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Valorisation des argilites du Callovo-Oxfordien sous forme de liant alcalinement activé dans le but de développer un coulis injectable.

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INTRODUCTION GENERALE

Cigéo (Centre industriel de stockage géologique) est le projet français de centre de stockage profond de déchets radioactifs. Il est conçu pour stocker les déchets hautement radioactifs et à durée de vie longue, produits par l'ensemble des installations nucléaires actuelles (jusqu'à leur démantèlement) et par le traitement des combustibles usés utilisés dans les centrales nucléaires. Ce centre de stockage (**Figure 1.A**) est prévu pour être construit à Bure, à 500 m sous terre, dans une couche géologique vieille d'environ 160 millions d'années datant du Callovo-Oxfordien (COx). Cette couche présente une très faible perméabilité, ce qui lui confère des propriétés intéressantes en terme de rétention des radionucléides. Les argilites qui la composent sont des mélanges de minéraux argileux (kaolinite, illite, smectite, interstratifiés illite-smectite et chlorite), d'espèces carbonatées (calcite et dolomite), de quartz et de pyrite. La demande d'autorisation de construction du site de Cigéo doit être déposée au cours de l'année 2020.

Si cette demande est acceptée, des millions de tonnes d'argilites du COx vont être excavées lors de la mise en place du site et de son exploitation. Le recyclage de cette immense quantité d'argilites est donc un des enjeux du projet Cigéo. Dans une visée d'économie circulaire, il faudrait que les argilites soient directement valorisées au sein du site de stockage. Pour cela, il est déjà envisagé d'utiliser les argilites comme matériau de comblement lors de la fermeture du site, mais cette solution ne permet pas la valorisation de l'intégralité des argilites excavées.

Lors du creusement des structures de stockage, l'exposition à l'air des argilites en paroi va provoquer l'oxydation d'un certain nombre de composés, en particulier les pyrites contenues dans les argilites. Cette oxydation peut conduire à l'apparition d'un milieu acide, entretenu par la déstabilisation des minéraux carbonatés. Dans Cigéo, les alvéoles de stockage des déchets de haute activité (HA) sont prévues pour être chemisées avec un tube en acier. Le milieu acide généré par l'oxydation des argilites pourrait entraîner une dégradation très rapide de ce chemisage en acier. Afin de neutraliser ce transitoire oxydant/acide, il est prévu d'injecter un matériau alcalin à l'interface chemisage acier/milieu géologique.

Ce « matériau » correspond à un coulis injecté entre le chemisage des déchets de haute activité et les argilites géologiques (**Figure 1.B**), et vise ainsi à neutraliser l'acidité du milieu géologique oxydé. Dans ces conditions, le liant de remplissage ainsi défini doit pouvoir être injecté, et donc présenter une durée pratique d'utilisation de l'ordre de 24 heures, ainsi qu'une viscosité faible (0,5-5,0 Pa.s). De plus, sa localisation, entre les déchets et le milieu géologique, conduit à deux spécificités : le liant ne doit pas comporter de composés organiques et présenter une valeur de pH après consolidation de l'ordre de 10-11.

Parmi les alternatives étudiées, l'utilisation des argilites dans la composition de ce « *matériau de remplissage de l'espace annulaire à l'extrados de l'alvéole de déchets de haute activité* » peut être envisagée.

(A) (B)

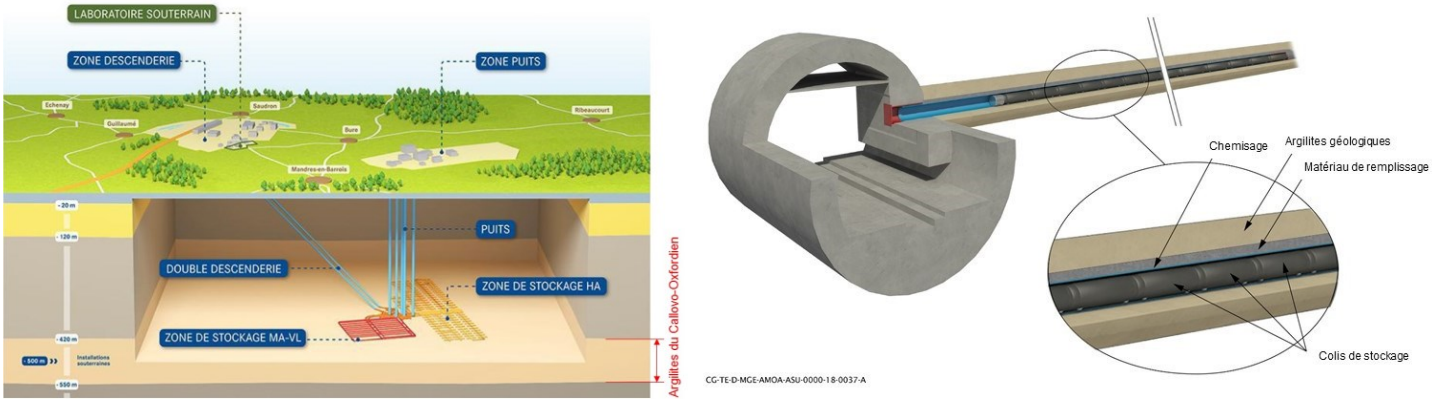


Figure 1. Schémas 3D **(A)** du site de Cigéo et **(B)** d'une alvéole de stockage de déchets HA.

Afin de développer un tel liant à base d'argilites, la voie envisagée est l'activation alcaline. Celle-ci est basée sur le mélange réactif d'une source minérale et d'une solution alcaline silicatée. A titre d'exemple, un métakaolin se dissout en présence d'une solution alcaline silicatée, conduisant à la formation d'un matériau consolidé de type géopolymère. Ces matériaux présentent une structure aluminosilicatée amorphe, proche de celle des verres, et des propriétés similaires à celles des matériaux céramiques. Un des principaux atouts de ce type de matériau est la possibilité de les synthétiser à partir de très nombreuses sources minérales. Ainsi les argilites du COx, pouvant contenir jusqu'à 50 % de minéraux argileux, peuvent être activées alcalinement. Pour cela, un traitement préalable des argilites est probablement nécessaire afin de favoriser l'activation alcaline. Le développement d'un liant présentant toutes les spécificités requises, nécessite une forte optimisation de la formulation et probablement l'incorporation d'additifs.

Afin de présenter le développement du coulis alcali-activé à base d'argilite, cette thèse s'articule autour de quatre chapitres. Le premier présente une synthèse bibliographique des minéraux argileux, des argilites du COx, des réactions de géopolymérisation et des données relatives au contrôle des valeurs de pH et de durée pratique d'utilisation des liants alcali-activés. Le second chapitre décrit les différentes matières premières utilisées, les protocoles de synthèses et les techniques de caractérisation employées. Une troisième partie présente une synthèse des différents travaux menés, à savoir l'activation alcaline de l'argilite, la formulation

d'un coulis à partir d'un mélange géopolymère de référence, puis à base d'argilite. Le dernier chapître regroupe les différentes publications rédigées, à savoir 8 articles scientifiques et 2 actes de congrès. Enfin, la conclusion rassemble les différents résultats obtenus au cours de ces travaux de thèse ainsi que les perspectives envisagées.

Liste des publications scientifiques :

ACL 1. The effect of furnace and flash heating on COx argillite for the synthesis of alkali-activated binders; Journal of Cleaner Production, 156 (2017) 970-978; A. Gharzouni, C. Dupuy, I. Sobrados, E. Joussein, N. Texier-Mandoki, X. Bourbon, S. Rossignol

ACL 2. Alkali-activated materials based on Callovo-Oxfordian Argillite: formation, structure and mechanical properties; Journal of Ceramic Science and Technology, 9 (2018) 127-140; C. Dupuy, A. Gharzouni, N. Texier-Mandoki, X. Bourbon, S. Rossignol

ACL 3. Thermal resistance of argillite-based alkali-activated materials. Part 1: effect of calcination processes and alkali cation; Materials chemistry and Physics, 217 (2018) 323-333; C. Dupuy, A. Gharzouni, N. Texier-Mandoki, X. Bourbon, S. Rossignol

ACL 4. Thermal resistance of argillite-based alkali-activated materials. Part 2: identification of the formed crystalline phases; Materials chemistry and Physics, 228 (2018) 262-271; C. Dupuy, A. Gharzouni, N. Texier-Mandoki, X. Bourbon, S. Rossignol

ACL 5. Metakaolin-based geopolymer: formation of new phases influencing the setting time with the use of additives; Construction and Building Material, 200 (2019) 272-281; C. Dupuy, J. Havette, A. Gharzouni, N. Texier-Mandoki, X. Bourbon, S. Rossignol

ACL 6. ^{29}Si, ^{27}Al, ^{31}P and ^{11}B magic angle spinning nuclear magnetic resonance study of the structural evolutions induced by the use of phosphor- and boron–based additives in geopolymer mixtures; Journal of Non-Crystalline Solids, 521 (2019) 119541; C. Dupuy, A. Gharzouni, I. Sobrados, N. Texier-Mandoki, X. Bourbon, S. Rossignol

ACL 7. Determination of the reactivity degree of various alkaline solutions: a chemometric investigation; Accepted by Applied Spectroscopy (10.1177/0003702819867956), M. Arnoult, C. Dupuy, M. Colas, J. Cornette, L. Duponchel, S. Rossignol

ACL 8. Formulation of an alkali-activated grout based on Callovo-Oxfordian argillite for an application in geological radioactive waste disposal, Submit to Construction and Building Materials, C. Dupuy, A. Gharzouni, I. Sobrados, N. Tessier-Doyen, N. Texier-Mandoki, X. Bourbon, S. Rossignol

ACLN 1. Thermal resistant alkali-activated materials using argillite and two types of solution; Ceramic Engineering and Science Proceedings, 39 (2019); C. Dupuy, M. Fricheteau, M. Ellie, A. Gharzouni, N. Texier-Mandoki, X. Bourbon, S. Rossignol

ACLN 2. Géopolymères à base de métakaolin : impact de l'addition d'acide orthophosphorique dans le mélange réactif; Actes du colloque NoMaD 2018, R-045 (2018); C. Dupuy, J. Havette, N. Texier-Mandoki, X. Bourbon, S. Rossignol

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I. INTRODUCTION

Afin d'étudier la valorisation des argilites du Callovo-Oxfordien sous forme de coulis alcalinement activé, il est nécessaire d'identifier les différentes réactions ayant lieu lors de la calcination d'un mélange argileux, et lors de son attaque par une solution basique. Ainsi, ce chapitre introduit dans un premier temps les minéraux argileux et les argilites du Callovo-Oxfordien. Les matériaux de type géopolymère et les solutions alcalines silicatées seront ensuite décrits, puis les coulis d'injection, ainsi que leurs propriétés, seront détaillés. Enfin, la structure des aluminosilicates amorphes sera abordée. Pour finir, l'objectif et les moyens mis en œuvre seront présentés.

II. LES MINERAUX ARGILEUX

Les minéraux argileux peuvent présenter des structures ainsi que des compositions chimiques différentes, qu'il est nécessaire d'identifier afin d'optimiser leur utilisation comme matière première.

1. Les phyllosilicates

a. Généralités

Les minéraux argileux peuvent être définis de différentes manières. En géologie, ils sont définis tels des minéraux d'une granulométrie inférieure à 2 µm [1] ou comprise entre 1 et 4 µm [2]. En minéralogie, ils sont définis par leur composition chimique, à base de silicates, et leur structure cristallographique. C'est cette dernière définition qui sera retenue et présentée.

Les minéraux argileux sont des silicates de la catégorie des phyllosilicates. Les silicates sont des espèces formées à base de tétraèdres d'atomes d'oxygène ayant au centre un atome de silicium [3]. Ces tétraèdres sont généralement présents sous différentes formes qui définissent les catégories de silicates. Ainsi, les silicates peuvent former des structures où les tétraèdres sont isolés les uns des autres (les nésosilicates), appariés (les sorosilicates) ou associés par cycles (les cyclosilicates). Cependant la majorité des silicates sont basés sur des alignements de tétraèdres en une dimension (les inosilicates), deux dimensions (les phyllosilicates) ou trois dimensions (les tectosilicates) [4, 5].

b. Classification

Les phyllosilicates étant composés de feuillets, leur structure doit être définie par la composition des différents feuillets s'alternant, plus ou moins périodiquement, afin d'atteindre

leur neutralité électronique. Celle-ci est usuellement obtenue par l'association d'un feuillet de tétraèdre (T) de silicium avec un feuillet d'octaèdre (O) d'aluminium (ou de magnésium) hydraté. Cette association peut être simple, avec uniquement un feuillet de tétraèdre et un feuillet d'octaèdre (phyllosilicate T-O) mais peut aussi comporter plus de feuillets [2], adoptant alors une structure T-O-T ou T-O-T-O. Cette notation décrit l'agencement des feuillets de tétraèdres (T) et d'octaèdres (O) (**Figure 1**).

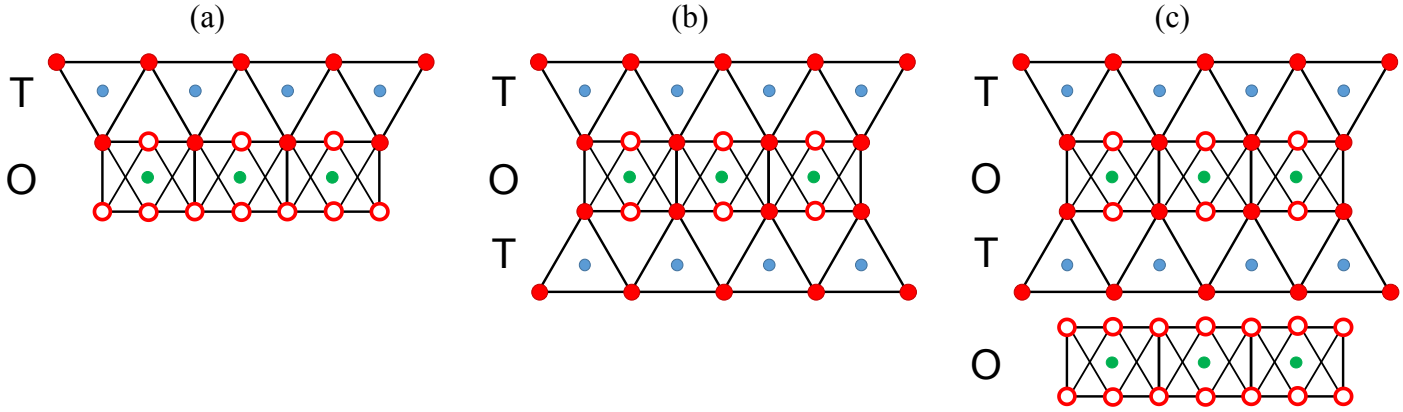


Figure 1. Schéma des différentes structures des phyllosilicates **(a)** T-O, **(b)** T-O-T et **(c)** T-O-T-O avec ● Si (ou Al), ● Al (ou Mg), ● O et ○ OH.

Les feuillets élémentaires ainsi formés (7-15 angström de hauteur) sont ensuite associés pour former les particules de phyllosilicates de taille micrométrique [5]. Les liaisons interfoliaires dépendent fortement de la nature du phyllosilicate. Par exemple, la kaolinite est un phyllosilicate T-O composé uniquement de tétraèdres d'atomes de silicium et d'octaèdres d'atomes d'aluminium. Ces différents feuillets de kaolinite sont associés par des liaisons hydroxyles pour former des particules microscopiques [6]. L'espace interfoliaire peut aussi contenir des molécules d'eau, dans le cas des phyllosilicates dit hydratés, comme l'halloysite (phyllosilicate T-O de composition chimique proche de la kaolinite) [7]. Dans les phyllosilicates de type T-O-T, les principales familles sont associées aux montmorillonites (T-O-T hydratés) et aux illites. Ces deux familles présentent d'importantes substitutions au sein de leur couche octaédrique (atomes de Mg ou Fe à la place des atomes d'Al) et tétraédrique (atome d'Al à la place des atomes de Si) conduisant à des défauts de charge. Ces défauts sont compensés par la présence de cations dans l'espace interfoliaire. Enfin, les T-O-T-O, tels que la chlorite, sont en réalité composés de feuillets T-O-T avec la présence d'un feuillet d'octaèdres en position interfoliaire [8]. Un dernier cas d'arrangement structural peut être identifié : les interstratifiés. Ceux-ci présentent un empilement de feuillets de différente nature.

Cette alternance de type de feuillet peut être périodique (interstratifié régulier) ou aléatoire (interstratifié irrégulier) [9].

Enfin, les phyllosilicates sont nommés en fonction de leur composition chimique précise et de leur structure. Leur nomination tient ainsi compte du taux et de la nature des substitutions des différents octaèdres et tétraèdres, mais aussi de la structure T-O, T-O-T ou T-O-T-O et de la composition interfoliaire.

2. Les argilites du Callovo-Oxfordien

a. Origines

Les argilites du Callovo-Oxfordien sont associées à une couche géologique, datant de l'époque du Callovo-Oxfordien (~ -160 millions d'années) et localisée dans l'est du bassin parisien (à la limite des départements de la Meuse et de la Haute Marne) [10]. Cette couche, située entre -420 et -540 m, a été sélectionnée pour accueillir le projet de centre industriel de stockage géologique (Cigéo), pour les déchets radioactifs français de moyenne activité à vie longue et de haute activité. En effet, cette couche géologique présente une très faible perméabilité, formant ainsi une barrière naturelle pour limiter la diffusion des radionucléides et des toxiques chimiques [11].

Le terme d'argilite fait référence à des minéraux argileux, issus de particules sédimentaires indurées. Les argilites du Callovo-Oxfordien contiennent ainsi environ 50 % de minéraux argileux associés principalement à du quartz et à de la calcite. Cependant la composition minéralogique de l'argilite dépend fortement de la profondeur à laquelle elle a été prélevée. Les deux tiers inférieurs de la couche d'argilite, -460 à -540 m, présentent une composition relativement homogène : 45-55 % de minéraux argileux, 20-30 % d'espèces carbonatées et 20-25 % de quartz. La couche supérieure présente une plus grande hétérogénéité, ainsi qu'une quantité de calcite très importante, pouvant atteindre jusqu'à 70 % [11, 12]. On parle alors d'unité carbonatée (UC) par opposition aux strates riches en argiles, ou unités argileuses (UA). Les argilites étudiées lors de ce travail proviennent intégralement de la couche inférieure, riche en minéraux argileux, dans l'unité identifiée UA2 [13].

b. Composition structurale

Le **Tableau 1** présente la composition pondérale de l'argilite en masse d'oxyde et de soufre [11]. L'argilite est ainsi composée de près de 48,8 % de silice et de 13,5 % d'alumine, provenant du quartz et des minéraux argileux. Cela en fait un aluminosilicate de rapport molaire Si/Al de

3,1. Le troisième oxyde le plus présent dans l'argilite est l'oxyde de calcium, 10,8 %, provenant principalement des calcites et dolomites, mais pouvant être aussi présent au sein des tectosilicates et des minéraux argileux. Ces silicates contiennent également des cations potassium, principalement dans les feuillets des phyllosilicates. Des oxydes de fer sont aussi présents (4,5 %), sous forme d'hématite ou bien issus des minéraux argileux. Les oxydes de magnésium proviennent, eux, essentiellement des espèces carbonatées mais aussi des phyllosilicates (T-O-T et T-O-T-O). Les traces de soufre observées, 0,8 %, proviennent de la pyrite présente dans l'argilite à environ 0,8 % massique. La perte au feu (PF) de l'argilite à 1000 °C est de l'ordre de 14,7 %. Elle correspond à l'élimination de l'eau physisorbée, de l'eau structurale des argiles ainsi qu'aux décompositions des carbonates et des sulfures.

Tableau 1. Composition élémentaire de l'unité UA2 de l'argilite, rapportée en oxydes [14].

Composé	**SiO_2**	**Al_2O_3**	**MnO**	**MgO**	**CaO**	**Na_2O**	**K_2O**	**TiO_2**	**Fe_2O_3**	**P_2O_5**	**S**	**PF**
Teneur ($\%_{mass}$)	48,78	13,44	0,03	2,50	10,75	0,20	3,27	0,73	4,52	0,07	0,84	14,73

La composition minéralogique de l'argilite, issue de multiples travaux menés par l'Andra, est décrite dans le **Tableau 2** [11].

L'argilite est principalement composée de minéraux argileux (52,0 %). Ces phyllosilicates sont en majorité des T-O-T, sous forme d'illite (16,7 % de l'argilite) mais surtout sous forme d'interstratifiés (28,6 % de l'argilite). Ces interstratifiés sont composés de feuillets d'illite et de smectite (T-O-T hydratés) organisés de façon régulière (87 % des interstratifiés sont réguliers). D'autre phyllosilicates sont présents en plus faible quantité avec 4,0 % de kaolinite (T-O) et 2,7 % de chlorite (T-O-T-O).

L'argilite présente aussi une importante quantité de tectosilicates (19,0 %), dont 16,6 % de quartz [15]. De faibles quantités de feldspath potassique peuvent être identifiées (1,4 %) ainsi que des plagioclases riches en sodium et calcium (1,0 %) [5, 16].

En plus des silicates, l'argilite présente une large quantité d'espèces carbonatées, dont 22,2 % de calcite ($CaCO_3$). Une fraction de l'argilite peut aussi être associée à de la dolomite à 3,7 % ($CaMg(CO_3)_2$).

D'autres phases peuvent aussi être présentes, telles que l'hématite (Fe_2O_3) ou divers minéraux à base de titane ou de fer et de la pyrite (FeS_2, 0,8 %). La fraction organique y est inférieure à 1,0 % [11].

Tableau 2. Composition minéralogique de l'unité UA2 de l'argilite [14].

Catégorie	Phase minérale	Quantité ($\%_{mass}$)
Minéraux argileux	Illite/Muscovite	16,7
	Interstratifiés Illite/Smectite	28,6
	Kaolinite	4,0
	Chlorite	2,7
Espèces carbonatées	Calcite	22,2
	Dolomite	3,7
Tectosilicates	Quartz	16,6
	Feldspaths	1,4
	Plagioclase	1,0
Autres minéraux	Pyrite	0,8
	Autres	2,3

3. Réactivité des argiles et argilites

a. Traitement thermique des argilites

Afin d'accroitre leur réactivité lors de l'activation alcaline, les argiles peuvent être calcinées. En effet, l'activation alcaline nécessite l'utilisation d'une source aluminosilicatée déstructurée, dont la plus commune est le métakaolin [17]. Cette déstructuration s'effectue à des températures comprises entre 530 et 590 °C pour la kaolinite, 500 et 550 °C pour la chlorite, 550 et 620 °C pour les illites et 500 et 600 °C pour les interstratifiés [18,19]. Cependant ces températures présentent une importante variabilité en fonction de la cristallinité, de l'érosion et des altérations temporelles des différentes espèces ainsi que des procédés de calcination [19]. Il est aussi nécessaire de ne pas calciner à trop haute température, pour éviter la formation d'autres minéraux tels que la mullite, la cordiérite ou des phases de type spinelle [19].

Afin de caractériser et de quantifier cette déhydroxylation des minéraux argileux, la résonnance magnétique nucléaire de l'aluminium 27 est souvent utilisée. Ainsi la **Figure 2** illustre l'évolution de la coordinence des atomes d'aluminium dans un kaolin. Initialement le

kaolin est cristallisé et présente des atomes d'aluminium en coordinence IV. Lors de la calcination, la coordinence passe à V et IV et le taux de transformation dépend de la température [20].

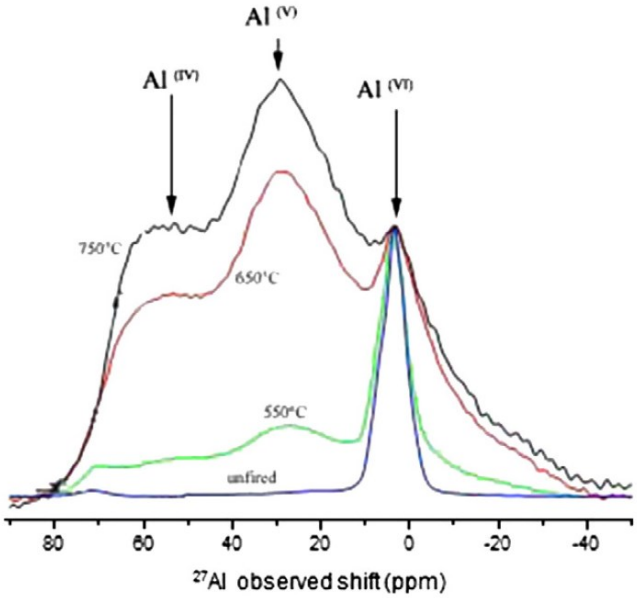


Figure 2. Spectre RMN de l'aluminium 27 d'un kaolin en fonction de la température de calcination (figure issue de l'article de B. Fabbri *et al.* [20]).

Le traitement thermique de l'argilite entraîne aussi la décomposition des espèces carbonatées. La calcite se décompose en oxyde de calcium à des températures comprises entre 600 et 950 °C (selon la cristallinité, l'érosion et les altérations temporelles) [19]. La dolomite se décompose à une température plus faible que la calcite, en formant de l'oxyde de magnésium et du carbonate de calcium [21]. La pyrite contenue dans l'argilite subit aussi une oxydation entre 400 et 500 °C [19].

b. Utilisation pour la synthèse de matériaux alcalinement activés

Dans le but de valoriser les argilites du Callovo-Oxfordien sous forme de matériaux alcalinement activés, il est nécessaire d'identifier le rôle de chaque phase vis-à-vis de l'activation alcaline.

L'activation alcaline se base sur la dissolution des espèces aluminosilicates amorphes afin de former un nouveau réseau amorphe [22]. Au sein de l'argilite, les aluminosilicates potentiellement réactifs sont les phyllosilicates. Cependant leur cristallinité va induire une faible dissolution/réactivité lors de l'activation alcaline, qu'il est nécessaire de compenser à l'aide d'une calcination [23]. La faible fraction de kaolinite, 4,0 %, se transforme alors en

métakaolinite, qui est la source minérale idéale pour l'activation alcaline [24]. La déstructuration des autres phyllosilicates, quasiment uniquement des T-O-T (interstratifiés ou non), peut conduire à des minéraux partiellement réactifs [25, 26]. Cependant cette réactivité n'est pas systématique et devra être vérifiée.

Le principal tectosilicate présent dans l'argilite est le quartz, qui demeure stable au cours des réactions d'activation alcaline. Il reste donc spectateur des réactions et peut uniquement jouer le rôle d'un renfort mécanique au sein du matériau consolidé [27, 28]. Cependant les particules de quartz disponibles dans l'argilite présentent une granulométrie assez faible, ce qui risque de limiter cet effet [12].

Les espèces carbonatées (26 %) disponibles dans l'argilite sous forme de calcite et de dolomite ne sont pas impactées par l'activation alcaline [29]. S. Samira a mis en évidence une stabilité de la calcite dans les solutions alcalines utilisées pour la synthèse de matériaux géopolymères [30]. Cependant si l'argilite subit un traitement thermique, les produits de décomposition de la calcite et de la dolomite, CaO et MgO, peuvent réagir lors de l'activation alcaline [31]. En fonction de la nature des matières premières et des quantités de CaO, plusieurs interactions peuvent être possibles.

(i) L'activation alcaline de sources minérales très riches en CaO, telles que des scories de fonderie ou des cendres volantes, peut conduire à la formation de phases secondaires, en plus du réseau géopolymère. La formation de silicates de calcium hydratés (CSH) ou d'aluminosilicates de calcium hydratés (CASH) peut être observée [32, 33]. Ces phases sont initiées par la présence d'hydroxyde de calcium, $Ca(OH)_2$, dans le mélange réactif [32]. Dans des conditions d'alcalinité modérée, la formation de ces phases est favorisée ainsi que la recarbonatation des oxydes de calcium et de magnésium [34, 35].

(ii) Pour des taux d'oxyde de calcium plus modérés (< 15 $\%_{mass}$) et des solutions d'alcalinités supérieures (valeur de pH de l'ordre de 12,8), aucun CSH n'a pu être détecté mais la formation de silicate de calcium non hydraté est observée [36]. Ainsi A. Gharzouni *et al.* a mis en évidence par spectroscopie IRTF la formation de liaisons silicium-oxygène-calcium, en parallèle de la formation des liaisons silicium-oxygène-aluminium caractéristiques du réseau géopolymère [37]. Cette formation semble d'autant plus favorisée que la quantité d'aluminium dans la source minérale est faible [37, 38]. La **Figure 3** illustre ainsi la formation de ces liaisons (Si-O-Ca à 920 cm^{-1}) au cours de la formation des matériaux alcalinement activés. La recarbonatation du matériaux, probablement le calcium, au cours du temps est aussi visible à 1400 cm^{-1} [36].

(iii) La présence de calcium et/ou de magnésium peut aussi conduire à la présence de ces cations au sein du réseau poral, afin de compenser les charges électroniques du réseau [39]. Des travaux ont également montré que ces cations pouvaient être échangés après consolidation du géopolymère, comme cela peut être le cas avec les zéolithes [40].

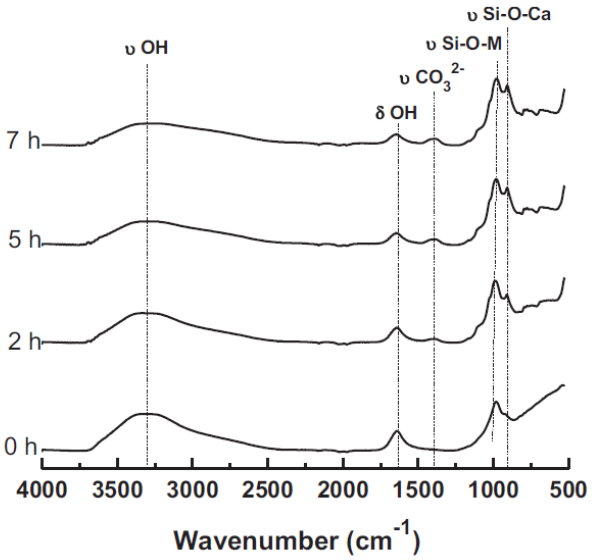


Figure 3. Exemple de suivi IRTF sur liant alcalinement activé à base d'une source minérale contenant une quantité modérée de CaO (3-10 $\%_{mass}$) (figure issue de l'article de J. Peyne *et al.* [36]).

Afin d'activer alcalinement des matériaux hétérogènes, tels que les minéraux argileux, il est nécessaire d'identifier les différents cations alcalins et alcalino-terreux en présence ainsi que la quantité de kaolinite.

III. LES MATERIAUX GEOPOLYMERES

Les matériaux géopolymères ont été introduits dans les années 70 par J. Davidovits [22]. Ces matériaux appartiennent à la catégorie plus générale des matériaux alcalinement activés, qui ont été étudiés dès 1940 par A.O. Purdon [41] et en 1957 par V.D. Glukhovsky [42]. Ces matériaux sont synthétisés à partir de précurseurs silicatés et sont donc associés à des applications de grande diffusion. Leurs propriétés caractéristiques sont une résistance mécanique en compression élevée, une tenue en température, une résistance aux attaques acides et une faible conductivité thermique [43, 44].

1. Mécanisme de géopolymérisation

a. Généralités

Les géopolymères sont des aluminosilicates amorphes basés sur un réseau tridimensionnel de tétraèdre de silicium et d'aluminium [45]. J. Davidovits a proposé la formule suivante pour décrire ces systèmes : $M_n [(SiO_2)_z (AlO_2)]_n wH_2O$; où M correspond au cation alcalin ($M = Na^+$ ou K^+), n au degré de polycondensation, z au rapport molaire Si/Al et w à la quantité d'eau [46]. Ces matériaux sont synthétisés à température ambiante, ou à une température modérée (< 100 °C), par dissolution d'une source aluminosilicatée dans une solution de silicate alcalin [46].

Parmi les sources aluminosilicatées possibles, le métakaolin est la source minérale la plus commune. D'autres minéraux argileux peuvent être utilisés, ainsi que de nombreux coproduits industriels ou déchets [45, 47, 48]. Ces minéraux présentent différentes réactivités en fonction de leur rapport Si/Al et de leur cristallinité. En effet, la source minérale devant se dissoudre dans la solution alcaline silicatée, un minéral déstructuré présente une dissolution favorisée et donc une meilleure réactivité [24]. Dans le cas des minéraux argileux, cette déstructuration est caractérisée par la déhydroxylation, qui conduit à la transformation des atomes d'aluminium en coordinence VI, en atomes de coordinence V et/ou IV.

Les solutions de silicate alcalin sont caractérisées par leur rapport molaire Si/M. En effet, ce rapport ainsi que le taux d'eau gouvernent la réactivité de la solution, qui est détaillée dans la partie **III.2** [49].

b. Réactions de géopolymérisation

Les réactions de géopolymérisation sont complexes et différents auteurs ont proposé des mécanismes [22, 44, 45, 50]. Ceux-ci sont décrits à partir de trois principales étapes : la dissolution de la source minérale, la formation des oligomères et les réactions de polycondensation conduisant à la polymérisation d'un réseau tridimensionnel (**Figure 4)**. La très forte alcalinité de la solution silicatée entraîne la dissolution de la source minérale. Cela conduit à la formation de monomères $Al(OH)_4^-$ et $Si(OH)_4$ [45]. Ces différentes espèces en solution vont interagir pour former des oligomères qui vont polycondenser et conduire à la formation d'un réseau solide de type gel [44]. La structure de ce gel est initiée par les oligomères des espèces siliceuses initialement présentes au sein de la solution alcaline [51]. Le réseau solide se réorganise pour conduire à une polymérisation, où la connectivité des atomes de silicium et d'aluminium est optimale.

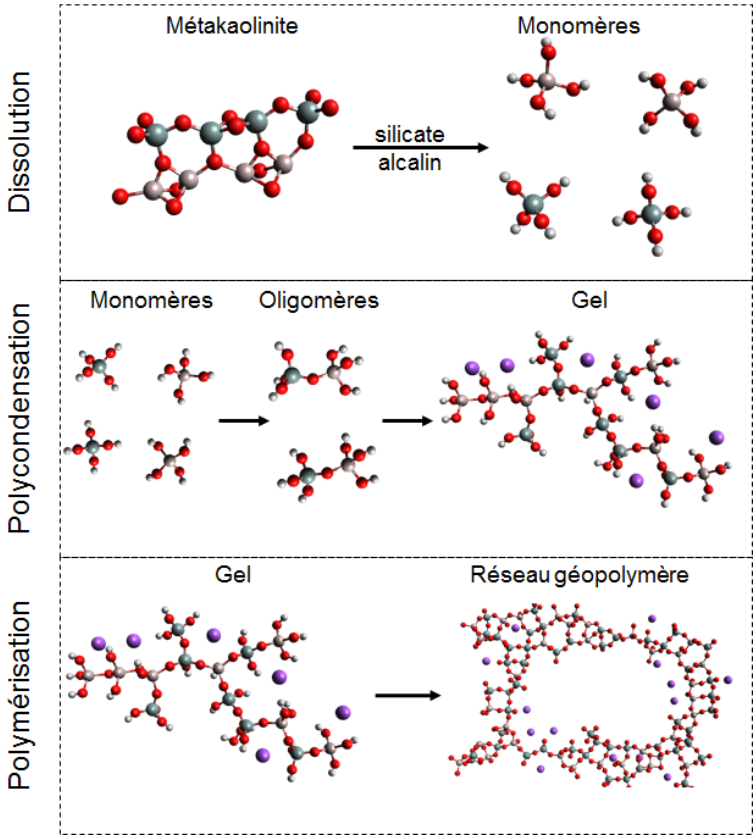


Figure 4. Schémas des différentes étapes de géopolymérisation (● Si^{4+}, ● Al^{3+}, ● Na^{+}, ● H^{+} et ● O^{2-}).

c. Caractérisation structurale des géopolymères

La structure finale d'un géopolymère consolidé est donc composée de tétraèdres de silicium et d'aluminium, pontés par les atomes d'oxygène avec la présence d'alcalin pour équilibrer les défauts de charge [22]. L'étude de cette structure s'effectue usuellement à l'aide de techniques spectroscopiques, telles que la spectroscopie IRTF et Raman ou la résonnance magnétique nucléaire (RMN). C'est cependant la RMN (du ^{27}Al et ^{29}Si) qui donne le plus d'information sur la connectivité des atomes de silicium et d'aluminium au sein du réseau [52].

La **Figure 5.a** présente un spectre RMN typique de l'aluminium (^{27}Al). Deux contributions à 60 et 0 ppm sont respectivement associées à l'aluminium en coordinence IV et VI [53, 54]. L'aluminium présent sous forme tétraédrique, $Al^{[4]}$, est largement majoritaire et correspond à l'aluminium du réseau géopolymère [52]. La faible quantité d'aluminium sous forme octaédrique, $Al^{[6]}$, provient de la fraction non-déstructurée de la source aluminosilicatée et n'intègre pas le réseau géopolymère [20]. Il n'est généralement pas observé d'$Al^{[5]}$ dans les géopolymères. En effet, l'aluminium en coordinence V (**Figure 2**) correspond à une fraction

très réactive de l'aluminium. Sa présence dans le spectre RMN d'un géopolymère est donc synonyme d'une géopolymérisation incomplète [52].

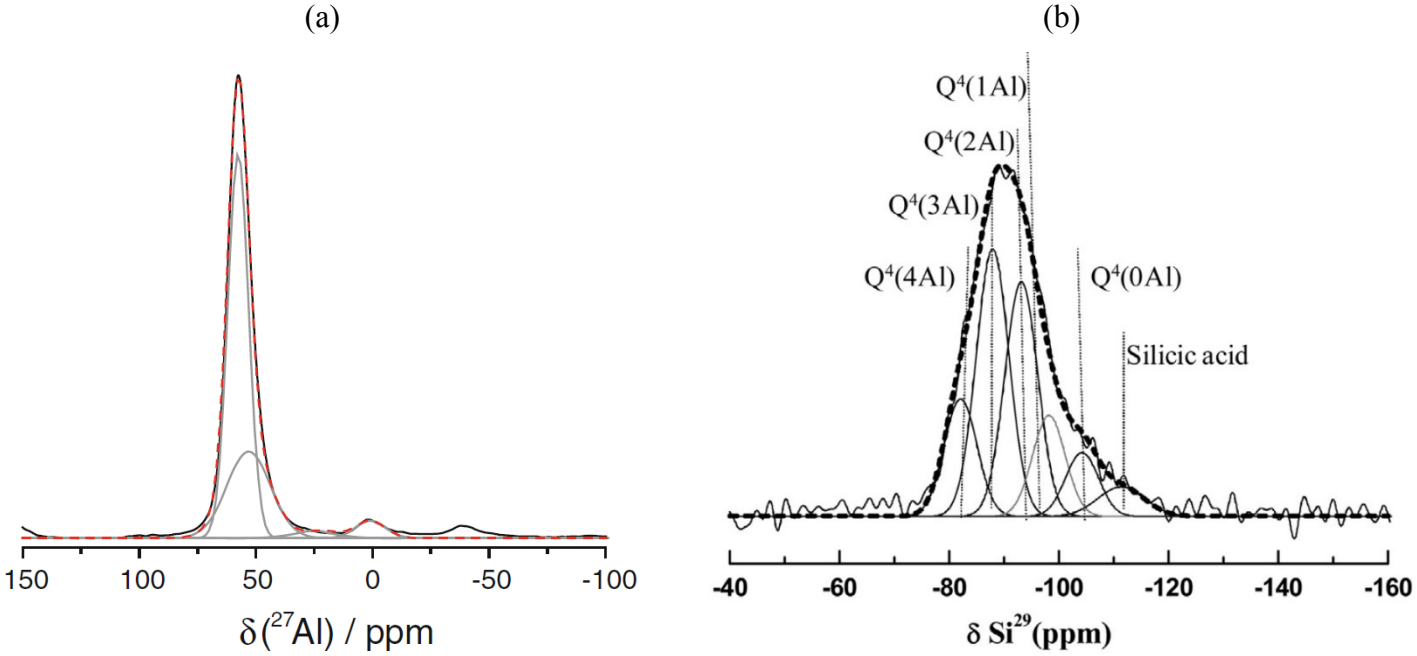


Figure 5. Spectres RMN typiques du **(a)** ^{27}Al et **(b)** ^{29}Si d'échantillons de géopolymère (figures respectivement issues des articles de E. Prud'Homme *et al.* et de A. Gharzouni *et al.* [53, 55]).

Le spectre RMN du ^{29}Si présente un très large pic s'étendant sur plus de 30 ppm, qui peut se décomposer en de nombreuses contributions (**Figure 5.b)** [55]. G. Engelhardt a largement étudié la RMN du silicium, et mis en évidence la possibilité d'identifier la coordinence du silicium mais aussi la quantité d'atomes d'aluminium liés à chaque atome de silicium [56]. La connectivité du silicium est notée Q^n , où n correspond au nombre d'atomes d'oxygène pontants liés à l'atome de silicium [57]. Cette valeur, comprise entre 0 et 4, décrit le taux de polymérisation générale des atomes de silicium. Les spectres RMN du ^{29}Si des géopolymères sont souvent décomposés d'après l'hypothèse que l'intégralité des atomes de silicium sont en coordinence IV (Q^4), afin d'identifier la connectivité silicium-aluminium [58]. Il est alors possible de décomposer le large pic en 6 contributions, qui correspondent aux atomes de silicium connectés à des atomes d'aluminium et à l'acide silicique. Les cinq premières contributions, à -84, -89, -94, -99 et -104 ppm, sont associées aux atomes de silicium en Q^4 liées à 4, 3, 2, 1 et 0 atomes d'aluminium [55]. La contribution à -111 ppm est attribuée à la présence d'acide silicique, issu d'espèces siliceuses n'ayant pas réagi [59]. Dans certains cas, il peut aussi être distingué une contribution de quartz à -107 ppm [60].

2. Solutions de silicate alcalin

a. Généralités

Les solutions de silicate alcalin sont utilisées pour plusieurs applications industrielles, telles que les défloculants, l'agglomération de sable, le traitement du bois, les peintures ou les liants basses températures [61, 62, 63]. Elles peuvent être produites par deux procédés industriels. Le premier consiste à former un verre de silicate alcalin puis de le dissoudre par autoclave. Le second consiste à dissoudre à chaud de la silice amorphe dans une solution alcaline concentrée [64, 65].

Ces solutions sont caractérisées par leur quantité d'eau, la nature de leur cation alcalin (noté M, usuellement M = Na^+ ou K^+) et leur rapport molaire Si/M. Les solutions utilisées comme précurseur pour la synthèse des matériaux alcalinement activés doivent être fortement alcalines, de rapport Si/M faible (0,5-0,8), afin de faciliter la dissolution de la source aluminosilicatée [66]. Pour atteindre de telles valeurs de rapport Si/M, des hydroxydes alcalins sont généralement ajoutés aux solutions commerciales [67].

b. Espèces silicatées en solution

Les espèces silicatées sont présentes sous forme de monomères et d'oligomères. Leur polymérisation ainsi que leur nature dépendent fortement de la quantité d'alcalin présente dans la solution (rapport Si/M), mais aussi de la quantité d'eau [68]. Afin de comprendre cette polymérisation, il est donc nécessaire d'étudier la nature des différentes espèces.

Pour cela, des techniques spectroscopiques telles que la résonnance magnétique nucléaire (RMN) du silicium 29 ainsi que la spectroscopie Raman peuvent être utilisées. Elles permettent de caractériser la connectivité du silicium, Q^n, et de décrire le taux de polymérisation générale des atomes de silicium des solutions alcalines [57]. En plus de la connectivité du silicium, la RMN permet également de différencier les espèces linéaires (notées Q^n) et cycliques (notées Q^{nc}) illustrées en **Figure 6.a**. Ces espèces sont ainsi nommées en fonction du nombre d'atomes de silicium les composant (mono-, di-, tri-, tetra-, … -mère) et de leur géométrie (cyclique, cubique, prismatique…) [69, 70]. La spectroscopie Raman donne des informations plus complètes sur la nature des espèces présentes, permettant d'identifier la présence de cycle de 3, 4 ou 5 tétraèdres ou de chaines composées de 5 à n tétraèdres (**Figure 6.b**) [49, 71, 72].

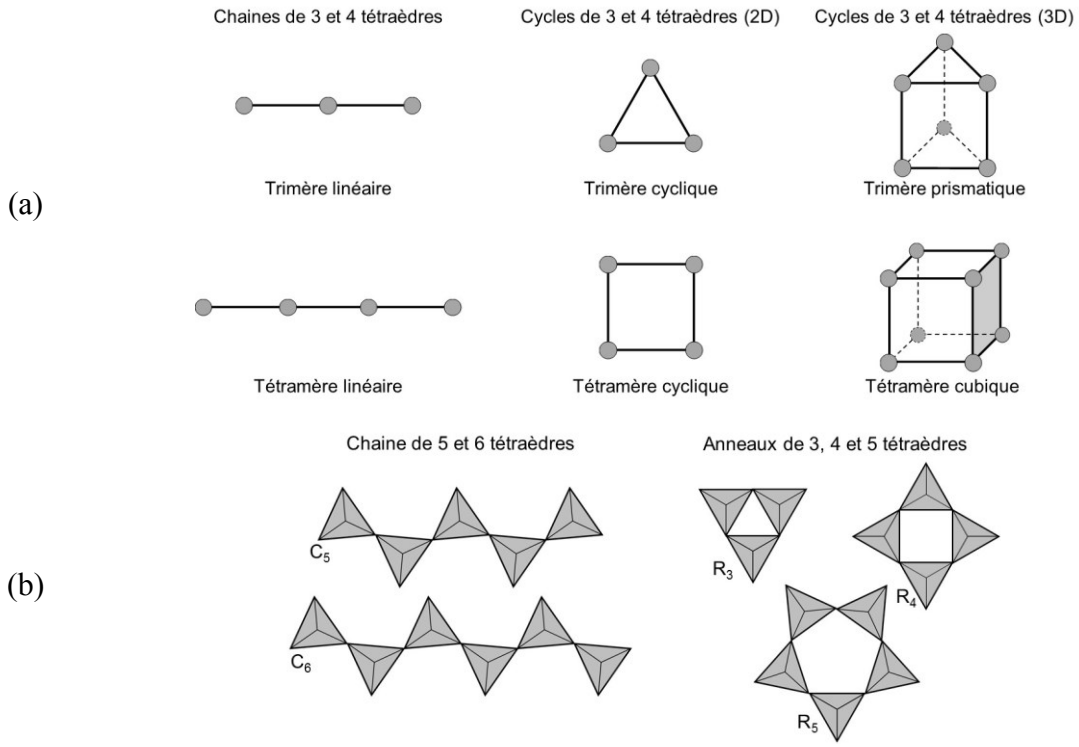


Figure 6. Représentation schématique des différentes espèces silicatées observées en **(a)** RMN et **(b)** en spectroscopie Raman [71, 72].

c. Réactivité et influence des solutions

La réactivité des solutions dépend tout d'abord de la nature des espèces disponibles. La présence d'atomes de silicium de coordinence Q^0, Q^1 et Q^2 conduit à une réactivité plus élevée [49]. Celle-ci s'explique par l'augmentation de la quantité d'atomes d'oxygène non-pontants (NBO) au sein de la solution [73]. Cette quantité est optimale pour des rapports Si/M de l'ordre de 0,5-0,8 [49]. En effet, le rapport Si/M de la solution conditionne directement la polymérisation de la solution (**Figure 7**) [74]. M. Arnoult *et al.* ont aussi mis en évidence l'importance de la nature de ces espèces, en montrant que la présence d'anneaux de 3-4 tétraèdres (R_3 et R_4) conduisait à une réactivité optimale alors que les chaines de 5-6 tétraèdres ($C_{5,6,7}$) limitent la réactivité [75]. L. Vidal a montré que le rapport entre ces quantités d'anneaux et de chaines ($(R_3+R_4)/C_{5,6,7}$) permettait de décrire la réactivité des solutions alcalines silicatées [76]. Cette réactivité est illustrée sur la **Figure 8** en fonction de la durée pratique d'utilisation des liants géopolymères [75].

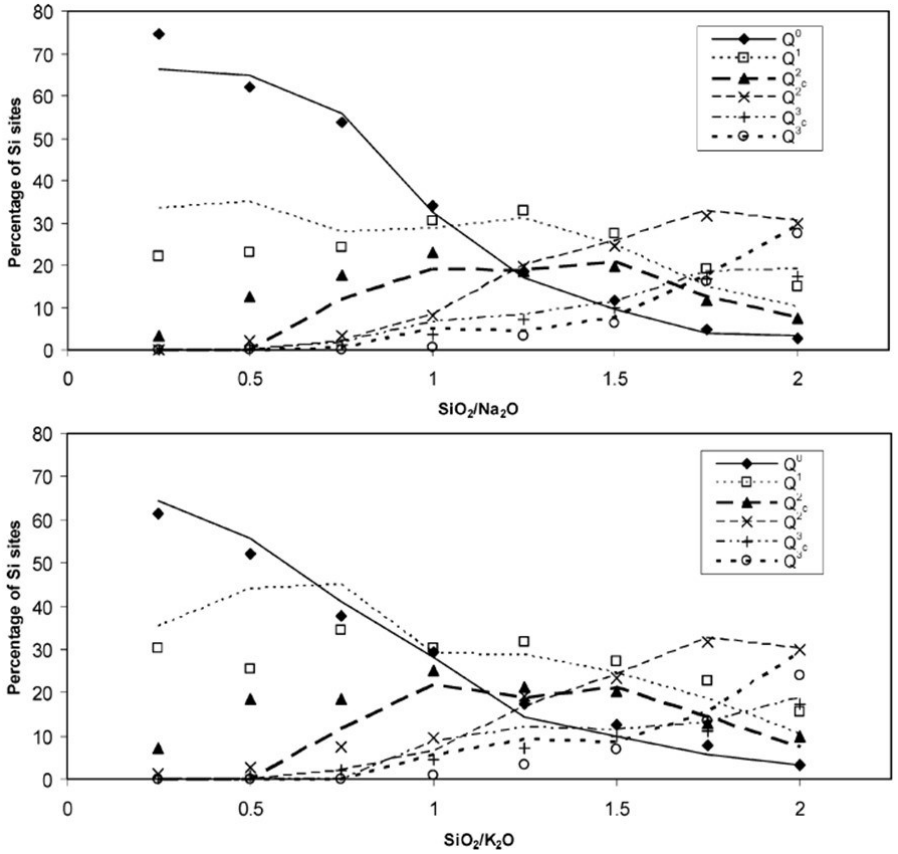


Figure 7. Evolution de la connectivité des atomes de silicium dans des solutions alcalines silicatées sodique et potassique (figure issue de l'article de J.L. Provis *et al.* [74]).

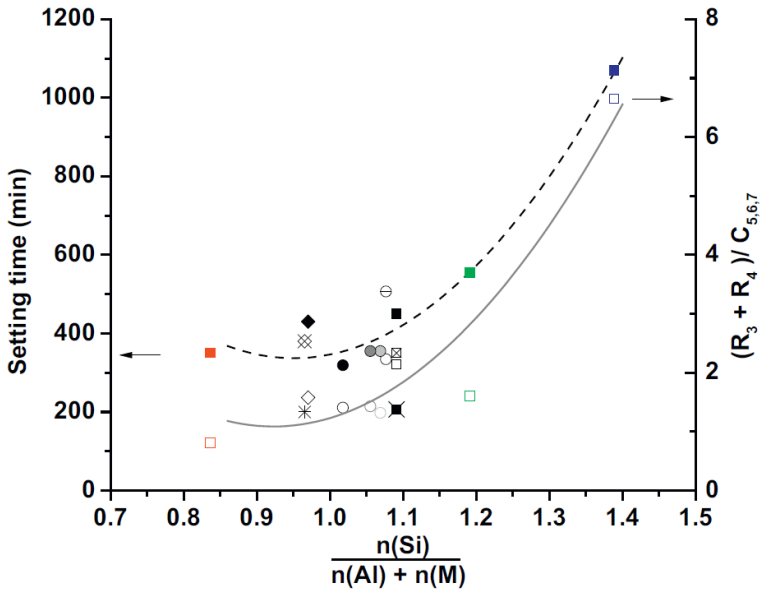


Figure 8. Evolution de la durée pratique d'utilisation et du rapport $(R_3+R_4)/ C_{5,6,7}$ en fonction de la composition chimique du mélange (figure issue de l'article de M. Arnoult *et al.* [75]).

La nature du cation alcalin utilisé influe aussi sur la réactivité des solutions alcalines silicatées. En effet, en présence de cations potassium la connectivité des espèces silicatées est plus importante qu'en présence de sodium (**Figure 7**) [77]. Ces variations sont liées à la taille des cations alcalins. Les cations sodium, de par leur plus petite taille, conduisent à une plus grande dépolymérisation que les cations potassium. Il en résulte en une plus grande quantité de silicium Q^0 et Q^1. L'influence du cation alcalin peut aussi être directement observée lors de la caractérisation des liants. Par exemple, la stabilité thermique est fortement liée à la nature du cation. P. Duxson *et al.* ont ainsi mis en évidence que l'utilisation d'une solution potassique limite fortement le retrait des échantillons lors du traitement thermique (**Figure 9.A**) [78]. En effet, la sphère d'hydratation du sodium est nettement supérieure à celle du potassium ce qui conduit à une quantité d'eau plus importante. A. Favier a aussi démontré que la viscosité initiale des solutions alcalines silicatées sodiques est deux fois supérieure à celle obtenue avec des solutions potassiques [79]. A. Arnoult *et al.* ont confirmé cette tendance sur les liants géopolymères (**Figure 9.B**) [75]. Une durée pratique d'utilisation plus faible est aussi observée avec l'utilisation d'une solution silicatée sodique [80].

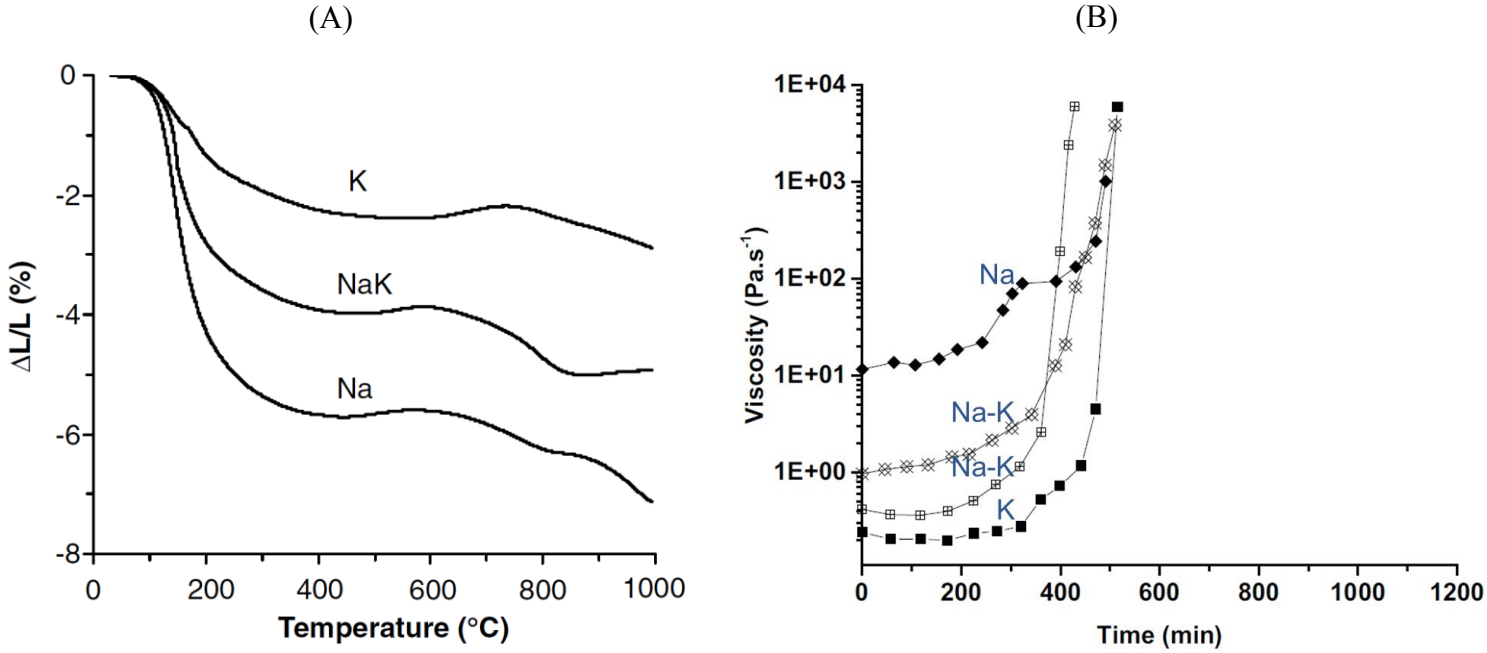


Figure 9. Evolution **(A)** du retrait lors d'un traitement thermique et **(B)** de la viscosité apparente de géopolymères mis en formes à partir de solutions potassique et sodique (figures issues des articles de P. Duxson *et al.* [78] et de M. Arnoult *et al.* [75]).

La maîtrise de la réactivité des solutions alcalines silicatées est nécessaire pour adapter les formulations géopolymères aux applications ciblées.

3. Valeur de pH des liants

a. Alcalinité des géopolymères

Il vient d'être démontré que la synthèse des liants géopolymères est directement liée à l'utilisation de solutions alcalines silicatées, de très fortes valeurs de pH. Cette forte alcalinité impose des précautions supplémentaires lors de la synthèse de quantités industrielles de géopolymères, et peut aussi limiter l'utilisation de ces liants pour certaines applications [81]. Dans le cadre du liant visé par cette thèse, la valeur de pH doit être légèrement basique (valeur de pH de 10-11) afin de pouvoir être utilisé au sein du site de Cigéo. Cette alcalinité permet de compenser l'acidité de l'argilite (oxydée lors du creusement des alvéoles), de respecter la passivité de l'acier du chemisage et, à terme, de préserver l'intégrité des colis vitrifiés [82]. La valeur de pH caractérise l'activité des ions en solution. Quand il est fait référence à la valeur de pH d'un solide, cela correspond à la valeur de pH résultant de l'immersion du solide. C'est ainsi que les valeurs de pH naturelles des minéraux argileux sont mesurées, comme le décrit la norme NF ISO 10390 [83]. Cette méthode a aussi été appliquée lors de la mesure de la valeur de pH de différents liants consolidés [84, 85]. Afin d'étudier plus précisément la valeur de pH de l'eau porale du géopolymère, l'échantillon peut aussi être pressé pour en extraire l'eau porale. Ce procédé nécessite cependant du matériel de pressage extrêmement conséquent [86].

b. Optimisation de la valeur de pH des géopolymères

Afin de réduire la valeur de pH d'un liant alcalinement activé, il est possible de limiter l'apport de cations alcalins dans le mélange réactif. L'alcalinité de la solution alcaline silicatée peut ainsi être optimisée pour réduire la valeur de pH finale. Cependant, afin de préserver une réactivité minimale, la solution ne peut pas présenter de valeur de pH inférieure à 13 [49]. La source aluminosilicatée n'a qu'une influence limitée sur la valeur de pH. L'utilisation d'une source minérale dite acide, telle que le métakaolin, permet d'atteindre des valeurs de pH légèrement plus faibles que des sources minérales riches en calcium, qui tendent à augmenter l'alcalinité [5, 87].

Néanmoins, pour conduire à une importante diminution de la valeur de pH, il ne suffit pas de réduire l'apport d'éléments alcalins. Il est aussi nécessaire de contrôler les réactions de géopolymérisation, afin de les optimiser pour augmenter la consommation d'alcalins lors des

réactions. En effet, A. Gharzouni *et al.* ont mis en œuvre des suivis de valeur de pH de géopolymères au cours de la consolidation. Il a ainsi été mis en évidence que la valeur de pH initiale du mélange réactif ne conditionne pas la valeur de pH du matériau consolidé [88]. La valeur de pH finale dépend de la réactivité du couple solution alcaline/source aluminosilicatée et de sa capacité à former un réseau développé. A. Gharzouni *et al.* ont démontré qu'afin d'obtenir un réseau homogène, avec une porosité de taille minimale, il est nécessaire de favoriser les étapes de dissolution et de polycondensation [89]. Ainsi la réactivité du mélange réactif doit être équilibrée afin de ne pas conduire à une consolidation trop rapide (limitant le développement du réseau géopolymère, et donc la consommation d'alcalins) tout en permettant une dissolution totale de la source aluminosilicatée.

L'utilisation d'additifs permet aussi de contrôler les valeurs de pH des géopolymères, avec des résultats variables. L'incorporation d'acide orthophosphorique dans des matériaux alcalinement activés a déjà été étudiée, mais il perturbe les réactions de prise et n'a donc qu'une influence limitée sur l'alcalinité du matériau [90]. Il a aussi été montré que le tétraborate de sodium permet de diminuer la valeur de pH de matériaux cimentaires [91]. Cependant le tétraborate de sodium peut aussi être utilisé pour former des borosilicates alcalinement activés, ce qui suppose qu'il peut aussi influer sur la nature du réseau géopolymère et conduire à une diminution plus importante de la valeur de pH [92]. Enfin, J. Wang *et al.* ont démontré que l'incorporation de zéolites (5-25 $\%_{mass}$) permet de diminuer significativement la valeur de pH (de 13 à 11) de liants alcalinement activés [93]. Cette diminution s'explique par l'incorporation des cations alcalins dans la structure zéolitique, par substitution du calcium qui précipite ensuite dans l'eau porale.

Les géopolymères sont des matériaux dont la formulation requiert la maitrise des précurseurs afin de contrôler la valeur de pH.

IV. LES COULIS D'INJECTION

1. Notion de coulis

a. Définition générale

Tout d'abord la notion de coulis est associée à un mélange à l'état frais, c'est-à-dire d'un liant liquide qui va à terme avoir une prise physique ou mécanique. Il est ainsi caractérisé par une durée pratique d'utilisation (DPU), qui définit la plage temporelle dans laquelle il peut être utilisé. Usuellement cette DPU est de l'ordre de quelques heures (5-15 heures) [94]. Les coulis

sont ensuite associés à leur utilisation : le comblement de cavités et de fractures (du sol ou d'un ouvrage). Celles-ci peuvent présenter des tailles et des formes très variées mais requièrent systématiquement d'être comblées par un matériau fluide ($\eta \sim 0{,}1\text{-}5{,}0$ Pa.s), souvent injecté sous pression jusqu'à la cavité [95]. Le coulis doit ainsi être composé de particules fines afin de limiter sa sédimentation, principalement lors de l'application d'une pression d'injection [96]. Pour les applications nécessitant de combler des interstices de faible taille, les liants cimentaires sont, par exemple, composés exclusivement de particules fines (< 3 mm) et de minéraux argileux, tels que la bentonite, sont utilisés comme charge minérale [97]. Enfin, les coulis sont très souvent associés aux liants cimentaires, mais cela ne correspond pas à leur spécificité. Les coulis cimentaires sont simplement les plus répandus actuellement. Leur formulation est maitrisée et permet l'incorporation d'une importante quantité d'eau et de plastifiant afin de contrôler leurs propriétés rhéologiques [98, 99].

b. Application visée

Dans le cadre du projet Cigéo il est nécessaire de développer un coulis répondant à des spécificités particulières, nommé « matériau de remplissage de l'espace annulaire à l'extrados de l'alvéole de déchets de haute activité » [100]. Ce matériau est développé afin d'être injecté au niveau des alvéoles de stockage des déchets de haute activité (HA), entre l'argilite géologique et le chemisage des déchets. La **Figure 10** représente la coupe d'une alvéole de stockage de déchets HA, où le matériau de remplissage comble l'interstice de quelques centimètres autour du chemisage de l'alvéole.

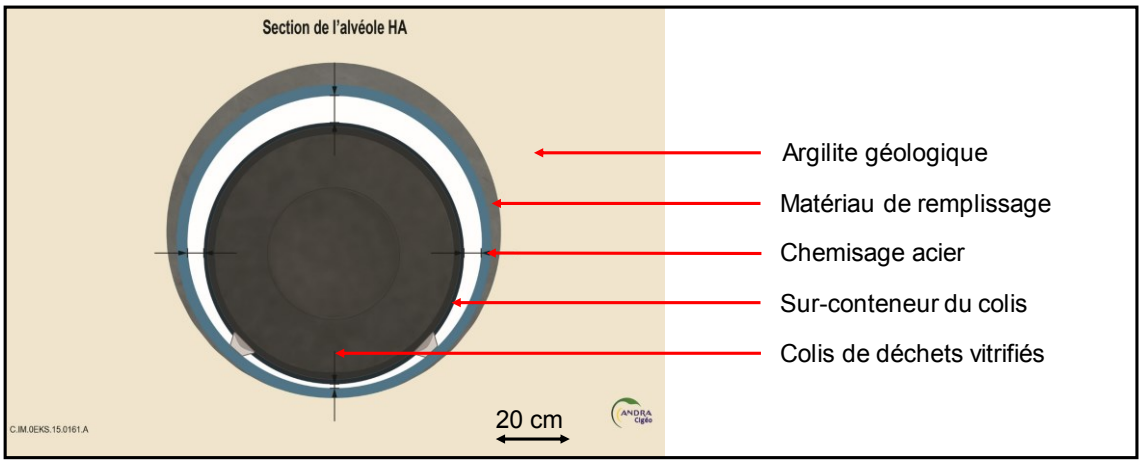


Figure 10. Schéma en coupe de l'alvéole de déchets HA (figure issue de l'Andra).

La position particulière du matériau de remplissage, à la frontière de l'argilite géologique et à quelques centimètres du déchet vitrifié, nécessite une formulation particulière. Le liant doit

ainsi être formulé sans additif organique, contrairement à la quasi-totalité des coulis cimentaires, et être totalement stable jusqu'à 90 °C (température des colis de déchets HA) [101]. Le liant doit également présenter une valeur de pH après consolidation de l'ordre de 10-11, et cela pour plusieurs raisons [82]:

(i) En présence d'air, les pyrites contenues dans l'argilite géologique s'oxydent, ce qui entraîne la formation d'une importante quantité d'acide dans la couche géologique (valeur de pH jusqu'à 4,5). Cette acidité peut engendrer une dissolution des espèces carbonatées (calcite, dolomite) ce qui résulterait en un dégagement gazeux néfaste. Le matériau de remplissage doit donc présenter une basicité suffisante pour la neutralisation l'argilite, mais cependant limitée pour éviter toute dégradation du milieu argileux [82].

(ii) Le matériau de remplissage est prévu pour être positionné en contact direct avec le chemisage en acier de l'alvéole HA. Afin de préserver le chemisage (au moins durant la période d'exploitation de Cigéo), le liant doit présenter une valeur de pH compatible avec la zone de passivation de l'acier (valeur de pH de 9,5-12,5) [102].

(iii) Le coulis n'est séparé du colis vitrifié que par deux couches métalliques et quelques centimètres. Il est donc nécessaire de limiter la réserve alcaline du coulis (et plus généralement de toute l'alvéole HA), afin de limiter le potentiel de dégradation du verre [82].

Du point de vue de la mise en place du coulis d'autres contraintes apparaissent. Pour enrober une seule alvéole HA, une quantité de 20 à 35 m^3 de coulis est nécessaire. Cette préparation sera probablement réalisée à la surface du site de Cigéo, pour être acheminée à 500 m sous terre et être injectée au niveau des alvéoles. Cela nécessitera une DPU importante, idéalement supérieure à 24 heures. De plus, l'injection est prévue pour être effectuée à une pression inférieure à 10 Bars, ce qui limite la gamme de viscosité possible (0,5-5,0 Pa.s).

2. Viscosité et durée pratique d'utilisation

a. Définition de la viscosité

Afin de mieux appréhender la formulation d'un coulis, il est nécessaire de définir la notion de viscosité et de sa mesure. Le terme viscosité fait référence aux capacités d'écoulement d'un fluide sur une surface solide. Pour des raisons de simplicité, la viscosité est souvent définie dans le cadre de l'écoulement d'un plan de fluide sur un autre, symbolisant ainsi les deux surfaces de la couche de fluide. Il est fait l'hypothèse que le plan inférieur est considéré comme immobile et assimilé à la surface solide. La **Figure 11** schématise l'écoulement d'un fluide de surface A

soumis à une force F, où le rapport F / A correspond à la contrainte de cisaillement appliquée sur le fluide. Cette contrainte est définie en fonction d'un plan du fluide caractérisé ici par la hauteur z, vis-à-vis de la surface d'écoulement. Il résulte de cette contrainte l'apparition d'un gradient de vitesse v, lui aussi dépendant de z [103, 104].

La viscosité, η, est la grandeur la plus couramment utilisée pour qualifier la rhéologie d'un fluide. Elle correspond au coefficient reliant la contrainte de cisaillement, appliquée sur le fluide, à son écoulement (**Eq. 1**).

$$\frac{F}{A} = \eta \frac{dv}{dz} \qquad \textbf{Eq. 1}$$

La viscosité ainsi définie, correspondant à un fluide Newtonien, est dite dynamique (ou de cisaillement). Dans le cadre plus commun d'un fluide contenant des molécules ou particules hétérogènes, l'écoulement est différent et correspond à un fluide non Newtonien. Dans ce cas la proportionnalité entre le gradient de vitesse et la contrainte de cisaillement disparait et la viscosité est qualifiée d'apparente. En effet, la viscosité est fonction de la contrainte de cisaillement appliquée ou du temps et non plus d'une constante du fluide [104].

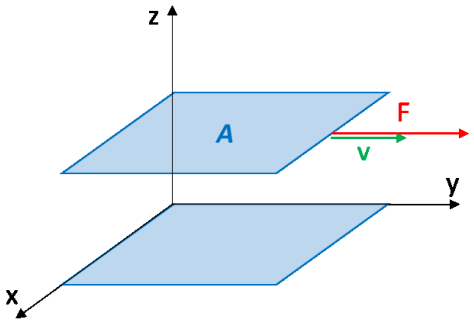


Figure 11. Schéma de l'écoulement d'un plan sur un autre.

Les valeurs de viscosité, paramètres rhéologiques de base, sont usuellement mesurées à l'aide de viscosimètre. Pour la mesure de coulis, de viscosité faible, la méthode la plus simple consiste à utiliser un viscosimètre à rotation, de géométrie de type cylindre [104]. Dans ce cas, un mobile cylindrique est plongé dans le fluide à analyser et mis en rotation à une vitesse, ou une contrainte, imposée. Le couple de torsion et la vitesse de rotation qui résultent du mouvement du mobile dans le fluide, permettent de déterminer la viscosité apparente du fluide [104, 105].

b. Notion de durée pratique d'utilisation

Les mélanges réactifs géopolymères ne sont pas des mélanges simples, puisque les réactions de polycondensation y interviennent très rapidement. En effet, ils présentent une importante réactivité qui entraîne l'augmentation progressive de la viscosité en fonction de l'évolution des

réactions de polycondensation et de géopolymérisation [106, 107, 108]. Afin de caractériser la viscosité d'un mélange réactif, il est donc indispensable d'associer la valeur mesurée à une durée de vieillissement, ou mieux de suivre l'évolution de la viscosité au cours du temps [109].

Dans le cadre du développement d'un coulis, les deux paramètres caractérisés sont la viscosité initiale et la durée pratique d'utilisation (DPU). Celle-ci correspond à la durée pendant laquelle la viscosité reste assez faible pour utiliser le coulis [110, 111]. La viscosité initiale correspond donc à la viscosité du liant durant toute la DPU. Elle peut être exprimée par la viscosité moyenne observée ou juste par la viscosité maximale observée (valeur maximale requise pour chaque étude) [75]. A titre d'exemple, la **Figure 12** présente l'évolution de la viscosité d'un mélange réactif de géopolymère potassique. La viscosité reste constante (0,2 Pa.s) durant 325 min, augmente progressivement durant 125 min puis augmente drastiquement jusqu'à la consolidation totale du liant. Afin de déterminer la DPU, la méthode des tangentes est couramment utilisée et conduit ici à une valeur de DPU de 450 min, avec une viscosité moyenne de l'ordre de 0,4 Pa.s et maximale de 1,0 Pa.s [75, 109].

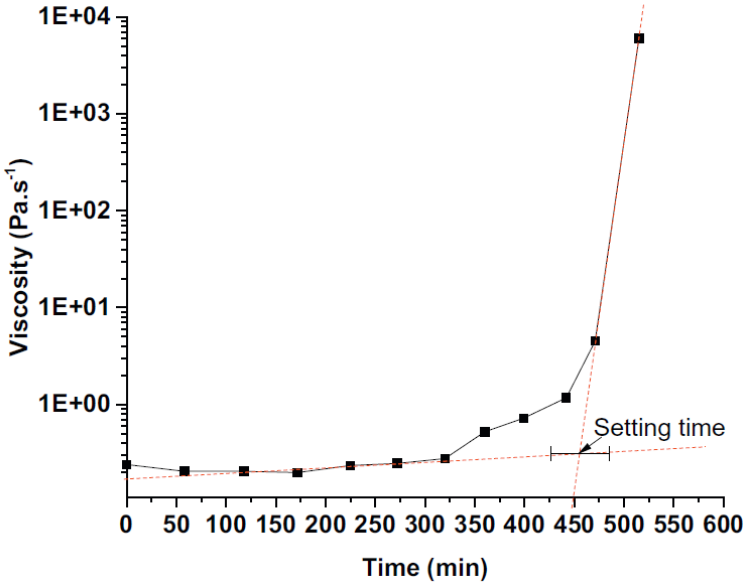


Figure 12. Courbe montrant l'évolution de la viscosité d'un mélange réactif géopolymère au cours du temps (figure issue de l'article de M. Arnoult *et al.* [75]).

3. Rôle des additifs

a. Généralités

Afin de contrôler à la fois la viscosité et la DPU d'un liant géopolymère, il est nécessaire de modifier la formulation du liant. La nature de la solution alcaline silicatée influence la viscosité et la DPU. Il faut donc prendre en compte la nature du cation alcalin, sa concentration

ainsi que le taux d'eau présent dans la solution alcaline silicatée [112, 113]. La réactivité de la source aluminosilicatée doit aussi être contrôlée, principalement par l'optimisation du taux de métakaolinite et de la concentration en atomes d'aluminium [114].

Afin d'adapter la solution alcaline silicatée pour obtenir une valeur de DPU plus élevée et limiter la viscosité du mélange réactif, il faut tout d'abord choisir le cation alcalin. En effet, une solution à base de cations potassium induit une viscosité plus faible et une valeur de DPU supérieure à celles observées en présence de cations sodium [79]. A. Poulesquen *et al.* ont mis en évidence que l'utilisation d'une solution à base de sodium accélérait la dissolution du métakaolin ainsi que la formation des oligomères, ce qui entraînait une prise plus rapide, associée à une valeur de DPU inférieure [80]. K. Vance *et al.* ont mis en évidence que la diminution du rapport Si/M conduit à une diminution de la viscosité, qui atteint une valeur minimale pour un rapport Si/M compris entre 0,50 et 1,00 (**Figure 13.A**) [115]. Cependant N.K. Lee *et al.* ont également montré que l'accroissement de la concentration en alcalin, de 4 à 8 mol/L, entraîne une diminution drastique de la DPU, de 160 à 50 min (**Figure 13.B**) [116] en accord avec les résultats de M.B. Karakok *et al.* [112] Ainsi l'augmentation de la concentration en alcalin conduit à une diminution de la valeur de DPU, et à une augmentation de la viscosité.

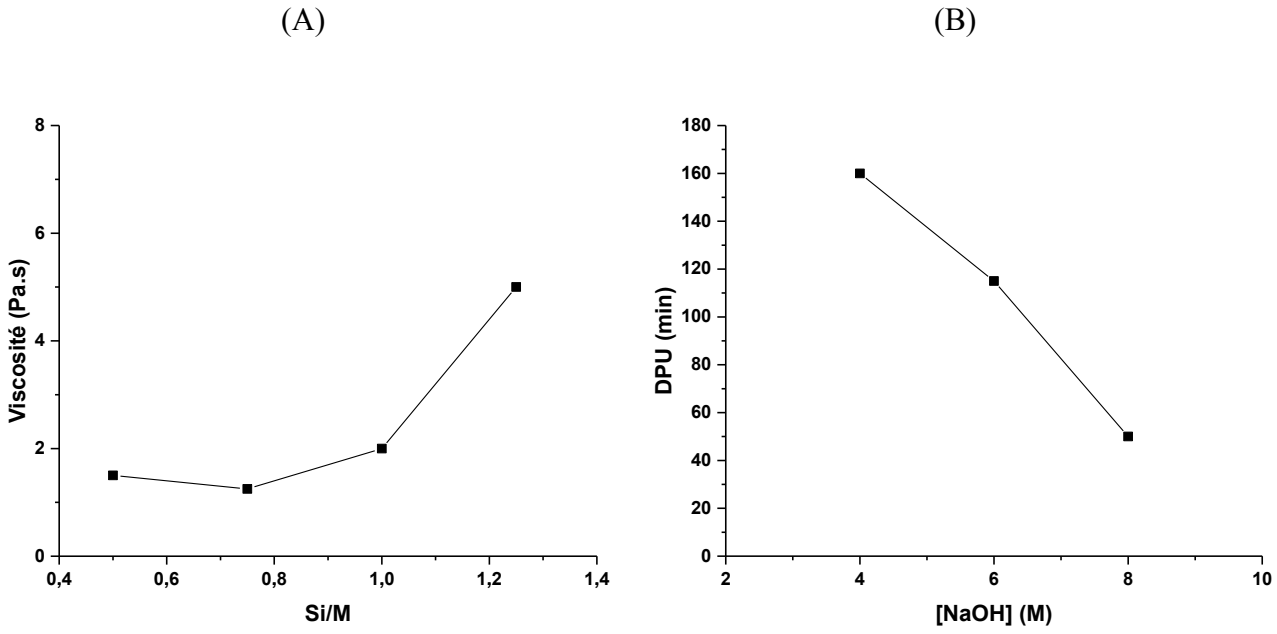


Figure 13. Evolution de **(A)** la viscosité du géopolymère en fonction du rapport Si/K_2O de la solution alcaline silicatée et de **(B)** la DPU du géopolymère en fonction de la concentration en hydroxyde de sodium utilisée lors de la préparation de la solution alcaline silicatée (données issues des articles de K. Vance *et al.* et H.K. Lee *et al.* [115, 116]).

Le contrôle de la source aluminosilicatée est aussi déterminant pour optimiser ces valeurs de DPU et de viscosité. Le paramètre clé pour le contrôle de la viscosité est la charge en matière, caractérisée par le rapport de la masse de solution alcaline silicatée sur la masse de source aluminosilicatée (l/s). L'augmentation du rapport l/s conduit à une diminution de la viscosité du mélange réactif et à un accroissement de la DPU (**Figure 14.A**) [101, 110, 117]. Ces variations s'expliquent par l'augmentation de la quantité d'eau disponible, fluidifiant les mélanges [118]. De plus, la nature de la source aluminosilicatée a un impact direct sur les valeurs de DPU (**Figure 14.B**). En effet, l'utilisation de coproduits industriels, tels que les scories de fonderies ou les cendres volantes, comme source aluminosilicatée est très répandue mais conduit à des réactions différentes au sein des mélanges réactifs [119]. Ainsi K. Hemra *et al.* et I. Perna *et al.* ont respectivement mis en évidence que l'incorporation de 50 % de cendres volantes réduit la DPU de 190 à 25 min et que l'introduction de 33 % de scories induit une diminution de 720 à 120 min [120, 121]. Ces évolutions sont liées à l'augmentation de la quantité d'espèces à base de calcium, qui conduisent à la précipitation rapide de phases intermédiaires [37]. De plus, cette augmentation se fait au détriment de la quantité d'aluminosilicate et d'aluminium réactif, limitant la quantité de réseau formé [114].

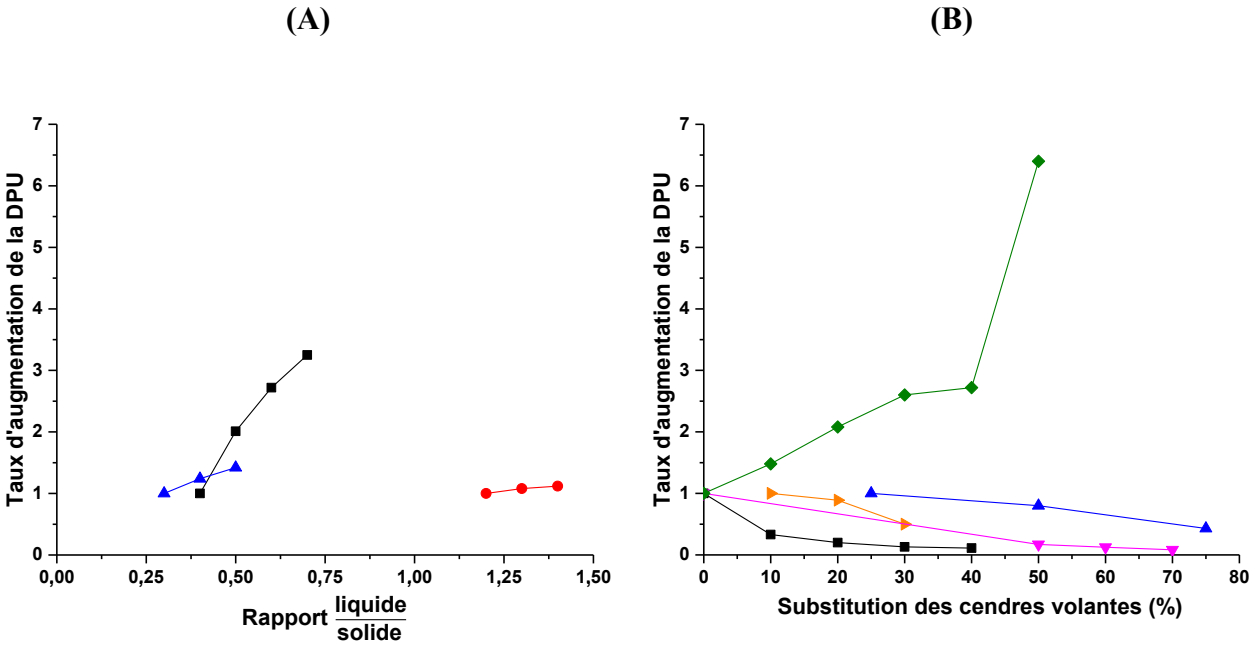


Figure 14. Taux d'augmentation de la DPU ($DPU_{finale}/DPU_{initiale}$) en fonction **(A)** du rapport l/s de mélanges réactifs à base de (■, ▲) cendres volantes et scories et (●) perlite et **(B)** du taux de substitution de cendres volantes par des scories (■, ▲, ▶), du métakaolin (◆) et par des mélanges scories-argiles (▼) (valeurs issues des différents articles (■) [122], (●) [110], (▲) [123], (▶) [116], (▼) [121] et (◆) [120]).

Afin d'obtenir la valeur de DPU visée, il est nécessaire de contrôler la concentration en alcalin, le rapport l/s ainsi que la nature de la source aluminosilicatée.

b. Utilisation d'additifs inorganiques

Le cahier des charges de l'Andra limite l'usage des composés organiques au niveau des alvéoles HA, ce qui exclut l'utilisation des plastifiants couramment utilisés lors de la formulation de liants [107, 124]. Les additifs inorganiques pouvant influer sur la DPU ont été peu étudiés dans la littérature. Certaines études ont néanmoins mis en évidence l'efficacité de certains additifs dans des mélanges réactifs à base de cendres volantes ou de scories de fonderies, contenant un fort taux de calcium (présentant un temps de prise extrêmement faible) [125]. La **Figure 15** regroupe les différentes de valeurs de DPU issues de la littérature.

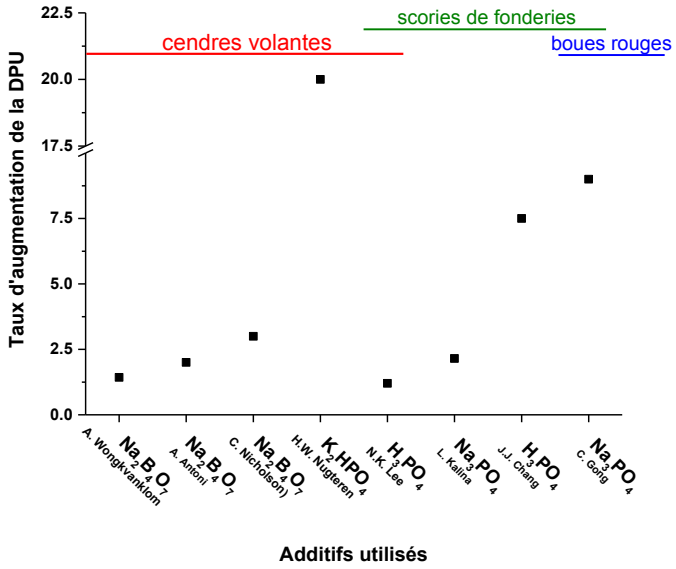


Figure 15. Taux d'augmentation de la DPU ($DPU_{finale}/DPU_{initiale}$) en fonction de la nature de la source aluminosilicatée utilisée (valeurs provenant des différents articles [116, 125, 126, 127, 129, 130, 131, 132]).

Parmi ces additifs, le tétraborate de sodium ($Na_2B_4O_7$) permet d'augmenter significativement le temps de prise [128]. D'après A. Antoni *et al.*, l'ajout de 5 $\%_{mass}$ de tétraborate de sodium dans la solution alcaline permet d'obtenir une forte augmentation du temps de prise (de 45 à 90 min) sans dégradation des propriétés mécaniques (σ~85 MPa avec et sans $Na_2B_4O_7$) [125]. Une augmentation de la DPU en présence de tétraborate de sodium, de 400 à 560 min, a été ainsi identifiée par Wongkvanklom *et al.* et attribuée à la faible réactivité des atomes de bore lors des réactions de polycondensation [129]. Lors de la synthèse de

borosilicate alcalinement activé, de l'acide borique a aussi pu être utilisé comme précurseur. Il est supposé que son usage conduit aux même interactions entre le bore et les réactions de polycondensation, résultant en une augmentation de la DPU [92].

Les principaux autres additifs inorganiques permettant une augmentation de la DPU, sont à base de composés phosphatés. Ainsi C. Gong *et al.* ont mis en évidence un effet retardant du composé Na_3PO_4, qui peut augmenter la DPU d'un facteur 8 [130]. Ce retard de consolidation est lié à la présence d'une importante quantité d'atomes de calcium dans la source minérale. En effet, ceux-ci peuvent réagir pour former des phosphates de calcium, limitant les réactions de polycondensation par la formation d'un gel [131]. L'utilisation d'acide phosphorique conduit également à de fortes augmentations de la valeur de DPU, comprises entre 200 et 400 % [127, 116]. Dans ces mélanges, le calcium présent en solution réagit avec les ions phosphates et forme le composé $Ca_3(PO_4)_2$, qui perturbe ensuite les différentes réactions et ralentit la consolidation [116]. D'après H.W. Nugteren *et al.*, l'hydrogènophosphate de potassium (K_2HPO_4) permet lui aussi de retarder la consolidation des mélanges réactifs (de 15 min à 5 h) [132]. Cette augmentation de la DPU peut s'expliquer par la formation de phase apatitique, avec le calcium présent dans le mélange, qui perturbe la géopolymérisation [132].

L'ajout d'additifs peut induire des modifications des réactions de polycondensation, ou la formation de composés secondaires, pouvant inhiber les différentes réactions de consolidation.

V. LA STRUCTURE DES ALUMINOSILICATES AMORPHES

Afin de comprendre l'impact des additifs sur la formation du réseau géopolymère, il est nécessaire d'étudier la structure des géopolymères mais aussi celles des verres silicatés. En effet, ceux-ci peuvent être synthétisés à partir d'alcalins modificateurs et de cations formateurs de verre tels que le phosphore et le bore. Il peut donc être supposé que certaines similitudes existent entre ces matériaux et les géopolymères en présence d'additifs.

1. Structure des verres silicatés

Les géopolymères sont basés sur un réseau tridimensionnel de tétraèdres de silicium et d'aluminium avec la présence de cations alcalins pour compenser les charges dans la structure [22]. Cette structure est donc proche de celle des verres silicatés, contenant généralement une fraction d'alcalin (sodium) ou d'alcalino-terreux (calcium) [133]. En effet, les verres oxydes

peuvent ainsi présenter une large plage de composition chimique que W.H. Zachariasen a divisé en trois catégories [134].

(i) Les cations formateurs de réseaux, qui forment la base du réseau vitreux. Ces atomes sont sous forme de polyèdres (centrés sur le cation formateur) connectés par les atomes d'oxygène (majoritairement pontants) localisés au niveau des sommets [135]. Ces cations, de coordinence III et IV, proviennent des oxydes SiO_2, GeO_2, B_2O_3, As_2O_3 et P_2O_5 [136, 137].

(ii) Les cations modificateurs de réseaux, dont la présence conduit usuellement à une dépolymérisation du réseau formé par les cations formateurs [138]. En effet, ces cations modificateurs sont des alcalins ou alcalino-terreux, de degrés d'hydratation IV ou VIII, qui viennent rompre les ponts entre les différents cations formateurs [136]. Il en résulte des atomes d'oxygène non-pontants, chargés négativement, compensés par les cations modificateurs [137]. Cette dépolymérisation entraîne une diminution des températures de fusion facilitant la synthèse de certaines compositions vitreuses [133, 139].

(iii) Les cations intermédiaires correspondent aux cations pouvant, selon les cas, agir comme formateurs ou modificateurs de réseaux [136]. Ils correspondent à des atomes pouvant présenter une coordinence IV (formateur) ou supérieure, VI (modificateur), tels que les atomes d'aluminium, de fer, de titane ou de zinc [135, 137].

2. Les verres borosilicatés

Les verres borosilicatés présentent une structure basée sur des atomes de silicium et de bore (en coordinence III et IV) pontés par des atomes d'oxygène [137]. Cependant, contrairement à ceux de la plupart des cations formateurs, les réseaux à base d'atome de bore ne sont pas systématiquement dépolymérisés en présence de cations modificateurs. Comme l'illustre la **Figure 16**, l'incorporation de cations alcalins dans un verre borosilicaté conduit à l'augmentation de la quantité de bore en coordinence IV [137]. P.J. Bray *et al.* ont décrit cette augmentation par le taux de N_4 (quantité de $B^{[4]}/(B^{[4]}+B^{[3]})$, usuellement quantifié par RMN [140]. Cette formation de $B^{[4]}$ augmente en fonction de la quantité d'alcalin, jusqu'à un maximum (obtenu pour un rapport alcalin/bore ~0,5) et présente un taux de N_4 maximal si la taille du cation alcalin est faible [141, 142]. De plus, l'augmentation du nombre de $B^{[4]}$ conduit à une augmentation du nombre d'atomes d'oxygène non-pontants (NBO) liés au bore et au silicium [138, 143]. Cette augmentation requiert alors une quantité importante de cations afin d'équilibrer les charges du réseau. Les atomes de bore en coordinence III présents dans les verres borosilicatés peuvent être de deux types [136].

(i) Les atomes de $B^{[3]}$ symétriques, définis par le taux N_{3A} ($N_{3A}= B^{[3]}_{sym} / (B^{[3]}+ B^{[4]})$)

(ii) Les atomes de $B^{[3]}$ asymétriques, définis par le taux N_{3S} ($N_{3S}= B^{[3]}_{asym} / (B^{[3]}+ B^{[4]})$).

En effet, les atomes de $B^{[3]}$ sont usuellement organisés symétriquement sous forme d'anneaux [144]. Ceux-ci sont typiquement formés à partir de 3 ou 5 atomes de bore, dont un ou plusieurs de ces atomes peuvent être en coordinence IV [136]. Les autres atomes de $B^{[3]}$, asymétriques, présentent une structure moins régulière ainsi qu'une quantité de NBO supérieure [140]. Cependant, au sein des structures symétriques les atomes de $B^{[3]}$ possèdent 0 ou 3 NBO [144].

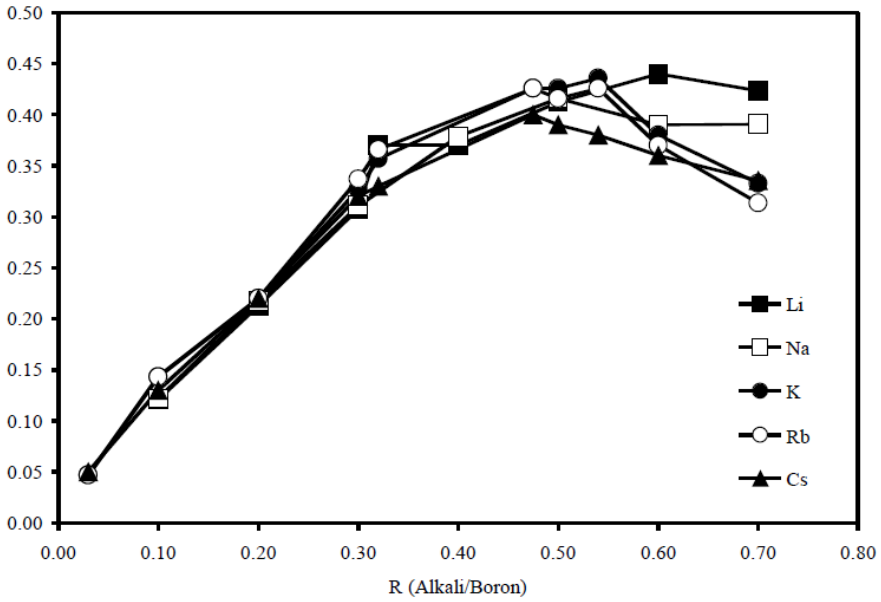


Figure 16. Evolution du taux de N_4 en fonction du rapport molaire alcalins/bore introduit dans la composition vitreuse (figure issue de l'article de S. Kroeker *et al.* [141]).

Afin d'identifier la connectivité du bore et du silicium, la méthode la plus utilisée est la spectroscopie RMN. L'identification des liaisons avec la RMN du ^{29}Si est possible dans le cas des borosilicates. Cependant, en présence d'aluminium, il n'est pas possible de distinguer les liaisons Si-O-Al des liaisons Si-O-B [145]. Dans le cadre de l'étude de géopolymères en présence de bore, la RMN du ^{11}B est donc privilégiée. La **Figure 17** présente un spectre de RMN du ^{11}B dans lequel deux zones sont identifiables. Entre 20 et 5 ppm, un large pic contient deux contributions de $B^{[3]}$, qui sont respectivement attribuées aux atomes de $B^{[3]}$ symétriques (15 ppm) et asymétriques (10 ppm) [146]. K.J.D Mackenzie a aussi identifié, vers 5 ppm, une contribution liée à des atomes de $B^{[3]}$ asymétriques présentant un atome d'oxygène non-pontant [54]. La zone centrée à 0 ppm est associée aux atomes de $B^{[4]}$ et L.S. Du *et al.* ont montré qu'il était possible d'identifier la connectivité entre les atomes de bore et de silicium dans cette zone

[147]. Les contributions des atomes de $B^{[4]}$ liés à 2, 3 ou 4 atomes de Si sont ainsi visibles à environ 2, 0 et -2 ppm respectivement [146].

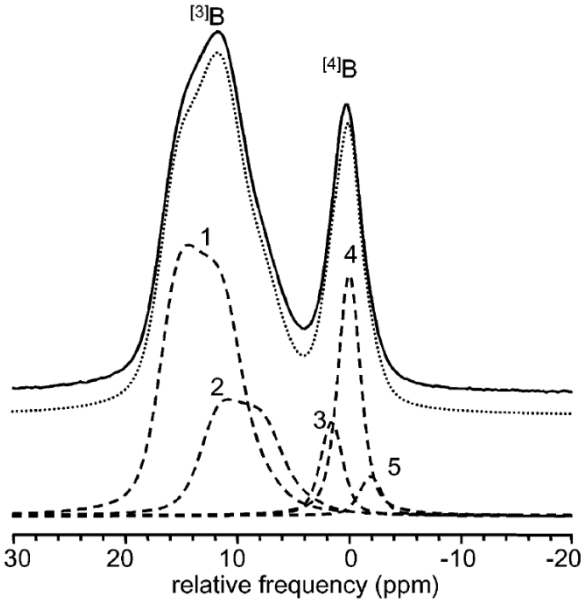


Figure 17. Spectre RMN du ^{11}B décomposé en cinq contributions associées à des atomes de (1) $B^{[3]}$ sous forme symétrique, (2) $B^{[3]}$ sous forme asymétrique, (3) $B^{[4]}$ lié à 2 atomes de Si, (4) $B^{[4]}$ lié à 3 atomes de Si et (5) $B^{[4]}$ lié à 4 atomes de Si (figure issue de l'article de L.S. Du *et al.* [146]).

Les verres borosilicatés sont composés d'un mélange d'atomes de bore en coordinence III et IV, avec notamment des environnements symétrique ou asymétrique pour les atomes de $B^{[3]}$.

3. Les verres phosphoaluminosilicatés

Les verres de phosphates sont composés de tétraèdres de phosphore dont la liaison avec l'un des atomes d'oxygène est double [148]. Au sein d'un réseau vitreux, ces tétraèdres peuvent présenter jusqu'à trois atomes d'oxygène pontants [54]. Ils sont ainsi définis comme les orthophosphates (PO_4^{3-}, Q^0, isolés), les pyrophosphates ($P_2O_7^{4-}$, Q^1, isolés), les polyphosphates (PO_4^{3-}, Q^2, chaines) ou cyclophosphates (PO_4^{3-}, Q^2, anneaux) et les ultraphosphates (PO_4^{3-}, Q^3, structure tridimensionnelle) [149, 150]. Au sein des compositions vitreuses, le phosphore est généralement associé à des cations alcalins/alcalino-terreux, de l'aluminium, du fluor, du bore ou des aluminosilicates [151].

Les verres phosphoaluminosilicatés sont ceux qui se rapprochent le plus des matériaux géopolymères. Au sein de ces verres, les atomes de phosphore forment préférentiellement un

réseau avec les atomes d'aluminium disponibles, et n'interagissent pas avec les atomes de silicium [152]. Ainsi les atomes d'aluminium, quelle que soit leur coordinence, se lient avec les différentes entités de phosphate, mais le taux de liaisons Al-O-P dépend des taux d'introduction respectif d'aluminium et de phosphore [153, 154]. L'ajout de cation alcalin, le plus couramment du sodium, entraîne une dépolymérisation du système et favorise la présence d'atomes de phosphore Q^1 et Q^2 [151]. Cette présence de cation alcalin peut cependant conduire à la formation de liaisons entre les atomes de silicium et d'aluminium [155]. La structure des verres phosphoaluminosilicatés résulte donc en un réseau aluminophosphaté, où les tétraèdres de phosphore et d'aluminium sont fortement connectés. La formation de ce réseau nécessite une importante quantité d'alcalin pour la compensation de charge, ce qui résulte en l'augmentation de la polymérisation du réseau silicaté [152].

De manière à caractériser les différents réseaux présents dans ces verres, la RMN est couramment utilisée. En effet, l'étude des spectres de la RMN du ^{31}P permet d'identifier le nombre d'atomes d'oxygène pontants pour chaque atome de phosphore : Q^0 (de 12 à -7 ppm), Q^1 (de 6 à -20 ppm), Q^2 (de -18 à -25 ppm) et Q^3 (de -32 à -47 ppm) (**Figure 18.A**) [54, 156]. L'étude de la position précise de chaque contribution permet d'identifier la nature des espèces liées aux atomes de phosphore. Par exemple, les atomes de phosphore Q^1 peuvent présenter une contribution à 5,5, 4,0 ou 1,1 ppm selon qu'ils soient liés à des atomes d'aluminium, de silicium ou de phosphore [154, 157, 158]. La connectivité entre les atomes d'aluminium et de phosphore peut aussi être observée avec la RMN du ^{27}Al (**Figure 18.B**) [157]. En effet, les contributions d'$Al^{[4]}$, $Al^{[5]}$ et $Al^{[6]}$ sont respectivement à environ 58, 30 et 0 ppm dans les structures aluminosilicatées [54]. Mais lorsque l'aluminium est lié à du phosphore, ces contributions se décalent à 47, 14 et -13 ppm [159, 160].

Les verres phosphoaluminosilicatés présentent différents réseaux, à base de phosphore-aluminium et d'aluminium-silicium, avec peu d'interactions phosphore-silicium.

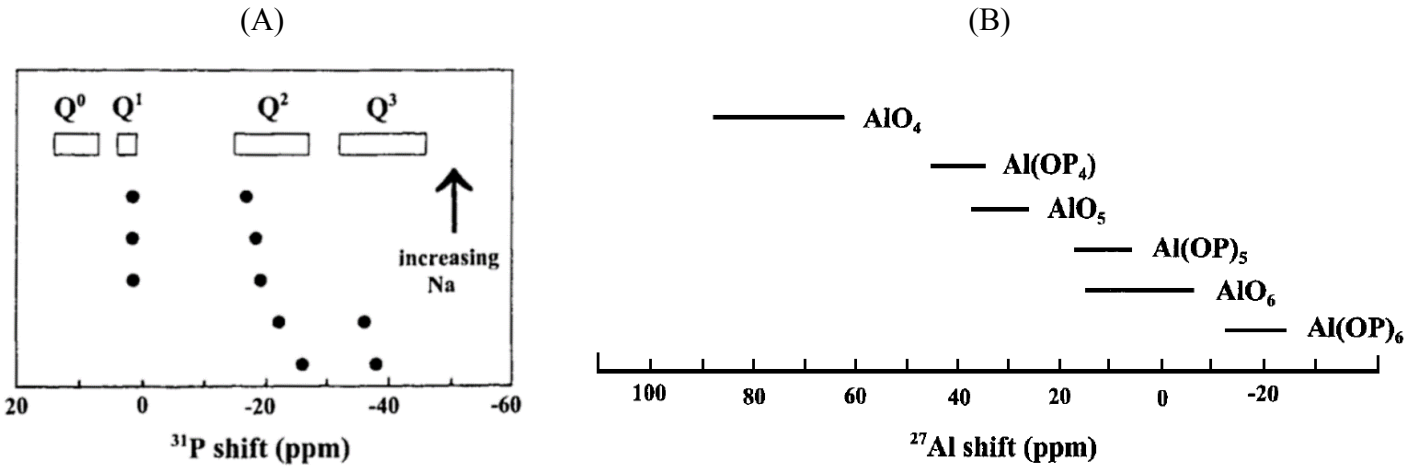


Figure 18. Position des contributions RMN **(A)** des espèces Q^0, Q^1, Q^2 et Q^3 du ^{31}P, en fonction de la quantité de sodium présent dans un verre de phosphate et **(B)** du ^{27}Al lié ou non à des atomes de phosphore (figures issues des articles de R.K. Brow *et al.* [156] et K.J.D Mackenzie [54]).

VI. L'OBJECTIF DE L'ETUDE

L'objectif de cette thèse est de valoriser les argilites du Callovo-Oxfordien (excavées lors de la mise en place et du fonctionnement de Cigéo) sous forme d'un coulis injectable pouvant être utilisé au sein du site de Cigéo. Le coulis ainsi développé doit présenter une viscosité modérée (0,5-5,0 Pa.s), une durée pratique d'utilisation élevée (> 24 heures) et une valeur de pH après consolidation comprise entre 10 et 11. Afin d'atteindre ces spécificités, une valorisation sous forme de liant alcalinement activé a été envisagée. Le développement de ce liant à base d'argilites, s'est organisé selon trois axes d'étude :

(i) Déterminer les évolutions structurales des argilites lors du traitement thermique et lors de l'activation alcaline des argilites du Callovo-Oxfordien.

(ii) Comprendre l'effet des différents additifs sur un géopolymère de référence afin d'optimiser sa valeur de pH et sa durée pratique d'utilisation.

(iii) Valider la formulation finale du liant (à partir d'argilite, de métakaolin et d'additif inorganique), au vu de ses propriétés d'usage et de sa structure.

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CHAPITRE II

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I. INTRODUCTION

Ce chapitre introduit les différentes matières premières utilisées, les protocoles expérimentaux associés à la fonctionnalisation de l'argilite, la synthèse des matériaux de type géopolymère ainsi que les traitements thermiques des échantillons consolidés. Il décrit aussi les techniques de caractérisation physico-chimiques, structurales, microstructurales et thermiques employées, ainsi que les méthodes d'évaluation des propriétés d'usage et d'analyse de données mises en œuvre.

II. MATIERES PREMIERES UTILISEES

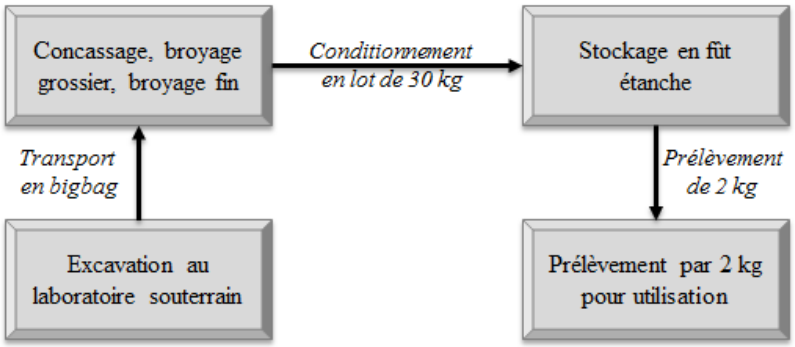
1. Sources minérales

Le **Tableau 1** regroupe les caractéristiques des différentes sources minérales utilisées au cours de ces travaux.

Les argilites du Callovo-Oxfordien et le métakaolin M1000 sont utilisés comme sources aluminosilicatées pour la synthèse des matériaux alcali-activés. Les argilites proviennent de la couche UA2 [1] du laboratoire souterrain[1] de l'Andra[2] et le **Schéma 1.** résume les différentes étapes de conditionnement et de préparation des argilites [2]. Par ailleurs, dans le but d'accroître leur réactivité, en vue d'une activation alcaline, ces argilites ont subi différents traitements thermiques détaillés en partie **III.1** (les évolutions résultantes de ces traitements seront développées dans le **Chapitre III**).

Le sablon et la chamotte sont employés comme renfort minéral inerte dans la formulation des matériaux alcalinement activés.

Schéma 1. Etapes du traitement et conditionnement de l'argilite.



[1] Commune de Bure, Meuse/Haute-Marne, France
[2] Agence nationale pour la gestion des déchets radioactifs, 92298 Châtenay-Malabry, France.

Plusieurs additifs minéraux sont utilisés dans les différentes formulations et leurs caractéristiques sont regroupées dans le **Tableau 2.**

Tableau 1. Caractéristiques des sources minérales.

Nom	Abréviation	Fournisseur	d_{50} (µm)	S_{BET} (m^2/g)	Composition ($\%_{mass}$)
Argilites du Callovo-Oxfordien	A25	Andra[2]	17	38	SiO_2 : 57,1 Al_2O_3 : 15,7 CaO : 12,6
Métakaolin M1000	M1	Argical[3]	6	17	SiO_2 : 55,0 Al_2O_3 : 40,0
Sablon	Sd	Argeco[4]	190	6	SiO_2 : 95,6 $CaCO_3$: 4,6
Chamotte	Cc	Argical[3]	180	1	SiO_2 : 56,7 Al_2O_3 : 38,5

Tableau 2. Données relatives aux additifs minéraux utilisés.

Nom	Abréviation	Formule chimique	Fournisseur	Pureté ($\%_{mass}$)
Hydrogénophosphate de potassium	KP	K_2HPO_4	Acros-Organics[5]	99,0
Acide ortho phosphorique	P	H_3PO_4	VWR Chemicals[6]	85,0
Tétraborate de sodium	NaB	$Na_2B_4O_7$, 10 H_2O	Alfa Aesar[7]	99,0
Tétraborate de lithium amorphe	LiB	$Li_2B_4O_7$	Claisse[8]	99,5
Tétraborate de lithium cristallisé	LiB_{cr}	$Li_2B_4O_7$	Sigma-Aldrich[9]	98,0
Acide borique	B	H_3BO_3	Acros-Organics[5]	99,0
Colémanite	CaB	$Ca_2B_6O_{11}$, 5 H_2O	Ceradel[10]	76,2

[3] Imerys AGS, F-17270 Clérac, France.
[4] Argeco Développement, 47500 Fumel, France.
[5] Acros-Organics, Thermo Fisher Scientific, Geel, Belgique.
[6] VWR, F-94126, Fontenay sous-bois, France.
[7] Alfa Aesar, Haverhill, Massacchusetts, USA.
[8] Claisse, Malverne Panalytical, Malvern WR14 1XZ, United Kingdom.
[9] Sigma-Aldrich, Saint-Louis, Missouri, USA.
[10] Céradel, ZA du Prouet, Panazol, France.

2. Solutions alcalines silicatées

Les solutions alcalines silicatées employées sont préparées à partir de quatre solutions commerciales et de deux hydroxydes alcalins. Les données relatives à ces précurseurs sont regroupées dans le **Tableau 3**. Les solutions sont préparées par dissolution de l'hydroxyde alcalin (MOH, où M = Na ou K) dans la solution alcaline silicatée commerciale (S1, S2, S3 ou S4). Usuellement l'hydroxyde alcalin utilisé correspond à l'alcalin présent dans la solution. Dans le cas contraire, ou en présence de la solution mixte S4, il est nécessaire de préciser la nature de l'hydroxyde alcalin utilisé (voir partie **III.4**).

Tableau 3. Données relatives aux solutions de silicates et aux hydroxydes alcalins.

Nature	Abréviation	Fournisseur	Taux d'eau ($\%_{mass}$)	Masse volumique (g / cm^3)	Pureté ($\%_{mass}$)	Si/M (M = Na et/ou K)
Silicate de sodium	S2	Woellner[11]	64,2	1,36		1,70
Silicate de potassium	S1		76,0	1,18		1,70
	S3		59,4	1,51		0,67
Silicate mixte sodium-potassium	S4		62,0	1,38		1,79
Hydroxyde de potassium	KOH	Sigma-Aldrich[9]			97,0	
Hydroxyde de sodium	NaOH				85,2	

III. PROTOCOLES EXPERIMENTAUX

1. Protocole de préparation des argilites

Les argilites du Callovo-Oxfordien sont tout d'abord préparées par une succession de trois traitements mécaniques : un concassage grossier (d_{50} < 5 cm), un broyage fin (d_{50} < 1 mm) et un broyage très fin (d_{50} < 100 µm). Ces trois traitements sont effectués sur l'intégralité du lot d'argilite sélectionné, sans fractionnement. Ceux-ci sont mis en œuvre après séchage à 40 °C du minerai, à l'aide d'un broyeur à mâchoires produit par Fritsch, puis d'un broyeur à pâles produit par Retsch et enfin d'un broyeur à billes (Φ = 4 cm).

[11] Woellner GmbH, Wöllnerstraße 26, D-67065 Ludwigshafen, Germany

Les argilites sont ensuite calcinées à des températures comprises entre 600 et 800 °C selon trois procédés différents dont les cycles thermiques sont présentés dans la **Figure 1.**

- La calcination en four statique s'effectue sous air par lot de 110 grammes dans une gazette réfractaire (lit de poudre de moins de 10 mm) (**Figure 1**).
- Le traitement en four rotatif est réalisé par lot de 700 grammes dans une cuve cylindrique, remplie à 25-30 %, maintenue en rotation (**Figure 1**).
- Le procédé flash[4] correspond à une calcination en continu, où la poudre est mise en mouvement par flux d'air et n'est exposée à la température cible (de 600 à 750 °C) qu'une fraction de seconde, conduisant à un cycle thermique très court (**Figure 1**).

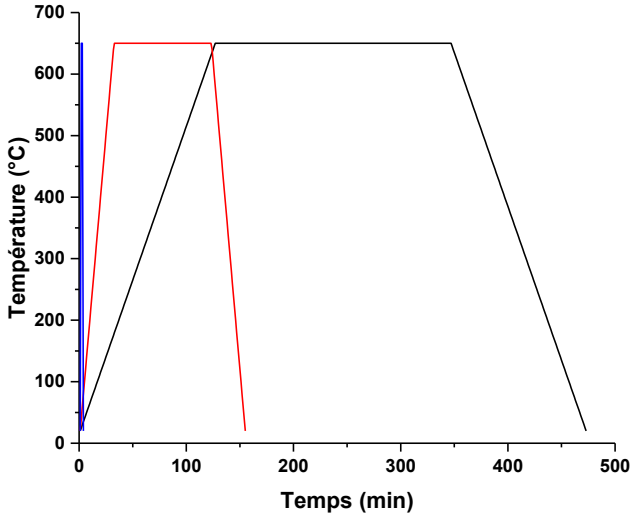


Figure 1. Cycles thermiques utilisés lors des calcinations à 650 °C en (—) four statique, (—) four rotatif et (—) four flash.

2. Protocole de synthèse des liants

Le protocole d'activation alcaline est présenté dans la **Figure 2.** Il consiste à malaxer la solution alcaline silicatée et la source aluminosilicatée (composée d'une ou d'un mélange de plusieurs sources) afin d'obtenir le mélange réactif. Si nécessaire, le ou les additifs sont incorporés dans le mélange réactif au cours du malaxage. Il est ensuite possible de couler le mélange réactif qui est conservé à température ambiante jusqu'à consolidation.

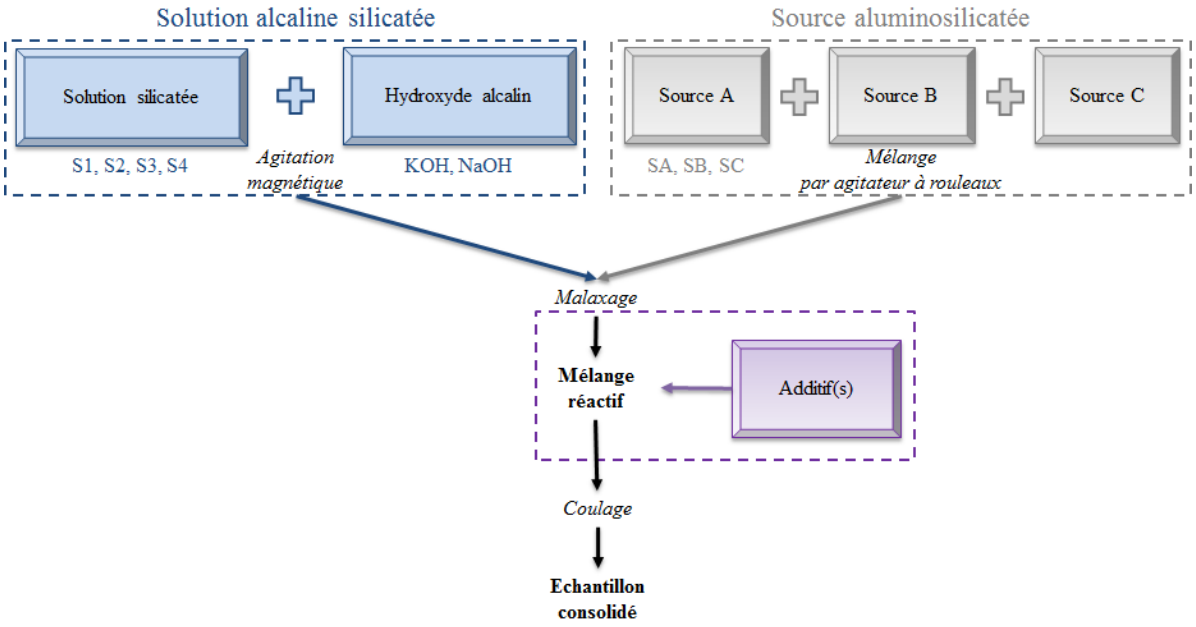


Figure 2. Protocole de préparation des différents échantillons.

3. Protocole de coulage d'échantillons au sein de bloc d'argilites

Afin de caractériser les interactions entre ces nouveaux liants et le milieu argileux, des essais de coulage dans des blocs d'argilites de Bure ont été réalisés.

Le **schéma 2** représente les différentes étapes de préparation des échantillons de liants coulés dans de l'argilite massive. Pour cela, des blocs d'argilites (Φ = 300 mm et H = 150 mm) fournis par l'Andra sont carottés (Φ = 30 mm et H = 80 mm). Les liants sont ensuite injectés à l'aide d'une pompe péristaltique au fond de ces réservations afin de les combler intégralement (a), ou d'enrober un cylindre (en géopolymère) symbolisant un élément qui serait mis en place *in situ* (b). Les échantillons sont ensuite conservés durant une durée variable (95 % HR et 20 °C).

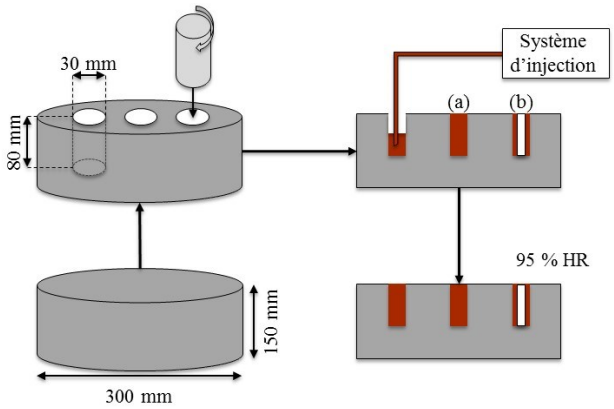


Schéma 2. Protocole de coulage de liants alcalinement activés dans un bloc d'argilites.

4. Protocoles de traitement thermique des échantillons consolidés

Des traitements thermiques à 800 °C sont effectués sur une partie des échantillons consolidés (après sept jours de consolidation à 20 °C et 95 % HR) afin d'étudier leur résistance thermique et les évolutions structurales induites par un flux thermique. Pour cela deux types de test sont mis en œuvre : une augmentation progressive de la température (1 °C/min) (**Figure 3**) et une exposition immédiate à 800 °C à l'aide d'un four ascenseur (**Figure 3**).

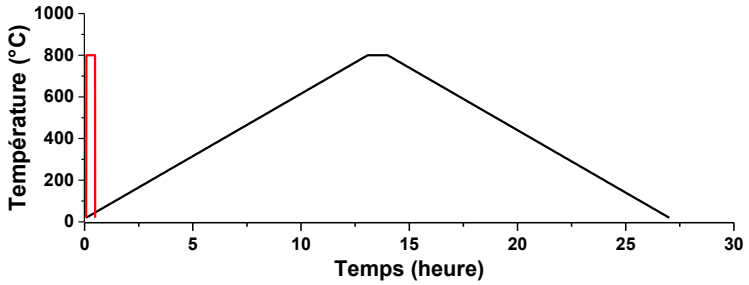


Figure 3. Protocoles de traitement thermique d'échantillons consolidés par (—) calcination classique et (—) choc thermique.

5. Nomenclature

Au cours de ce travail deux nomenclatures ont été utilisées et décrites dans le **Tableau 4.** La première décrit les solutions de silicates alcalins et la seconde la composition des différents mélanges réactifs. Dans le **Chapitre III**, pour plus de lisibilité, les nomenclatures utilisées pourront être simplifiées, dans ce cas les modifications seront précisées en en-tête de partie.

Tableau 4. Nomenclature décrivant les principaux échantillons.

Echantillonnage	Nomenclature
Solutions alcalines silicatées	S_M^r
Mélanges réactifs	$S_L SA_{1-x-y} SB_x SC_y^r \, Ad^{\%}$

Les codes utilisés correspondent à :

S : la solution alcaline silicatée commerciale (S1, S2, S3 et S4).

M : le cation alcalin (K, Na) ajouté sous forme d'hydroxyde.

r : le *ratio* Si/M, caractéristique de la quantité d'hydroxyde alcalin ajoutée.

L : le rapport solide sur liquide du mélange réactif.

SA, SB, SC : les sources aluminosilicatées.

x, y : respectivement, les taux d'insertion de source B et C.

Ad : le ou les additifs introduits dans le mélange.

% : le pourcentage massique d'additif inséré.

Par exemple, l'échantillon $S1_{1,02}M1_{0,5}A650_{0,5}^{0,7}$ + B^2 correspond à un mélange réactif mis en forme à partir d'une solution S1 (dont le rapport Si/K a été fixé à 0,7 par ajout d'hydroxyde de potassium) mélangée à une source minérale (composé de 50 $\%_{mass}$ de métakaolin M1 et de 50 $\%_{mass}$ d'argilite A650) dans un rapport liquide sur solide de 1,02. A ce mélange est ensuite ajouté 2 $\%_{mass}$ d'acide borique.

Afin d'illustrer les matériaux alcalinement activés, le **Tableau 5** regroupe des photos d'échantillons mis en forme à partir des différentes argilites calcinées à 650 °C et de la solution $S1_K^{0,58}$.

Tableau 5. Photographies des échantillons $S1_{1,17}A650^{0,58}$, $S1_{1,17}AR650^{0,58}$ et $S1_{1,17}AF650^{0,58}$.

Echantillon	**$S1_{1,17}A650^{0,58}$**	**$S1_{1,17}AR650^{0,58}$**	**$S1_{1,17}AF650^{0,58}$**
Photographie			

IV. TECHNIQUES DE CARACTERISATION

1. Caractérisations physico-chimiques

a. Mesure de la mouillabilité (demande en eau)

La mouillabilité d'un solide pulvérulent s'exprime en µL / g et correspond au volume d'eau nécessaire pour saturer en eau une masse de poudre. A cet équilibre, le système peut être assimilé à une association de particules dont l'ensemble des pores (intrinsèques et interparticulaires) est comblé par le liquide. Cette grandeur est ainsi directement liée à la granulométrie, la surface spécifique et la morphologie des particules composant la poudre. Il est ainsi possible de caractériser la réactivité de la poudre étudiée vis-à-vis du liquide utilisé.

La mesure de la mouillabilité est effectuée par la pesée d'un gramme de poudre dans une coupelle de verre, puis par l'ajout progressif de l'eau (par pallier de 10 µL) à l'aide d'une micropipette. Une fois la saturation en eau atteinte (observation visuelle illustrée par la **Figure 4**), la valeur de mouillabilité peut être calculée. Chaque mesure est réitérée trois fois et les variations observées ne sont pas supérieures à 20 µL/g.

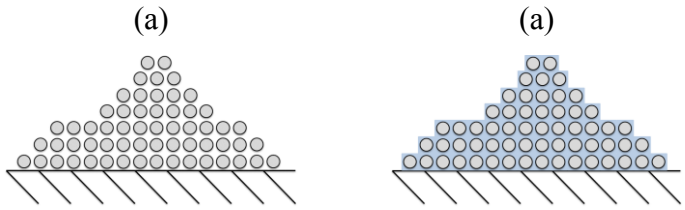


Figure 4. Observation d'une masse de poudre **(a)** avant et **(b)** après sa saturation en eau.

b. Analyse de la distribution granulométrique

Les analyses granulométriques sont utilisées afin d'évaluer la distribution en tailles des particules constituant un échantillon pulvérulent. Ces analyses sont effectuées à l'aide d'un granulomètre par diffraction laser de type Mastersizer 2000 (société Malvern), équipé d'un module de mesure en voie sèche. La poudre est ainsi portée par un flux d'air d'une pression de trois Bars à travers le faisceau laser. L'étude de la diffraction du faisceau permet ensuite de déterminer la distribution granulométrique de l'échantillon. Pour chaque analyse, une série de trois acquisitions est effectuée puis moyennée.

c. Mesure de la surface spécifique (BET)

La surface spécifique d'une poudre, ou d'un solide poreux, correspond à la surface totale d'un échantillon rapportée à sa masse, et s'exprime en m² / g. Elle peut être mesurée à l'aide de la méthode BET (Brunauer, Emmett et Teller [3, 4]) qui consiste à déterminer le volume de gaz (usuellement de l'azote) nécessaire pour former une monocouche de molécules de gaz en surface de l'échantillon. A partir du volume de gaz adsorbé à la surface de l'échantillon, il est possible de calculer la surface de la monocouche formée et de calculer la surface spécifique de l'échantillon (**Eq. 1**).

$$S = \frac{\mathrm{Vm} * \mathrm{Na} * \mathrm{s}}{\mathrm{VM} * \mathrm{m}} \qquad \textbf{Eq. 1}$$

Avec S : la surface spécifique en m²/g., V_m : le volume d'azote adsorbé (correspondant au volume de la monocouche) en cm^3/mol, Na : le nombre d'Avogadro en mol^{-1}, s : la surface occupée par une molécule du gaz adsorbée (soit 16,2 $10^{-20} m^2$ pour l'azote) en m², V_M : le volume molaire du gaz adsorbé en cm^3 et m : la masse de l'échantillon en g.

Les mesures ont été réalisées à l'aide d'un dispositif Tristar II 3020 produit par Micrometrics et fonctionnant par adsorption d'azote à très basse température (-196 °C). Préalablement, les échantillons subissent une étape de dégazage (15 heures à 200 °C).

d. Mesure de la masse volumique par pycnométrie

Les masses volumiques des matériaux pulvérulents sont mesurées à l'aide d'un pycnomètre à hélium AccuPyc 1340 (Micrometrics). Il permet de mesurer le volume d'un échantillon, de masse connue, en comblant la totalité de l'espace (porosité interne et externe comprises) à l'aide d'hélium gazeux. Pour cela, une masse connue d'échantillon est introduite sous forme pulvérulente dans une cellule de volume de 3,5 cm^3, qui est ensuite remplie d'une quantité d'hélium. La pression d'hélium résultante permet de remonter au volume disponible dans la cellule, puis au volume de poudre et enfin à la masse volumique de la poudre. Pour chaque échantillon, la masse volumique mesurée correspond à la moyenne de cinq cycles de mesure. Les déviations constatées sont inférieures à 0,005 g/cm^3.

e. Mesure des valeurs de pH

Les valeurs de pH des échantillons sont mesurées après sept jours de consolidation, par immersion des échantillons durant sept jours dans une masse d'eau deux fois supérieure à celle de l'échantillon utilisé. Un pH mètre 3310 fabriqué par WTW est ensuite utilisé avec une sonde spécifique pour les valeurs de pH alcalin (produite par Fisher Scientific, référence U402 S7 A120), afin de mesurer la valeur de pH de l'eau dans laquelle l'échantillon a été immergé. Le pH mètre est préalablement calibré à l'aide de solutions tampons certifiées de valeurs de pH de dix et treize.

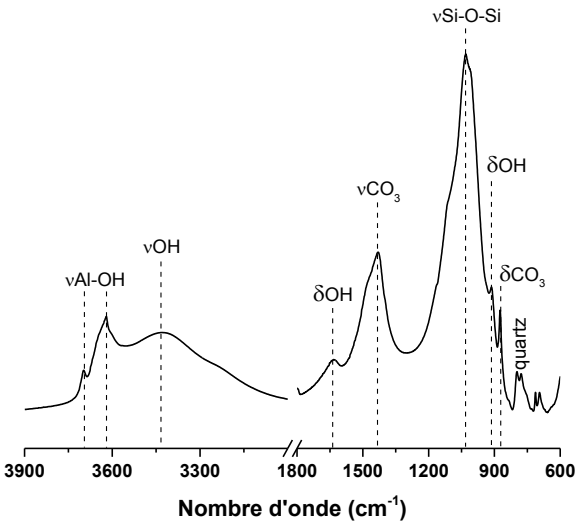
Afin de simuler les conditions d'utilisation du liant dans les alvéoles HA de Cigéo, des mesures sont aussi faites sur des échantillons ayant été exposés à une température de 90 °C. Pour cela, les échantillons sont stockés quinze heures en étuve, puis immergés durant sept jours avant que l'alcalinité de l'eau d'immersion soit mesurée.

2. Analyses structurales

a. Spectroscopie infrarouge à transformée de Fourrier (IRTF)

La spectroscopie IRTF étudie le phénomène d'absorption qui se produit lorsqu'un rayonnement infrarouge traverse un matériau, qu'il soit liquide ou solide. Celui-ci est alors absorbé sélectivement selon les vibrations excitées dans l'échantillon. En effet, chaque molécule présente un niveau de vibration associé à une énergie spécifique. Le spectre d'absorption ainsi obtenu permet donc d'identifier les différents groupements moléculaires présents dans le matériau.

(A)



(B)

(a) (b)

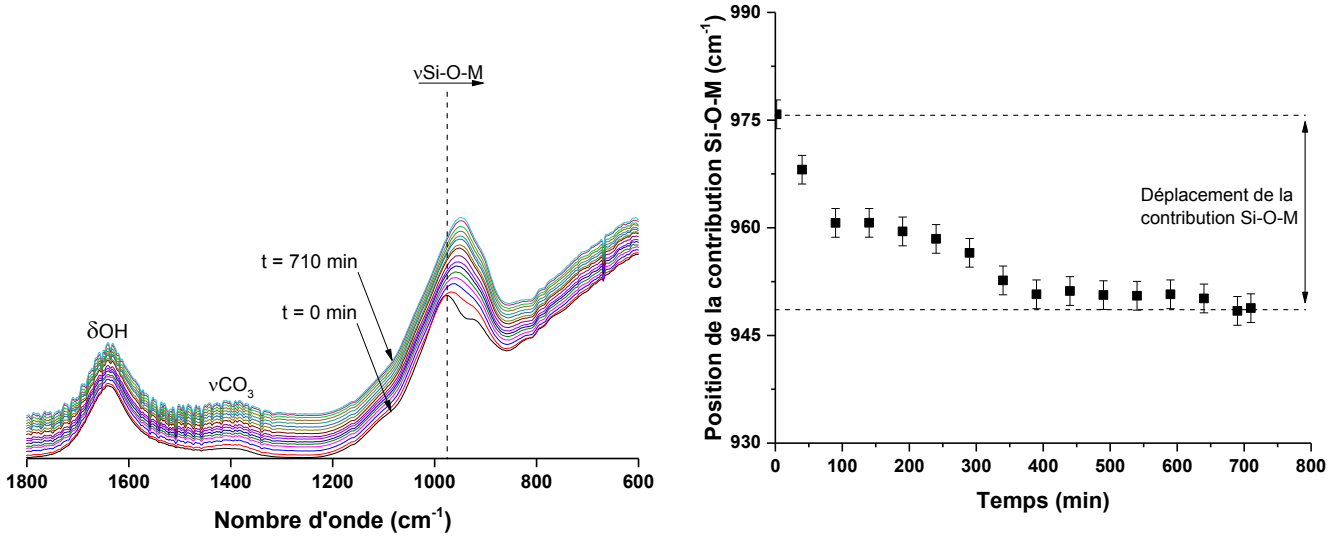


Figure 5. Données IRTF de **(A)** l'argilite crue A25 et **(B)** du suivi cinétique de la consolidation du mélange réactif $S1_{1,17}A750^{0,58}$ **(a)** spectres et **(b)** récapitulatif de l'évolution de la position de la contribution Si-O-M au cours du temps.

Les analyses sont effectuées avec un spectromètre Nicolet 380 (ThermoFicher Scientific) entre 4000 et 600 cm^{-1}, avec une résolution 4 cm^{-1}. Le spectre obtenu correspond à la moyenne de 64 acquisitions corrigé par le bruit de fond. Pour l'analyse des matériaux argileux, le spectromètre est utilisé en mode transmission au travers de pastille de bromure de potassium

(pressage de 100 mg de KBr et de 5 mg d'échantillon). Le traitement des spectres est ensuite effectué avec le logiciel OMNIC. La zone du spectre comprise entre 2400 et 2280 cm^{-1} présentant des perturbations dues au dioxyde de carbone atmosphérique, est corrigée par une ligne droite.

Les sources aluminosilicatées, telle que l'argilite crue (**Figure 5.A**), présentent principalement des vibrations associées aux liaisons Si-O-Si, ainsi qu'aux groupements hydroxydes et carbonates. La liste des principales contributions étudiées est disponible en **Annexe II – A.**

La spectroscopie infrarouge peut aussi être utilisée afin d'effectuer des analyses cinétiques *in-situ* lors de la formation des liants. Pour cela le spectromètre est utilisé en mode ATR (Attenuated Total Reflectance) et quelques gouttes de mélange réactif sont déposées sur le diamant de l'appareil. Les acquisitions sont ensuite effectuées toutes les 10 minutes durant 13 heures et l'évolution du liant est décrite par un ensemble de 72 spectres (**Figure 5.B,a**). La transformation de la liaison Si-O-Si en Si-O-M (où M= Si ou Al), correspondant à la formation du réseau géopolymère, est ainsi étudiée [5]. Le tracé de la position de la contribution Si-O-M en fonction du temps (**Figure 5.B,b**) permet d'obtenir la pente de la courbe au cours des premières minutes de réaction, et d'en évaluer la cinétique. Ce suivi permet aussi d'observer le phénomène de géopolymérisation mis en évidence par le déplacement de la bande Si-O-M.

b. Spectroscopie Raman

La spectroscopie Raman se focalise sur les phénomènes de diffusions résultant de l'excitation d'un matériau (liquide ou solide) par un puissant rayonnement monochromatique de type laser. La diffusion Raman correspond à une fraction très minoritaire du signal qui est associée à la diffusion inélastique d'un photon. Les acquisitions sont effectuées à l'aide d'un spectromètre In Via Reflex, produit par Renishaw, équipé d'une source laser d'une longueur d'onde de 532 nm avec une puissance de 40 mW. Le rayonnement diffusé est détecté à l'aide d'un triple monochromateur (grilles de 2400 lignes/mm), sur la gamme spectrale de 200 à 1400 cm^{-1}. La **Figure 6.a** regroupe les spectres bruts de deux solutions alcalines silicatées, présentant des signatures spectrales caractéristiques de différentes réactivités (détail des contributions en **Annexe II – B)**.

Afin de quantifier la réactivité des solutions alcalines silicatées, les spectres peuvent être traités et décomposés à l'aide du logiciel Wire (Renishaw), **Figure 6.b** [6]. Pour cela, les spectres sont étudiés sur la zone spectrale 300-800 cm^{-1}, après soustraction d'une ligne de base

(simulée par un polynôme d'ordre 5), et décomposés en six contributions décrites dans le **Tableau 6.**

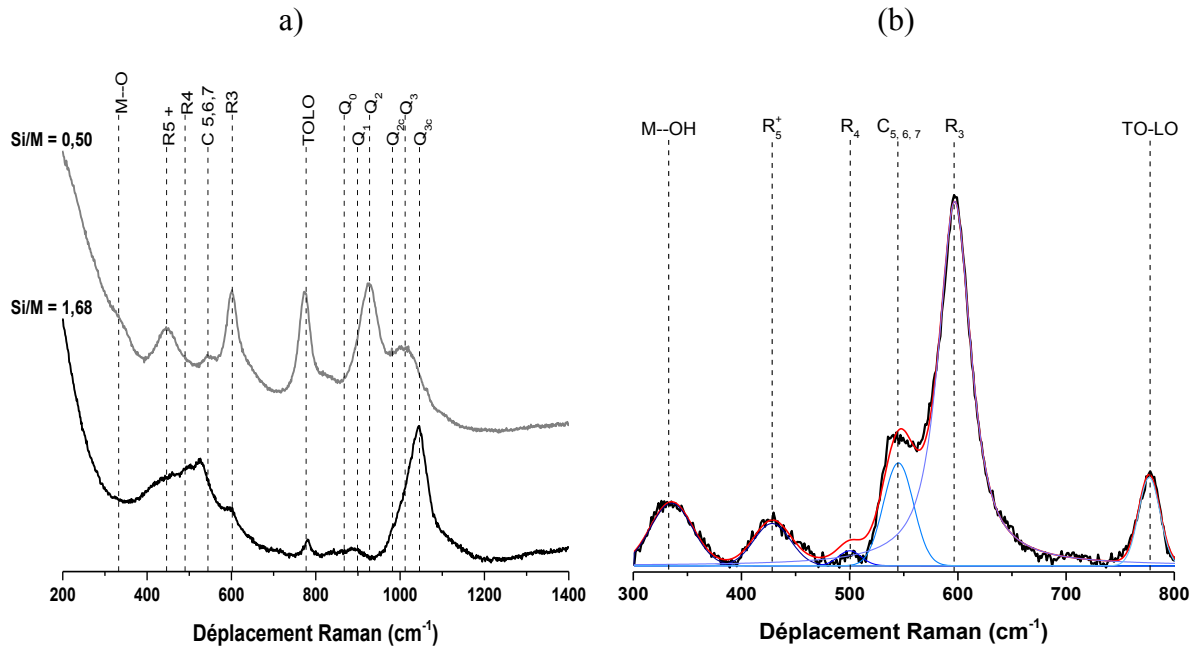


Figure 6. Exemple de spectres Raman illustrant **(a)** l'évolution du spectre de la solution potassique S1 avec l'augmentation du rapport Si/M et **(b)** un exemple de décomposition sur la solution sodique S2.

Tableau 6. Contributions Raman des solutions alcalines silicatées entre 300 et 800 cm^{-1}.

Contributions	Position (cm^{-1})	Références
M-O	340–360	[7]
$\delta[R_{5\ et\ plus}]$	400–490	[8]
D_1 ($\delta[R_4]$)	453–550	[8]
υ_s (Si-O-Si) $C_{5,6,7}$	515–535	[9]
D_2 ($\delta[R_3]$)	587–606	[10, 11]
υ Si-O-Si (TO-LO)	650–850	[12]

c. Résonance Magnétique Nucléaire (RMN)

La spectroscopie par résonance magnétique nucléaire étudie les phénomènes de résonnances induits par l'exposition des noyaux atomiques à un champ magnétique. En effet, lors de l'application d'un champ magnétique, les spins des noyaux atomiques peuvent changer de niveau énergétique, conduisant à l'émission ou à l'absorption d'un photon résonnant à une

fréquence précise [13]. L'étude de cette fréquence permet de tracer le spectre RMN et de caractériser l'environnement électronique du noyau. Cependant cette caractérisation ne peut s'effectuer que sur des atomes présentant un spin nucléaire non nul. Au cours de ce travail les environnements des noyaux du bore (^{11}B), de l'aluminium (^{27}Al), du silicium (^{29}Si) et du phosphore (P^{31}) ont été analysés et les informations relatives à leur noyau sont regroupées dans le **Tableau 7.**

Tableau 7. Données relatives aux noyaux étudiés.

Noyau	**Spin**	**Abondance (%)**	**Fréquence de résonnance (Hz) pour un champ de 9,4 T**
^{11}B	3/2	80,1	128,38
^{27}Al	5/2	100,0	104,26
^{29}Si	1/2	4,7	79,50
^{31}P	1/2	100,0	161,98

Les matières premières et les échantillons alcali-activés ont été analysés par un spectromètre AVANCE 400 (Brucker) de type MAS (Magic Angle Spinning) sous un champ magnétique de 9,4 T. Les échantillons sont préalablement broyés et séchés à 40 °C, puis placés dans un rotor en zircone sous une vitesse de rotation de 10 kHz au cours de l'analyse. Les spectres ainsi obtenus sont traités à l'aide du logiciel Winfit (Brucker) puis décomposés à l'aide du logiciel dmfit (CNRS) [14]. La **Figure 7** présente des exemples de décomposition (associés aux noyaux ^{27}Al - ^{29}Si et ^{11}B - ^{31}P) pour l'échantillon $S1_{1,01}M1^{0,7}$, seul et en présence de tétraborate de sodium ou d'hydrogénophosphate de potassium. Les données relatives à l'indexation de ces spectres sont regroupées dans l'**Annexe II – C**.

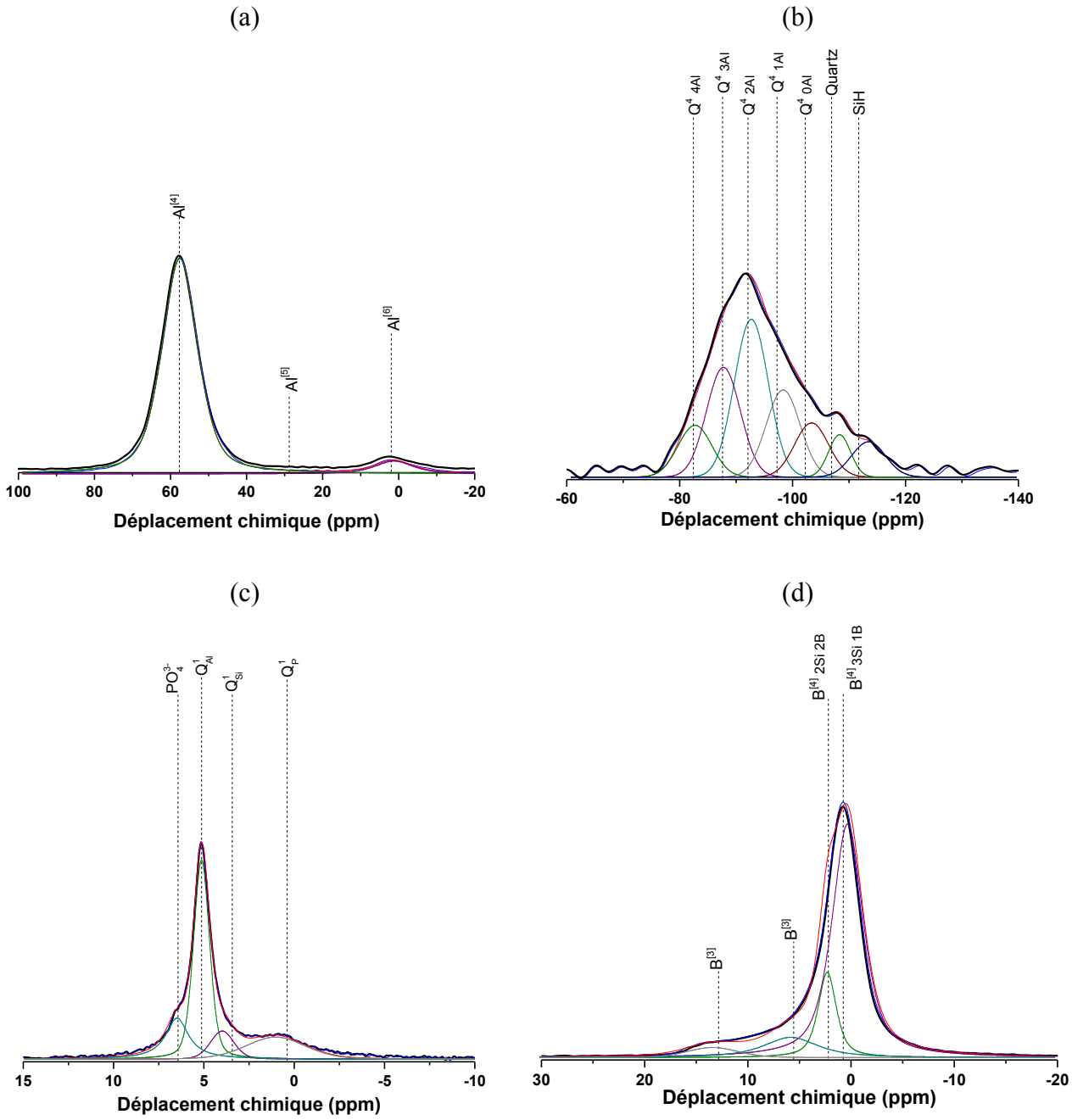


Figure 7. Spectres RMN MAS du **(a, b)** ^{27}Al - ^{29}Si de l'échantillon $S1_{1,01}M1^{0,7}$, **(c)** ^{31}P de l'échantillon $S1_{1,01}M1^{0,7}$ $KP^{9,3}$ et **(d)** ^{11}B de l'échantillon $S1_{1,01}M1^{0,7}$ NaB^{10}.

d. Diffraction des rayons-X

La diffraction des rayons X (DRX) est une technique de caractérisation structurale basée sur l'interaction entre un faisceau de rayons X et un matériau. Cette technique se focalise sur un rayonnement monochromatique X en contact avec les plans atomiques constituant le matériau. Cette diffraction est possible si la longueur d'onde du rayonnement incident est du même ordre de grandeur que les distances interatomiques. La loi de Bragg (**Eq. 2**) permet alors

de calculer la distance inter-réticulaire entre deux plans atomiques (hkl) grâce à l'angle de diffraction (θ) et la longueur d'onde du rayonnement X (λ). Il est ainsi possible d'identifier des phases cristallines, de déterminer les paramètres de mailles d'une structure connue, de quantifier la cristallinité d'un composé et même de quantifier les phases présentes dans un échantillon.

$$2d_{hkl} * \sin\theta = \lambda \qquad \textbf{Eq. 2}$$

Les diffractogrammes ont été obtenus à l'aide d'un diffractomètre D8 (Brucker) équipé d'un montage Bragg-Brentano. La source de rayons X est composée d'une anode en cuivre (λK_α= 1,54056 Å) et d'un détecteur composé de 192 cellules. Les échantillons sont préalablement broyés au mortier en agate puis analysés sur la plage 10-50 ° (2 θ). L'utilisation d'un temps de palier de 1,5 s et d'une résolution angulaire de 0,019 ° (2 θ), a permis d'obtenir des résultats exploitables. L'identification des phases cristallines est effectuée avec le logiciel EVA (Brucker) à l'aide des fiches de référence PDF (Powder Diffraction File) du ICDD (International Center for Diffraction Data). La **Figure 8.a,b** présente les diffractogrammes de l'argilite crue (A25) et du géopolymère $S1_{1,01}M1^{0,7}$décomposé. L'**Annexe II – D** regroupe la liste des différentes fiches PDF utilisées lors de ce travail.

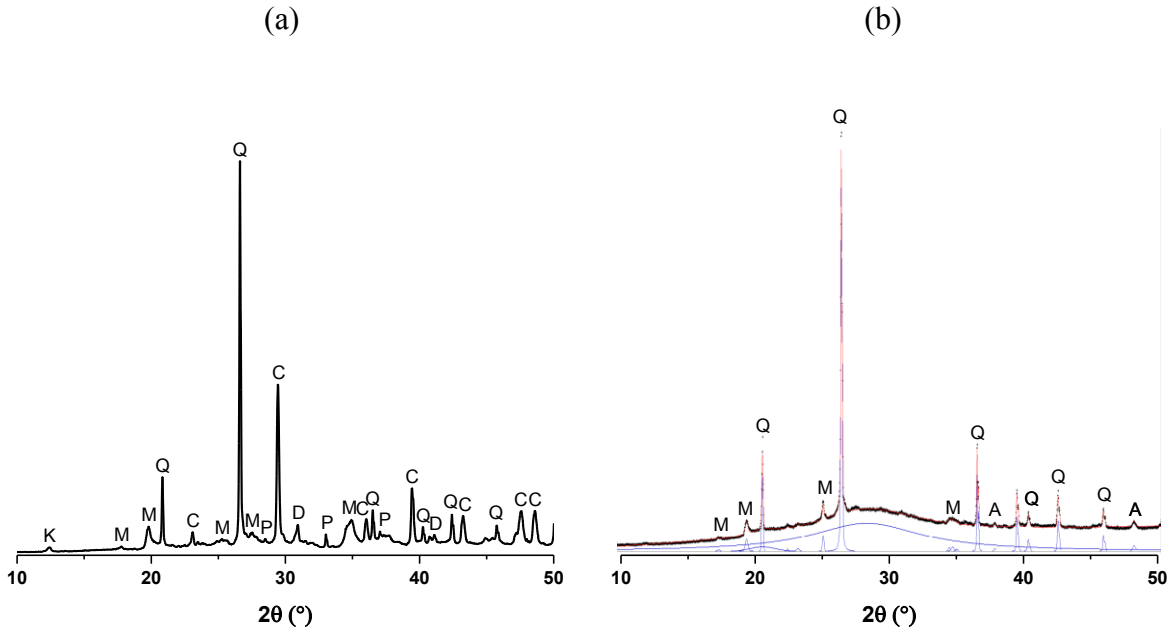


Figure 8. (a) Diffractogramme de l'argilite crue A25 et **(b)** décomposition du diffractogramme de l'échantillon $S1_{1,01}M1^{0,7}$ (avec K – kaolinite, M – illite/muscovite, Q – quartz, C – calcite, P – pyrite, D – dolomite et A – anatase).

La fraction amorphe des échantillons alcali-activés occasionne une déformation de la ligne de base, entre 20 et 35 ° (2 θ). Cette fraction d'amorphe est étudiée à l'aide de décompositions de diffractogrammes, qui sont effectués à l'aide du logiciel Peakoc (IRCER) et d'une fonction de Voigt tenant compte des rayonnements $K_{\alpha 1}$ et $K_{\alpha 2}$ [15].

3. Analyse microstructurale

L'analyse par microscopie électronique à balayage (MEB) est une technique d'analyse microstructurale permettant l'observation d'échantillon jusqu'à une résolution de l'ordre de quelques nanomètres. Celle-ci s'effectue par l'exposition de l'échantillon à un faisceau électronique conduisant, grâce aux interactions rayonnement-matière, à l'émission d'électrons secondaires ou rétrodiffusés. L'étude de ces derniers donne des informations sur le contraste morphologique (électron secondaire) ou élémentaire (électron rétrodiffusé).

Les observations sont effectuées à l'aide d'un microscope IT300 (JEOL) équipé d'une source en tungstène et d'une sonde chimique X. Les échantillons sont préalablement métallisés à l'aide de platine (ou de carbone pour les analyses chimiques X) et fixés sur les porte échantillons à l'aide de pastilles et/ou pâte carbone. Cela permet de faciliter la conduction électronique et de limiter les effets de charge en surface. Les analyses chimiques X permettent d'identifier et d'évaluer les éléments chimiques présents au sein de l'échantillon. L'**Annexe II – E** regroupe les énergies associées aux différents éléments.

4. Comportement thermique

a. Analyse par dilatométrie

Les analyses de dilatométrie permettent de déterminer les variations dimensionnelles d'un échantillon en fonction de la température. Les essais sont effectués sur des cylindres de géopolymère (Φ = 5 mm / H = 6 mm), disposés dans le sens de la hauteur dans un dilatomètre vertical Setsys (Setaram Instrumentation). Les cylindres sont positionnés entre deux cales de platine de façon à limiter les phénomènes de diffusion entre l'échantillon et les cales d'alumine. Les essais sont ensuite effectués sous air avec un cycle thermique composé d'une rampe de chauffe à 5 °C/min jusqu'à 1000 °C, puis d'un refroidissement à 20 °C/min jusqu'à 20 °C. Les essais sont ensuite corrigés par un « blanc » (manipulation sans l'échantillon) afin de soustraire les variations dimensionnelles dues à l'équipement et aux cales.

La **Figure 9** présente une courbe de dilatométrie, associée à l'échantillon $S1_{1,23}AF750^{0,58}$.

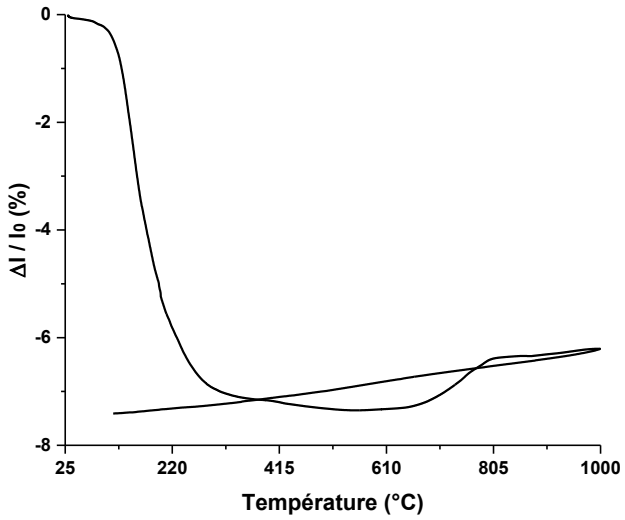


Figure 9. Variation dimensionnelle en fonction de la température pour l'échantillon $S1_{1,23}AF750^{0,58}$.

b. Analyses thermodifférentielle et thermogravimétrique (ATD-ATG)

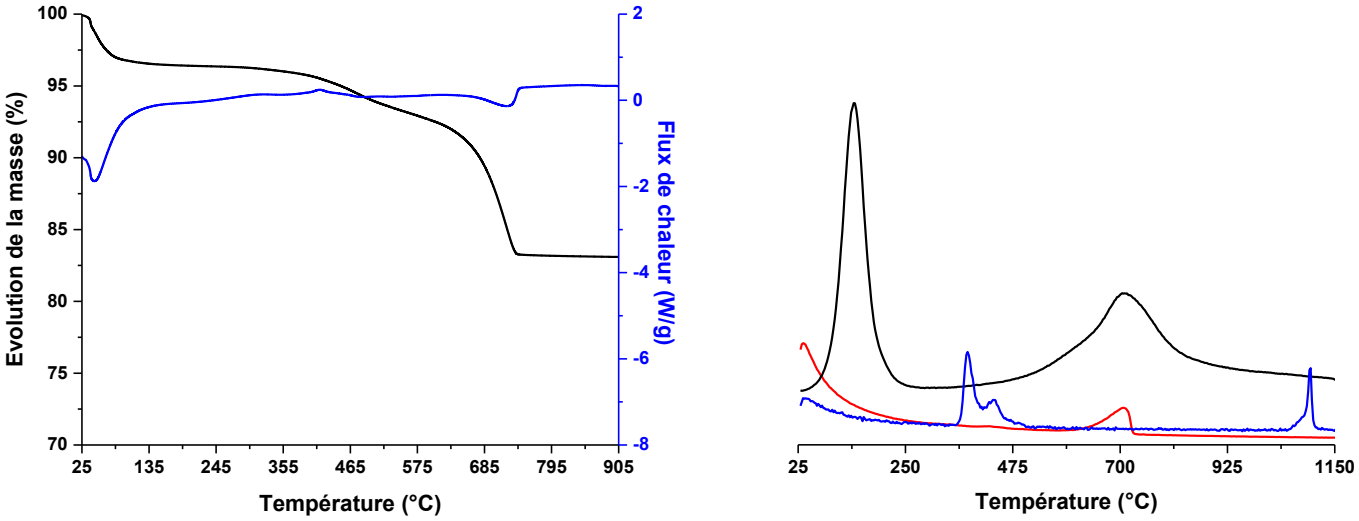
L'analyse thermique, thermodifférentielle (ATD) et thermogravimétrique (ATG), est une technique permettant d'évaluer le comportement d'un matériau en fonction de la température. Le couplage des deux analyses permet de mettre en évidence les changement d'états physicochimiques des composés analysés. Les changements d'états ou transformations polymorphiques sont caractérisés par des phénomènes exothermique ou endothermique (ATD). La différence de température entre les deux creusets (mesure et référence) permet de mesurer le flux de chaleur lié aux évolutions de l'échantillon par différence. Les pertes de masses mesurées permettent d'identifier et de quantifier des pertes d'eau ou des décompositions d'échantillons. La technique d'ATD-ATG peut aussi être couplée à un spectromètre de masse permettant d'analyser les gaz issus des décompositions, ou réactions, intervenant dans un échantillon lors de l'augmentation de température.

Les analyses d'ATD-ATG ont été effectuées à l'aide d'un équipement SDT Q600 produit par TA Instrument. Les analyses sont effectuées sous un balayage d'air (100 cm^3/min) dans des creusets en platine contenant de 20 à 70 mg d'échantillon. Les analyses ATD-ATG couplées à un spectromètre de masse sont effectuées avec un dispositif STA 449F produit par Netzsch, dans des conditions opératoires identiques. Trois contributions de m/z ont été identifiées pour les composés H_2O (m/z = 18), CO_2 (m/z = 44) et SO_2 (m/z = 64).

La **Figure 10.A.a,b** présente ainsi les courbes d'analyses thermiques de l'argilite crue ainsi que les résultats de spectrométrie de masse associés (m/z = 18, 44 et 64). Cela permet d'identifier les températures de déhydroxylation (H_2O, m/z = 18) et de décomposition des espèces carbonatées (CO_2, m/z = 44) et sulfatées (SO_4, m/z = 64) [16]. La **Figure 10.B** présente le thermogramme d'un échantillon alcali-activé à base d'argilite, $S1_{1,17}A750^{0,58}$.

(A)

(a) (b)



(B)

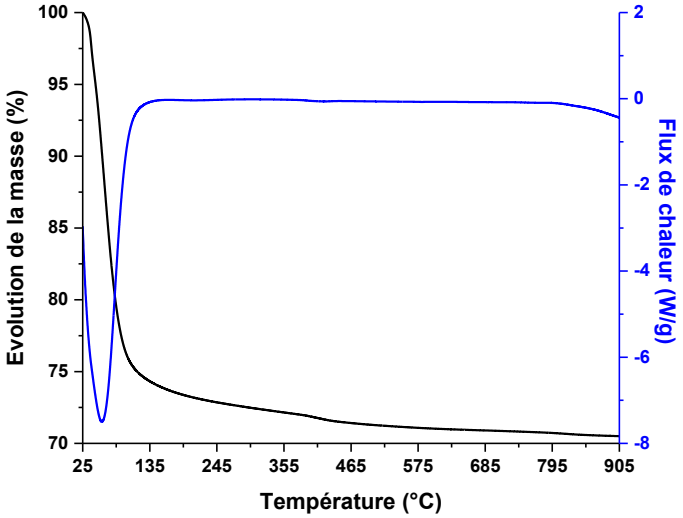


Figure 10. (A,a) Thermogramme de l'argilite crue (A25) et **(A,b)** courbes d'intensités relatives à (—) H_2O (m/z = 18), (—) CO_2 (m/z = 44) et (—) SO_2 *10^3(m/z = 64) obtenues par spectrométrie de masse couplée à l'analyse thermique de A25 et **(B)** thermogramme de l'échantillon $S1_{1,17}A750^{0,58}$.

5. Mesures de viscosités

Les mesures de viscosités sont effectuées sur les mélanges réactifs afin d'évaluer leur caractéristique d'écoulement et leur évolution en fonction du temps. Pour cela, un viscosimètre DV2T (Brookfield), fonctionnant par mesure de la contrainte de cisaillement entrainée par la rotation d'un mobile immergé dans le mélange réactif, est utilisé. Le mobile est entrainé à une vitesse de 100 tr/min dans un flacon de 65 mL. Pour la mesure de viscosité élevée (> 6 Pa.s), il est nécessaire de diminuer la vitesse de rotation, afin de ne pas dépasser la contrainte maximale mesurable. Les mesures sont alors possibles jusqu'à 600 Pa.s. Les mesures de viscosités étant effectuées sur des mélanges réactifs, qui par définition évoluent au cours du temps, la viscosité n'est significative que si elle est associée à une durée de vieillissement. Dans ce but, des suivis de viscosités dans le temps sont effectués, à l'aide de mesures ponctuelles (usuellement toutes les trente minutes). Entre chaque mesure, les mélanges sont maintenus sous agitation par un mélangeur à rouleau (60 tr/min) et à une température de 20 °C. La **Figure 11** montre deux exemples de courbes de viscosités pour des liants $S1_{1,01}M1^{0,58}$ avec une solution $S1_{Na}{}^{0,58}$ et $S1_{K}{}^{0,58}$. L'utilisation de la solution sodique conduit à un accroissement constant de la viscosité au cours du temps et ne sera donc pas étudiée au cours de ce travail. Cependant l'utilisation de la solution potassique permet de définir une zone de viscosité constante (η_c), associée à la durée pratique d'utilisation (DPU), puis une zone d'augmentation de la viscosité, correspondant à la consolidation du mélange. Il est ainsi possible d'estimer la valeur de DPU à l'aide des courbes de viscosité et de la méthode des tangentes, l'erreur résultante est de l'ordre de 30-60 minutes.

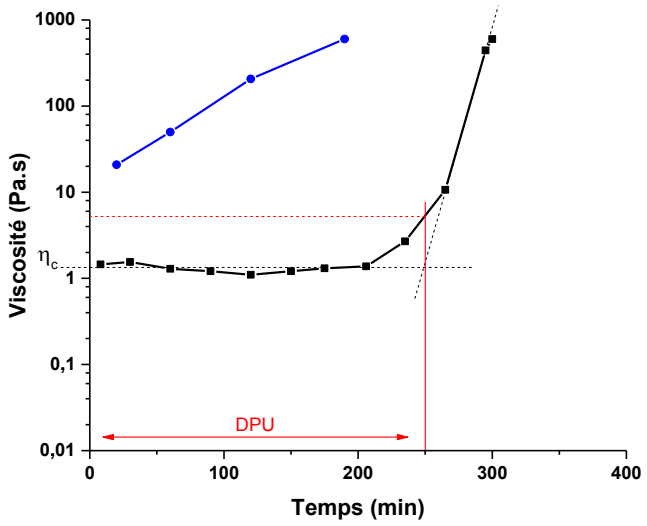


Figure 11. Valeurs de viscosité en fonction du temps pour des mélanges $S1_{1,01}M1^{0,58}$ à base de solutions (■) $S1_{K}{}^{0,58}$ et (●) $S1_{Na}{}^{0,58}$.

6. Propriétés d'usage

Les propriétés d'usage sont estimées à l'aide d'essais de résistance mécanique en compression simple. Ils consistent à appliquer une charge croissante, de manière normale par rapport à la surface de l'échantillon (cylindrique ou cubique). L'essai est mené jusqu'à la rupture de celui-ci. Il est alors possible d'obtenir la contrainte à la rupture, σ_{max}, de l'échantillon dans la direction de sollicitation.

Pour chaque échantillon, les essais sont effectués sur au minimum cinq éprouvettes cylindriques qui sont démoulées, rectifiées ($\Phi/H = 2$) et testées après 7 ou 28 jours de consolidation endogène. L'appareillage de mesure utilisé est un bâti universel 5969 (Instron), équipé d'un capteur de force d'une portée de 50 kN et opérant à une vitesse de 0,5 mm/min. La **Figure 12** présente les courbes associées à l'analyse de l'échantillon $S1_{1,17}A750^{0,58}$ après 7 et 28 jours de consolidation. Une légère augmentation de la contrainte à la rupture est observée entre 7 et 28 jours, les essais à 28 jours sont donc privilégiés. L'erreur sur la contrainte à rupture est comprise entre 2 et 4 MPa.

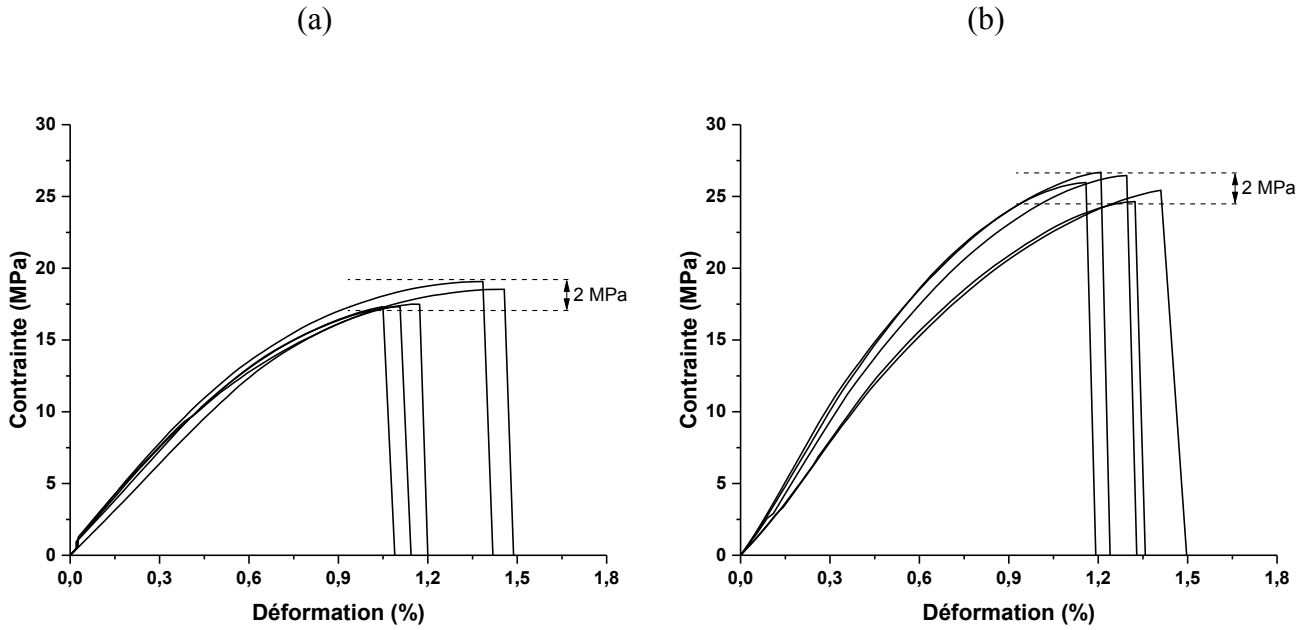


Figure 12. Valeurs de contrainte en fonction de la déformation pour l'échantillon $S1_{1,17}A750^{0,58}$ après **(a)** 7 et **(b)** 28 jours de consolidation.

7. Chimiométrie

Afin d'interpréter de nombreux et complexes jeux de données, la chimiométrie peut être utilisée. Elle consiste à appliquer des outils mathématiques permettant d'analyser des données

multivariées, telles que les données spectroscopiques, à l'aide de calculs statistiques [17]. En effet, un spectre d'analyse spectroscopique, par exemple Raman (**Figure 13.A**), peut être assimilé à un ensemble de variables « X » correspondant à l'ensemble des intensités mesurées à chaque valeur de déplacement Raman. L'utilisation d'outils mathématiques adaptés permet de créer un modèle à partir de cette série de variables, qu'il peut être possible d'associer à un paramètre de sortie « Y ». Dans le cadre des solutions alcalines silicatées, ce paramètre Y peut être le rapport Si/M, la valeur de pH, la réactivité de la solution… Selon les jeux de données et les outils mathématiques utilisés, les modèles élaborés peuvent permettre de discriminer les valeurs de X (domaines spectraux) lors des évolutions des valeurs de Y (données de sorties) ou même de prédire cette valeur de Y.

Lors de ce travail, la chimiométrie a été appliquée sur des spectres Raman afin d'étudier la réactivité des solutions alcaline silicatées. Les spectres Raman des solutions de silicates sont complexes et difficilement interprétables (**Figure 6.a**). L. Vidal *et al.* a mis en place un modèle de décomposition afin d'identifier et de quantifier les espèces siliceuses présentes en solution [6]. Un exemple de ces décompositions est présenté en **Figure 6.b**. Ce procédé est cependant chronophage et nécessite l'utilisation d'une ligne de base, ce qui induit une erreur non négligeable. La chimiométrie est donc utilisée afin d'analyser les solutions alcalines silicatées (pour déterminer leur réactivité) en s'affranchissant de l'étape de décomposition spectrale. Pour cela, deux outils d'analyses ont été utilisés :

(i) des analyses par composantes principales (ACP), qui regroupent les variables par « composantes principales », afin d'expliquer le maximum de la variance du jeu de données [17]. Cela conduit à un nombre limité de variables (usuellement moins d'une dizaine), très discriminantes, avec lesquelles il est plus aisée de décrire le jeu de données. La chimiométrie peut effectivement discriminer une valeur Y en fonction des données X.

(ii) des analyses correspondant à des « régressions des moindres carrés partiels » (PLSR – Partial Least Squares Regression) [18]. Elles consistent en « l'apprentissage » d'un jeu de données complet (X-Y), afin de pouvoir à terme prédire la valeur de Y d'un échantillon (**Figure 13.B**).

Ces outils ont été appliqués sur un jeu de données comportant 65 solutions alcalines silicatées (chacune préparée trois fois), combinant les quatre solutions de base (S1, S2, S3 et S4) mélangées avec de l'hydroxyde de potassium et/ou de sodium (voir **Annexe II – F**). Les solutions sont ensuite analysées par spectroscopie Raman (partie **II.2.b**) et l'analyse est effectuée sous le logiciel SOLO (Eigenvector) [19].

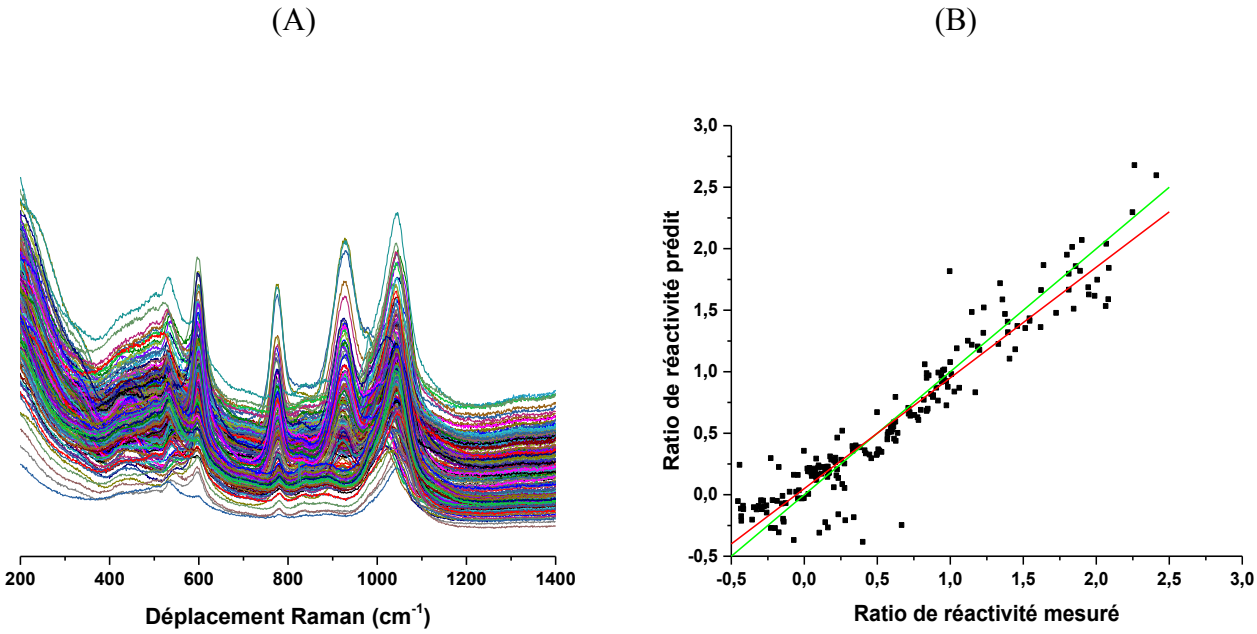


Figure 13. (A) Spectres Raman d'un lot de solutions alcalines silicatées et **(B)** résultat de l'analyse en régression linéaire associée à ce lot de solutions.

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CHAPITRE III

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I. INTRODUCTION

Ce chapitre synthétise les études liées à la valorisation de l'argilite du Callovo-Oxfordien, sous forme de liant alcali-activé. La première partie regroupe les informations liées à l'activation alcaline de l'argilite. Dans un premier temps, les données relatives aux traitements thermiques de l'argilite et à la caractérisation des évolutions structurales induites sont présentées. Les essais associés à la faisabilité d'échantillons à base d'argilite sont ensuite détaillés, ainsi que la caractérisation de ces matériaux. La seconde partie traite d'un géopolymère « de référence », à base de métakaolin, pour le développement d'un coulis. Les informations relatives à la formulation du liant et à l'usage d'additifs, mais aussi à la caractérisation des différents mélanges réactifs sont développées. Ces caractérisations portent sur les propriétés d'usage ainsi que sur les évolutions structurales, afin de pouvoir décrire l'action des additifs sur les réactions de géopolymérisation. Enfin, la dernière partie décrit la formulation du coulis à base d'argilite et ses interactions avec de l'argilite massive.

II. DE L'ARGILITE AU MATERIAU ALCALI-ACTIVE

1. Traitement de l'argilite

Afin d'activer alcalinement l'argilite, il est nécessaire de la fonctionnaliser afin de modifier sa structure ainsi que ses caractéristiques physico-chimiques. L'argilite est ainsi préalablement broyée puis différents types de traitements thermiques sont appliqués.

a. Modes de calcination

Le thermogramme de l'argilite (**Figure 1.a)** révèle cinq zones de perte de masse. Jusqu'à 350 °C (zone **I**), les pertes de masse sont associées à la déshydratation des différents minéraux. Entre 350 et 620 °C (zones **II** et **III**) plusieurs pertes de masse sont dues aux déhydroxylations des différents minéraux argileux (kaolinite, chlorite, illite et interstratifié illite/smectite) [1]. Enfin au-delà de 620 °C, deux pertes de masse sont dues à la décomposition des espèces carbonatées (décarboxylation). La perte de masse à la température la plus basse dans ce domaine (< 750 °C), zone **IV**, est principalement due à la décomposition de la dolomite en $CaCO_3$ et en oxyde de magnésium (**Eq. 1**). Pour des températures croissantes, en zone **V**, la décomposition de la calcite, plus réfractaire, est observée (**Eq. 2**) [2] (**Chapitre IV, ACL 1 et ACL 2**).

$$CaMg(CO_3)_2 \rightarrow MgO + CaCO_3 + \overrightarrow{CO_2} \qquad \textbf{Eq. 1}$$

$CaCO_3 \rightarrow CaO + \overrightarrow{CO_2}$ **Eq. 2**

Suite à cette analyse, trois procédés de calcination, en four statique (A), rotatif (AR) et flash (AF), ont été appliqués à des températures comprises entre 600 et 800 °C. Dans cette partie, seules les températures de 650 et 750 °C seront détaillées. Ainsi les thermogrammes des argilites calcinées en four statique à 650 et 750 °C sont reportés sur les **Figures 1.b,c**.

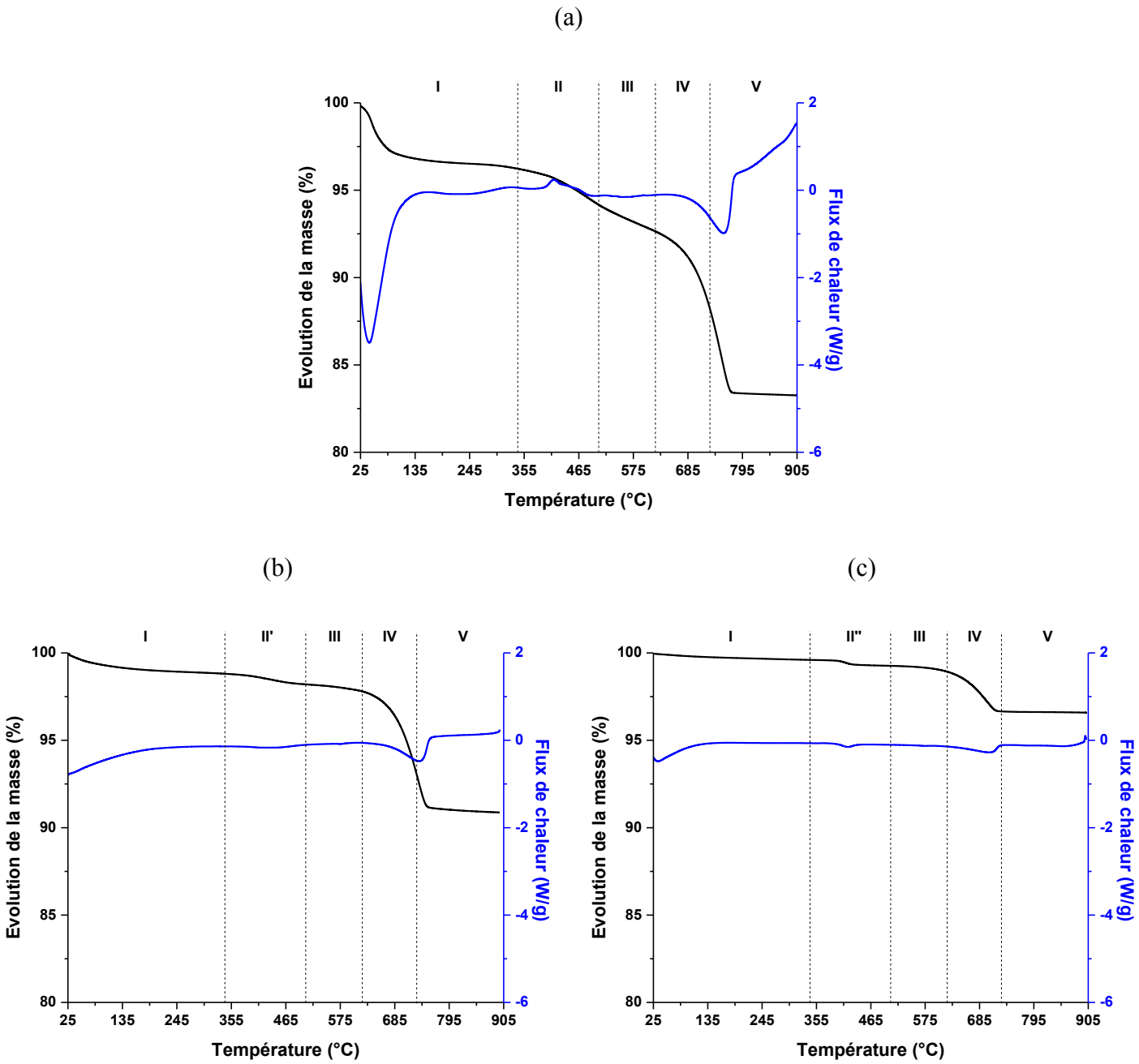


Figure 1. Thermogrammes de **(a)** l'argilite crue (A25) et des argilites calcinées en four statique à **(b)** 650 et **(c)** 750 °C.

L'analyse des échantillons calcinés à 650 °C montre une importante diminution des pertes de masse en dessous de 600 °C (zones **I**, **II** et **III**). Par ailleurs, une nouvelle perte (**II'**) est visible vers 400 °C, et correspond à la déhydroxylation du $Mg(OH)_2$ formé à partir du cation alcalino-terreux (Mg^{2+}), libéré lors de la décomposition de la dolomite (**Eq. 3**) [3]. Au-delà de 600 °C, la perte **IV**, liée à la décomposition des espèces carbonatées, est plus faible. La calcination à 750 °C (A750), entraîne uniquement deux pertes de masse. La perte **II''** est associée à la déhydroxylation du $Mg(OH)_2$ mais aussi du à celle du $Ca(OH)_2$ (**Eq. 4**), formé à la suite de la décomposition de $CaCO_3$. La perte de masse **IV** correspond à la fin de la décomposition de la calcite, mais aussi à la décomposition d'espèces pouvant s'être re-carbonatées à l'issue de la calcination [4].

$$Mg(OH)_2 \rightarrow MgO + \overrightarrow{H_2O} \qquad \textbf{Eq. 3}$$

$$Ca(OH)_2 \rightarrow CaO + \overrightarrow{H_2O} \qquad \textbf{Eq. 4}$$

Les valeurs des différentes pertes de masse observées lors de l'analyse thermique des argilites calcinées en four statique, rotatif et flash sont regroupées en **Annexe III – A**. Il ressort que l'usage du four flash conduit aux pertes de masse les plus importantes, et donc aux décompositions les plus faibles. Le four rotatif conduit à des décompositions plus importantes, qui sont maximales dans le four statique.

La calcination de l'argilite conduit principalement à la déhydroxylation des minéraux argileux (< 650 °C) et à la décomposition des espèces carbonatées (> 650 °C). Ces évolutions sont maximales en four statique, plus limitées en four rotatif et faibles en four flash.

b. Evolutions structurales

Les différents types d'argilites calcinées sont analysés par diffraction des rayons X et par spectroscopie IRTF (**Figure 2**).

Initialement l'argilite crue, A25, présente des raies de diffraction associées à des phases de kaolinite, d'illite/muscovite, de quartz, de calcite, de pyrite et de dolomite (**Figure 2.A**). Quel que soit le procédé de calcination, à 650 °C la pyrite est décomposée (en fer réactif et oxyde de soufre). La kaolinite est décomposée lors des traitements en fours statique et rotatif mais reste présente après le traitement flash. Les contributions des espèces carbonatées, calcite et dolomite, évoluent peu. Après calcination à 750 °C, la kaolinite est décomposée dans toutes les argilites et les contributions d'illite/muscovite s'affinent, à cause de leur déhydroxylation [5].

Ces différentes déhydroxylations ont pu être étudiées par RMN de l'aluminium 27 dont les spectres sont disponibles en **Annexe III – B**. Lors de ces transformations, les atomes d'aluminium en coordinence VI passent en coordinence IV (**Chapitre IV, ACL 1**). Le taux de transformation est plus élevé lors des calcinations en fours statique et rotatif (passage de 30 à plus de 80 % d'$Al^{[4]}$) et très limité en four flash (seulement 43 % d'$Al^{[4]}$). Les principales différences identifiables sur les diffractogrammes des argilites calcinées à 750 °C sont liées aux espèces carbonatées. La dolomite est presque intégralement décomposée lors des traitements en fours statique et rotatif, mais reste présente dans l'argilite calcinée en four flash. La calcite est aussi quasi-totalement décomposée dans le four statique. Cependant le four rotatif ne permet qu'une décomposition partielle et le four flash n'induit pas d'évolutions significatives des contributions de la calcite. Ces résultats sont corroborés par la formation d'une phase d'oxyde de calcium, qui n'est détectée que dans l'argilite calcinée en four statique (A750).

Le spectre IRTF de l'argilite crue (**Figure 2.B**), présente différentes contributions associées aux groupements hydroxyles des minéraux argileux (3700-3400 cm^{-1}) [6, 7], aux espèces carbonatées (1550-1400, 870 et 710 cm^{-1}) [8], aux liaisons silicatées (1050-650 cm^{-1}) [9] et aux sulfates (1160 cm^{-1}) [10] (**Annexe II – A**).

Les calcinations à 650 °C conduisent principalement à la perte des groupements hydroxyles, notamment dans les fours statique et rotatif, comme noté précédemment. Les contributions associées aux espèces carbonatées n'évoluent que sur l'argilite calcinée en four statique (A650). À 750 °C, les évolutions les plus significatives sont centrées sur les espèces carbonatées. La contribution à 1450 cm^{-1}, associée à la dolomite, diminue significativement pour tous les échantillons. Les contributions des espèces carbonatées CO_3^{2-} à 1510, 1430 et 870 cm^{-1}, associées au cation Ca^{2+}, diminuent. Cependant, quel que soit l'échantillon, une contribution de calcite est toujours visible à 1430 cm^{-1}. Pour les échantillons A750 et AR750, présentant les contributions de carbonates les moins intenses, une nouvelle contribution centrée autour de 1550-1500 cm^{-1} apparaît. Celle-ci peut être due à des groupements carbonates adsorbés à la surface de l'argilite, par des réactions d'état solide avec les cations Ca^{2+} et Mg^{2+} libérés lors de la décomposition des espèces carbonatées [4].

Les évolutions structurales, liées à la déstructuration des minéraux argileux et à la décomposition des espèces carbonatées, sont maximisées lors du traitement en four statique.

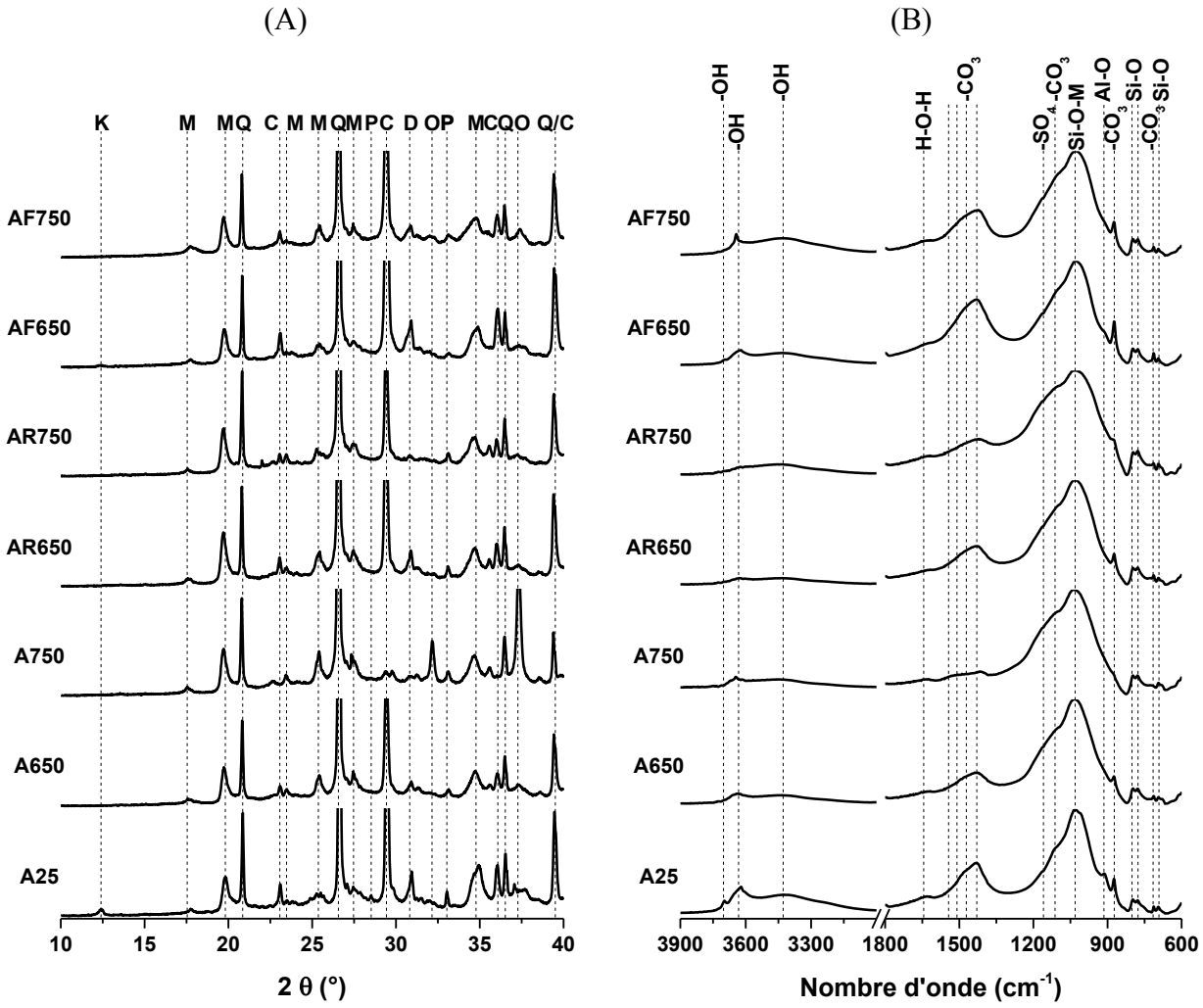


Figure 2. (A) Diffractogrammes et **(B)** spectres IRTF des différents types d'argilites crue et calcinées (K : kaolinite, M : illite/muscovite, Q : quartz, C : calcite, P : pyrite, D : dolomite et O : oxyde de calcium).

Les différents traitements thermiques entraînent aussi des variations physico-chimiques (d_{50}, mouillabilité, masse volumique et S_{BET}) de l'argilite (**Annexe III – C**.) Les valeurs de d_{50} et de S_{BET} en fonction des différents traitements thermiques sont présentées dans la **Figure 3.**

Les valeurs de granulométrie (d_{50}) après une calcination à 650 °C évoluent faiblement et sont de 21, 27 et 28 µm, respectivement pour argilites calcinées AF650, AR650 et A650. L'augmentation de la température de calcination à 750 °C, n'entraîne pas de modification pour les argilites AF650 et AR650. En revanche, pour l'échantillon A750, il est noté une très forte augmentation de la granulométrie, de 28 à 161 µm. Cet accroissement granulaire observé en four statique est lié à des phénomènes de coalescence de grains intervenant dans le lit de poudre à 750 °C.

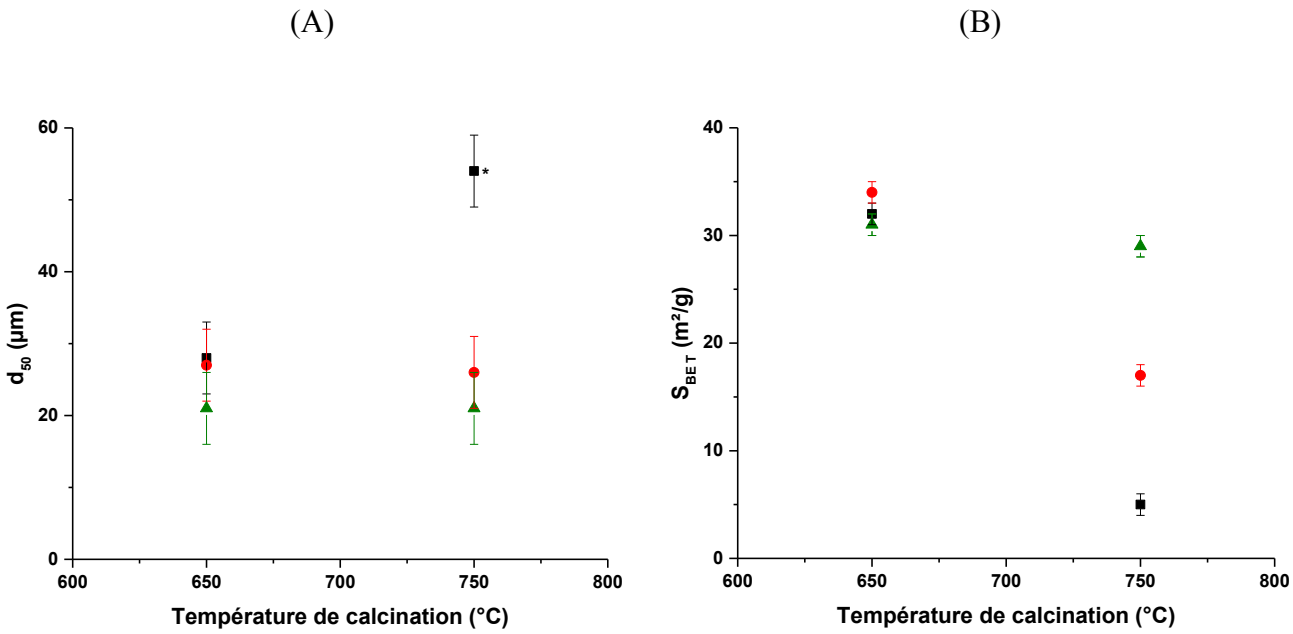


Figure 3. Valeurs de **(A)** granulométrie (d_{50}) et **(B)** de surface spécifique BET des argilites calcinées en (■) four statique, (●) four rotatif et (▲) four flash, en fonction de la température de calcination (* valeur divisée par 3 pour plus de lisibilité) .

Quel que soit le procédé utilisé, à 650 °C les valeurs de surface spécifique sont de l'ordre de 30 m²/g. La calcination à 750°C induit une très faible diminution pour l'échantillon AF750. Pour les deux autres échantillons, la valeur de S_{BET} diminue jusqu'à 17 et 5 m²/g, respectivement pour les argilites AR750 et A750. Les variations observées à 750 °C sont liées aux différents régimes de calcination induits par l'utilisation des différents procédés.

Les évolutions des propriétés physico-chimiques soulignent ainsi que l'argilite subit une densification associée à un accroissement granulaire, principalement en four statique. Dans le cas des réactions de géopolymérisation envisagées, cet accroissement pourrait limiter la dissolution de l'argilite dans la solution alcaline silicatée [11].

Les calcinations en fours flash et rotatif induisent des évolutions limitées des caractéristiques physico-chimiques de l'argilite, alors que celles en four statique entraîne une importante densification et agrégation des particules d'argilite.

c. Influence du type de four

Les variations structurales et physico-chimiques sont directement liées au type de four utilisé et au régime associé. En effet, les caractéristiques physico-chimiques de l'argilite A750

(four statique) sont caractéristiques d'un accroissement granulaire. Celui-ci est lié à un régime cinétique chimique, dû à la présence d'un lit de poudre favorisant la coalescence. Le four rotatif, dynamique, limite cet effet, qui disparaît complètement dans le four flash.

Ces différences de régime induisent des transformations structurales et physico-chimiques distinctes. En effet, le four statique conduit à des décompositions totales, favorisées par le régime cinétique chimique [12]. A l'inverse, lors de l'utilisation des fours rotatif et flash, le régime prédominant est de type diffusionnel. Les différences observées entre ces deux modes sont liées au temps de séjour. En effet, le four rotatif, effectuant un pallier d'une heure et demie, permet aussi la présence d'un régime chimique, alors que le four flash ne permet qu'un régime cinétique diffusionnel [13]. Ce changement de régime peut expliquer les degrés d'avancement des différentes décompositions au cours des traitements.

Afin de résumer l'influence des différentes calcinations de l'argilite sur les évolutions structurales, le taux d'atomes d'aluminium en coordinence IV en fonction du taux d'amorphe (estimé par quantification Rietveld, [14]) est reporté sur la **Figure 4**. En effet, le taux d'atomes d'$Al^{[4]}$ et le taux d'amorphe permettent d'estimer la réactivité de l'argilite [15]. Le taux d'atomes d'aluminium en coordinence IV augmente proportionnellement avec le taux d'amorphe. Cette augmentation de la réactivité est principalement liée à l'augmentation de la température de calcination mais aussi au procédé. Ainsi les argilites calcinées en four flash présentent les réactivités les plus faibles.

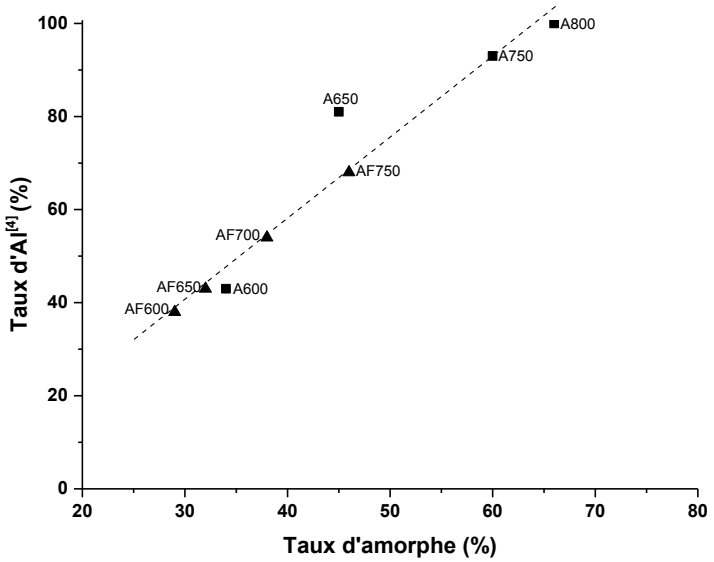


Figure 4. Evolution du taux d'$Al^{[4]}$ en fonction de la quantité d'amorphe des différentes calcinations d'argilite.

Afin de faciliter l'activation alcaline, les argilites les plus réactives, calcinées à haute température, sont sélectionnées. La température de 750 °C est retenue pour les fours statique et flash.

2. Activation alcaline

Afin d'étudier l'effet des différents traitements thermiques de l'argilite (A750 et AF750) en présence de solutions alcalines de réactivité variable ($S1_K^{0,58}$, $S2_{Na}^{0,70}$ et $S3_K^{0,50}$), différents mélanges ont été testés (incluant l'argilite crue), en conservant un rapport solide sur liquide s/l = 1,17. La nomenclature ne reprend que le nom de la solution et des argilites utilisées ; ainsi l'échantillon S1A25A750 correspond au mélange $S1_{1,17}A25_{0,5}A750_{0,5}^{0,58}$ (**Chapitre II, III.5**).

a. Essais de faisabilité

La faisabilité d'échantillons à base d'argilite a été évaluée par la détermination des différentes zones (absence de consolidation, consolidation en moins de deux minutes ou consolidation optimale) au sein du ternaire de faisabilité A25-A750-AF750 (**Figure 5.a,b,c** et **Tableau 1**) établi à l'aide de différentes solutions. En effet, l'incorporation d'argilite crue, A25, permet de s'affranchir de la consommation énergétique nécessaire à la calcination, et doit donc être étudiée. Pour favoriser la consolidation, l'utilisation d'argilites très réactives doit être privilégiée, comme celles calcinées à une température de 750 °C (partie **I.1.b**). Ainsi, l'argilite issue de calcination en four statique, A750, est retenue pour sa très forte réactivité et celle issue de calcination flash, AF750, pour sa similitude avec un produit industriel (four pilote industriel).

L'utilisation d'une solution silicatée sodique, S2 ([Na]~8,3 mol/L) (**Figure 5.a),** ne permet une consolidation optimale qu'en présence d'une majorité d'argilite A750. L'utilisation d'argilite AF750 et de la majorité des mélanges d'argilites (tel que l'échantillon S2A25AF750A750) permet une consolidation très rapide, voir immédiate, limitant la mise en forme et donc la faisabilité (**Tableau 1**). De plus, l'utilisation d'une majorité d'argilite crue (tel que l'échantillon S1A25) inhibe la consolidation du liant. L'emploi d'une solution potassique concentrée, S3 ([K]~8,7 mol/L), conduit à des résultats similaires (**Figure 5.b**). A l'inverse, une solution potassique de plus faible concentration, S1 ([K]~5,2 mol/L), permet d'obtenir une faisabilité optimale (**Figure 5.c**) [16, 17]. En effet, les solutions moins réactives présentent un nombre d'atomes d'oxygène non-pontants limité, conduisant à une dissolution plus faible de la source aluminosilicatée (**Chapitre I, III.2**) [18].

La consolidation de l'argilite est donc seulement possible en utilisant une majorité d'argilite calcinée. L'argilite A750 permet une consolidation optimale quelle que soit la solution alcaline. En effet, les mélanges contenant de l'argilite crue ou flashée présentent une granulométrie plus faible (**Figure 3.A**), accélérant la cinétique de consolidation [11], déjà très rapide en présence d'argilite (**Chapitre IV, ACL 3**).

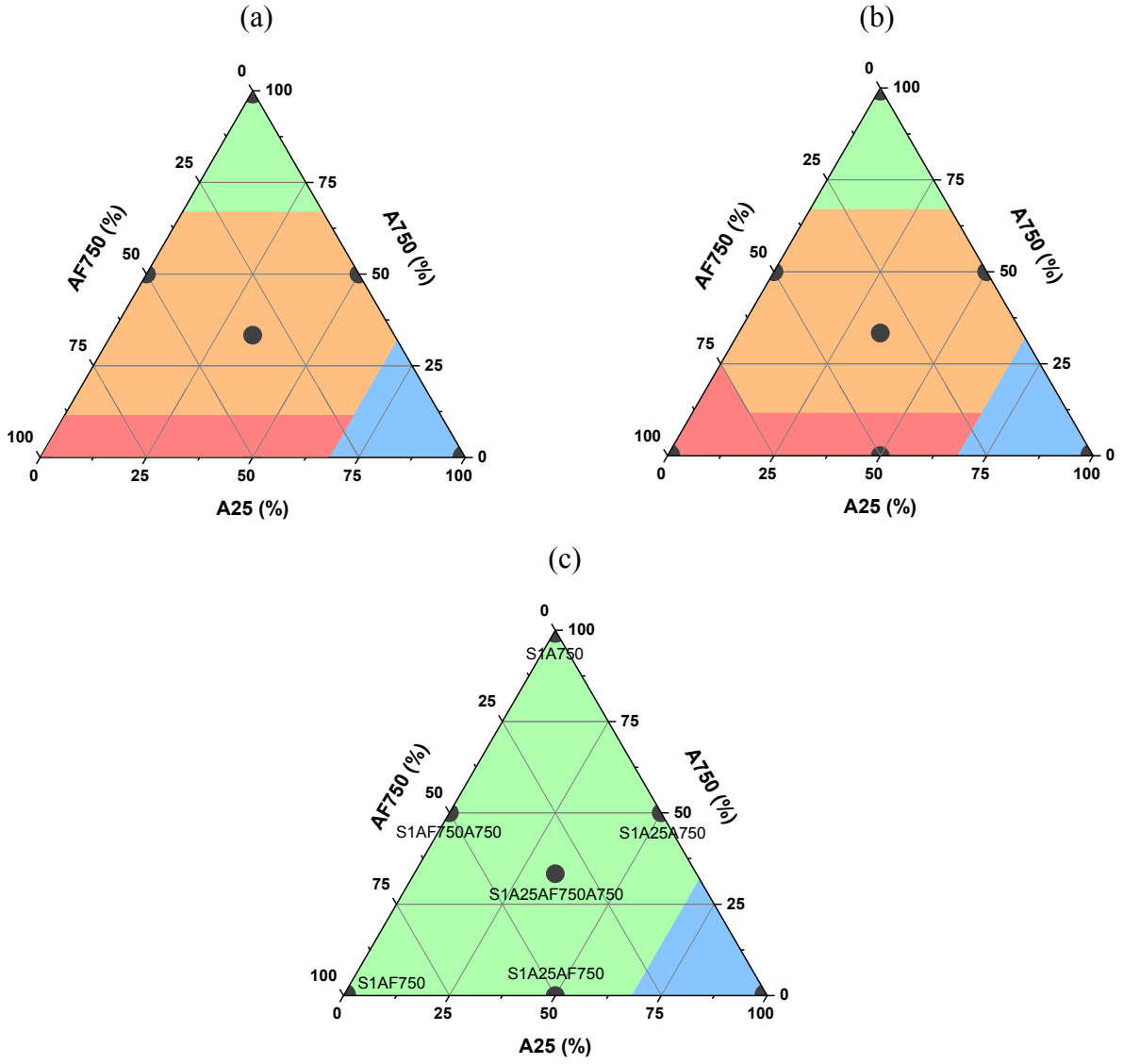
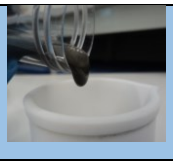
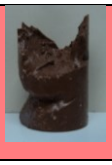


Figure 5. Ternaire de faisabilité d'échantillons consolidés à partir des argilites A25 - A750 - AF750 en présence des solutions de silicates **(a)** $S2_{Na}^{0,70}$, **(b)** $S3_{K}^{0,50}$ et **(c)** $S1_{K}^{0,58}$. (consolidation (🟩) optimale, (🟥) immédiate, (🟧) très rapide et (🟦) impossible).

Il faudra donc privilégier une solution potassique de concentration modérée (~5 mol/L) afin d'obtenir une consolidation optimale et de meilleures propriétés.

Tableau 1. Exemples de photographies d'échantillons en fonction du niveau de consolidation.

Echantillon	S1A25	S2A25AF750A750	S3AF750A750	S1A750
Photographie				
Type de consolidation	Impossible	Très rapide	Immédiate	Optimale

b. Etude de la géopolymérisation

La consolidation des échantillons à base d'argilite a pu être mise en évidence par des essais de faisabilité. Cependant, il est nécessaire de déterminer la nature des réactions mises en jeu.

Formation du réseau géopolymère

Parmi les techniques permettant la détermination des environnements locaux, la résonnance magnétique nucléaire a été sélectionnée pour différents échantillons (**Figure 6)**. Les décompositions de ces spectres sont disponibles en **Annexe III – C**.

Le spectre associé à l'argilite crue, A25, présente deux contributions d'atomes d'aluminium en coordinence VI, $Al^{[6]}$, et deux contributions d'atomes d'aluminium en coordinence IV, $Al^{[4]}$ (l'identification du spectre est détaillée en **Annexe III – B**). L'échantillon S1A25AF750 présente deux contributions associées aux atomes $Al^{[6]}$, identiques à celles observées sur l'argilite crue, localisées à 2,4 et -6,0 ppm (respectivement associées aux illites/smectites et à la kaolinite) [19, 20]. Deux autres contributions, associées aux atomes d'$Al^{[4]}$, sont aussi notables. La plus intense, à 66,0 ppm, correspond à des atomes d'aluminium insérés dans un réseau géopolymère alors que l'épaulement détecté à 72,6 ppm correspond à des liaisons Al-O-Ca [19, 21]. Celle-ci met en évidence la réactivité du calcium au sein des liants à base d'argilite. En effet, les atomes de calcium peuvent réagir avec les espèces présentes en solution (principalement à base d'aluminium ou de silice) afin de former des phases amorphes ou des composés cristallisés [22]. L'échantillon ne contenant que de l'argilite calcinée, S1AF750, présente des contributions similaires, mais la quantité d'$Al^{[4]}$ est plus élevée.

La décomposition de ces spectres (**Annexe III – D)** permet de quantifier la quantité d'aluminium associée au réseau. L'échantillon S1A25AF750 présente ~39 % d'$Al^{[4]}$ attribués au réseau géopolymère alors que l'échantillon S1AF750 en présente jusqu'à ~62 %. L'utilisation d'une source minérale composée intégralement d'argilite calcinée, permet donc

d'obtenir un réseau géopolymère plus important qu'en présence d'une source comportant de l'argilite crue, A25.

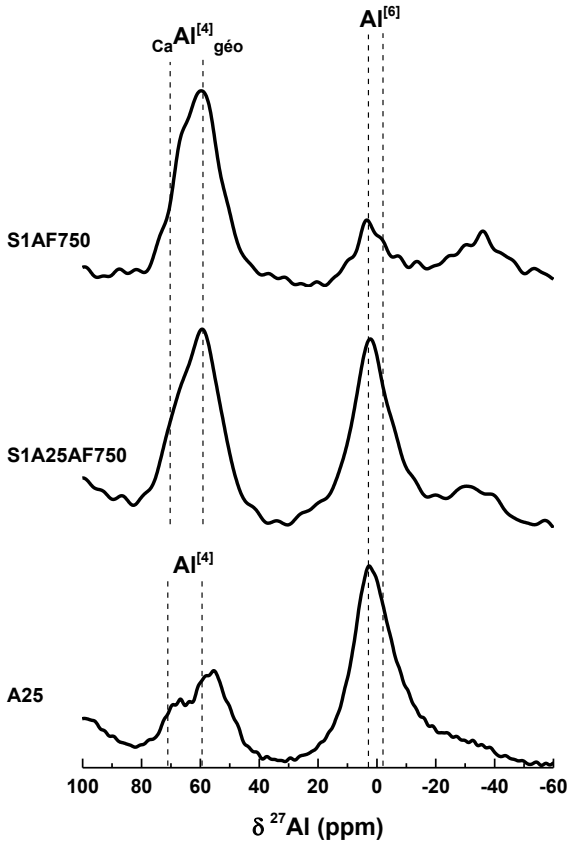


Figure 6. Spectre RMN MAS du ^{27}Al de l'argilite crue, A25, et des échantillons S1A25AF750 et S1AF750.

Il vient d'être démontré que certains échantillons présentent des atomes d'aluminium de degrés de coordinence IV différents, dont l'un d'entre eux correspond aux atomes d'aluminium dans le réseau géopolymère. Afin de conclure sur la formation du réseau géopolymère, les données telles que les valeurs de contrainte à la rupture, de déplacement de la bande Si-O-M (IRTF) en relation avec la formulation ([Al]) sont reportées sur la **Figure 7** (**Chapitre IV, ACL 2**). En effet, ces différentes grandeurs ont souvent été confrontées pour valider les réactions de polycondensation au sein de ces matériaux [23, 24].

La comparaison de ces grandeurs permet de distinguer deux groupes.

(i) Les échantillons contenant une fraction d'argilite crue (50 ou 33 $\%_{mass}$) présentent une valeur de déplacement proche de 10 cm^{-1} associée à des réactions de silicatage entraînant des valeurs de résistance mécanique inférieures à 10 MPa [25, 26].

(ii) Les échantillons contenant uniquement de l'argilite calcinée (A750 ou AF750) présentent un déplacement de l'ordre de 20 cm^{-1}, associé à une contrainte à la rupture d'environ 15 MPa et à une concentration en aluminium supérieure à 7 mol/L. Ces données sont en faveur des réactions de polycondensation conduisant à un réseau géopolymère [22].

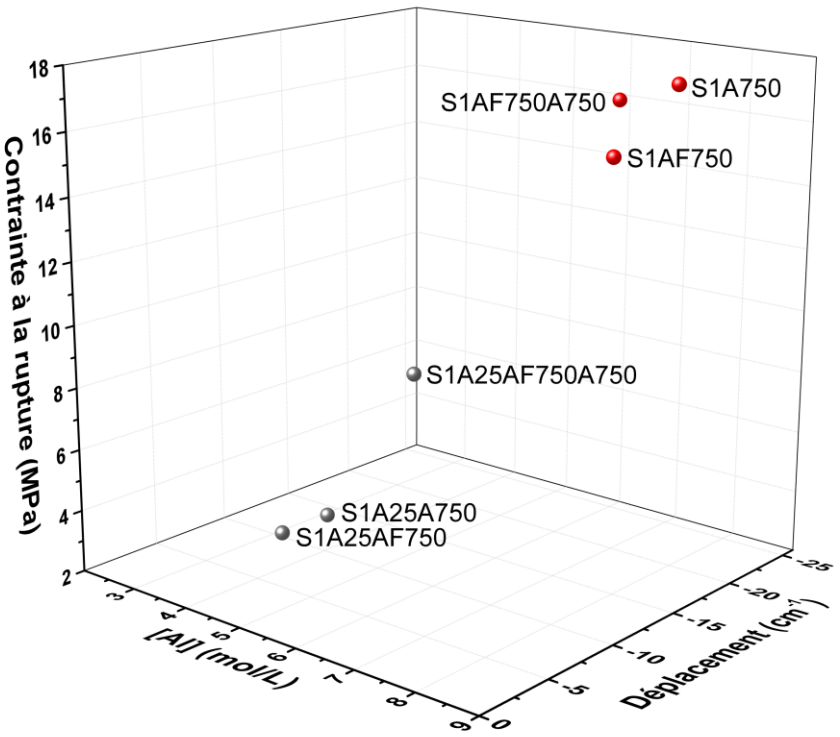


Figure 7. Valeurs de contrainte à la rupture et du déplacement de la liaison Si-O-M (IRTF) en fonction de la concentration en aluminium pour les échantillons du ternaire A25-AF750-A750 en présence de la solution S1.

L'activation alcaline de l'argilite permet donc d'obtenir des matériaux consolidés présentant un réseau géopolymère, dont le développement est supérieur en présence d'argilite calcinée.

Influence du calcium dans les liants

La partie **I.1.b** a mis évidence l'importance des modifications structurales liées aux espèces carbonatées, calcite et dolomite, lors du traitement thermique. Il en résulte la formation d'oxydes de calcium et de magnésium (quantifiée dans le **chapitre IV, ACL 2**), qualifiés de

réactifs en présence d'une solution d'activation. Il est donc nécessaire d'identifier et de comprendre l'évolution de ces espèces dans les échantillons alcali-activés.

La **Figure 8** présente ainsi les pertes de masse observées par analyse thermique sur une sélection d'échantillons (S1A750, S1AF750 et S1A25AF750A750). Ces pertes de masse peuvent être divisées en trois domaines de température.

(i) Le premier, entre 25 et 600 °C, correspond principalement aux pertes d'eau contenue dans l'échantillon, mais aussi aux décompositions d'hydroxydes ($Ca(OH)_2$ / $Mg(OH)_2$), de composés sulfures (pyrite) et à la déshydratation des minéraux argileux (A25) [1].

(ii) Le second, entre 600 et 750 °C, est associé à la décomposition du $CaCO_3$ et de la dolomite résiduels présents dans les argilites A25 et AF750 [1, 2].

(iii) Le dernier, au-delà de 750 °C, correspond à la décomposition de la calcite la plus réfractaire.

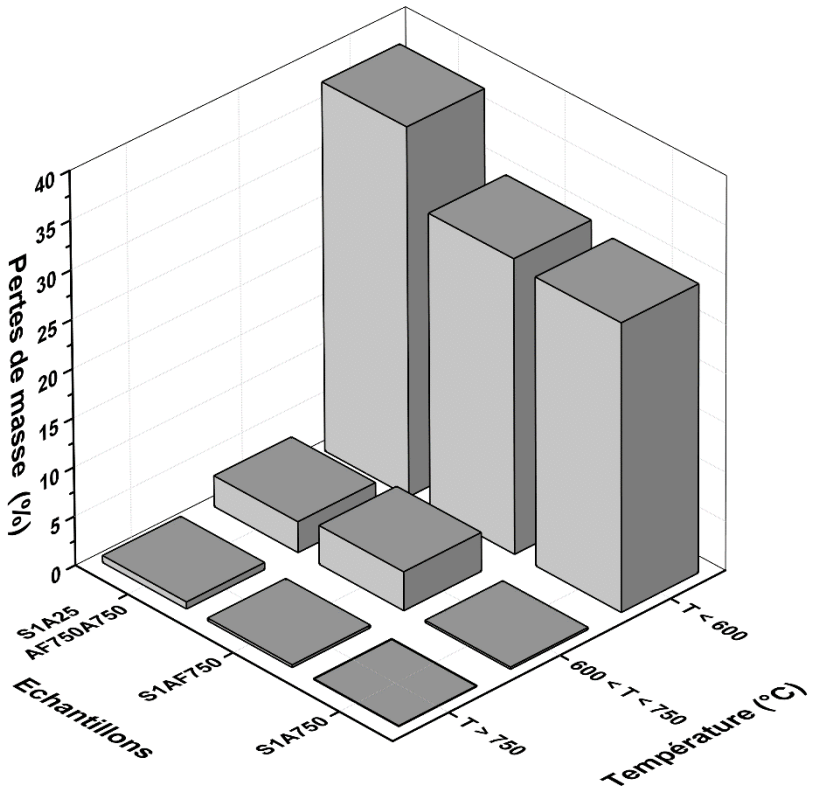


Figure 8. Valeurs des pertes de masse déterminées par analyse thermique, inférieures à 600 °C, comprises entre 600 et 750 °C et supérieures à 750 °C, pour les échantillons S1A25AF750, S1AF750 et S1A750.

Les pertes de masse pour une température inférieure à 600 °C, sont de l'ordre de 35 % pour l'échantillon S1A25AF750A750 (contenant de l'argilite crue) et de 30 % pour les échantillons S1AF750 et S1A750 (ne contenant que de l'argilite calcinée). Les pertes les plus faibles, relatives aux échantillons à base d'argilite calcinée, s'expliquent par la présence d'un réseau géopolymère plus conséquent [22]. La perte de masse observée entre 600 et 750 °C est presque nulle (< 0,5 %) pour l'échantillon S1A750, alors qu'elle est respectivement de 3,0 et 4,0 % pour les autres échantillons. Cela s'explique par la présence de composés carbonatés non décomposés au sein des argilites A25 et AF750. Au-delà de 750 °C les pertes sont très faibles, seul l'échantillon contenant de l'argilite crue, S1A25AF750A750, présente une perte de masse significative.

Afin d'identifier les composés carbonatés, des caractérisations ont été réalisées par spectroscopie infrarouge (IRTF) et par diffraction des rayons X (**Figure 9**). Celles-ci se focalisent sur la sélection d'échantillons précédemment étudiés et sont comparées aux données de l'argilite AF750 (contenant de la dolomite et de la calcite).

Le spectre IRTF de l'argilite AF750, **Figure 9.A**, présente trois contributions d'espèces carbonatées, à 1510, 1455 et 1430 cm^{-1}, respectivement associées à de la calcite, de la dolomite et de la calcite (**Annexe II – B**). L'activation alcaline des échantillons S1A25AF750A750 et S1AF750 conduit à la diminution des deux premières contributions (1510 et 1455 cm^{-1}) au profit d'une unique contribution. Cette large contribution est localisée entre 1415 et 1380 cm^{-1}, entre la position de la contribution de la calcite et celle du carbonate de potassium. Cela souligne la présence de réactions entre les différents cations alcalins et alcalino-terreux. Le spectre de l'échantillon S1A750 présente la même contribution, de moindre intensité due à la faible quantité d'espèces carbonatées présentes dans l'argilite A750. Il est ainsi supposé que lors de l'activation alcaline, les espèces carbonatées réagissent avec un excès d'élément potassium apporté par la solution S1, formant ainsi des carbonates mixtes calcium-magnésium-potassium [27].

Le diffractogramme de l'argilite AF750 (**Figure 9.B**) présente une large raie associée à la calcite (29,4 ° 2θ). Après activation alcaline, les échantillons S1A25AF750A750 et S1AF750 présentent un léger décalage de ce pic, vers la position de la butschliite à 29,5 ° 2θ ($K_2Ca(CO_3)_2$). De même, l'échantillon S1A750 présente aussi ce décalage, faiblement discernable de par la très faible intensité du pic, ainsi qu'une contribution de l'arcanite (K_2SO_4). Le décalage du pic de calcite à une position intermédiaire entre la calcite et la butschliite

confirme les observations faites en IRTF sur la formation d'un carbonate mixte au sein de l'échantillon. La formation d'arcanite dans l'échantillon A750, est issue d'une réaction entre les atomes de potassium (solution alcaline silicatée) et les atomes de soufre issus de la décomposition de la pyrite. Cela souligne à nouveau que l'élément potassium est capable de diffuser au sein du mélange réactif. Les carbonates mixtes sont donc également formés par les atomes de potassium présents dans le mélange réactif.

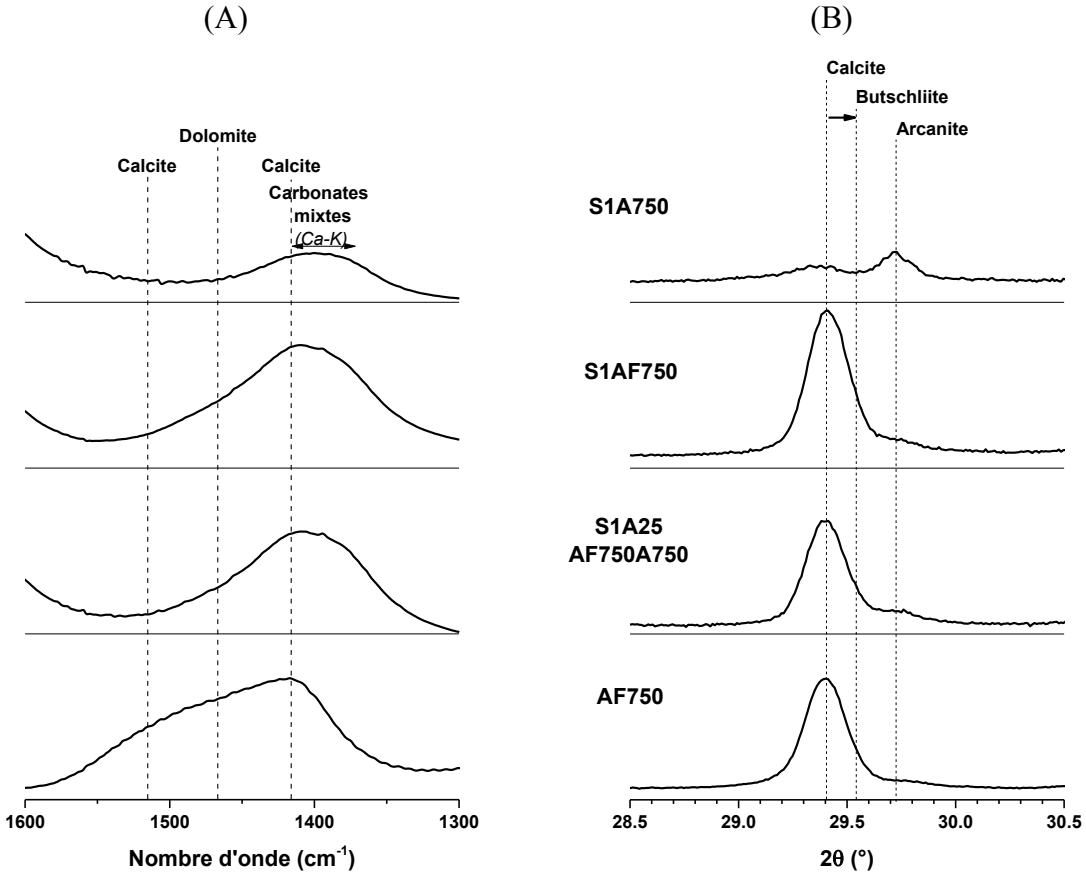


Figure 9. (A) Spectres IRTF et **(B)** diffractogrammes centrés sur le domaine angulaire (28,5-30,5 ° 2θ) relatifs aux espèces carbonatées des échantillons AF750, S1A25AF750A750, S1AF750 et S1A750.

La **Figure 10** résume les différentes réactions ayant lieu lors de la calcination de l'argilite et de son activation alcaline.

(i) Les minéraux argileux contenus dans l'argilite sont déstructurés lors de la calcination, ce qui conduit respectivement à la formation de 94 et 68 % d'$Al^{[4]}$ pour les argilite A750 et AF750. La pyrite est décomposée lors du traitement thermique, conduisant à l'apparition d'oxyde de fer et de diffèrents sulfates qui s'associent aux cations calcium et magnésium « libres ». Les

espèces carbonatées sont partiellement décomposées lors du traitement thermique, respectivement de 68 et 13 % pour l'argilite A750 et AF750 (**Chapitre IV, ACL 2**).

(ii) L'activation alcaline de ces minéraux conduit à la formation du réseau géopolymère, mais quel que soit le type d'argilite utilisée une fraction d'illites/smectites ne réagit pas. Les cations alcalino-terreux réactifs forment des hydroxydes ou réagissent avec les sulfates. Lors de l'activation alcaline, ceux-ci réagissent avec le potassium afin de former un carbonate mixte potassium-alcalino-terreux. Le calcium en excès peut aussi réagir avec les espèces siliceuses afin de former des liaisons Si-O-Ca (**Chapitre IV, ACL 2**).

(iii) Enfin, les tectosilicates ne présentent pas d'évolutions significatives lors de la calcination et de l'activation alcaline.

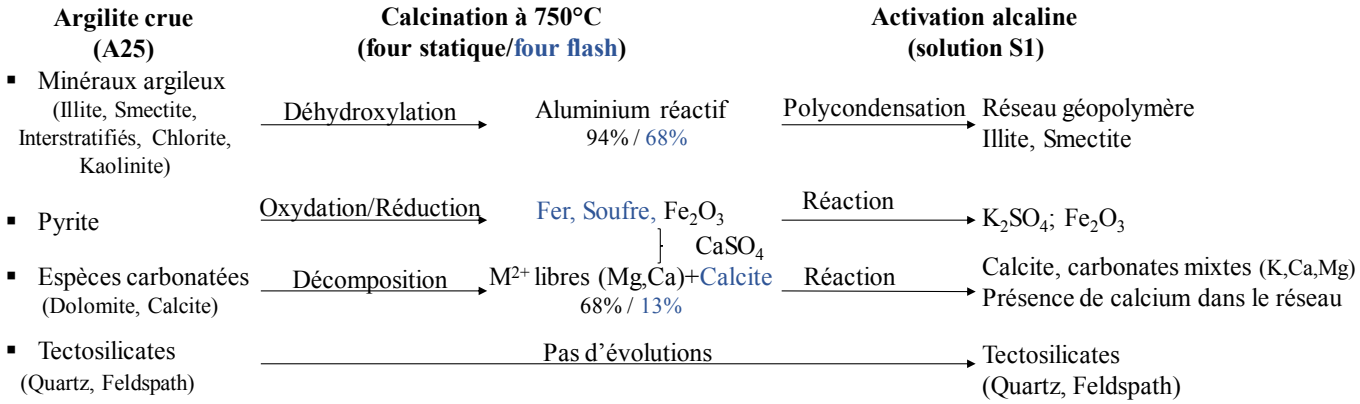


Figure 10. Bilan des évolutions structurales observées sur l'argilite lors de la calcination puis de l'activation alcaline.

L'activation alcaline des argilites conduit à la formation d'un réseau géopolymère mais aussi de différents composés cristallisés (carbonates, sulfates). Il est ainsi nécessaire d'identifier l'évolution de ces composés au cours de leur vieillissement, ou de la simuler en température.

c. Evolution en température

De manière à étudier les évolutions des phases secondaires au sein des échantillons, des traitements en température sont effectués sur les échantillons $S1_{1,49}AF750^{0,58}$ et $S1_{1,28}A750^{0,58}$. Ceux-ci sont respectivement nommés S1AF750 et S1A750 dans la partie **II.2.c** pour plus de lisibilité. Ces échantillons ont été traités à 800 °C, par un traitement en four classique et par un

choc thermique réalisé dans un four ascenseur (**Chapitre II, III.4**). Ces deux traitements seront respectivement notés « classique » et « choc », et les échantillons non traités en température seront notés « brut ».

Évolutions structurales suite au traitement thermique

Des essais de résistance mécanique en compression ont été effectués sur l'échantillon S1AF750 avant et après traitement thermique classique et choc (**Figure 11.A**). L'échantillon de référence présente une contrainte à la rupture de 12 MPa qui augmente de plus de 100 % lors du traitement thermique classique, et s'effondre à ~3 MPa après le choc thermique. Cette dernière valeur est essentiellement due à la fissuration généralisée de l'échantillon. Les micrographies de l'échantillon S1AF750 brut et après traitement classique à 800°C (**Figure 11.B.a,b)** sont caractéristiques d'un échantillon géopolymère et d'un composé présentant des renforts créés in situ (**Chapitre IV, ACL 3**).

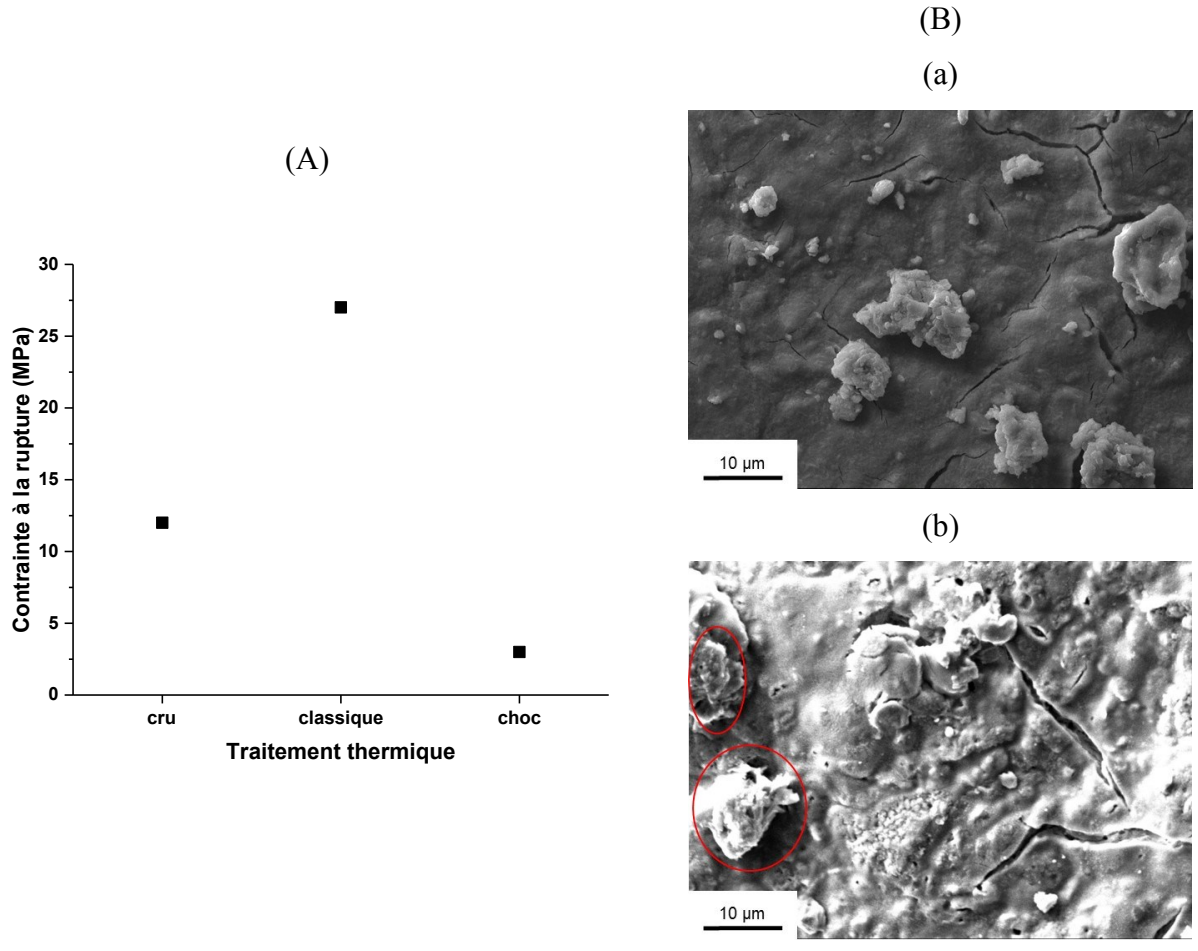


Figure 11. (A) Valeurs de la résistance mécanique en compression pour l'échantillon S1AF750 brut et après différents traitements thermiques et **(B)** micrographies de l'échantillon S1AF750 **(a)** avant et **(b)** après traitement thermique en four (les phases cristallisées formées sont entourées de rouge).

Le diffractogramme de l'échantillon S1AF750 brut (**Figure 12.A)** présente des phases argileuses (illite/muscovite et muscovite déhydroxylée), du quartz, de la calcite/carbonate mixte et de l'arcanite. Après un traitement thermique classique, la calcite est intégralement décomposée et la muscovite déhydroxylée est partiellement décomposée. Ceci entraîne la formation de nouvelles phases comme la wollastonite $CaSiO_3$ (particules aciculaires correspondant aux observations de la **Figure 11.B.b**) et une phase de type zéolite, $KAlSiO_4$. Le traitement en choc thermique conduit à des évolutions similaires. La formation de wollastonite est cependant plus faible et d'autres phases silico-calciques apparaissent, comme la kilchoanite, $Ca_6Si_3(SiO_4)O_{10}$, et la diopside, $CaMgSi_2O_6$ (**Chapitre IV, ACL 4**).

Les évolutions en température présentent des variations qui pourraient être similaires à celles observées lors du vieillissement. Afin de le vérifier, la **Figure 12.B** présente les diffractogrammes de l'échantillon S1A750 à 7 jours, dix-huit mois et après traitement thermique classique. Initialement l'échantillon S1A750 présente des phases similaires à celles de l'échantillon S1AF750 (**Figure 12**), sans présence de calcite. Après un an et demi de vieillissement, le diffractogramme de l'échantillon S1A750 présente une nouvelle phase, associée à un large dôme vers 29 ° 2θ. Cette contribution peut être attribuée à la kilchoanite, mais aussi à différents types de silicates dus au large dôme. Le traitement thermique classique sur cet échantillon, conduit à la cristallisation de la pseudo-kilchoanite formée au cours du temps ainsi qu'à la formation de wollastonite. Cela confirme donc la métastabilité de la phase de kilchoanite. L'échantillon S1A750 traité en four classique présente les mêmes évolutions que l'échantillon S1AF750 traité en température.

Le vieillissement de l'échantillon entraîne la présence de phases similaires à celles observées lors d'un traitement thermique. Les phases en présence sont légèrement différentes, plus proches du traitement choc que du four, soulignant des évolutions très lentes. Les études en température peuvent donc être la signature du comportement lors du vieillissement.

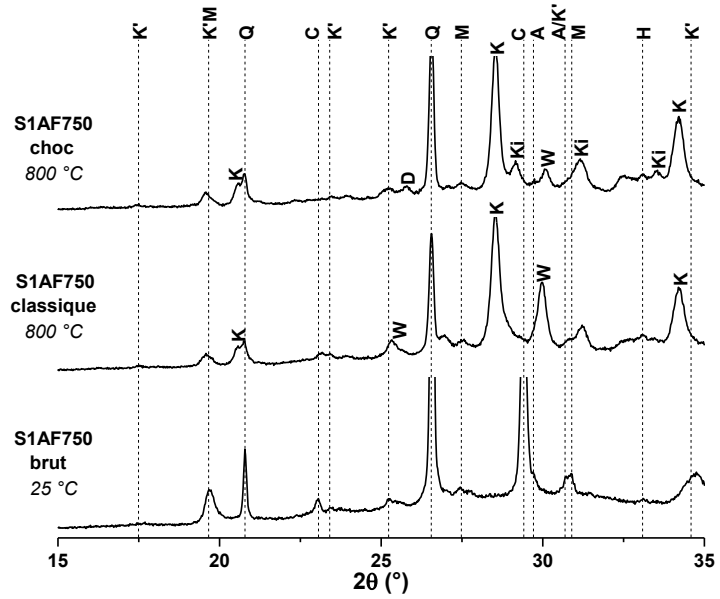
Proposition d'un modèle de réactions

L'évolution structurale des échantillons au cours du temps étant un paramètre très important dans le cadre du projet Cigéo, il a été décidé d'approfondir l'étude des variations structurales en température. Un modèle des réactions pouvant avoir lieu a été établi à partir des données d'analyses thermiques et de diffraction des rayons X (**Figure 13**).

Les premières pertes de masse (déterminées par ATD-TG) sont associées à la décomposition des hydroxydes (respectivement à 380 et 430 °C), conduisant à des cations Mg^{2+}

et Ca^{2+}réactifs. A partir de 600 °C les minéraux argileux s'amorphisent et les cations Al^{3+}, Si^{4+} et K^{+} deviennent réactifs. Les composés carbonatés se décomposent au-delà de 700 °C (**Chapitre IV, ACL 4**).

(a)



(b)

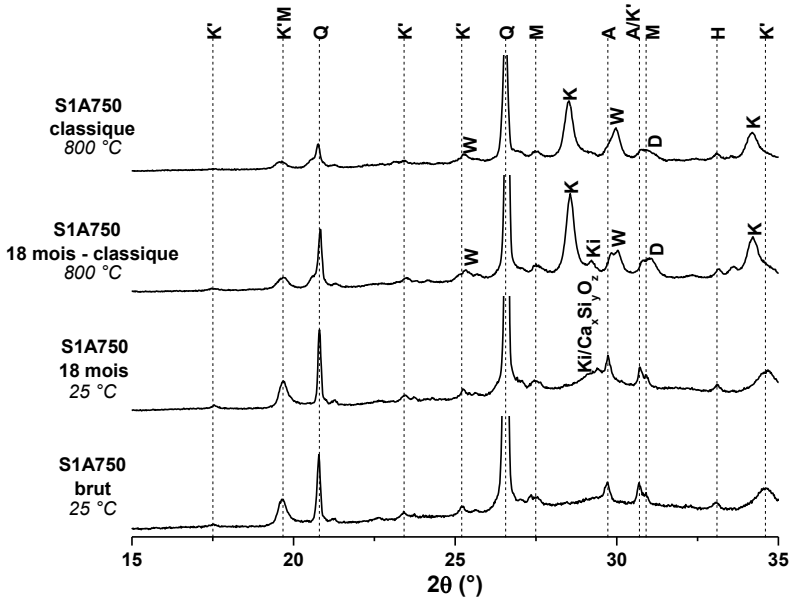


Figure 12. Diffractogrammes de **(a)** l'échantillon S1AF750 brut, après traitement thermique classique et après choc thermique et **(b)** l'échantillon S1A750 brut, après 18 mois de vieillissement et après traitement thermique classique pour les deux échantillons (K' : muscovite déhydroxylée, M : illite/muscovite, K : zéolite, Q : quartz, C : calcite/carbonates mixtes, D : diopside, W : wollastonite, Ki : kilchoanite et H : hématite).

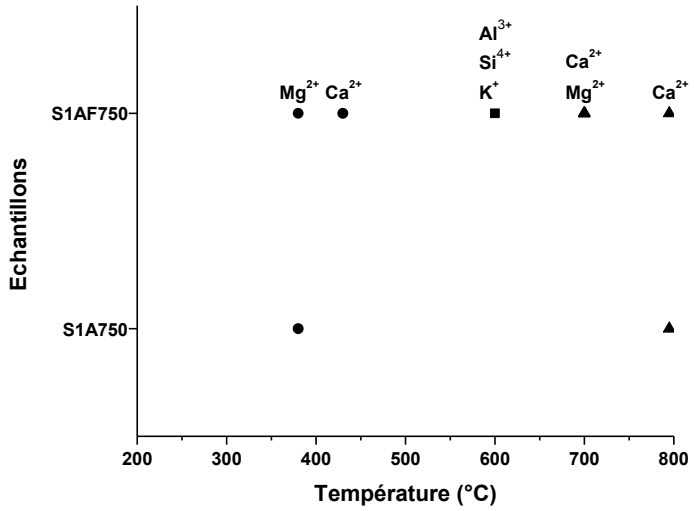


Figure 13. Valeurs des températures de décomposition et nature des espèces identifiées lors de la décomposition des (●) hydroxydes, (■) minéraux argileux et (▲) espèces carbonatées.

Les produits formés lors de ces décompositions conduisent à la formation de deux principales phases.

(i) Les produits de décomposition issus de la déhydroxylation des minéraux argileux, non incorporés dans le réseau géopolymère, réagissent pour former la phase zéolitique $KAlSiO_4$ (**Eq. 5**). Cette phase se forme par insertion des atomes de potassium, provenant du réseau géopolymère et/ou des carbonates mixtes, entre un feuillet de tétraèdres d'aluminium (AlO_4) et un feuillet de tétraèdres de silicium (SiO_4) [28]. Cette phase usuellement formée à 1200 °C peut se former à plus basse température du fait de la présence de cations alcalins [29, 30].

$$KAl_3Si_3O_{11} + K_2O \rightarrow 3\,KAlSiO_4 \qquad \textbf{Eq. 5}$$

(ii) Les produits de décomposition des hydroxydes (**Eq. 6** et **Eq. 7**) et des espèces carbonatées (**Eq. 8** et **Eq. 9**) réagissent avec la silice afin de former la wollastonite (**Eq. 10**). En effet, cette phase cristallise à 780 °C et sa formation a déjà été observée dans des matériaux alcali-activés [31, 32]. Les atomes de magnésium contenus dans l'échantillon, très minoritaires vis-à-vis du calcium, réagissent pour former la diopside (**Eq. 11**) [33].

$$Ca(OH)_2 \rightarrow CaO + \overrightarrow{H_2O} \qquad \textbf{Eq. 6}$$

$$Mg(OH)_2 \rightarrow MgO + \overrightarrow{H_2O} \qquad \textbf{Eq. 7}$$

$CaMg(CO_3)_2 \rightarrow MgO + CaCO_3 + \overrightarrow{CO_2}$ **Eq. 8**

$CaCO_3 \rightarrow CaO + \overrightarrow{CO_2}$ **Eq. 9**

$CaO + SiO_2 \rightarrow CaSiO_3$ **Eq. 10**

$CaO + MgO + 2\,SiO_2 \rightarrow CaMgSi_2O_6$ **Eq. 11**

Les transformations observées lors du traitement choc sont similaires, seule la phase à base de calcium diffère. Ce traitement très rapide ne permet pas la formation de la wollastonite, mais celle d'un silicate de calcium métastable, la kilchoanite (**Eq. 12**) [34, 35]. Par ailleurs cette phase, qui n'apparaît que pour des raisons cinétiques, est également détectée lors du vieillissement de l'échantillon S1A750 (dix-huit mois). Cela conforte l'hypothèse que les évolutions structurales induites par le traitement thermique et par le vieillissement présentent des similitudes.

$6\,CaO + 4\,SiO_2 \rightarrow Ca_6Si_3(SiO_4)O_{10}$ **Eq. 12**

L'argilite a ainsi pu être activée thermiquement et alcalinement, ce qui a conduit à des matériaux consolidés présentant un réseau géopolymère et des phases secondaires, dont l'évolution en température permet de prévoir le vieillissement.

Il est donc nécessaire d'optimiser les propriétés des liants développés, afin d'atteindre le cahier des charges (viscosité, durée pratique d'utilisation et valeur de pH).

III. FORMULATION D'UN COULIS GEOPOLYMERE

L'activation alcaline de l'argilite conduit à des échantillons consolidant très rapidement, en moins de dix minutes avec de l'argilite calciné à 750 °C. La formulation du coulis visé nécessite un liant présentant une viscosité de l'ordre de 0,5-5,0 Pa.s, une durée pratique d'utilisation (DPU) supérieure à 24 heures et une valeur de pH, après consolidation, comprise entre 10 et 11. Au vu de la très faible valeur de DPU des liants à base d'argilite, le développement d'un coulis à base de métakaolin a été envisagé, afin de faire une étude « modèle » sur un mélange de référence. Ceci a été fait afin de développer le coulis répondant au cahier des charges, et de comprendre les évolutions structurales induites par les additifs utilisés.

1. Contrôle des valeurs de pH et de DPU

a. Définition d'un mélange de base

Afin de développer le coulis, il est nécessaire de définir la formulation du liant de référence. Compte tenu de la faible réactivité de l'argilite calcinée, le métakaolin sélectionné est un métakaolin peu réactif, nommé M1, utilisé depuis près de onze ans au laboratoire [36]. La solution alcaline silicatée S1, ayant permis l'activation alcaline optimale de l'argilite, a été privilégiée. Par conséquent, la formulation S1M1, dont les caractéristiques (rapport s/l, Si/M et cation alcalin) restent à déterminer, est choisie.

Les courbes de viscosité en fonction du temps de mélanges $S1M1^{0,58}$ présentant des rapports s/l de 0,64 à 1,17 sont regroupées sur la **Figure 14**. Les valeurs de viscosité initiale des échantillons de rapport l/s compris entre 0,85 et 1,07 sont dans la gamme requise. De plus, la valeur de DPU augmente de manière significative lorsque le rapport s/l diminue. L'utilisation d'une faible valeur (0,85 ou 0,90) devrait être choisie. Néanmoins les études antérieures au laboratoire, axées sur la valeur s/l = 1,01, sont nombreuses et c'est cette valeur qui est retenue.

Le second paramètre ajustable est le rapport Si/M de la solution, qui définit la concentration en espèces alcalines. Différents essais ont été effectués sur le mélange $S1_{1,01}M1$ avec des solutions $S1_K$ de rapport Si/M compris entre 0,50 et 1,00 (**Tableau 2**). Tous les échantillons présentent une consolidation. Au-delà d'un rapport Si/M de 0,80 la consolidation est lente et conduit à des échantillons ne présentant pas l'aspect d'un géopolymère (pas de brillance ni de surface lisse/homogène). Ces résultats sont en accord avec les différents travaux effectués au sein du laboratoire, qui préconisent une valeur du rapport Si/M comprise entre 0,50 et 0,80,

quel que soit le cation M [37]. Il est donc choisi de travailler avec un rapport Si/M compris entre 0,60-0,80 pour préserver une durée de consolidation faible.

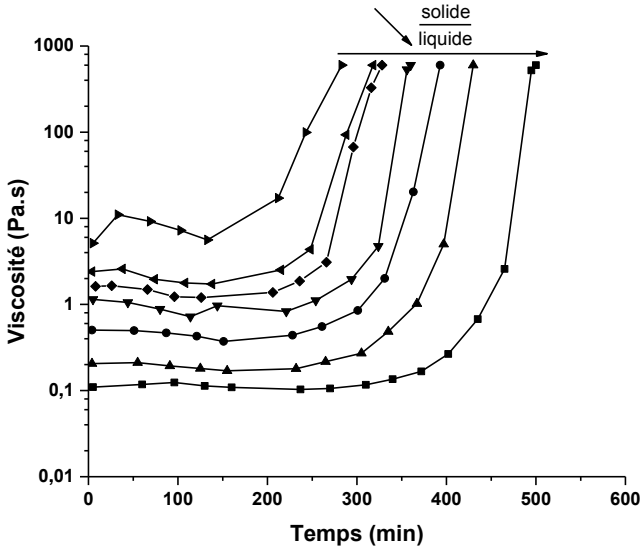


Figure 14. Courbes de viscosité en fonction du temps des mélanges $S1M1^{0,58}$ présentant des rapports s/l de (■) 0,64, (▲) 0,75, (●) 0,85, (▼) 0,90, (◆) 1,01, (◀) 1,07 et (▶) 1,17.

Tableau 2. Caractéristiques des mélanges $S1_{1,01}M1$ synthétisés avec différentes valeurs de rapport Si/M.

Si/M	**0,5**	**0,6**	**0,7**	**0,8**	**0,9**	**1,0**
Valeur de pH de S1	14,00	13,95	13,90	13,65	13,35	13,05
Temps de consolidation (heures)	< 24				< 40	< 100
Photo (Φ ~35 mm)						

L'impact du rapport Si/M de la solution sur la durée pratique d'utilisation a donc été quantifié, afin de sélectionner le rapport optimal pour atteindre la DPU ciblée. La nature du cation alcalin (K ou Na) a également été étudiée (**Figure 15**). L'utilisation d'un hydroxyde sodique, lors de la préparation de la solution S1, conduit systématiquement à des valeurs de viscosité supérieures à 10 Pa.s, bien supérieures à la valeur requise. La valeur de la DPU

diminue fortement avec l'utilisation de la solution $S1_{Na,}$ imposant l'utilisation d'une solution potassique [38]. Les deux solutions potassiques $S1_K^{0,70}$ et $S1_K^{0,80}$ présentent une valeur de DPU similaire. L'utilisation de la solution $\underline{S1_K^{0,70}}$, de viscosité initiale plus faible, est privilégiée.

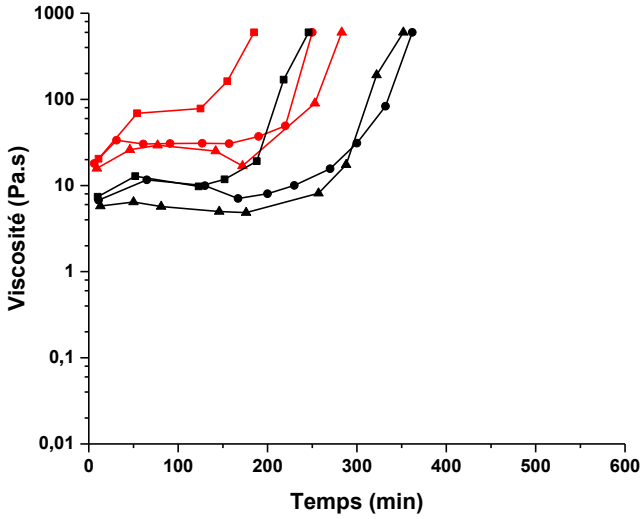


Figure 15. Evolution de la viscosité en fonction du temps des mélanges S1M1 à base de solution $S1_K$ (noir) et $S1_{Na}$ (rouge) pour des rapport Si/M de (■) 0,58, (●) 0,70 et (▲) 0,80.

Le mélange de référence utilisé est donc potassique, de rapports Si/K = 0,70 et s/l = 1,01, correspondant au liant $S1_{1,01}M1^{0,70}$.

b. Utilisation d'additifs

Afin d'atteindre les valeurs ciblées par le liant, l'utilisation d'additifs est indispensable. Ces additifs, minéraux, sont tous à base de cations formateurs de verres (B ou P) sous forme acide ou associés à un cation alcalin/alcalino-terreux. En effet, les atomes de bore ou de phosphore, pouvant être en coordinence IV, peuvent potentiellement participer au réseau géopolymère et les cations alcalin/alcalino-terreux peuvent compenser les chaînes ainsi formées [39, 40].
Le mélange de référence utilisé, $S1_{1,01}M1^{0,70}$, sera nommé S1M1 jusqu'à la fin de la partie **III**. L'ajout d'additif s'effectuant uniquement sur ce liant, les mélanges à base d'additif seront uniquement nommés par le nom de l'additif et son pourcentage d'insertion. NaB^{10} correspondra donc à l'échantillon $S1_{1,01}M1^{0,70}\,NaB^{10}$.

L'influence de l'ajout de différentes quantités d'hydrogénophosphate de potassium ($KHPO_4$), d'acide orthophosphorique (H_3PO_4), d'acide borique (H_3BO_3), de tétraborate de

sodium ($Na_2B_4O_7$, 10 H_2O), de tétraborate de lithium ($Li_2B_4O_7$) et de colémanite ($Ca_2B_6O_{11}$, 5 H_2O) sur les valeurs de DPU et pH est donnée sur la **Figure 16**.

Afin d'augmenter la DPU des mélanges réactifs, **Figure 16.A**, l'utilisation de bore ou de phosphore, sous forme acide, conduit aux variations les plus importantes. L'augmentation de la quantité d'additif permet d'augmenter la valeur de DPU au-delà de 1400 min, pour des quantités d'additifs introduits très limitées (< 3 $\%_{mass}$). En présence de composés à base de cations alcalins ou alcalino-terreux, des quantités supérieures (5-15 $\%_{mass}$) conduisent à des évolutions plus contrastées. Pour le tétraborate de lithium et la colémanite, quelle que soit la quantité, la valeur de DPU n'est pas affectée. A l'inverse, l'insertion d'hydrogénophosphate de potassium permet une augmentation continue de la DPU, jusqu'à la doubler. Seul le tétraborate de sodium permet une importante augmentation de DPU, jusqu'à plus de 500 %.

(A) (B)

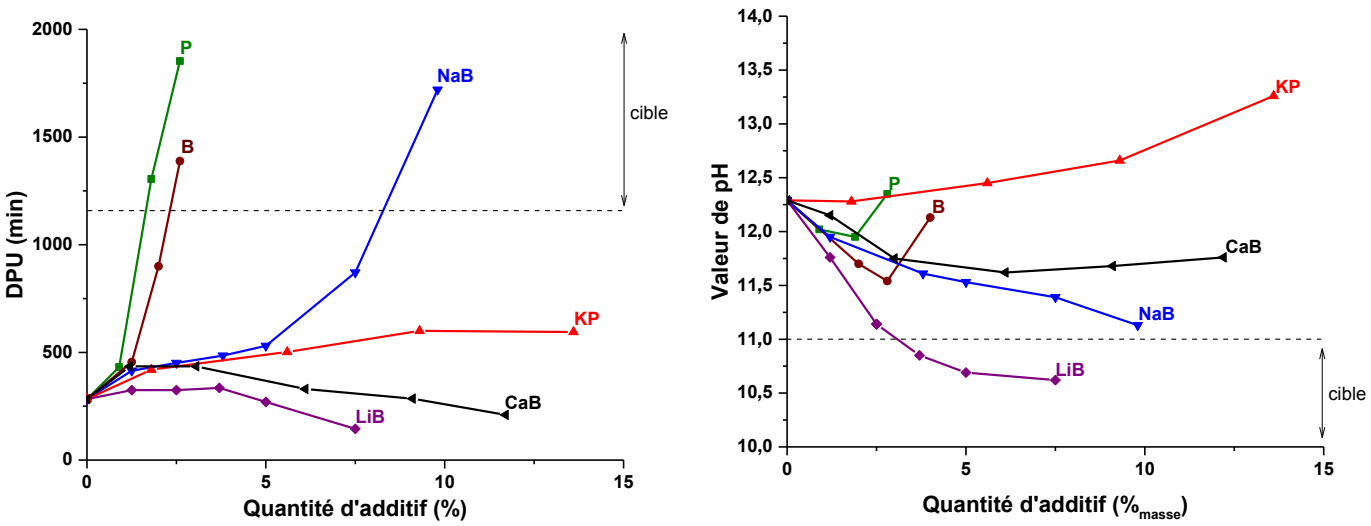


Figure 16. Valeurs de **(A)** DPU et **(B)** pH de l'échantillon S1M1 en fonction de l'introduction de différentes quantités de (▲) KP, (■) P, (●) B, (▼) NaB, (◆) LiB et (◀) CaB.

Les évolutions de la valeur de pH des liants (**Figure 16.B)**, ne présentent pas les mêmes variations. L'ajout d'acide induit des évolutions très dépendantes de la quantité d'additif introduit. Les valeurs de pH passent par un minimum de 12,0 (P) et 11,5 (B). L'augmentation observée peut être due à une quantité d'acide excédentaire, inhibant les réactions de polycondensation (**Chapitre 4, ACL 4**). Les composés à base d'alcalins/alcalino-terreux présentent des comportements différents de ceux observés sur la DPU. L'hydrogénophosphate de potassium conduit à une augmentation de la valeur de pH. Pour les autres additifs, il y a une

diminution de la valeur de pH en fonction du taux d'additif. Les deux tétraborates, de lithium et de sodium, sont les seuls à conduire à une valeur de pH proche des valeurs ciblées (respectivement 10,8 et 11,2).

Les variations des valeurs de DPU et de pH sont divergentes en fonction du type d'additif introduit. Cela est dû à la nature des cations formateurs, des contre-cations et de la quantité introduite. Cependant, un additif permet d'atteindre des caractéristiques ciblées par l'Andra, à savoir le tétraborate de sodium. Pour chaque additif, une composition optimale a été sélectionnée, en tenant en compte des valeurs de DPU et de pH. Les mélanges ainsi retenus ($KP^{9,3}$, $P^{2,8}$, $B^{2,8}$, $NaB^{10,0}$, $LiB^{3,7}$ et $CaB^{6,1}$) vont être maintenant analysés.

Les valeurs de résistance mécanique en compression ainsi que la quantité d'eau (perte de masse < 300 °C), déterminée par analyse thermique de chacun de ces échantillons, ont été reportées sur la **Figure 17** [41]. Des observations microstructurales sont aussi disponibles en **Annexe III – E**.

Le géopolymère de référence, S1M1, présente une valeur de résistance mécanique de l'ordre de 42 MPa associée à une perte de masse de l'ordre de 15 %, ce qui est en accord avec les travaux antérieurs [42].

L'ajout d'additifs à base de phosphate, P et KP, conduit à la présence d'une très grande quantité d'eau, supérieure à 20 $\%_{mass}$, induisant une diminution de la résistance mécanique, jusqu'à 5 MPa (**Chapitre 4, ACN 2**). Il en est de même lors de l'introduction d'acide borique et de tétraborate de lithium, mais la valeur de résistance en compression observée, ~12 MPa, reste acceptable. Cette diminution, non linéaire avec la quantité d'eau présente dans l'échantillon, ne correspond pas au comportement général des géopolymères [42, 43]. Ceci peut s'expliquer par le pouvoir polarisant des atomes d'hydrogène et de lithium, supérieur à celui des éléments potassium, sodium ou calcium [11]. En effet, cela induit de plus fortes interactions entre les cations et l'eau présente au sein du réseau géopolymère, limitant la perte d'eau. Il en résulte une dégradation des propriétés mécaniques des échantillons.

L'utilisation de la colémanite et du tétraborate de sodium entraîne une faible diminution de la résistance mécanique, jusqu'à environ 32 MPa, s'accompagnant d'une diminution linéaire de la teneur en eau.

Par conséquent, afin de préserver une tenue mécanique minimale des échantillons, les additifs à base de phosphate sont à exclure.

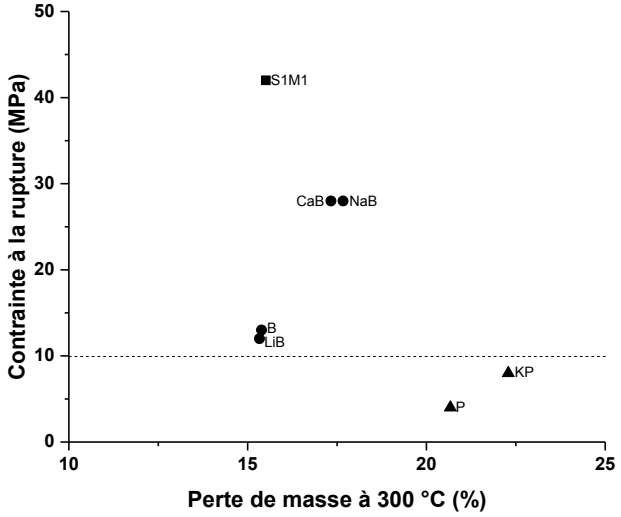


Figure 17. Valeurs de résistance mécanique en compression en fonction de la perte de masse à 300 °C pour les échantillons S1M1 en présence de $KP^{9,3}$, $P^{2,8}$, $B^{2,8}$, $NaB^{10,0}$, $LiB^{3,7}$ et $CaB^{6,1}$.

Le contrôle des valeurs de DPU et de pH des échantillons S1M1 est réalisable par l'ajout de tétraborate de sodium. Afin d'établir un modèle des évolutions des valeurs de DPU/pH en fonction de la nature et de la quantité d'additifs introduits, des études structurales doivent être réalisées.

2. Compréhension des évolutions structurales

Afin d'étudier les évolutions structurales induites par l'ajout d'additifs, il est nécessaire de se focaliser sur le réseau aluminosilicaté amorphe composant le géopolymère de référence, S1M1. Les additifs sont à base de bore ou de phosphore, atomes qui ont la particularité d'être des cations formateur de verres [44]. Ces derniers peuvent donc interagir au sein du réseau géopolymère en coordinence tétraédrique. Pour vérifier ces hypothèses, des études structurales par spectroscopie RMN ont été réalisées.

a. Etude de l'environnement du ^{11}B, ^{27}Al, ^{29}Si et ^{31}P par RMN

La **Figure 18** regroupe les évolutions des différentes contributions des noyaux ^{27}Al et ^{29}Si pour les échantillons S1M1 en présence des différents additifs. Pour chaque échantillon, les différentes contributions sont associées au rapport de l'intensité de l'échantillon sur la référence, S1M1 (intensités obtenues par décomposition des spectres, **Chapitre II, IV.2.c**). Le

détail des différentes contributions indexées et décomposées est disponible en **Annexe II – D** et au **Chapitre IV, ACL 6**.

Les différents environnements de l'atome d'aluminium, ^{27}Al, (**Figure 18.A**) sont l'aluminium en coordinence VI ($Al^{[6]}$), associé à des atomes d'aluminium n'ayant pas réagi, et l'aluminium en coordinence IV ($Al^{[4]}$) caractéristique du réseau géopolymère (**Chapitre II, IV.2.c**). L'ajout d'additif à base de phosphates (**Figure 18.A.a**) conduit à une augmentation de la quantité d'aluminium en coordinence VI. Celle-ci est très importante avec l'ajout d'acide orthophosphorique (-50 % d'$Al^{[4]}$) mais reste limitée avec l'utilisation de l'hydrogénophosphate de potassium (-4 % d'$Al^{[4]}$). L'introduction d'additif à base de bore (**Figure 18.A.b**) induit aussi une faible augmentation de la quantité d'$Al^{[6]}$. Que ce soit en présence d'additif à base de bore ou de phosphore, l'augmentation de la quantité d'$Al^{[6]}$ signifie qu'une quantité inférieure d'espèces alumineuses est présente au sein du réseau géopolymère [45].

Les spectres de l'atome de silicium, ^{29}Si, des différents échantillons ont pu être décomposés en sept contributions (**Figure 18.B**) : le silicium en coordinence IV (Q^4) associé à 4, 3, 2, 1 et 0 atomes d'aluminium, le silicium provenant du quartz (Q^4 0Al) et l'acide silicique (**Chapitre II, IV.2.c**) [46, 47, 48]. L'ajout d'additif à base de phosphate, **Figure 18.B.a**, dans le géopolymère S1M1 conduit à une diminution de l'intensité des contributions associées aux atomes de silicium liés à de nombreux atomes d'aluminium (Q^4 4Al, Q^4 3Al et Q^4 2Al). Cette diminution s'effectue au bénéfice des contributions des atomes de silicium liés à peu d'atomes d'aluminium (Q^4 1Al et Q^4 0Al). L'utilisation d'acide orthophosphorique conduit aux variations les plus importantes. L'ajout d'additif à base de bore, **Figure 18.B.b**, entraîne des évolutions similaires, minimales en présence de colémanite et de tétraborate de sodium. Ces variations mettent en évidence que l'ajout d'additif, quel qu'il soit, conduit à un réseau géopolymère présentant une plus faible connectivité des atomes de silicium avec les atomes d'aluminium. Cette tendance confirme celle observée lors de l'étude du ^{27}Al : la présence d'additif limite légèrement la formation du réseau géopolymère (fortement lors de l'ajout d'acide orthophosphorique) (**Chapitre IV, ACL 6**).

Afin de pouvoir identifier les phénomènes à l'origine de la diminution de la quantité de réseau géopolymère en présence d'additif, l'étude des noyaux ^{11}B et ^{31}P a été initiée. Les spectres RMN ^{11}B (**Chapitre IV, ACL 6** et **Figure 19.a**) sont constitués d'atomes de bore en coordinence IV ($B^{[4]}$ liés à deux ou trois atomes de silicium) et d'atomes de bore en coordinence III ($B^{[3]}$ symétrique ou asymétrique) [49, 50]. Les contributions majoritaires sont celles des atomes de $B^{[4]}$ connectés à deux atomes de silicium (pour la colémanite et le tétraborate de

lithium) ou à trois atomes de silicium (pour l'acide borique et le tétraborate de sodium). La présence d'atomes de $B^{[3]}$ résiduels est aussi détectée, principalement sous forme symétrique. Pour les deux tétraborates (échantillon $NaB^{10,0}$ et $LiB^{3,7}$) une quantité significative de $B^{[3]}$ asymétrique (disposant d'un atome oxygène non pontant, NBO) est observée [51]. Les atomes de bore sont donc principalement en coordinence IV, intégrés au réseau géopolymère, avec une connectivité bore-oxygène-silicium majoritaire (**Chapitre IV, ACL 6**).

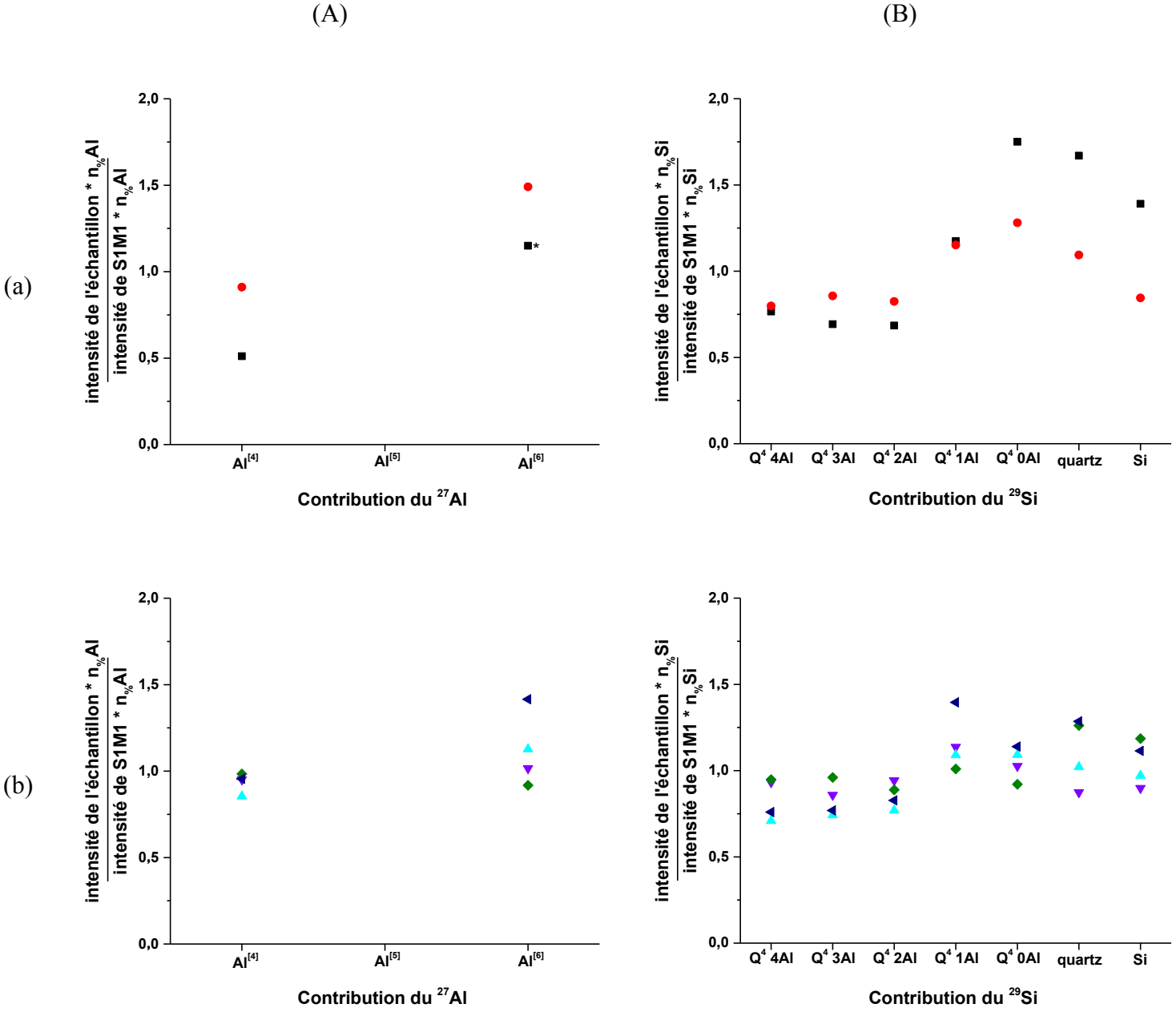
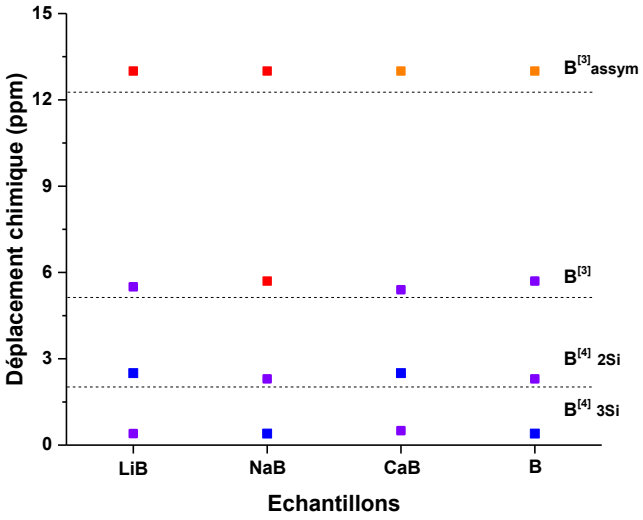


Figure 18. Rapport d'intensité des contributions RMN du **(A)** ^{27}Al et **(B)** ^{29}Si pour les échantillons S1M1 en présence d'additif à base de **(a)** phosphate et **(b)** bore : ● $KP^{9,3}$, ■ $P^{2,8}$, ◀ $B^{2,8}$, ▲ $NaB^{10,0}$, ▼ $LiB^{3,7}$, ◆ $CaB^{6,1}$ (* rapport d'intensité divisé par quatre)

(a)



(b)

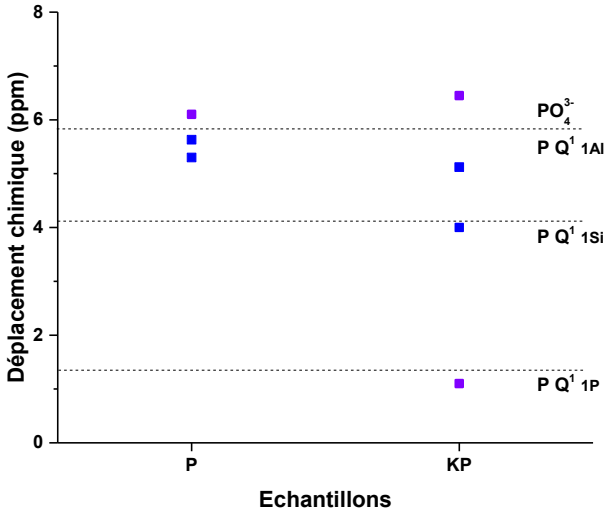


Figure 19. Valeurs du déplacement chimique et des intensités associées des différentes contributions RMN du **(a)** ^{11}B pour les échantillons LiB^{3,7}, NaB^{10,0}, CaB^{6,1} et B^{2,8} et **(b)** du ^{31}P pour les échantillons P^{2,8} et KP^{9,3} (■ intensité forte, ■ intensité moyenne, ■ intensité faible et ■ intensité très faible).

L'étude des spectres RMN du ^{31}P permet l'identification de quatre contributions (**Chapitre IV, ACL 6** et **Figure 19.b**). La plus intense, quel que soit l'additif introduit, est associée à des atomes de phosphore liés à un atome oxygène pontant à un atome d'aluminium [52]. La seconde contribution, la plus intense, correspond aux groupements phosphates, PO_4^{3-}, présents dans l'échantillon [53]. Deux faibles contributions de ^{31}P, présentant respectivement un oxygène

pontant à du silicium et du potassium, peuvent être observées sur l'échantillon contenant de l'hydrogénophosphate de potassium (**Chapitre II, IV.2.b**). L'utilisation d'additifs à base de phosphate, conduit principalement à la présence d'atomes de phosphore faiblement connectés à des atomes d'aluminium et à des groupements phosphates (**Chapitre IV, ACL 6**).

L'incorporation d'additif conduit à un réseau géopolymère dépolymérisé en atomes d'aluminium. Les atomes de B [4] sont dans le réseau et ceux de B [3] induisent des atomes d'oxygène non-pontants. Les additifs à base de phosphore forment des groupements phosphates connectés (Q^1) ou isolés.

b. Influence des additifs sur la durée pratique d'utilisation

Ces données structurales ont été comparées aux valeurs de DPU et de pH. La **Figure 20** représente l'évolution de la valeur de DPU en fonction de la quantité relative de réseau géopolymère. Celle-ci est calculée à partir de la quantité de réseau géopolymère (déterminée à partir de la quantité de Si Q^4 4Al, Si Q^4 3Al, Si Q^4 2Al et $Al^{[4]}$) à laquelle est soustraite la quantité de réseau liée aux cations formateurs introduits (déterminée à l'aide des quantités de P Q^1 1Al et $B^{[4]}$) (**Annexe III – F**).

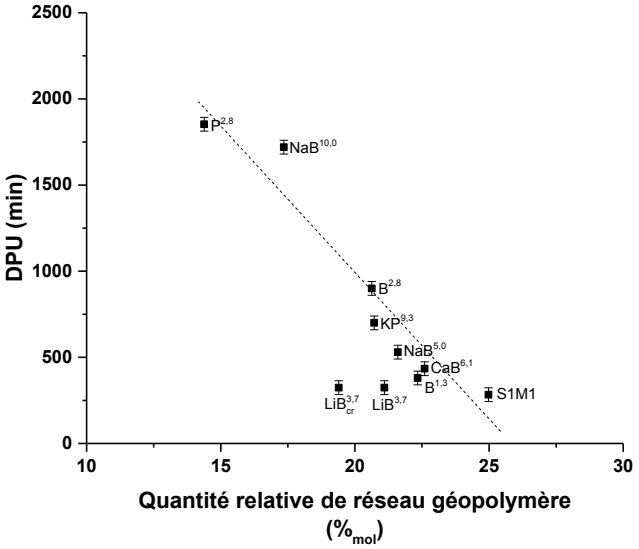


Figure 20. Valeurs de DPU des différents liants S1M1 en présence d'additifs en fonction de la différence entre la quantité de réseau géopolymère et la quantité de réseau secondaire à base de cations formateurs (P et B).

La diminution de cette quantité relative de réseau géopolymère est directement liée à l'augmentation de la valeur de DPU des liants. La formation d'un réseau secondaire, à base des cations formateurs de verres introduits par l'intermédiaire des additifs, diminue les réactions de géopolymérisation et retarde donc la consolidation. Seuls les échantillons à base de tétraborate de lithium, LiB et LiB_{cr}, ne suivent pas cette tendance. En effet, les deux tétraborates de lithium, dont les spectres Raman sont décrits en **Annexe III – G**, présentent des différences. Effectivement, les spectres Raman de solutions de silicates $S1_k^{0,70}$ en présence d'additif (**Chapitre IV, ACL 6**), montrent que l'introduction de tétraborate de lithium modifie très faiblement la quantité d'espèces siliceuses réactives présentes, contrairement aux autres additifs. Cette évolution limitée des espèces réactives en solution explique l'absence de variation de DPU en présence de tétraborate de lithium.

La durée pratique d'utilisation des liants est contrôlable par la détermination du réseau secondaire, à base de cations formateurs de verres, formé au détriment du réseau géopolymère.

c. Impact des additifs sur les valeurs de pH

La quantité d'atomes de bore ($B^{[3]}$) asymétriques présents dans les échantillons a été tracée en fonction de leur valeur de pH (**Figure 21)**.

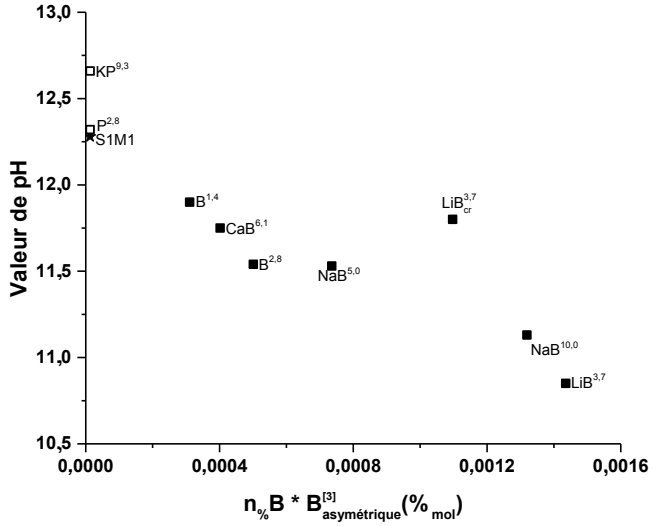


Figure 21. Evolution des valeurs de pH des différents liants S1M1 en présence d'additifs en fonction de la quantité de $B^{[3]}$ asymétrique.

Les échantillons à base de bore, conduisent à une diminution linéaire de la valeur de pH. En effet, les espèces $B^{[3]}$ asymétriques ont pour particularité de présenter un atome d'oxygène non-pontant (NBO), qui est compensé par un cation alcalin au sein du réseau [51]. Cela conduit à une diminution des cations alcalins disponibles dans l'échantillon et donc à une diminution de la valeur de pH du liant (**Chapitre IV, ACL 6**). Cette tendance n'est pas observée avec le tétraborate de lithium cristallisé (LiB_{cr}), qui présente une dissolution limitée dans les mélanges réactifs (**Annexe III – G**).

La présence d'atomes de bore ($B^{[3]}$) asymétriques, dont l'un des atomes d'oxygène est non-pontant (NBO), permet de contrôler la valeur de pH.

3. Proposition d'un modèle d'interactions additif – réseau géopolymère

Les environnements des atomes de bore, aluminium, silicium et phosphore identifiés par RMN peuvent permettre de proposer un modèle décrivant l'action des additifs sur les réactions de polycondensation. La **Figure 22** illustre ainsi le modèle proposé sur une chaîne d'aluminosilicate (les anions O^{2-} y sont représentés avec une faible taille pour plus de lisibilité). Initialement le système de référence présente deux chaines aluminosilicatées liées et compensées par les cations potassium (**Figure 22.a**).

L'introduction de bore conduit à la formation d'atomes de $B^{[4]}$ liés à deux ou trois atomes de silicium, ce qui correspond à l'insertion du bore dans le réseau géopolymère. Les atomes $B^{[3]}$ asymétriques, présentant un atome d'oxygène non pontant, nécessitent la présence de cations alcalins pour équilibrer les charges. Ces entités sont isolées des chaînes aluminosilicatées (**Chapitre IV, ACL 6**).

(i) L'ajout d'acide borique (**Figure 22.b)**, présente comme principale modification l'introduction d'atomes de $B^{[4]}$ (majoritairement liés à trois atomes de silicium) dans le réseau géopolymère.

(ii) L'addition de tétraborate de lithium (**Figure 22.c)**, conduit aussi à l'insertion d'atomes de $B^{[4]}$ (principalement connectés à deux atomes de silicium) mais également à la formation d'atomes $B^{[3]}$ asymétriques. Ils sont compensés par les alcalins présents dans le mélange, parmi lesquels se trouve le lithium introduit avec l'additif.

(iii) L'ajout de tétraborate de sodium (**Figure 22.d**) conduit à des évolutions similaires, avec cependant une connectivité des atomes de $B^{[4]}$ plus élevée (majoritairement connectés à 3 atomes de silicium).

L'incorporation d'additif à base de phosphore dans les mélanges réactifs conduit à la formation d'entités phosphates isolées (compensées par des cations alcalins) ou présentant une connectivité faible (Q^1, en très grande majorité liées avec un atome d'aluminium). Pour que ces entités présentent une si faible connectivité, il est supposé que les atomes de phosphore se positionnent aux extrémités des chaînes aluminosilicatées, limitant ainsi la polycondensation (**Chapitre IV, ACL 6**).

(i) L'ajout d'acide orthophosphorique (**Figure 22.e**) induit la formation d'une importante quantité d'entités phosphatées se positionnant en terminaison de chaîne, coupant ainsi une partie de la chaîne aluminosilicatée. La présence de phosphates isolés, et compensés par des cations potassium, est aussi notable.

(ii) L'introduction d'hydrogénophosphate de potassium (**Figure 22.f**) conduit à des évolutions similaires, avec une quantité supérieure de phosphates isolés et de cations potassium.

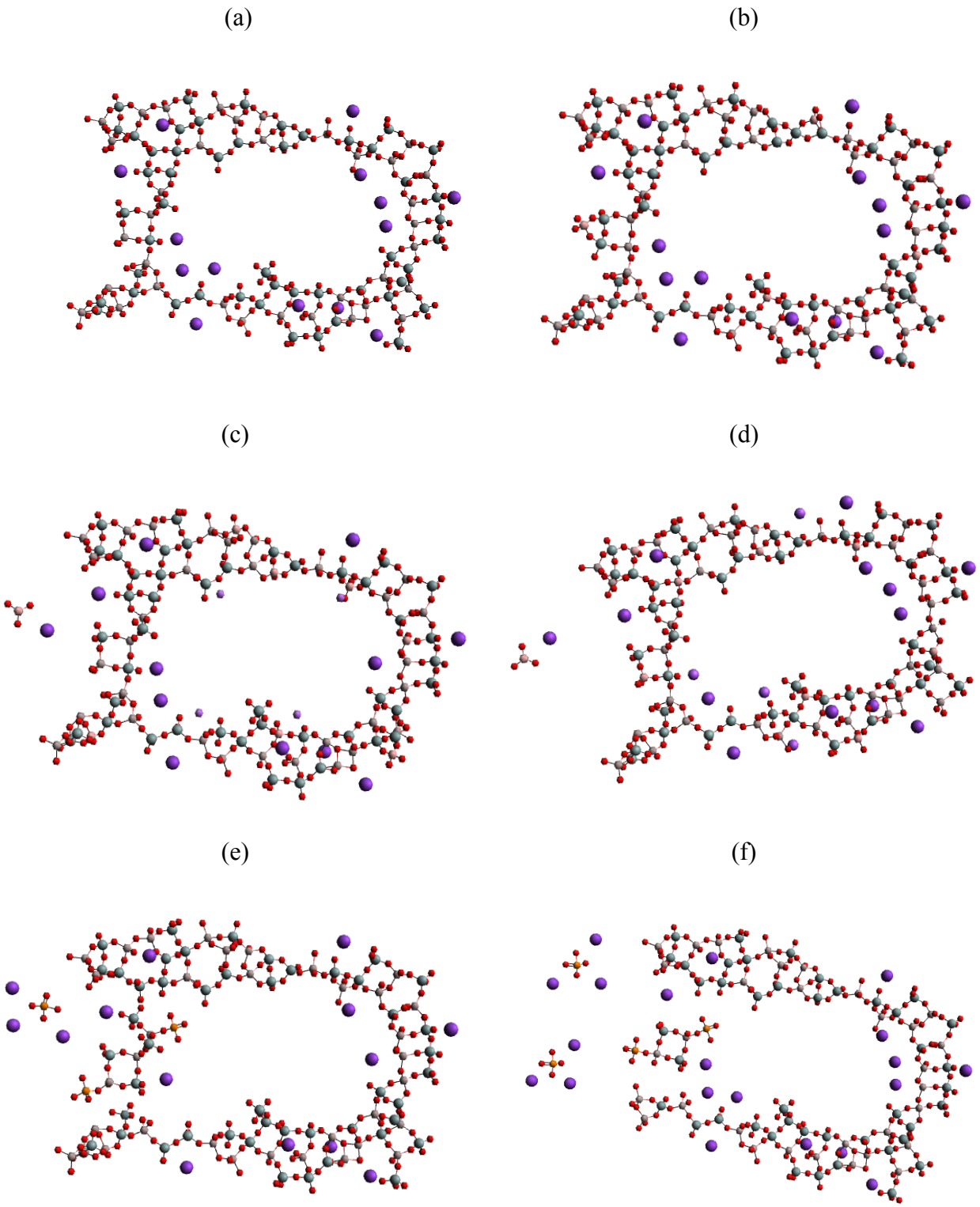


Figure 22. Schéma des échantillons **(a)** S1M1, **(b)** $B^{2,8}$, **(c)** $LiB^{3,7}$, **(d)** $NaB^{10,0}$, **(e)** $P^{2,8}$ et **(f)** $KP^{9,3}$ (● Si^{4+}, ● Al^{3+}, ● B^{3+}, ● P^{5+}, ● K^{+}, ● Na^{+}, ● Li^{+} et ● O^{2-}).

IV. INTERACTIONS EN PRESENCE DES ARGILITES

Il a ainsi été démontré qu'il était possible de développer un coulis géopolymère présentant les caractéristiques visées (viscosité, DPU et valeur de pH). Dans le but de valoriser les argilites, il est nécessaire d'incorporer celles-ci au sein du coulis géopolymère précédemment développé. Pour cela, le géopolymère de référence $S1_{1,01}M1^{0,70}$ a été utilisé en présence d'additifs (principalement des tétraborates de lithium ou de sodium et de l'acide borique).

1. Coulis à base d'argilite

Afin de développer le coulis répondant au cahier des charges (DPU > 24 heures et valeur de pH de 10-11) et contenant de l'argilite, il est nécessaire d'adapter la formulation. Pour cela, il faut tout d'abord sélectionner la source minérale optimale, optimiser la solution alcaline silicatée puis le rapport s/l, et enfin incorporer les additifs, afin d'atteindre les objectifs visés.

a. Choix de la source minérale

Pour déterminer la source minérale optimale pour l'application visée, de multiples essais de faisabilité ont été menés sur des échantillons synthétisés à partir de solutions $S1_K$ et $S1_{Na}$ (de rapport Si/M compris entre 0,5 et 1,0) et de sources minérales M1, A750, AF750, A650, A600, M1A25, M1A25A650, M1A25A600, A25A650 et A25A600 (les mélanges sont tous préparés dans des proportions équimassiques). Leur faisabilité est ensuite déterminée par une observation visuelle (**Tableau 3**). A titre d'exemple, l'échantillon $S1_{Na}A750^{0,5}$ correspond à une consolidation optimale. Il présente un aspect lisse et brillant ainsi qu'une parfaite consolidation (et tenue mécanique). Le remplacement de l'argilite A750 par A600 ($S1_{Na}A600^{0,5}$) induit aussi une consolidation, mais le temps de prise est plus long. L'augmentation du rapport Si/M de cette composition ($S1_{Na}A600^{1,0}$) ne permet pas d'obtenir une consolidation complète. De même, la consolidation insuffisante de l'échantillon $S1_{Na}A25A600^{0,7}$ souligne l'impact de l'utilisation d'un mélange de source aluminosilicatée moins réactive, qui traduit un phénomène de « collage » et non de géopolymérisation [25, 26].

Tableau 3. Exemple des différents types de consolidation observés.

Echantillon	**$S1_{Na}^{0,5}A750$**	**$S1_{Na}^{0,5}A600$**	**$S1_{Na}^{1,0}A600$**	**$S1_{Na}^{0,7}A25_{0,5}A600_{0,5}$**
Aspect				
Consolidation	optimale	correcte	faible	insuffisante

La **Figure 23** regroupe tous les résultats des différents essais effectués : à savoir une variation du cation alcalin (solutions $S1_K$ et $S1_{Na}$), du rapport Si/M (de 0,5 à 1,0) et des sources aluminosilicatées utilisées.

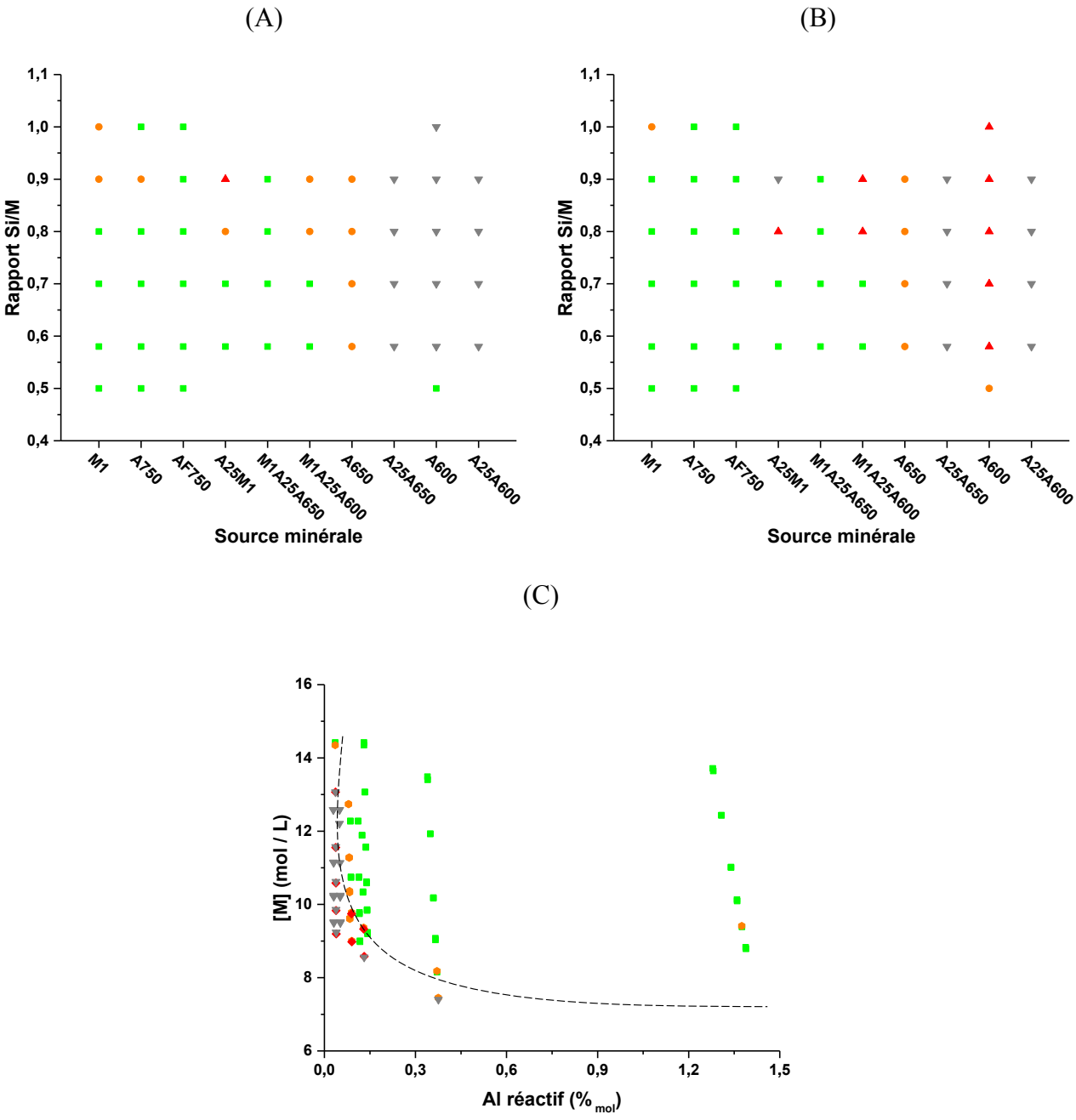


Figure 23. Faisabilité des échantillons synthétisés à partir de différents mélanges de sources minérales et de solutions **(A)** $S1_K$ et **(B)** $S1_{Na}$; **(C)** tracé de la concentration en cations M du mélange réactif en fonction de la quantité d'aluminium réactif, pour une consolidation (■) optimale, (●) correcte, (▲) faible et (▼) limitée.

L'utilisation de la solution $S1_K$ (**Figure 23.A)** permet d'obtenir une large gamme de consolidation optimale pour les sources minérales les plus réactives (contenant de l'argilite calcinée à 750 °C et/ou du métakaolin M1). L'utilisation d'un rapport Si/M modéré (≤ 0,8) permet d'élargir la zone de consolidation optimale. Il en est de même pour une solution mixte potassium-sodium, $S1_{Na}$ (**Figure 23.B**). Cependant, les échantillons de rapport Si/M plus élevé (0,9 ou 1,0) présentent une faisabilité supérieure. Cela est du à la réactivité du silicate de sodium, optimale pour des rapports Si/M supérieurs [54]. Peu de variations sont observées pour les sources minérales peu réactives (principalement celles à base d'argilite A25 ou A600). La faisabilité est donc optimale avec une solution alcaline silicatée de rapport Si/M < 0,8 (quel que soit le cation alcalin) et un mélange de source aluminosilicatée à base d'argilite calcinée (au minimum à 650 °C) ou de métakaolin.
Un domaine de faisabilité est défini en traçant l'évolution de la concentration en cation alcalin ([M]) en fonction de la quantité d'aluminium réactif (quantité d'aluminium corrigée par le rapport des intensités $(Al^{[4]} + Al^{[5]})/Al^{[6]}$ obtenues en RMN) (**Figure 23.C**). Une consolidation correcte nécessite une concentration en cation alcalin d'au moins 8,5 mol/L. La fraction molaire d'aluminium réactif minimale pour obtenir une consolidation correcte est comprise entre 0,10 et 0,15 (selon la concentration en alcalin).

La faisabilité optimale des échantillons est obtenue pour des concentrations en alcalin supérieures à 9 mol/L et un pourcentage molaire d'aluminium réactif supérieur à 0,10.

Afin de développer le coulis et d'obtenir une DPU optimale, la source minérale la moins réactive, M1A25A650, est sélectionnée car elle présente le meilleur compromis entre une consolidation optimale et une réactivité limitée. Il a donc été établi des ternaires décrivant l'évolution des valeurs de pH et de DPU dans le système $S1_kM1_xA25_yA650_z^{0,70}$ (**Figure 24**).
La valeur de pH des liants (**Figure 24.A**) est minimale (12,5) pour les échantillons contenant une majorité de métakaolin M1. L'utilisation d'argilite calcinée, A650, permet d'obtenir des valeurs de pH légèrement plus faibles (-0,1 unité de pH) que l'argilite crue (A25).
La durée pratique d'utilisation (**Figure 24.B**) est maximale (1500-2000 min) pour les échantillons synthétisés à partir d'environ 75 $\%_{mass}$ d'argilite crue (A25), ce qui représente la limite au-delà de laquelle les échantillons ne peuvent plus consolider. Cependant l'utilisation d'une telle quantité d'argilite crue conduit à une consolidation insuffisante, son incorporation doit donc être limitée à 50 $\%_{mass}$. L'utilisation d'argilite calcinée, A650, induit une

consolidation rapide (environ 60 min) et doit donc également être limitée à 50 $\%_{mass}$. La source minérale doit ainsi comporter une importante fraction de métakaolin M1.

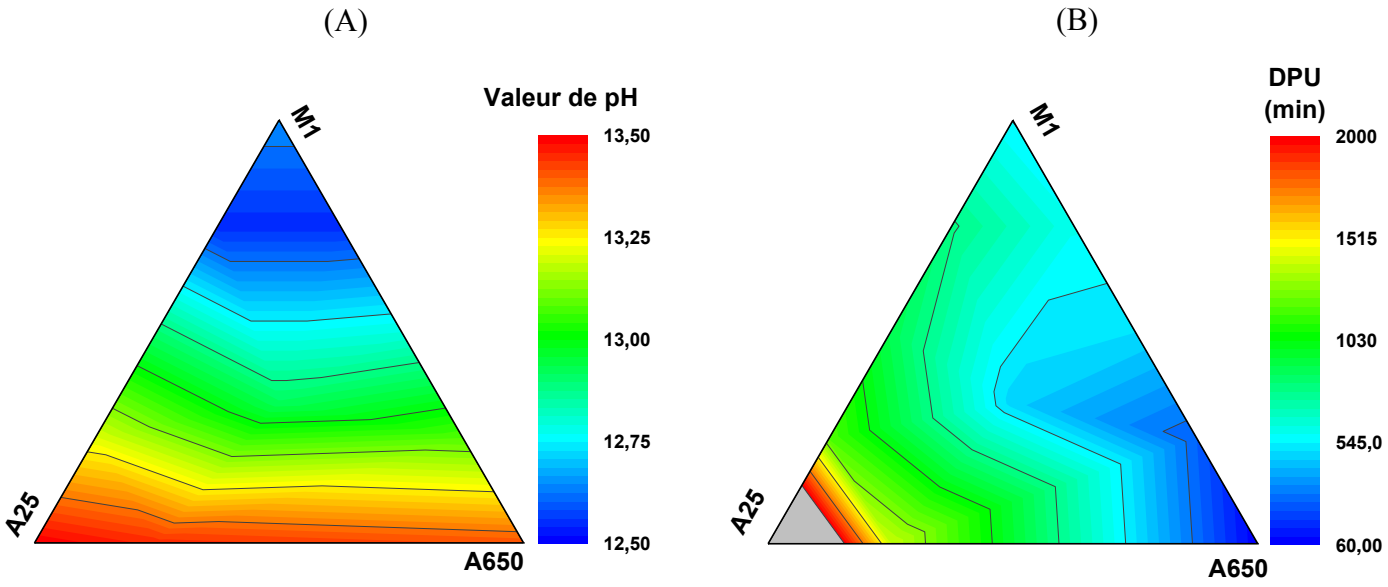


Figure 24. Valeurs de **(A)** pH et **(B)** DPU au sein du ternaire (M1 - A650 - A25) pour les échantillons $S1_kM1_xA25_yA650_z^{0,70}$.

La valeur de pH élevée (caractéristique critique) en présence d'argilite crue (A25) limite son utilisation. Le binaire $M1_xA650_y$ est donc sélectionné pour ses plus faibles valeurs de pH.

b. Développement du liant

Une fois la source minérale $M1_xA650_y$ sélectionnée, il est nécessaire d'optimiser le taux de métakaolin. Une solution alcaline silicatée potassique est choisie, pour sa viscosité faible et sa valeur de DPU élevée, mais le rapport Si/M doit être optimisé. Tous les mélanges sont préparés de façon à avoir une mouillabilité optimale. De plus, afin de se rapprocher des conditions industrielles, l'argilite A650 (four statique, difficile à produire industriellement) est remplacée par l'argilite AR650 (four rotatif).

Les évolutions des valeurs de pH et de DPU en fonction du taux de métakaolin et du rapport Si/M de la solution sont regroupées sur la **Figure 25**.

Pour le mélange $S1M1_{0,5}A650_{0,5}$, l'augmentation du rapport Si/M (de 0,58 à 0,70) permet de diminuer la valeur de pH de l'ordre de 0,2 unité de pH et d'augmenter la valeur de DPU d'environ 60 min. Le rapport Si/M le plus élevé, 0,70, doit ainsi être privilégié. L'augmentation du taux de métakaolin, M1, permet de diminuer la valeur de pH. Une variation maximale de

l'ordre de 0,2 unité de pH est observée avec une quantité de métakaolin supérieure à 60 $\%_{mass}$. Concernant la valeur de DPU, elle augmente (550 à 660 min) avec la quantité de métakaolin introduite.

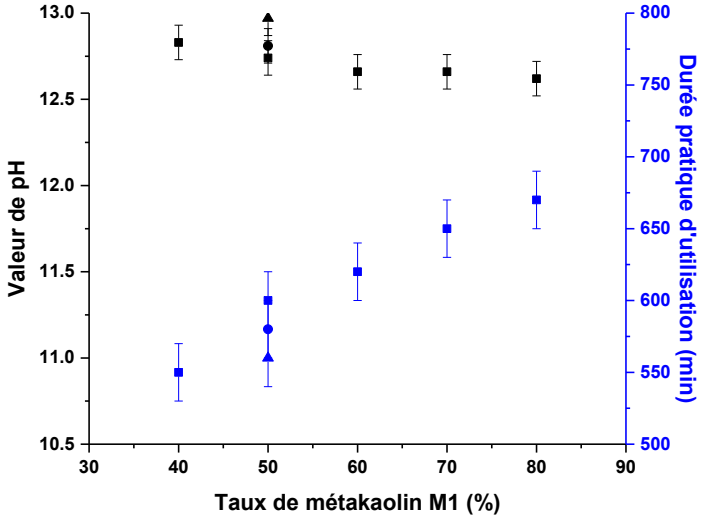


Figure 25. Valeurs de pH et de DPU de liants $S1M1A650^{0,7}$ présentant différents taux de métakaolin et mis en forme avec des solutions $S1_K$ de rapport Si/M (▲) 0,58, (●) 0,64 et (■) 0,70.

Afin d'optimiser les valeurs de pH et de DPU, les deux liants $S1_{0,88}M1_{0,7}A650_{0,3}^{0,7}$ et $S1_{0,98}M1_{0,5}A650_{0,5}^{0,7}$ sont retenus pour obtenir une valeur de pH faible et valoriser une quantité maximale d'argilite.

c. Impact des additifs

Dans la partie **III.2**, il a été montré que l'addition d'acide borique, ou de tétraborate de sodium, conduit au meilleur compromis entre la diminution de la valeur de pH et l'augmentation de la DPU. Ainsi ces deux additifs vont être ajoutés au liant $S1M1_{0,7}A650_{0,3}$. Afin de caractériser le liant dans des conditions les plus proches possibles de celles prévues lors de l'implantation de Cigéo, les valeurs de pH sont aussi mesurées sur des échantillons stockés à une température de 90 °C (température à laquelle le liant sera exposé après sa consolidation) et une humidité relative inférieure à 5%. La **Figure 26** regroupe les différentes valeurs de pH et de DPU du liant $S1M1_{0,7}A650_{0,3}$ sans additif et en présence d'acide borique, B (2,0-2,5 $\%_{mass}$), de tétraborate de sodium, NaB (5,5-8,5 $\%_{mass}$) et des deux additifs (1,2-2,0 et 7,0-8,5 $\%_{mass}$ de B et NaB respectivement).

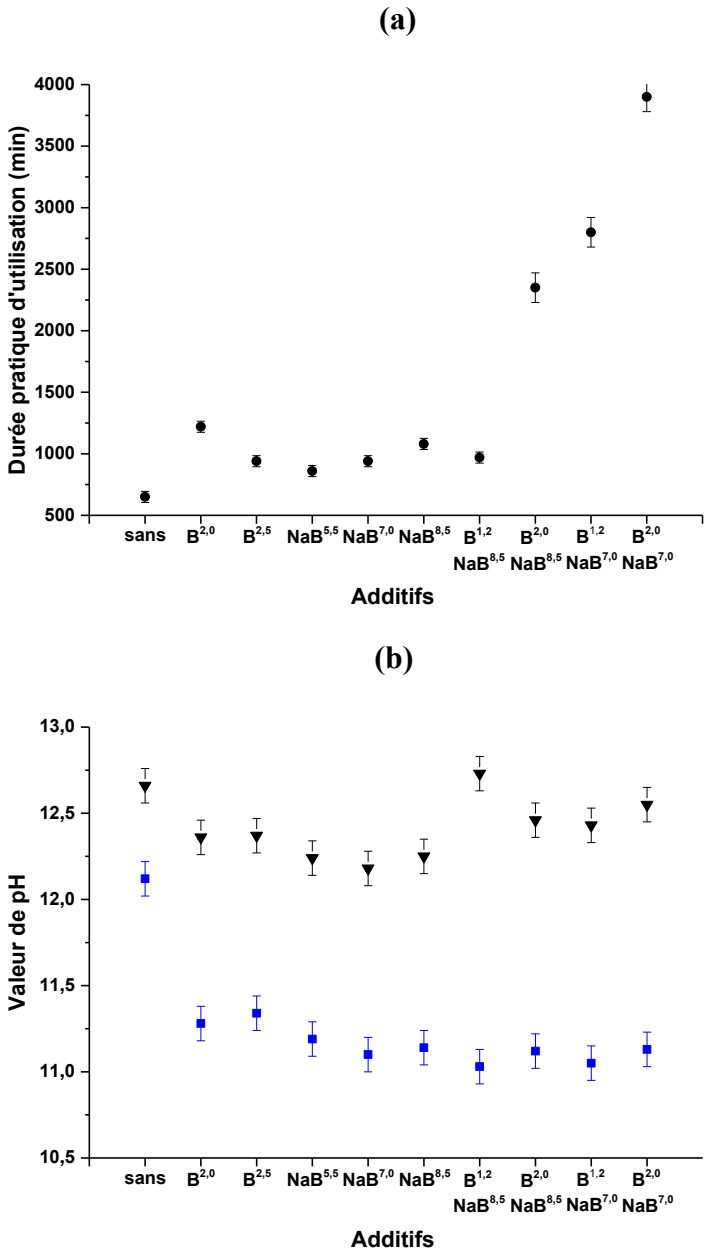


Figure 26. Evolution **(a)** des durées pratiques d'utilisation et **(b)** des valeurs de pH après exposition à (▼) 20 et (■) 90 °C des échantillons $S1M1_{0,7}A650_{0,3}$ en présence de différents additifs.

La durée pratique d'utilisation des différents liants, augmente en présence d'additifs (**Figure 26.a**). Pour les échantillons contenant un seul additif, l'ajout de 2,0 $\%_{mass}$ d'acide borique ou de 8,5 $\%_{mass}$ de tétraborate de sodium permet ainsi d'atteindre des valeurs supérieures à 1000 min, proches des valeurs visées. La combinaison de deux additifs permet d'atteindre des valeurs de DPU très élevées, supérieures à 2000 min. Seul l'échantillon $S1M1_{0,7}A650_{0,3}$ $B^{1,2}$ $NaB^{8,5}$, présente une variation de DPU limitée, probablement liée à des

interactions entre les deux additifs, présents en excès. L'insertion de 2,0 $\%_{mass}$ d'acide borique ou de 8,5 $\%_{mass}$ de tétraborate de sodium dans le liant $S1M1_{0,7}A650_{0,3}$, permet d'atteindre les valeurs cibles. La combinaison des deux additifs présente uniquement un intérêt pour augmenter la DPU au-delà de 2000 min.

A température ambiante, 20°C, l'insertion d'additif conduit à une diminution limitée de la valeur de pH (-0,3 à -0,5 unité de pH), qui est optimale en présence de tétraborate de sodium (**Figure 26.b**). L'utilisation simultanée des deux additifs entraîne de faibles variations de la valeur de pH, supposant que ceux-ci puissent être en excès. Quels que soient les échantillons, les valeurs de pH des échantillons stockés à la température de 90 °C sont plus faibles que celles des échantillons conservés à température ambiante. L'échantillon $S1M1_{0,7}A650_{0,3}$ sans additif présente une diminution modérée de sa valeur de pH, de 12,6 à 12,1. En présence d'additifs cette diminution s'accroît, avec des écarts pouvant dépasser l'unité de pH, et des valeurs de 11,1-11,0 sont atteintes ($S1M1_{0,7}A650_{0,3}$ $NaB^{7,0}$ et $S1M1_{0,7}A650_{0,3}$ $NaB^{8,5}$). La combinaison de deux additifs ($S1M1_{0,7}A650_{0,3}$ $B^{1,2}$ $NaB^{7,0}$ par exemple) entraîne une meilleure diminution de la valeur de pH à 90 °C qu'à 20 °C, similaire à celle obtenue avec un seul additif. Il est ainsi supposé, qu'en présence de différents additifs, l'élévation de température entraîne une modification du réseau géopolymère, permettant d'augmenter le seuil de saturation observé lors de la combinaison d'additifs à 20 °C.

Les valeurs de pH et de DPU les plus proches du cahier des charges sont obtenues avec les échantillons $S1M1_{0,7}A650_{0,3}$ $NaB^{8,5}$ et $S1M1_{0,7}A650_{0,3}$ $B^{2,5}$.

d. Données relatives à l'évolution du réseau géopolymère

Afin d'identifier les différences observées, des études par échographie ultrasonore ont été réalisées (**Chapitre IV, ACL 8**). Cette technique permet de mesurer le module d'Young d'un matériau par des mesures de vitesse de propagation d'ondes ultrasonores transversale et longitudinale dans un échantillon (technique présentée dans l'**Annexe III – H**). Il est important de savoir que le rapport V_T/V_L permet de décrire le caractère isotrope ou anisotrope d'un matériau. Un matériau isotrope présente un rapport V_T/V_L de l'ordre de 0,6. Les différentes données obtenues pour différents échantillons de la série $S1M1_{1-x}A650_x$ sont regroupées dans le **Tableau 4**. L'échantillon S1M1 a aussi été étudié ici à titre de comparaison car il présente une très faible variation de valeur de pH à la suite du traitement thermique.

Tableau 4. Valeurs des masses volumiques et données relatives aux différentes échographies ultrasonores effectuées.

Echantillon	$\rho_{apparente}$ (g/cm^3)		V_T (m/s)		V_L (m/s)		V_T / V_L		E (GPa)	
Température (°C)	*20*	*90*	*20*	*90*	*20*	*90*	*20*	*90*	*20*	*90*
S1M1	1,72	1,24	1067	1229	1703	2179	0,63	0,56	4,6	4,7
S1M1$_{0,5}$A650$_{0,5}$	1,71	1,23	1049	1331	1746	2254	0,60	0,59	4,6	5,4
S1M1$_{0,7}$A650$_{0,3}$	1,68	1,20	1006	1342	1761	2300	0,57	0,58	4,3	5,4
S1M1$_{0,7}$A650$_{0,3}$ B^{2,5}	1,66	1,19	968	1556	2200	2726	0,44	0,57	4,3	7,3
S1M1$_{0,7}$A650$_{0,3}$ NaB^{8,5}	1,72	1,20	914	1466	1856	2544	0,49	0,58	3,9	6,5

Initialement, tous les échantillons présentent une masse volumique de l'ordre de 1,7 g/cm^3. Après traitement à 90 °C, une diminution de masse volumique jusqu'à ~1,2 g/cm^3 est notée pour les différents échantillons. Cette diminution de masse volumique est liée à l'évacuation de l'eau porale lors du traitement à 90 °C [55, 56].

A 20 °C, les valeurs des vitesses de propagation des ondes longitudinales sont de l'ordre de 1750 m/s pour les échantillons sans additif et peuvent atteindre 2200 m/s en présence d'additifs (échantillons S1M1$_{0,7}$A650$_{0,3}$ B^{2,5} et S1M1$_{0,7}$A650$_{0,3}$ NaB^{8,5}). Les vitesses de propagation des ondes transversales sont inférieures, respectivement de 1050 et < 1000 m/s sans et avec additifs. Cela conduit à un rapport entre les vitesses transversales et longitudinales (V_T/V_L) de l'ordre de 0,6 sans additif et inférieur à 0,5 en présence d'additifs. L'incorporation d'additifs conduit donc à la présence d'une anisotropie au sein du matériau ($V_T/V_L < 0,6$) [57]. Après le traitement à la température de 90 °C, toutes les vitesses de propagation augmentent significativement, ce qui est du à la perte d'eau dans les échantillons lors du traitement [58]. Ces augmentations de vitesses sont encore plus importantes en présence d'additifs, ce qui conduit à des rapports V_T/V_L d'environ 0,6 pour tous les échantillons. Cela signifie qu'après un traitement à 90 °C, il y a perte de l'anisotropie dans les échantillons à base d'additifs. Ceci suppose que la structure du réseau géopolymère a été localement modifiée (**Chapitre IV, ACL 8**).

Les valeurs de module d'Young des différents échantillons sont initialement de l'ordre de 4,5 GPa et peuvent atteindre des valeurs maximales de 7,5 GPa après le traitement à 90 °C. Ce phénomène est significatif d'une rigidité plus forte du réseau géopolymère, apparaissant lors de l'incorporation d'argilite dans les mélanges réactifs (+ ~1 GPa) mais surtout lors de

l'incorporation d'additifs (+ ~3 GPa). Ces évolutions soulignent des modifications des réseaux géopolymères, qui subissent une réorganisation lors du traitement à 90 °C.

Les principales différences étant relatives aux vitesses de propagation des ondes transversales et aux valeurs de module d'Young, il a été tracé dans la **Figure 27** leur taux de variation en fonction des variations de valeur de pH. Pour chaque échantillon, la variation de la valeur de pH mesurée entre 20 et 90 °C semble évoluer linéairement avec les taux de variation de module d'Young et de vitesse transversale. L'évolution de la valeur de pH semble donc être la conséquence de modifications subies par le réseau géopolymère lors des variations de température.

Pour compléter ces données, des analyses de porosité mercure ont été réalisées sur les échantillons S1M1 et $S1M1_{0,7}A650_{0,3}$ $NaB^{8,5}$ avant et après traitement à 90 °C (**Annexe III – I**). Les valeurs de porosité de l'échantillon S1M1 sont de 42 % à 20 °C et de 48 % après traitement à 90 °C. L'augmentation simultanée de la taille des pores, de 10 à 15 nm, peut être expliquée par l'évacuation de l'eau porale induisant une coalescence des pores [59, 60]. En effet, bien que les échantillons soient consolidés P.S. Mangat *et al.* et G. Ya-min *et al.* ont mis en évidence que les conditions de séchage et stockage peuvent fortement influer sur la porosité [61, 62]. Dans le cas de l'échantillon $S1M1_{0,7}A650_{0,3}$ $NaB^{8,5}$, la taille des pores augmente légèrement (de 36 à 42 nm) et la porosité totale décroît de ~46 à ~40 %. L'augmentation de la taille des pores est aussi liée à l'évacuation de l'eau porale. En revanche, la diminution de la porosité totale est en opposition avec le comportement observé sur l'échantillon S1M1, supposant que d'autres phénomènes puissent intervenir. Afin d'expliquer cette variation, des analyses par spectroscopie IRTF ont été effectuées. Les spectres ont ainsi révélé la présence d'une contribution d'un groupement hydroxyle à 3735 cm^{-1}. Cette bande est attribuable à la liaison Si-OH d'une phase de zéolite (**Chapitre IV, ACL 8)** [63]. De plus, des bandes caractéristiques d'espèces carbonatées adsorbées sur ces mêmes matériaux ont pu être observées à 2245 et 1380 cm^{-1}**.** La formation de cette phase de zéolite peut être expliquée par la présence de pseudo-conditions hydrothermales lors du traitement à 90 °C [64]. Enfin, elle permet d'expliquer la diminution de porosité observée sur l'échantillons $S1M1_{0,7}A650_{0,3}$ $NaB^{8,5}$. En effet, cette phase aurait la particularité de piéger les cations alcalins dans les cages de zéolite, justifiant les diminutions de valeur de pH [65].

Le changement de température induit une réorganisation du réseau géopolymère. En présence d'argilite la formation de phase de type zéolite est supposée.

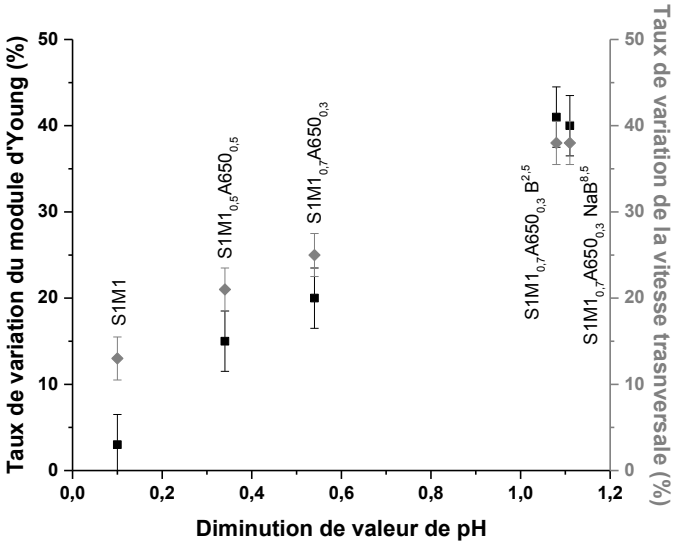


Figure 27. Taux de variation, entre 20 et 90 °C, du module d'Young et de la vitesse transversale observés en fonction de la diminution de la valeur de pH (de 20 à 90 °C) des échantillons S1M1, S1M1$_{0,5}$A650$_{0,5}$, S1M1$_{0,7}$A650$_{0,3}$, S1M1$_{0,7}$A650$_{0,3}$ B^{2,5} et S1M1$_{0,7}$A650$_{0,3}$ NaB^{8,5}.

2. Interaction liant/argilites

Il a été démontré qu'il était possible de formuler des liants (S1M1$_{0,7}$A650$_{0,3}$ NaB^{8,5} et S1M1$_{0,7}$A650$_{0,3}$ B^{2,5}) présentant des caractéristiques proches de celles requises pour le coulis. Ainsi le comportement de ces liants, injectés au contact de blocs d'argilites du Callovo-Oxfordien a été étudié. Pour cela, quatre liants ont été sélectionnés : S1$_{1,01}$M1^{0,70}, S1$_{0,88}$M1$_{0,3}$A650$_{0,7}$^{0,70}, S1$_{0,88}$M1$_{0,3}$A650$_{0,7}$^{0,70} B^{2,5} et S1$_{0,88}$M1$_{0,3}$A650$_{0,7}$^{0,70} NaB^{8,5}. Dans cette partie ces échantillons seront respectivement nommés S1M1, S1M1A650, S1M1A650 B et S1M1A650 NaB. Dans cette partie, le terme "argilites" réfère aux blocs d'argilites géologiques.

a. Echantillons de géopolymère au contact des argilites

Afin d'étudier les interactions liant/argilites du Callovo-Oxfordien, des échantillons ont été coulés dans des blocs d'argilites (**Chapitre II, III.3**). La **Figure 28** illustre l'interface obtenue entre les argilites et un liant alcali-activé. Lors du coulage du liant S1M1A650 au contact des argilites, deux phénomènes interviennent : une fissuration et un retrait en surface (**Figure 28.a**). Ce comportement peut être expliqué par des phénomènes de capillarité entre le liant et les argilites. En effet, en fonction des conditions de conservation après prélèvement *in situ*, les

argilites peuvent sécher. L'abaissement de la saturation en eau augmente les tensions capillaires au sein du matériau, permettant une absorption d'eau d'autant plus forte [66, 67]. Cet effet est renforcé lors de la présence de fractures (issues du prélèvement et de l'usinage, **Annexe III – J**) qui facilitent la perméation du mélange réactif au sein du bloc d'argilites. La **Figure 28.b** montre la base de l'échantillon. Cette photographie a pu être obtenue car le liant a pénétré dans une fracture du bloc d'argilites (zone d'étalement du liant sur la gauche de l'image). Cette propagation de liant dans la fracture, a facilité la rupture du bloc d'argilites, ce qui a permis d'observer la base de l'échantillon. L'échantillon S1M1A650 ne présente, lui, que des fissures millimétriques au niveau de l'interface liant/argilites du Callovo-Oxfordien. Le coulage des liants alcali-activés au contact des argilites semble donc n'occasionner que des dégradations au niveau de la surface, et des interfaces, en préservant l'intégrité globale du liant. Les dommages subis par les blocs d'argilites sont probablement davantage liés à la préparation des blocs (carottage, séchage et usinage) qu'à un impact direct du liant.

(a) (b)

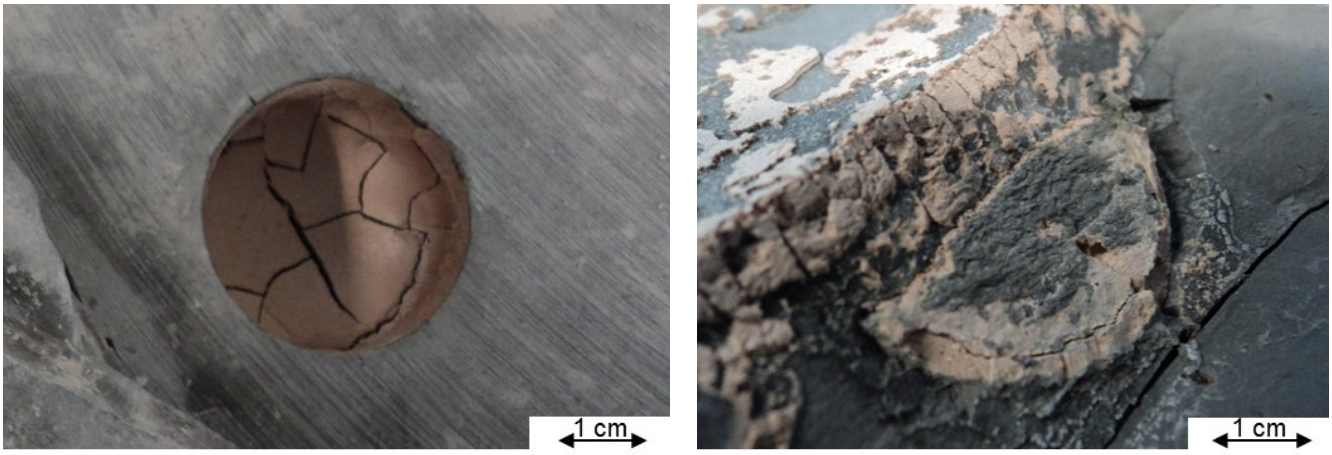


Figure 28. Photographies **(a)** en surface et **(b)** à cœur d'un échantillon S1M1A650 coulé dans un bloc d'argilites (coulage et stockage à 20 °C).

Après avoir caractérisé macroscopiquement l'interface liant/argilites du Callovo-Oxfordien, celle-ci a été étudiée par microscopie électronique et analyse chimique, afin d'identifier les différences de comportement à 20 et 90 °C. Ainsi, une cartographie X de la zone d'interface entre l'échantillon S1M1A650 et un bloc d'argilites est présentée en **Figure 29**. Les données relatives aux autres échantillons sont disponibles en **Annexe III – K**.

A la température de 20 °C, la cartographie élémentaire permet de distinguer quelques variations de composition chimique. L'étude de l'intensité des photons (K_{α}) du potassium (**Figure 29.A.b**)

permet de matérialiser l'interface entre le liant et les argilites. La quantité de potassium est largement supérieure dans le liant S1M1A650, mis en forme à partir d'une solution potassique. Les argilites présentent cependant une quantité de potassium significative et répartie uniformément. Cela est probablement lié à sa composition (minéraux argileux riches en potassium) et non à des phénomènes de transfert, du liant vers les argilites [68]. L'intensité K_α associée au calcium (**Figure 29.A.c**) est plus intense au niveau des argilites, ce qui s'explique par la présence de calcite et de dolomite [68]. Le liant, dont la source minérale est composée à 30 $\%_{mass}$ d'argilite, présente également du calcium, avec la même origine. Les intensités liées aux éléments silicium (K_α) et oxygène (K_α) sont assez homogènes sur toute la zone. De plus, l'intensité K_α de l'aluminium est légèrement plus importante au niveau du liant, du fait de la présence de métakaolin, riche en atomes d'aluminium. La cartographie des échantillons exposés à la température de 90 °C présente peu de modifications par rapport à celle obtenue à 20 °C, à l'exception de la répartition du potassium (**Figure 29.B.b**). Celui-ci apparaît réparti uniformément entre les deux matériaux.

b. Etude de la diffusion

Afin d'appréhender la diffusion de l'élément potassium au sein du milieu géologique, des profils de concentration en élément potassium ont été tracés sur les zones d'interfaces à 20 et 90 °C (**Figure 30**).

A la température de 20 °C, **Figure 30.a**, les profils de concentration en élément potassium des quatre échantillons étudiés présentent une zone de transition, d'une épaisseur de l'ordre de 50 µm, entre la zone associée aux argilites et au liant. La répartition de l'intensité totale mesurée sur l'échantillon est de l'ordre de 30-40 % sur la zone des argilites contre 60-70 % dans la zone du liant. Ces valeurs confirment la variation entre les deux zones. Cette variation disparaît après le traitement à 90 °C (**Figure 30.b**), traduisant une homogénéisation complète des teneurs en potassium dans les deux matériaux. L'interface n'est plus matérialisable avec cet indicateur. En effet, la répartition de l'intensité totale captée est de l'ordre de 50 % par zone (à 5 % près, variation peu significative). La diffusion de cations potassium dans le bloc d'argilites est donc observée, ce qui avait déjà été relevé dans des travaux antérieurs [69]. Cette diffusion est favorisée dans des milieux très humides, tels que les argilites, et par l'augmentation de la température [70, 71]. Il est ainsi supposé que l'augmentation de température permet de favoriser la diffusion de l'élément potassium au sein des argilites.

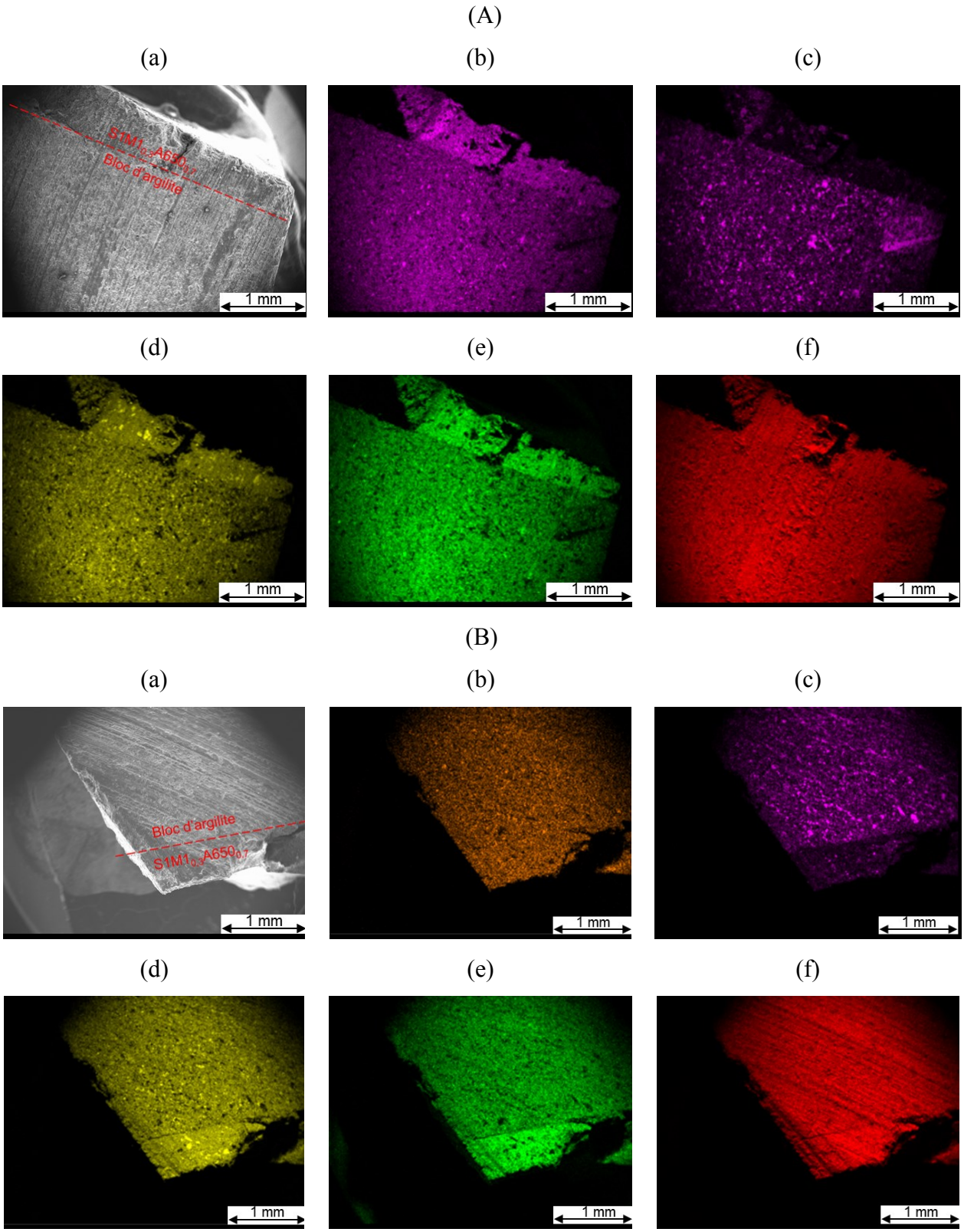


Figure 29. Cartographies X de l'échantillon S1M1A650 mis en contact avec un bloc d'argilites à **(A)** 20 et **(B)** 90 °C, avec **(a)** la photographie MEB, et l'intensité en pixel des raies **(b)** K (K_α = 3,312 keV), **(c)** Ca (K_α = 3,690 keV), **(d)** Si (K_α = 1,739 keV), **(e)** Al (K_α = 1,486 keV) et **(f)** O (K_α = 0,525 keV).

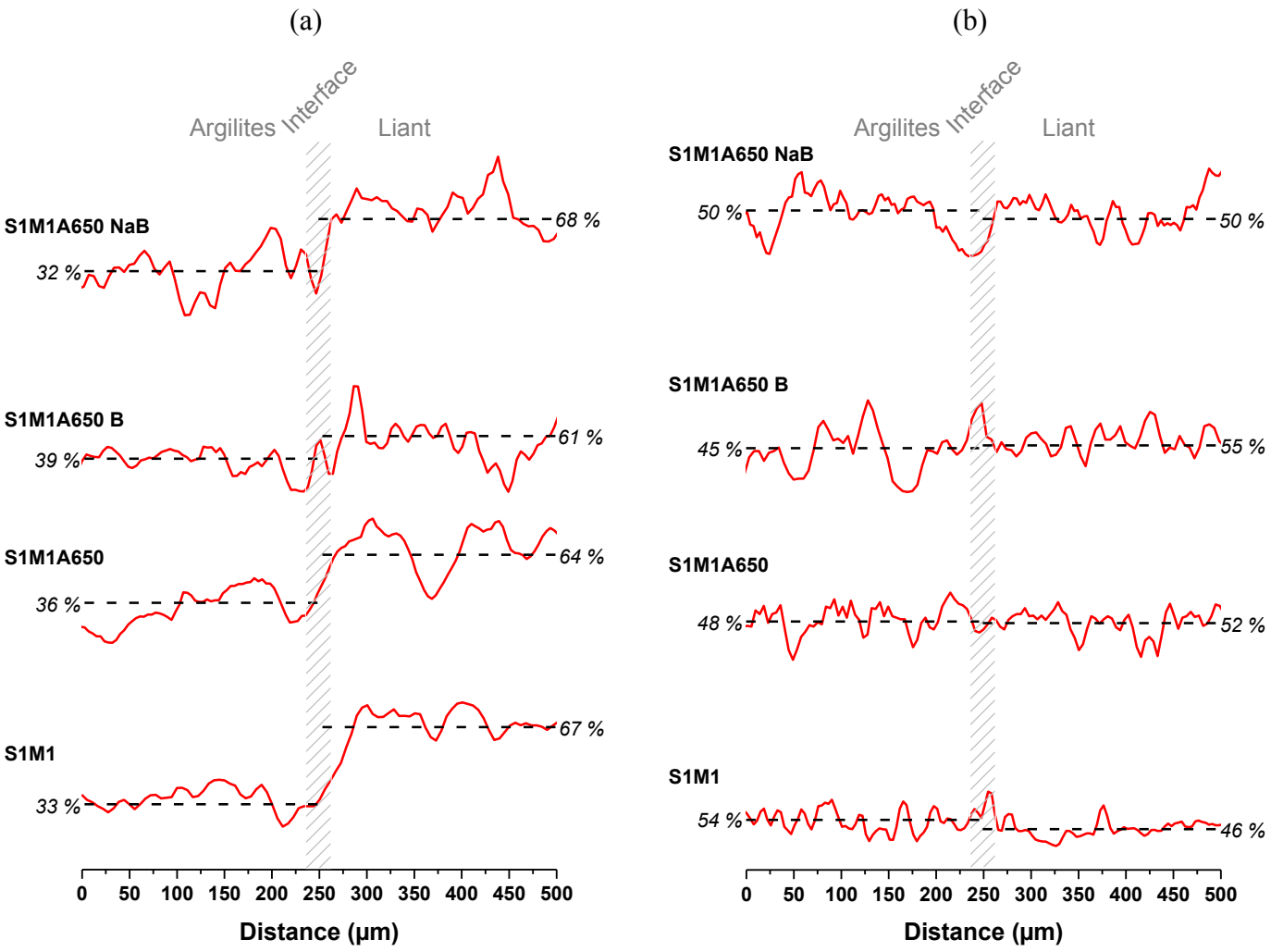


Figure 30. Profil de concentration de la raie K_α (3,312 keV) du potassium à **(a)** 20 °C et **(b)** après exposition à 90 °C, des interfaces argilites/liant en présence des différents liants S1M1, S1M1A650, S1M1A650 B et S1M1A650 NaB.

L'étude de l'interface argilites/liant révèle la formation d'une interface d'épaisseur très faible (~50 µm) et l'existence d'une diffusion de l'élément potassium après le traitement à 90 °C.

3. Résumé de la formulation du coulis

Afin de résumer les transformations des argilites permettant de les valoriser sous forme de coulis alcali-activé, les différentes étapes basées sur les évolutions des différents éléments sont regroupées sur la **Figure 31**.

(i) Tout d'abord, **Figure 31.A**, les argilites sont traitées à 650 °C en four rotatif, afin d'accroître la réactivité des espèces argileuses, tout en limitant la décarbonatation, pour éviter la présence de calcium réactif (décomposition des carbonates de calcium en oxyde de calcium). Les espèces carbonatées présentent peu de variation au cours de l'activation alcaline, mais la formation de carbonate de potassium, ou mixte potassium-calcium, est observée.

(ii) Puis un mélange de source aluminosilicatée contenant cette argilite et du métakaolin est activé alcalinement avec la solution $S1^{0,70}$, de manière à augmenter la DPU du coulis et à diminuer les valeurs de pH (**Figure 31.B**).

(iii) L'ajout d'un additif, tel que le tétraborate de sodium, permet de modifier la structure du géopolymère par l'intercalation d'atomes de bore en coordinence III ($B^{[3]}$) et IV ($B^{[4]}$) dans son réseau silicaté. La présence d'atomes de $B^{[3]}$, se liant aux cations potassium, permet la diminution de la valeur de pH (**Figure 31.B**).

(iv) La mise en contact des argilites avec un liant à 20 et 90 °C, a permis de montrer des transformations structurales avec l'accroissement de la quantité de bore en coordinence IV, la formation d'une zéolite ainsi que la diffusion du potassium dans les argilites (**Figure 31.C**).

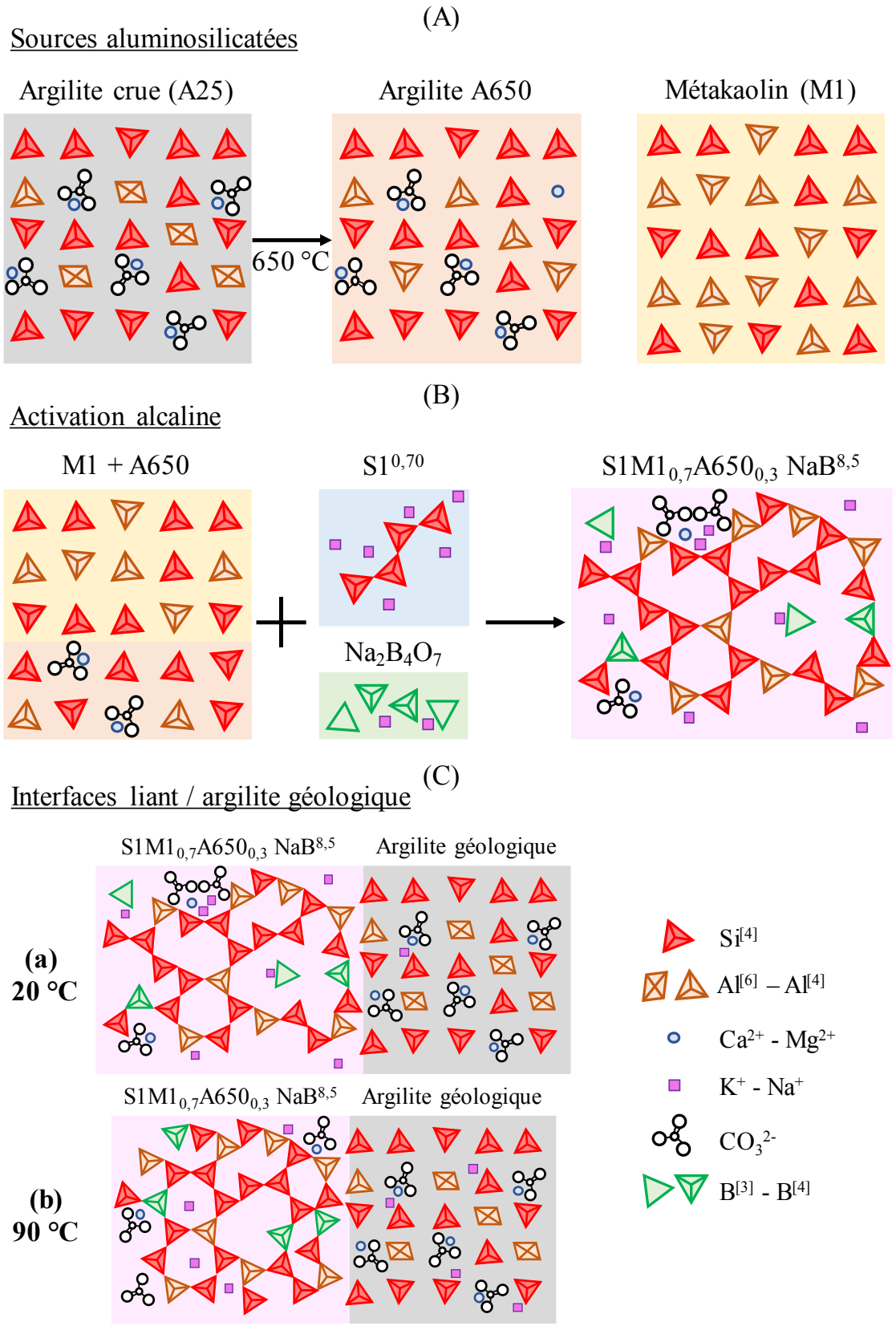


Figure 31. Schéma des différentes évolutions subies par les argilites au cours de la synthèse du liant $S1M1_{0,7}A650_{0,3}$ $NaB^{8,5}$ avec **(A)** l'activation thermique de l'argilite, **(B)** la formation du réseau géopolymère et **(C)** l'étude de l'interface liant/argilite géologique à **(a)** 20 et **(b)** 90 °C.

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Publication 1 (ACL1)

A. Gharzouni, C. Dupuy, I. Sobrados, E. Joussein, N. Texier-Mandoki, X. Bourbon, S. Rossignol

The effect of furnace and flash heating on COx argillite for the synthesis of alkali-activated binders.

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The effect of furnace and flash heating on COx argillite for the synthesis of alkali-activated binders

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ABSTRACT

A considerable quantity of Callovo-Oxfordian (COx) argillite will be excavated due to deep geological radioactive waste disposal. Till now, there is no viable solution to make use of the excavated argillite. This paper investigates the possibility of producing alkali-activated materials based on argillite. The raw argillite is mainly composed of illite, smectite, muscovite and traces of kaolinite and chlorite. In addition, it contains carbonates, quartz, plagioclase and pyrite.

At first, argillite was ground and thermally treated at different temperatures ranging from 600 °C to 800 °C and from 600 °C to 750 °C with furnace and flash processes, respectively. Then, a comparative study of the effect of the two heating processes on the physical, chemical and structural characteristics of argillite was undertaken. It was shown that in the case of furnace heat treatment, a heating between 700 °C and 800 °C leads to the full dehydroxylation of clay minerals (illite-smectite, illite/mica, kaolinite and chlorite) and the total transformation of octahedral aluminum to tetrahedral one. However, flash treatment induces partial structural dehydroxylation of argillite clay minerals regardless of the temperature. Finally, it was demonstrated that it is possible to produce alkali-activated materials from a mixture comprising of 50% of raw argillite and 50% of metakaolin and from calcined argillite regardless of the heat treatment process and the applied temperature.

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1. Introduction

Nuclear waste disposal is a major issue for all countries using nuclear energy. In France, the national radioactive waste management agency (Andra) is in charge of assessing the feasibility and the long-term safety for the disposal of Long Lived Intermediate Level (LL-IL) and High Level (HL) Wastes in deep geological strata. In this context, the Callovo-Oxfordian (COx) argillite was extensively studied in order to evaluate its suitability as a host rock for deep geological radioactive waste disposal. The COx argillite is a rock formation of 160 million years age, which lies under a limestone and marly rock formation in a depth between 420 m and 555 m below ground level in the Bure region (east of the Parisian basin - France) (Yven et al., 2007). Due to some advantageous properties, such as sufficient thickness, geological stability, homogeneity and low permeability, the COx argillite is potentially suitable as a host rock for the disposal of radioactive wastes (Montes et al., 2004). Nevertheless, the disposal will lead to the excavation of several million cubic meters of this clay host rock throughout the operating period. The main subjects of research on argillite deal with the physical (i.e. geomechanical) and the chemical properties of the host rock, to generate input data for the long term safety assessment. However, there are still no plans for the use of the excavated argillite. To propose a possible utilization of the excavated argillite, we studied the suitability of the COx argillite as a raw material for the production of alkali-activated binders.

Geopolymers are amorphous inorganic materials resulting from the activation of an aluminosilicate source by an alkaline solution at a temperature below 100 °C (Davidovits, 2008). These materials have the advantage of the possible use of different aluminosilicate

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sources such as clays, metakaolins and industrial co- or by-products. Geopolymers are currently regarded as a subgroup of alkali activated materials, which contain minor amount of calcium (Provis and van Deventer, 2014).

Despite the possibility of using crude aluminosilicate sources (Essaidi et al., 2014), thermal treatment is a crucial step in order to increase the reactivity of the source materials in alkaline solutions (Seiffarth et al., 2013). Many authors have focused on the thermal treatment of clays for geopolymer synthesis. For instance, Elimbi et al. (2011) evidenced that the optimal temperature for the calcination of kaolinite for geopolymer synthesis is 700 °C. However, the calcination temperature is not the only key parameter to control the reactivity of the aluminosilicates. The method of calcination plays also an important role on the chemical, physical and structural changes induced by thermal treatment and thus on the reactivity in alkaline medium. Recently, flash heat treatment is being employed increasingly. Many authors have studied the effect of flash calcination on kaolin (Meinhold et al., 1994; Salvador, 1995). They have demonstrated that flash-calcined metakaolin exhibits similar or better reactivity, lower density and higher light absorption capacity than soak-calcined metakaolin. Similarly, San Nicolas et al. (2013) have undertaken a comparative study between rotary and flash calcinations of kaolin and have shown that the method of thermal treatment influences the physical properties of resulting metakaolins and therefore their reactivity when they were used as supplementary cementitious material or for geopolymer synthesis. Furthermore, it was demonstrated that "flash" metakaolins have lower water demand than "rotary" metakaolins, which can be explained by the differences of morphological properties of the two calcined metakaolins. In fact, the angular shaped metakaolin particles derived from rotary-calcination have a higher specific surface area and thus adsorb more water. Autef et al. (2013a) highlighted the effect of dehydroxylation rate induced by flash heat treatment on metakaolin reactivity for geopolymer synthesis. Nanostructural differences were evident by TEM observations of three metakaolins produced by three different processes (rotary, flash and furnace). Flash calcined metakaolin mainly composed of amorphous aluminosilicate phases which made it more reactive than the two other studied metakaolins. According to previous data, flash calcination seems to be attractive (calcination time and cost are less for flash calcination compared to rotary or furnace calcination). However, the effect of flash calcination on clays, other than kaolinite, is not yet understood. Thus, the purpose of the present survey is to analyze and to compare the chemical, physical and structural changes induced by thermal treatment of argillite at different temperatures with two different processes, i.e. furnace and flash heat treatments.

It was demonstrated that the heat treatment process and temperature affect the physical and chemical characteristics, mineralogical composition and aluminum coordination. Then, it was evidenced that heat treated COx argillite is suitable for alkali-activated materials synthesis.

2. Experimental

2.1. Raw materials and sample preparation

Fig. 1 illustrates the different steps of sample preparation. A core of COx argillite rock (1 m of length) was dried, crushed and ground in order to obtain a particle size < 100 μm. The raw argillite was denoted as A. Then, the argillite was calcined according to two methods:

i) The argillite powder was heated in a laboratory furnace for 4 h at different temperatures (600 °C, 700 °C, 750 °C and 800 °C) with a heating rate of 5 °C/min. The argillite samples were denoted as ^{T}A (Table 1) where A refers to the COx argillite and T corresponds to the temperature of heat treatment.

ii) The argillite powder was heated with a flash prototype situated in Argeco (Fumel, France)[1]. Different temperatures (600 °C, 650 °C, 700 °C and 750 °C) were tested. The maximum temperature of calcination was imposed by the prototype design not permitting the increase of temperature above 750 °C. The argillite powder was preheated in cyclonic separators. After that, the powder is brought in the calcination chamber, at the desired temperature, where it turns around a flame for few seconds. Finally, the powder is cooled in cyclonic separators. F was added to the nomenclature (^{FT}A) in the case of flash heat treatment (Table 1). For example, ^{F700}A corresponds to argillite powder calcined at 700 °C with flash process.

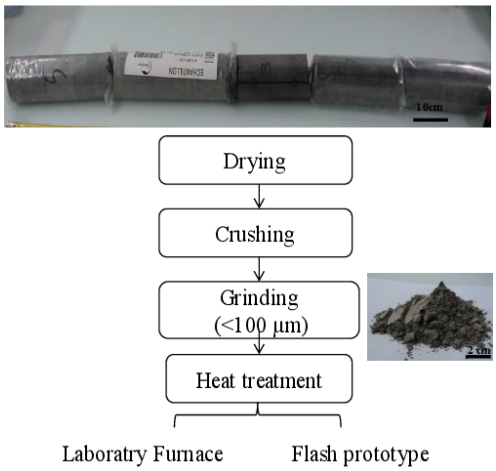


Fig. 1. Preparation steps of the different argillite samples.

Consolidated materials were synthesized according to formulation established in the work of Gharzouni et al. (2015) by mixing raw argillite and metakaolin (M, Si/Al = 1.17) or thermally treated argillite with a potassium alkaline solution (molar Si/K ratio = 0.5). The obtained mixtures were placed in a closed sealable polystyrene mold at room temperature (25 °C). Samples were denoted as AM, ^{T}A^{K} and ^{FT}A^{K} for samples based on raw argillite and metakaolin, furnace and flash-heated argillite, respectively.

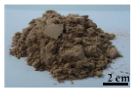
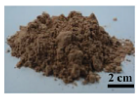
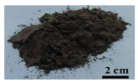
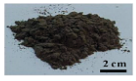
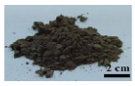
2.2. Sample characterization

The particle size distributions of the clays were measured using a laser particle size analyzer (Mastersizer-2000). The powder is suspended by an air current flowing through a glass cell with parallel faces illuminated by a beam of laser light. The measurement is made at a pressure of 3 bars.

Powder BET surface areas (m^2/g) were determined by N_2 adsorption at −195.85 °C using a Micrometrics Tristar II 3020 volumetric adsorption/desorption apparatus. Prior to the measurement, the samples were degassed at 200 °C under vacuum for 4 h.

[1] Argeco development, Rue Fournie Gorre 47500 FUMEL (France).

Table 1
Nomenclature, photos, chemical and physical properties of (A) raw, (B) furnace-heated and (C) flash-heated argillite at different temperatures.

Nomenclature	Photo	D_{50} (μm)	SBET (m^2/g)	Wettability (μL/g)
(A)				
A		17	38	453
(B)				
^{600}A		41	30	507
^{700}A		176	25	496
^{750}A		161	5	536
^{800}A		139	6	702
(C)				
^{F600}A		15	33	400
^{F650}A		21	31	420
^{F700}A		17	30	480
^{F750}A		21	29	530

The wettability value (μL/g) corresponds to the volume of water that can be adsorbed by one gram of powder before saturation. One gram of powder is deposited on a glass slide, water is then added to the powder using a micropipette until visual saturation.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed with a SDT Q600 apparatus from TA Instruments, in an atmosphere of flowing dry air (100 mL/min) in platinum crucibles. The signals were measured with Pt/Pt–10%Rh thermocouples. The raw argillite sample was heated up to 1200 °C with a rate of 5 °C/min.

FTIR spectra were obtained with a Fourier-transform infrared (FTIR) spectrometer. The spectra were acquired in transmission mode using KBr pressed discs (0.6 mg of sample and 100 mg of KBr). The IR spectra were recorded over a range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1}. Atmospheric CO_2 contribution was removed via a straight-line fit between 2400 and 2280 cm^{-1}. To enable comparison, the spectra were baseline corrected and normalized (Prud'homme et al., 2011).

X-ray diffraction (XRD) patterns were acquired with a Bruker-AXS D8 powder diffractometer using Cu Kα radiation (λKα = 0.154186 nm). The analytical range is between 5° and 55° (2θ), with a step width of 0.02° θ and a dwell time of 1 s. Joint Committee Powder Diffraction Standard (JCPDS) files were used for phase identification (Autef et al., 2013b).

High-resolution NMR experiments were performed at room temperature with the help of a Bruker AVANCE-400 spectrometer, operating at 104.26 MHz (^{27}Al signal). MAS experiments were carried out for powder samples, which were spun at 10 KHz. The number of scans was 400 (Autef et al., 2013c).

3. Results and discussion

3.1. Raw argillite: physical, chemical and structural characterization

The physical and chemical characteristics of the raw argillite are reported in Table 1 A. This raw material is characterized by a dark grey color. The D_{50} of the ground argillite is about 17 μm. The BET surface area value is 38 m^2/g which is in accordance with the value found in the literature (De Combarieu et al., 2007). This value is relatively high and suggests the presence of different 2:1 clay minerals known to have a high BET surface area such as illite and smectite (Aylmore et al., 1970). The wettability value of the raw argillite is equal to 453 μL/g.

Differential thermal analysis and thermal gravimetric analysis (DTA-TGA) were conducted on raw argillite to study the influence of heat on that material. The DTA-TGA curves of raw argillite are presented in Fig. 2. The curves show different peaks relative to different physical and chemical transformations associated to various mass losses. The first endothermic peak which is observed up to 200 °C is associated with a mass-loss of about 4% is due to the release of free and poorly physi-sorbed water. The destruction of organic compounds and the beginning of dehydration of illite is between 200 and 400 °C (Boulingui et al., 2015). The associated loss of mass is of the order of 4%. Between 400 and 600 °C, the mass loss (about 3%) corresponds to the dehydroxylation reaction of kaolinite, illite and chlorite (Humberto de Araújo et al., 2004). The endothermic peak between 600 °C and 800 °C accompanied with a weight loss of 9% is due to the decomposition of carbonates (Rodriguez-Navarro et al., 2009) and the dehydroxylation of smectite (Drits et al., 1995).

In order to obtain more accurate structural informations about the COx argillite, FTIR spectroscopy was performed. The FTIR spectrum of the argillite sample (A) is reported in Fig. 3 A. A sharp band is observed at about 3652 cm^{-1} in the area of stretching hydroxyl bonds (υ-OH) (between 3800 and 3600 cm^{-1}). This band corresponds to Al-Al-OH stretching vibration, however the bending vibration peak is situated at 917 cm^{-1}. These two bands are typical of dioctahedral clay and in this case probably smectite and illite (Srasra et al., 1994). The slight shoulder at 3692 cm^{-1} gives evidence of a very low amount of kaolinite that did not exceed 5% according to Joussein et al. (2001). Another broad band is detected at 3400 cm^{-1} and can be attributed to asymmetric υ_3 and symmetric υ_1 (H–O–H) stretching vibrations of H-bonded water, as mentioned by Madejova (2003). C-H bands are identified at 2934, 2982 and 2874 cm^{-1} indicating the presence of organic compounds (Schäfer et al., 2009). The bands at 2500, 1800, 1430, 873, 713 cm^{-1} are characteristic of carbonates and more precisely calcite (HuaNc and Konn, 1960). The intense band at 1033 cm^{-1} corresponds to υ (Si-O-Si). The bands at 1161 cm^{-1} and 1080 cm^{-1}, the doublet at 797 and 778 cm^{-1} and the peak at 694 cm^{-1} are a proof of the presence of quartz (Kramar and Lux, 2015). Complementary information concerning the mineralogical composition of argillite sample were given by XRD measurements. The XRD pattern shows the predominance of peaks related to clay minerals such as illite, smectite, muscovite and traces of kaolinite and chlorite (Fig. 3B). In addition, the argillite material shows X-ray reflections of calcite, magnesite and dolomite. Reflections of quartz, plagioclase and pyrite have also been identified.

XRD was useful to determine the mineralogy of the argillite but it did not permit to the differentiation of aluminum in tetrahedral and octahedral sites. That is why the sample was analyzed by ^{27}Al MAS-NMR spectroscopy. The only limitation of this technique is the presence of iron which is responsible of the spinning side and the broadening of the signal (Thompson, 1984). In the case of the raw argillite sample (Fig. 3C), two main contributions and a series of spinning sidebands, resulting from the iron content as mentioned previously, can be observed. In order to facilitate the exploitation of the spectrum, the data concerning the chemical shifts and the percentages of the curve area of the various contributions (Al^{IV} and Al^{VI}) are given in Table 2. The aluminum in argillite sample is predominantly in octahedral sites (about 70 wt %) and it corresponds mainly to aluminum present in smectite, illite, kaolinite and mica. No pentahedral aluminum (Al^{V}) was identified. The tetrahedral aluminum (Al^{IV}), in minor percentage (about 30 wt %), can be associated with plagioclase, kaolinite, smectite and mica (Kirkpatrick et al., 1985). These data are in accordance with mineralogical composition determined by XRD.

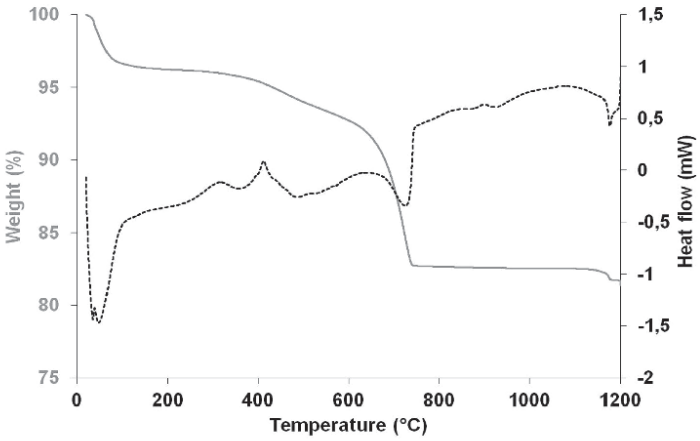


Fig. 2. (—) DTA (—) and TGA curves of the raw argillite sample.

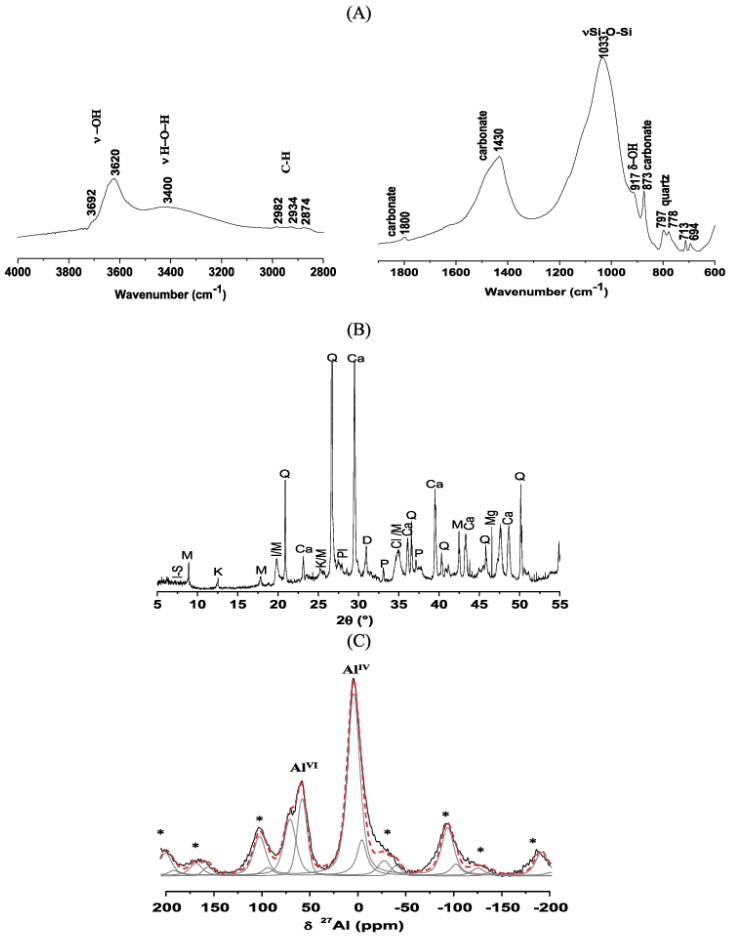


Fig. 3. (A) FTIR spectrum, (B) XRD pattern and (C) ^{27}Al NMR spectrum and its deconvolution of the raw argillite sample (* spinning side band). JCPDS files Q: Quartz (04-016-2085), I–S: Illite-Smectite, K: Kaolinite (00-003-0059), Cl: Chlorite (04-011-6114), P: Pyrite (04-007-2613), Mg: Magnesite (04-012-4920), Pl: Plagioclase (01-083-1370).

Table 2
Deconvolution details about the chemical shifts, the assignment and the percentages of the contributions areas for all samples.

Sample	Percentage of the area curve of contribution (%)			
	Al(IV)		Al$^{(VI)}$	
	≈67 ppm	≈56 ppm	≈2 ppm	≈ −6 ppm
A	17.2	13.11	54.46	15.22
^{600}A	10.11	33.49	41.85	14.56
^{700}A	17.76	60.6	18.24	3.41
^{750}A	12.04	81.57	4.85	1.54
^{800}A	30.92	69.08	0.00	0.00
^{F600}A	24.82	13.59	49.51	12.07
^{F650}A	26.85	16.44	41.75	14.96
^{F700}A	32.12	22.22	36.01	9.64
^{F750}A	34.07	33.77	30.41	1.76

3.2. Effect of thermal treatment: a comparative study between furnace and flash heat treatments

3.2.1. Physical and chemical data

A comparative study between two different heat treatment methods (classic thermal treatment in laboratory furnace and flash thermal treatment) was undertaken in order to determine their effect on the properties of argillite and therefore its reactivity for alkali-activated materials synthesis. Photos as well as physical and chemical characteristics of the different heated samples are given in Table 1B and C. Comparing the samples temperatures and by different calcination processes, two types of materials can be distinguished according to their color. On the one hand, furnace-heated samples (Table 1B) exhibit reddish-yellow color. On the other hand, flash-heated samples (Table 1C) keep the grey color of the raw argillite. However, the grey color seems to lighten with the

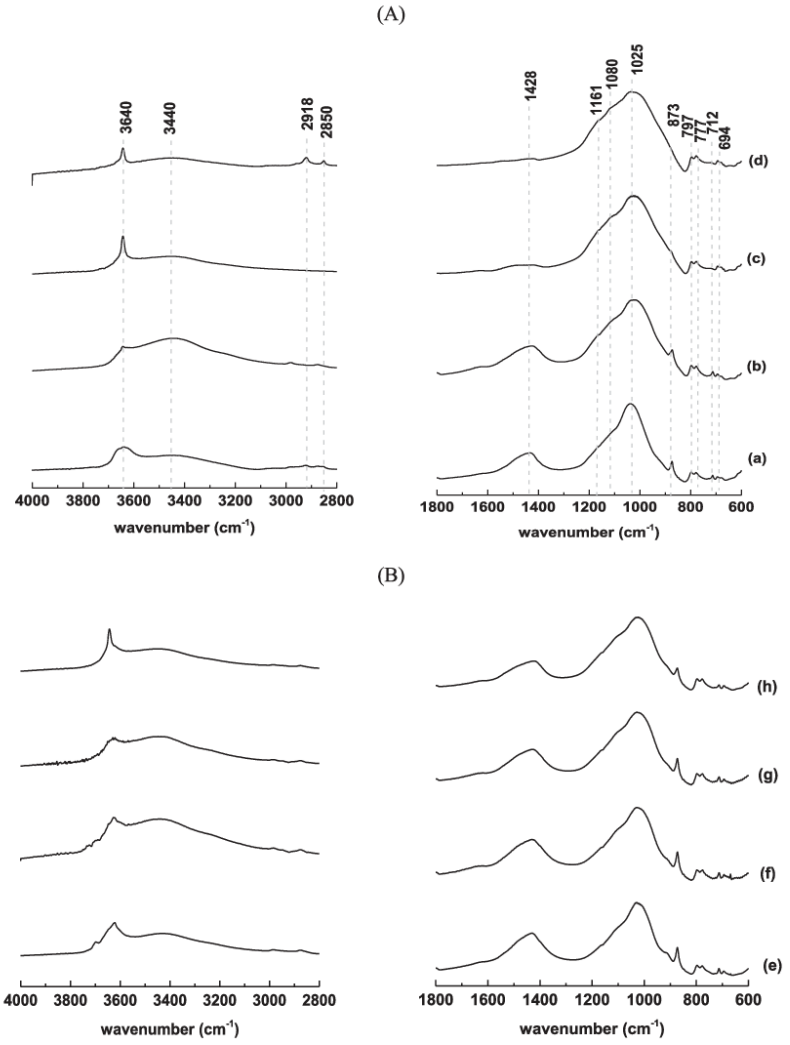


Fig. 4. FTIR spectra of (A) (a) ^{600}A, (b) ^{700}A (c) ^{750}A and (d) ^{800}A furnace heated argillite samples and (B) (e) ^{F600}A, (f) ^{F650}A (g) ^{F700}A and (h) ^{F750}A flash heated samples.

increase of temperature. These observations indicate different oxidation states of iron (Murad and Wagner, 1996) (mainly responsible of the color of the material at a dry state).

Moreover, particles of the furnace-heated samples showed an increased median diameter (D_{50}) and significantly a decreased BET surface area (S_{BET}) (Table 1B). The D_{50} increases from 41 μm at 600 °C to 139 μm at 800 °C while the S_{BET} value decreases from 30 m^2/g at 600 °C to 6 m^2/g at 800 °C. The coarsening of the particles may be resulted from sintering. In fact, He et al. (1995) have explained the decrease of the S_{BET} upon heating in the case of illitic clay by the agglomeration of particles and the closing of the pores. Similarly, Hu et al. (2017) evidenced that the increase of grain size and the decrease of specific surface area of illite-smectite clay after heating at 850 °C, which resulted from the sintering.

Nevertheless, this phenomenon is not observed in the case of flash heating process (Table 1C) and no changes were neither detected in the D_{50} nor in the S_{BET} values (the D_{50} varies between 15 μm at 600 °C and 21 μm at 800 °C and the S_{BET} values are about 33 m^2/g and 29 m^2/g at 600 °C and 750 °C, respectively). This different behaviour, compared to furnace calcination, is due to the suspension of the powder in the air and the very short time of heat treatment which avoids the agglomeration of particles (Medri et al., 2010). This fact is industrially advantageous since it allows to save time and energy and to reduce the cost of a supplementary post-

calcination grinding as it is the case of traditional heat treatment (Salvador et al., 1994).

The wettability value increases slightly when the argillite was calcined in furnace at 600 °C (from 453 to 507 μL/g for A and ^{600}A samples, respectively). More significant increase was observed at higher temperatures (702 μL/g for ^{800}A sample). However, slight increase is detected in the case of flash calcined samples.

3.2.2. Structural data

To elucidate the structural differences, the heated samples were studied using FTIR spectroscopy, XRD and ^{27}Al MAS-NMR. Compared to raw argillite (Fig. 3A), the FTIR spectra of samples heated in the laboratory furnace showed structural variations which are accentuated with increasing calcination temperature (Fig. 4A). Indeed, sharper and weaker OH stretching bands are detected. Moreover, The OH bending band, at about 917 cm^{-1}, is gradually attenuated after calcination at 750 °C. These results reveal the dehydroxylation of illite and smectite. According to the literature, the dehydroxylation of illite and interstratified illite-smectite occurs between 400 and 700 °C while their total structural breakdown is at around 800–900 °C (Kirkpatrick et al., 1985; He et al., 1995, 2000). Additionally, the disappearance of the small band at 3692 cm^{-1} indicates the total dehydroxylation of kaolinite (Frost and Vassallo, 1996). A significant decrease of the intensity of the band at 3420 cm^{-1}, is related to the removal of adsorbed water. The decomposition of calcite was observed at 700 °C. At that temperature, the absorption bands of calcite disappeared.

Above this temperature, the bands of carbonate disappear indicating the decomposition of calcite. The band at 1025 cm^{-1} broadened with the increase of the heating temperature and can be assigned to amorphous silica (Bich et al., 2009).

The diffractograms of the different heated argillite samples are presented in Fig. 5. The diffractograms of furnace heated samples (Fig. 5A) show the breakdown of the kaolinite structure with increasing temperature. The reflections related to quartz, illite, smectite, and muscovite seem not affected which indicates that the crystal structure of these minerals generally remained intact. The peaks associated with calcite and dolomite are still visible at 600 °C. However, they disappear from a temperature of 700 °C and peaks of lime appear indicating the decomposition of calcite (Boulingui et al., 2015). On the other hand, in the case of flash calcined samples (Fig. 5B), no significant changes were observed. Peaks associated with quartz, illite, smectite, and muscovite remained unchanged. Kaolinite, calcite and dolomite peaks persist, even after heat treatment at 750 °C, but their features change revealing some disorder of the structure (Ionescu et al., 2014). Lime reflections indicate the partial decomposition of calcite at 750 °C.

^{27}Al NMR results (Fig. 6) corroborate the XRD data. Indeed, the tetrahedral peak is increased to the detriment of the octahedral peak. At 800 °C, the octahedral aluminum disappears completely and all the aluminum became tetrahedrally coordinated. The transformation of octahedrally coordinated aluminum into tetrahedral coordination indicates the dehydroxylation of the clay minerals of the argillite rock (Roch et al., 1998). As a result, it can be deduced that at a temperature of 750 °C, the argillite clay minerals are fully dehydroxylated. However, in the case of flash calcined samples, the octahedral aluminum is present and only decreases in percentage area with the decrease of temperature. These results confirm that flash heat treatment leads to a partial dehydroxylation of the argillite clay minerals.

3.3. Feasibility of consolidated materials

The different argillite samples, raw and issued from the different heat treatments (temperature and process), were used as aluminosilicate sources in presence of a potassium alkaline solution. Consolidated materials (Table 3) were obtained from a mixture of 50% of raw argillite and 50% of metakaolin (AM^{K} sample). Moreover, whatever the heat treatment process, alkali-activated materials were obtained from calcined argillite (^{T}A^{K} and ^{FT}A^{K} samples). This finding is a promising way to use argillite as a raw material.

Based on their visual aspect and consolidated state, samples

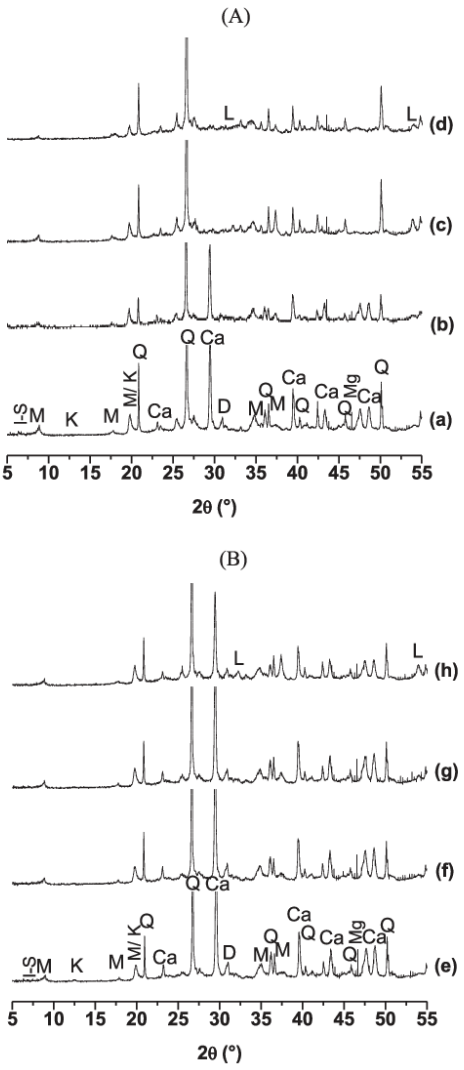


Fig. 5. XRD patterns of (A) (a) ^{600}A, (b) ^{700}A, (c) ^{750}A and (d) ^{800}A furnace heated argillite samples and (B) (e) ^{F600}A, (f) ^{F650}A, (g) ^{F700}A and (h) ^{F750}A flash heated samples. JCPDS files (Q: Quartz (04-016-2085), I–S: Illite-Smectite, K: Kaolinite (00-012-0447), M: Muscovite (00-003-0849), Ca: Calcite (00-005-0586), Mg: Magnesite (04-012-4921), L: Lime (01-082-1690), D: Dolomite (04-015-9852)).

based on argillite heated at high temperature (above 700 °C) seems to harden faster and to have better consolidation state. This fact can be explained by higher dissolution rate. Indeed, Buchwald et al. (2009) have demonstrated that the heat treatment at 750 °C of an illite/smectite clay induces the highest aluminate release. However, the heat treatment at 550 and 650 °C leads to lower

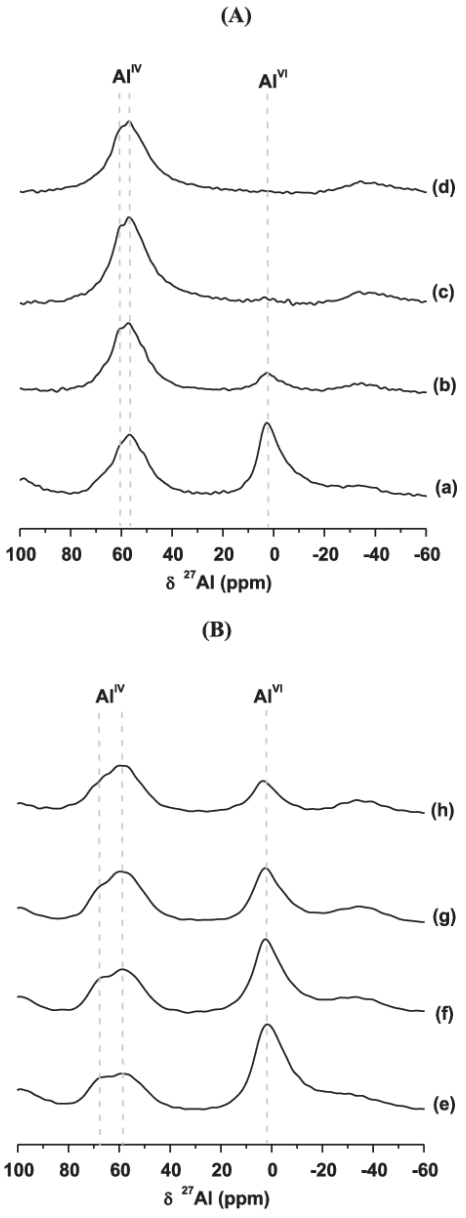
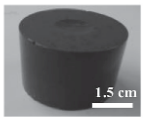
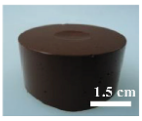
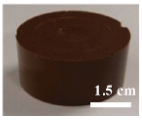
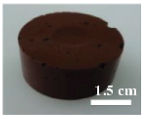
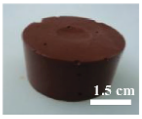
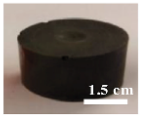
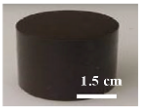
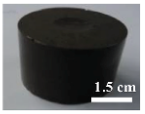
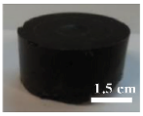


Fig. 6. ^{27}Al NMR spectra of (A) (a) ^{600}A, (b) ^{700}A (c) ^{750}A and (d) ^{800}A furnace heated samples and (B) (e) ^{F600}A, (f) ^{F650}A, (g) ^{F700}A and (h) ^{F750}A flash heated samples.

Table 3
Nomenclature and photos of different alkali-activated samples based on raw and heated argillite at different temperatures.

Nomenclature	Photo
(A) AM^K	
(B) $^{600}A^K$	
$^{700}A^K$	
$^{750}A^K$	
$^{800}A^K$	
(C) $^{F600}A^K$	
$^{F650}A^K$	
$^{F700}A^K$	
$^{F750}A^K$	

dissolution rate in alkaline solution indicating lower reactivity due to the presence of undehydroxylated clay minerals.

The structural evolution of the reactive mixtures as well as the working properties of the resulting alkali-activated materials will be further investigated in a future study.

4. Conclusion

The disposal of a nuclear waste in argillite clay host rock will lead to the excavation of huge quantities of argillite considered as by-products. In a context of circular economy, the suitability of argillite for alkali-activated materials synthesis was evaluated with emphasis on the thermal activation process.

In order to increase the reactivity of the argillite, it was thermally treated with furnace and flash processes. The present study focuses on the physical, chemical and structural changes induced by the two heat treatment processes at different temperatures. Initially, argillite was characterized by diverse mineralogical phases. Illite and smectite were the main clay minerals. The presence of carbonates (calcite and dolomite) was also evidenced.

In the case of furnace heat treatment, two behaviours were distinguished depending on the temperature. During furnace calcination at temperatures $\leq$700 °C, the clay minerals were partially dehydroxylated and the structure of calcite and dolomite basically remained intact. It was demonstrated that a temperature between 700 °C and 800 °C lead to full dehydroxylation of clay minerals and a total transformation of octahedral aluminum to tetrahedral one. In addition to that, the carbonates were fully decomposed. On the other hand, the flash treatment, regardless of the temperature and kinetic, induces partial dehydroxylation of clay minerals, and the transformation of octahedral aluminum to tetrahedral coordination as well as the decomposition of carbonates were incomplete. Consolidated alkali-activated materials were successfully obtained from a mixture of raw argillite and metakaolin or from calcined argillite whatever the treatment process. Thus, it is possible to make use of the excavated argillite in alkali-activated materials formulation. Moreover, the furnace and flash processes are suitable for thermal activation of the COx argillite. The different physical, chemical and structural characteristics induced by the two processes will allow the formulation of alkali-activated materials with adaptable working properties. This fact will also permit to widen the range of applications of the final materials.

Acknowledgments

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Alkali-Activated Materials Based on Callovo-Oxfordian Argillite: Formation, Structure and Mechanical Properties

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Abstract

If accepted, the construction of Cigéo, a French geological disposal facility for radioactive waste, will lead to the excavation of a large quantity of Callovo-Oxfordian (COx) argillite. The valorization of this raw material by alkaline activation was studied. For this, COx argillite without and with thermal treatment at 750 °C using furnace and flash processes were investigated. These treatments led mainly to the dehydroxylation of clay minerals and the decomposition of carbonate compounds. The feasibility of the alkali-activated samples based on different argillite samples and their mixtures was evaluated. Then, the consolidated samples were characterized by FTIR, X-ray diffraction, thermal analysis and compressive strength measurements. The results demonstrate that alkali activation is possible for all samples that contain at least 25 % calcined argillite (using both furnace and flash treatments). However, only samples without raw argillite indicate the formation of a geopolymer network and exhibit sufficient compressive strength. Lastly, the decomposition of the carbonate species (which produces free calcium and magnesium) was further studied. Indeed, the free alkaline earth cations led to structural modification in the alkali-activated samples.

Keywords: Callovo-Oxfordian, argillite, alkali-activated, heat treatment, carbonate, calcium

I. Introduction

High-level and intermediate-level long-lived wastes are the main products issued mainly from the nuclear industry and especially from the reprocessing of the nuclear spent fuel. The activity level and long half-lives of the waste justify deep geological disposal to ensure their confinement over several hundreds of thousands of years. In France, the French National Radioactive Waste Management Agency (Andra) is currently investigating the feasibility of a geological disposal site, called Cigéo, in eastern France between the Meuse and the Haute-Marne. The host geological layer, called Callovo-Oxfordian (COx) argillite, is located approximately 500 m under the ground level [1, 2]. If the construction of the disposal facility is accepted by the French authorities, the digging of the facilities will lead to the excavation of a total of millions of cubic meters of COx argillite, all along the Cigeo operating period (i.e., 100 years). Part of the excavated argillite will be used as backfill material. However, others methods for valorization are currently being assessed. In this study, the alkali-activation of COx argillite is investigated. The main mineral phases in COx argillite are clay minerals, but a high rate of carbonates and tectosilicates are also present [1].

Alkali-activated materials were introduced by Glukhovsky in 1957 and are more commonly called geopolymers (which is a subgroup of the alkali-activated materials). These materials are amorphous inorganic materials shaped at low temperature (< 100 °C) by the activation of an aluminosilicate source by an alkaline silicate solution [3, 4]. One advantage of these materials is the variety of aluminosilicate sources suitable for alkali activation. The possible use of crude aluminosilicate sources (without thermal treatment) has been demonstrated [5]. However, better working properties of the final synthesized materials were generally obtained using thermally treated aluminosilicate sources [6, 7]. Indeed, the thermal treatment induces the dehydroxylation of the clay minerals and a disorganization of the structure. Thermal treatment also leads to other transformations mainly on the carbonate species [8]. Recently, Gharzouni *et al.* [8] have studied the structural variations induced by the thermal treatment of argillite at different temperatures using furnace and flash processes to develop the alkali-activated materials. Gharzouni and coworkers demonstrated that at a temperature of 750 °C, furnace calcination leads to more complete clay mineral dehydroxylation and carbonate decomposition than does flash processing at the same temperature.

Particular interest is given to the decomposition of calcium carbonate, which results in the formation of lime and strongly influences the alkaline activation. Indeed, the presence of reactive calcium (free lime) in the mixture leads to a modification of the kinetics of polycondensation by decreasing the setting time [9]. Moreover, the structure of the final materials can be different with the appearance of

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a C-S-H phase due to the presence of large amounts of free lime and silica in this alkaline medium (this reaction is known as a pozzolanic reaction leading to the formation of C-S-H) [10, 11]. Moreover, the presence of calcium in the reactive mixture can also interfere with the geopolymerization reaction, which leads to Si-O-Ca bond formation [12]. Lastly, the carbonates can react with hydrated lime to form calcium carbonate [11, 13].

Despite the existing literature, the evolution of different carbonate compounds during alkali-activation is still not well understood and strongly depends on the raw materials that are used. The objective of this study is to investigate the formation, structure and mechanical properties of alkali-activated materials based on COx argillite and to focus on the evolution of the carbonate species. To do this, two different calcination processes (furnace and flash calcinations) and mixtures of raw and calcined argillite are studied. The study of various mixtures with different degrees of carbonate decomposition will allow a better understanding of the effect of calcium on alkali-activated samples based on COx argillite.

II. Experimental

(1) Raw materials

The COx argillite formation, where the Cigeo facilities will be implemented, is composed of 52 % clay minerals (interlayered illite/smectite, illite, kaolinite and chlorite), 26 % carbonate (calcite and dolomite) and 17 % quartz [1, 2]. The other components are mainly feldspar and pyrite. The chemical composition is reported in Table 1. The samples of argillite were ground and calcined in two different processes (furnace and flash), as described by A. Gharzouni *et al.* [8]. The furnace process is a classic calcination of the powder for four hours in a laboratory furnace, and the flash process consists of a very short exposure of the powder (by an airflow circulation) to a flame. In this paper, three different argillite powders were used: Ar (raw argillite), Ac (furnace-calcined argillite at 750 °C) and Af (flash-calcined argillite at 750 °C).

(2) Sample preparation

The consolidated samples were synthesized by mixing the powders of argillites with a potassium alkaline silicate solution (58 % water, and the molar ratio of Si/K = 0.58). The blends were cast in a closed polystyrene mold and maintained at room temperature for seven days (a classic procedure in the laboratory). The alkali-activated samples were referred to by the letter G, which is a reference to the raw materials. When several raw materials were used, the notation of the raw material was completed by the weight percent of each material. For example, $GAr_{0.5}Ac_{0.5}$ is a consolidated sample based on 50 % raw argillite and 50 % calcined argillite.

(3) Sample characterization

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were conducted with an SDT Q600, TA Instruments. Measurements were performed under a dry airflow (100 mL/min) in a platinum crucible. The samples were heated to 1200 °C at a rate of 5 °C/min. In addition, DTA-TGA coupled with mass spectrometry was performed with a Netzsch STA 449F3 analyzer. For these measurements, the samples were heated to 1200 °C at a rate of 10 °C/min under an argon flow. Only the H_2O (m/z = 18), CO_2 (m/z = 44) and SO_2 (m/z = 64) curves were selected from previous studies [8]. The apparatus does not allow quantitative measurements.

X-ray diffraction (XRD) patterns were obtained with a Bruker-D8 Advance diffractometer with a Bragg-Brentano geometry and a $CuK\alpha_1\alpha_2$ detector. The analytical range is between 5 ° and 55 ° (2θ) with a step width of 0.02 ° (2θ) and a dwell time of 1 s. Phase identification was performed with Joint Committee on Powder Diffraction Standards (JCPDS). A quantitative analysis was conducted via the Rietveld method using Topas software. For these measurements, the sample was mixed with 30 % ZnO.

Fourier-transform infrared (FTIR) spectra were obtained with a Thermo Fisher Scientific Nicolet 380 with an attenuated total reflectance (ATR) module. The spectra were recorded between 400 and 4000 cm^{-1} at a resolution of 4 cm^{-1}, and 64 scans were conducted. Atmospheric CO_2 was removed between 2280 and 2400 cm^{-1} and replaced by a straight line [14]. FTIR measurements were used to characterize the raw and activated materials but also for following the structural evolution during the first few hours of polycondensation (a spectrum was acquired every 10 minutes during a 13-hour period).

The compressive strengths of the samples were tested with a LLOYD EZ20 universal testing machine with a crosshead speed of 0.5 mm/min. For every composition, the measurements were performed on five cylindrical (15 mm diameter and 30 mm height) samples aged 28 days. The average compressive strength was expressed in MPa and represents the average of the five measurements.

The particle size distributions of the samples were obtained with a laser particle size analyzer, Mastersizer 2000. The powders were suspended by an airflow (3 Bars) through a glass cell with parallel faces illuminated by a beam of laser light.

Table 1: Chemical data of COx argillite (weight %).

SiO_2	Al_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	Fe_2O_3	P_2O_5	S	LOI (1000 °C)
48.68	13.41	0.03	2.50	10.73	0.20	3.26	0.72	4.51	0.07	0.83	15.06

The nuclear magnetic resonance (NMR) measurements were performed at room temperature with a Bruker Avance 400 spectrometer. The analyses were conducted with 400 scans at 104.26 MHz for ^{27}Al.

III. Results

(1) Raw materials

Different argillite samples, thermally treated or not, were investigated in this study. Table 2 lists the various physical, chemical and structural data about the argillite samples.

Table 2: Physicochemical and structural data of raw, calcined and flash argillite (M = Ca or Mg)

	Si/Al[8]	D_{50} (µm)[8]	Al^{IV} (%)[8]	Free MO (%)	Amorphous phase (%)
Ar	3,63	17	30	0	34
Ac	3,63	160	94	68	60
Af	3,63	21	68	13	46

The Si/Al ratio, the percentage of the Al^{IV} content determined from ^{27}Al MAS-NMR and the particle size were issued from a previous study [8]. Previous studies have demonstrated that furnace calcination (samples Ac) allows a more complete dehydroxylation of the clay minerals than does flash calcination. The percentages of amorphous phase (Table 2) agree with this finding. In fact, the amorphous phase content increases from 34 % to 46 % and 60 % for Ar, Af and Ac samples, respectively. To identify the different weight losses, the mass spectrometry coupled with thermal analysis curves (Fig. 1) that correspond to the Ar, Ac and Af samples are presented. The mass/charge ratios (m/z) of 18, 44 and 64 are selected, since they correspond to the release of H_2O, CO_2 and SO_2, respectively, as previously identified by thermal analysis [8]. The various notable outgassed molecules are related to several reactions occurring at various temperatures (H_2O from the departure of physisorbed water, CO_2 due to the decomposition of carbonate species and SO_2 from sulfate compounds). More precisely, for raw argillite (Ar sample, Fig. 1a), the first H_2O contribution with a high intensity was observed between 25 and 225 °C, which corresponds to the release of physisorbed water. At temperatures between 500 and 800 °C, the second large H_2O contribution with a smaller intensity is related to water departure from various clay minerals or from dihydroxylation [15]. Contributions linked to an m/z of 44 with a lower intensity at temperatures between 650 and 800 °C correspond to the release of CO_2 resulting from the decomposition of the carbonate species (calcite and dolomite) [15, 16]. Furthermore, the SO_2 contributions (m/z = 44) were detected at 400 °C and 1100 °C and are related to the presence of a sulfur compound. The first release of sulfate (400 °C) is related to the presence of pyrite [17]. Lastly, the release of sulfur dioxide at approximately 1100 °C is related to calcium sulfate decomposition [18, 19]. Calcium sulfate may be originally present in argillite and/or formed due to an *in-situ* reaction following the decomposition of carbonate compounds and the transformation of pyrite.

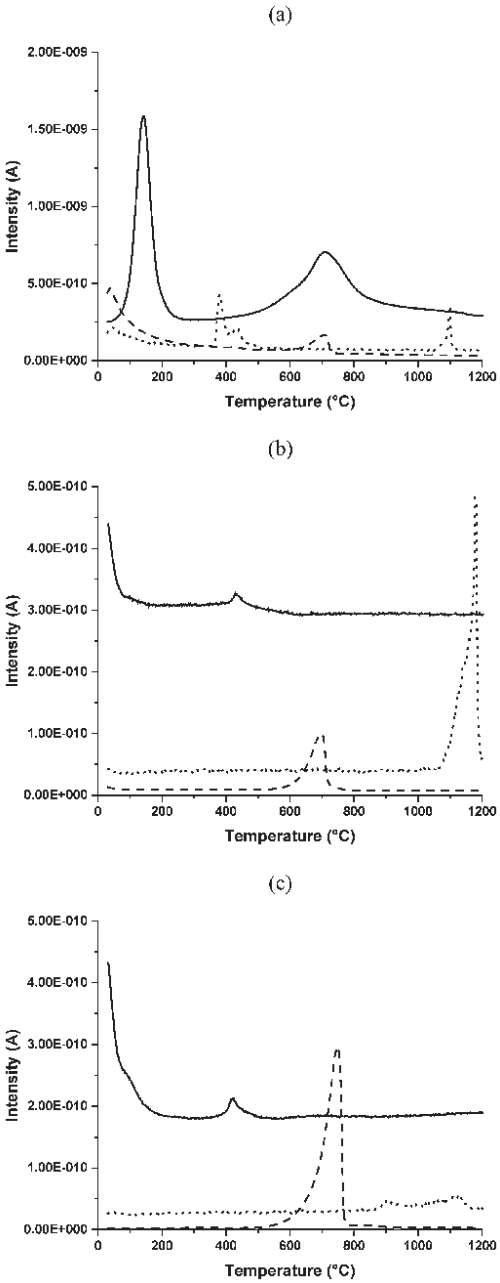


Fig. 1: Intensity of H_2O - m/z = 18 (–), CO_2 - m/z = 44 (---) and $SO_2 \times 10^2$ - m/z = 64 (···) as the function of the temperature get by thermal analysis coupled with mass spectrometer for (a) Ar, (b) Ac and (c) Af samples.

No matter what the thermal treatment of argillite is (Ac and Af samples, Fig. 1b and c, respectively), the H_2O contribution at approximately 500 – 800 °C disappears. However, a small contribution at a temperature less than 200 °C remains in the case of the Af sample and can be attributed to a hydrated compound (Mg or Ca based) or illite [15, 17, 18]. New contributions appear at temperatures of 390 and 410 °C for the Ac and Af samples, respectively. These contributions can be related to the $Mg(OH)_2$ transformation in the Af sample and $Ca(OH)_2$ decomposition in the Ac sample [15]. These data are in accordance with the different steps of dolomite decomposition previously observed [15, 16]. The contribution related to the carbon dioxide outgassing is always present at approximately 700 °C with various intensities and is characteristic of a carbonate species (calcite and dolomite), which is not completely decomposed. The Af sample presents a larger CO_2 contribution than does the Ac sample, which is greater in the presence of more available carbonates. For Af, an additional loss of SO_2 occurs at approximately 900 °C and is related to the outgassing of magnesium sulfate due to the solid-gas reaction between the magnesium, resulting from dolomite decomposition, and sulfate, resulting from pyrite decomposition [20, 21]. These data underscore the difference between the Af and Ac samples, notably in terms of the presence of the free alkaline earth cation (free lime and magnesia). To complete these data, the free alkaline earth compounds (Ca, Mg) were evaluated by thermal analysis (supplementary file) before and after calcination (Table 2). The value of 68 % for the Ac sample corresponds to the amount of the free alkaline earth cation divided by the total amount of M (Ca and Mg). This value, greater than that of the Af sample (13 %), is related to a high rate of decomposition for the carbonate species with a furnace treatment.

All these data highlight differences between the raw and calcined argillite samples with the various processes, especially in terms of the rate of dehydroxylation of the clay minerals and the presence of free alkaline earth cations dispensed from the carbonate species, suggesting a different reactivity for alkali activation.

(2) Alkali-activated materials based on COx argillite

(a) *Feasibility*

The feasibility of alkali-activated materials based on argillite was studied by the synthesis of several samples containing Ar, Ac and Af. The existence domains in an Ar-Ac-Af ternary diagram (Fig. 2) according to the weight percent of each argillite present in the sample were investigated. The feasibility is evaluated according to general characteristics, consolidation and water resistance. First, using pure Ac and Af argillites, the feasibility of the alkali-activated materials is optimal. However, for the Ar-based samples, there is no consolidation. Consequently, in the binary Ac-Af samples, consolidated materials are obtained, independent of the amount of Ac or Af used. In the Ac or Af samples with Ar, a limit of approximately 75 % of substitution is reached. In the following sections, six samples named A, B, C, D, E and F were selected to investigate their properties.

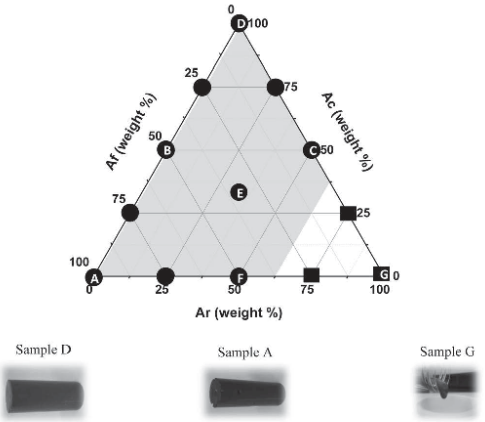


Fig. 2: Feasibility domains of Ar-Ac-Af alkali-activated materiel at room temperature: sufficient consolidation •, limited shaping ■.

(b) *Structural evolution during formation*

The local structural formations were followed by *in-situ* FTIR measurements. Three examples of the obtained spectra at the initial and final time of the measurement for the GAf, $GAf_{0.5}Ac_{0.5}$ and $GAr_{0.5}Ac_{0.5}$ samples are given in Fig. 3A. For the GAf sample, at the beginning of the reaction (t = 0 min), the large peak at 3400 cm^{-1} is associated with -OH stretching, and a sharper peak centered at 1630 cm^{-1} is related to -OH bending of a water molecule [22]. Small shoulders at 2980 and 2940 cm^{-1} correspond to τ -CH (from hydrogen carbonate) [23]. Additionally, contributions of the carbonate species are visible at approximately 1550 – 1450 cm^{-1} [24]. The intense and large peak at approximately 1000 cm^{-1} corresponds to Si-O-M bonds (M = Si, Al, etc.) [25]. During the first 13 hours of the reaction, several modifications occur. The intensity of the water contribution decreases, and the intensity of the carbonate species increases slightly as well as their bond positions. The Si-O-M bond also shifts to a lower wavenumber. The spectra of the $GAf_{0.5}Ac_{0.5}$ and $GAr_{0.5}Ac_{0.5}$ samples present similar curves at the initial and final times, but the intensity of the carbonate and the Si-O-M bond position shifts are not the same. This shift is related to the transformation of the Si-O-Si bonds. Indeed, alkali activation leads to a substitution of the silicon by aluminum in the silicate network to form a 3D network of the geopolymer materials. This network results in the formation of Si-O-Al bonds and a shift in the Si-O-M bonds, which is characteristic of a polycondensation reaction [26]. The evolution of the carbonate contributions will be discussed in section III(3).

To correlate the FTIR shift with the kinetics of the reaction, Fig. 3B displays the shift in the Si-O-M bonds for the six studied samples according to the slope value. This slope value corresponds to the kinetics of the FTIR shift during the first 13 hours of the polycondensation reaction, i.e., 13 hours after the preparation of the reactive mixture. Two behaviors are distinguished: on one hand, the GAc (D), GAf (A) and $GAf_{0.5}Ac_{0.5}$ (B) samples are characterized by high shift and slope values

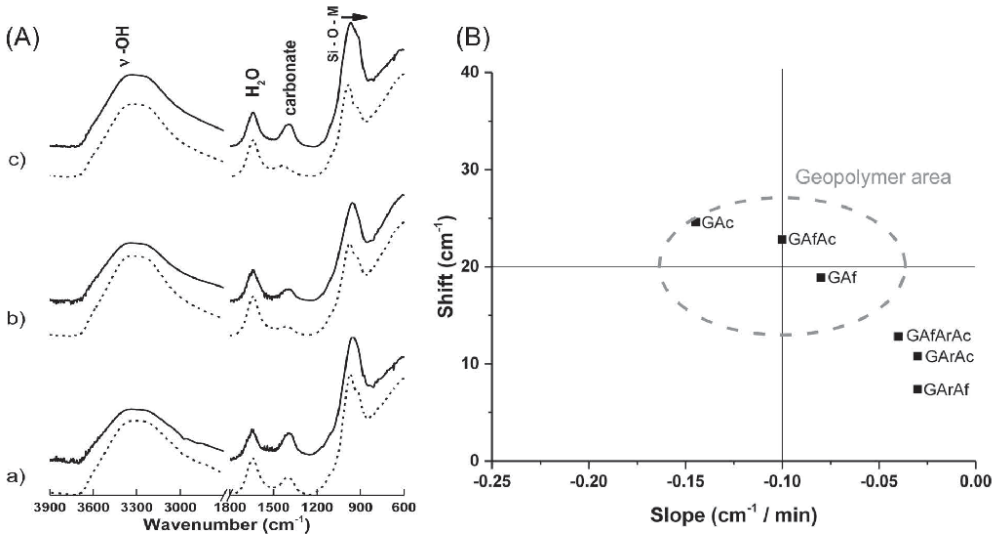


Fig. 3: (A) FTIR spectra of following in-situ measurement at initial time (---) and final time (–) for (a) GAf, (b) $GAf_{0.5}Ac_{0.5}$ and (c) $GAr_{0.5}Ac_{0.5}$ samples and (B) shift (Si-O-M) band value in function of the slope for the six samples.

(approximately 20 cm^{-1} and -0.10 cm^{-1}/min respectively); on the other hand, $GAf_{0.33}Ar_{0.33}Ac_{0.33}$ (E), $GAr_{0.5}Af_{0.5}$ (F) and $GAr_{0.5}Ac_{0.5}$ (C) exhibit lower shift and slope values (approximately 10 cm^{-1} and - 0.03 cm^{-1}/min respectively). Previously, A. Gharzouni *et al.* [27] defined an area of geopolymerization around a shift of 20 cm^{-1} and a slope of -0.10 cm^{-1} /min. According to these criteria, only the first group of samples, i.e. without Ar, leads to a polycondensation reaction. In the other samples, only a partial polycondensation reaction occurs. It is also notable that an increase in the calcined argillite proportion in the mixture increases the shift and the slope values favoring the geopolymerization reaction. Moreover, the increase in the proportion of raw argillite (Ar) in the mixture leads to a decrease in the shift and slope values. This fact can be explained by the higher reactivity of calcined argillite compared to raw argillite. Indeed, calcination allows the dehydroxylation of the clay minerals (kaolinite, illite, smectite, etc.), inducing an increase in the amorphous phase, which will be reactive in presence of an alkaline solution. This result agrees with the literature [8]. Indeed, it has been demonstrated that an improved reactivity is obtained by using a calcined clay at 750 °C.

The different behaviors observed during formation according to the used argillite samples suggest different structures and properties of the final alkali-activated materials.

(c) ***Structural and mechanical properties of the alkali-activated materials***

To compare the structure of the different synthesized samples, X-ray diffraction was performed. Fig. 4A. displays three example X-ray patterns of the different alkali-activated samples after seven days and the Ac, Af and Ar raw materials. Compared to the Af raw material, the GAf sample shows the presence of an amorphous dome centered at approximately 29 ° (2θ), demonstrating the polycondensation reaction observed for the geopolymer materials [28]. The diffraction peaks of illite/muscovite, quartz, calcite and dolomite present in the Af sample persist in the GAf alkali-activated material. Furthermore, the peaks that correspond to lime (i.e., the lime peaks) disappear. Additionally, for $GAf_{0.5}Af_{0.5}$, an amorphous dome is exhibited, and the lime peaks, initially observed in the Af and Ac raw materials, disappear. However, the carbonate peaks are well defined, which may be because the carbonates were not fully decomposed from the Af raw materials or new carbonates were formed during the alkali activation. The X-ray pattern of the $GAr_{0.5}Ac_{0.5}$ sample also shows an amorphous dome. The peaks attributed to lime disappear, and the pyrite and kaolinite peak intensities from the Ar raw materials are slightly discernible. To sum up, whatever the sample, alkali activation leads to the formation of an amorphous structure and the persistence of the crystalline phases initially present in the raw material(s) with the exception of lime for the Ac and Af-based samples [29]. The amorphous content strongly depend on the used argillite. An increase in the content of furnace-calcined and/or flash-calcined argillite favors the reaction and leads to the formation of a greater amorphous phase. This fact can be explained by the higher content of reactive aluminate and silicate in the calcined argillite (greater amorphous phase, Table 2) than in the non-calcined argillite. Moreover, the evolution of the carbonate species is different depending on the type and proportion of argillite.

More structural information was given by the FTIR measurements. The FTIR spectra of the argillite raw samples and alkali-activated materials aged seven days are presented in Fig. 4B. The summary of the positions and the assignment of the different contributions are provided in Table 3.

Compared to the Af sample, the GAf spectrum shows the disappearance of the νAl-OH of the illite, smectite and interlayered material initially detected at 3643 cm^{-1} [30, 31]. Moreover, a larger band at 3420 cm^{-1} of -OH stretching contribution is observed [22]. Concerning the carbonate species, a large band at approximately 1450 cm^{-1}, which is the result of the overlapping of several contributions from different carbonates, such as dolomite and calcite, is observed in the Af sample [24, 32]. After alkali activation (GAf), the intensities of dolomite and calcite located at approximately 1510 cm^{-1} decreased because of a new contribution link to the mixed carbonate species, which will be developed in section III(3)(b). The Si-O-Si bond initially located at 1028 cm^{-1} in the Af raw material shifts to 950 cm^{-1} [8, 33] and a new peak appears at approximately 930 cm^{-1}, related to Si-O-Ca formation [34]. The formation of $GAf_{0.5}Ac_{0.5}$ leads to the same transformation compared with that of GAf: i.e., an increase in the water contribution, the formation of a new carbonate speciesand a shift of Si-O-M to 943 cm^{-1}. Finally, $GAr_{0.5}Ac_{0.5}$ evolves similarly to the other samples. It is noticeable that the clay mineral initially present in the Ar sample (Al-OH stretching and bending modes at 3698 and 913 cm^{-1}, respectively) is not detectable on the spectrum after alkali activation [8].

The structural differences between the synthesized samples are directly linked to the used raw materials and their reactivity induced by thermal treatment. The observed differences will impact the mechanical properties of the resulting materials.

(d) ***Mechanical properties***

The mechanical properties of the different samples were evaluated by compressive strength measurements after 28 days of consolidation. To correlate the mechanical properties with the *in-situ* FTIR measurements, the evolution of the compressive strength and the FTIR shift in the Si-O-M peak position were plotted as a function of the Al concentration (calculated with the amount of aluminum and the volume of reactive mixture), as shown in Fig. 5. It is observed that the shift and the compressive strength values increase with an increase in the Al concentration. The samples containing non-calcined argillite, $GAr_{0.5}Ac_{0.5}$, $GAr_{0.5}Af_{0.5}$ and $GAf_{0.33}Ar_{0.33}Ac_{0.33}$

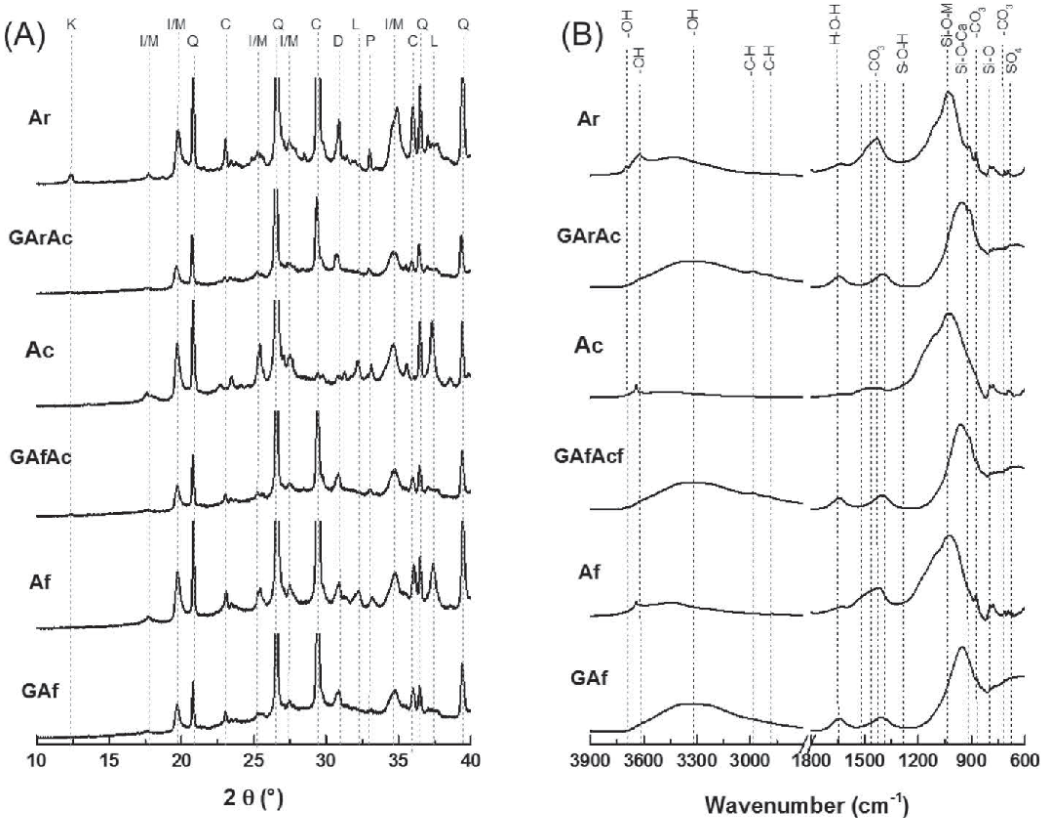


Fig. 4: (A) XRD pattern and (B) FTIR spectrum of GAf, Af, $GAf_{0.5}Ac_{0.5}$, Ac, $GAr_{0.5}Ac_{0.5}$ and Ar samples. JCPDS files: K: kaolinite (00–001–0527), I/M: Illite/muscovite (04–019–1573), Q: quartz (04–016–2085), C: calcite (04–012–0489), D: dolomite (04–011–9833), L: lime (04–002–6758) and P: pyrite (04–011–7328).

Table 3: Assignment of FTIR contribution in argillites and alkali-activated samples.

Wavenumber (cm^{-1})	Attribution	Mineral	Bibliography
3696	ν OH	Kaolinite	30
3640 – 3620	ν O-H	Illite, smectite, interstratified	31
3400	ν H-O-H	H-bonded water	22
2977, 2939	ν C-H	C-H bands	23
1630	δ OH	Water of crystallization	22
1510	ν CO_3	Calcite	32
1454	ν CO_3	Dolomite	24
1432	ν CO_3	Calcite	24
1378	ν CO_3	K_2CO_3	37
1160	ν SO_4	Sulfites	40
1033	ν Si-O-Si	Clay mineral	33
930	ν Si-O-Ca	Calcium silicate	34
910	δ Al-O	Kaolinite	8
870	δ CO_3	Calcite	23
796, 774	δ Si-O	Quartz	33
691	δ Si-O	Quartz	33
613	δ -SO_4	Calcium sulfate	40

present the lowest compressive strengths (2, 2 and 8 MPa, respectively) and the lowest shift values, which correspond to the lowest aluminum concentration (~ 4 mol/L). The aluminum content does not appear sufficient in this case to promote a sufficient polycondensation reaction. As previously demonstrated in section III(2)(b), the $GAr_{0.5}Ac_{0.5}$, $GAr_{0.5}Af_{0.5}$ and $GAf_{0.33}Ar_{0.33}Ac_{0.33}$ samples did not facilitate the formation of a geopolymer network. For the calcined argillite-based samples, GAc, GAf and $GAf_{0.5}Ac_{0.5}$, the compressive strength values and shift values increase to 16 MPa and 20 cm^{-1}, respectively, with an increase in the Al concentration (up to 7.4 mol/L). Indeed, these samples present a higher rate of the reactive phase, which favors the polycondensation and geopolymerization reactions leading to stronger structure and hence better compressive strength [26]. This difference in the reactive phase is directly linked to the proportion of calcined argillite in the mixture. In fact, an increase in Ac and/or Af leads to an increase in aluminum concentration and thus improves the reactivity of the mixture. The differences in the mechanical strengths can also be linked to the difference in carbonate species evolution after alkali activation, and this hypothesis needs to be confirmed.

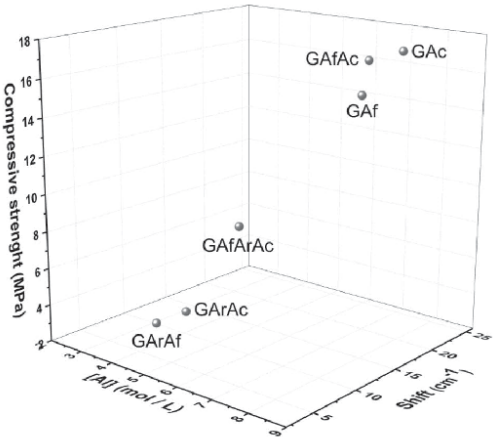


Fig. 5: Compressive strength (after 28 days) and FTIR shift of Si-O-M band values in function of the Al concentration for GAc, GAf, $GAf_{0.5}Ac_{0.5}$, $GAr_{0.5}Ac_{0.5}$, $GAr_{0.5}Af_{0.5}$ and $GAf_{0.33}Ar_{0.33}Ac_{0.33}$ alkali-activated samples.

(3) Study of the carbonate species

(a) *Thermal behavior*

To understand the thermal behavior of the alkali-activated samples and the evolution of the carbonate species, the weight losses of the different samples were studied by TGA analysis. Fig. 6A, presents three examples of the TGA curves for GAf, $GAf_{0.5}Ac_{0.5}$ and $GAr_{0.5}Ac_{0.5}$ samples after seven days. Independent of the sample type, the first weight loss of 25 % occurs at a temperature lower than 600 °C (I), which corresponds mostly to physisorbed water and structural water due to the geopolymer network that decomposed before 200 °C. Moreover, between 200 and 600 °C, there is a water loss due to the hydroxyl groups in the clay minerals (mainly in Ar). Two additional weight losses occur between 620 and 680 °C (II) and after 750 °C (III), which are related to carbonate species decomposition

and CO_2 formation [14, 15]. Differences can be detected between the different samples. The three weight losses of all the alkali-activated samples are presented in Fig. 6B. The first weight losses (I) are between 25 and 30 %, which is in accordance with the values commonly obtained for alkali-activated binders [25]. Lower weight loss values (~ 26 %) are obtained for samples based only on calcined argillite, which suggests a better geopolymer network. This result is in accordance with section III(2)(d) that shows a higher compressive strength in the case of these samples [26, 35].

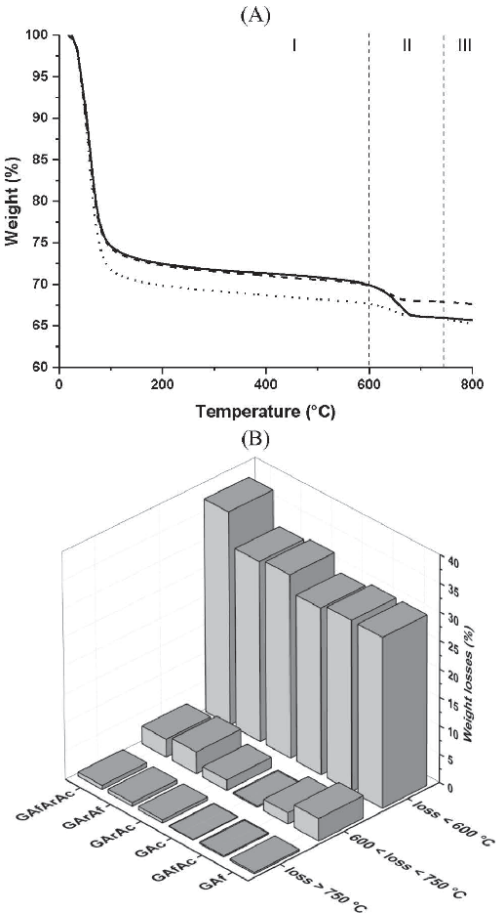


Fig. 6: (A) Example of thermal analysis curves for GAf (–), $GAf_{0.5}Ac_{0.5}$ (---) and $GAr_{0.5}Ac_{0.5}$ (…) samples after seven days and (B) weight losses for all alkali-activated samples at seven days.

The first CO_2 loss that occurs between 600 and 750 °C (II) is probably related to mixed carbonate species or carbonate compounds based on an alkaline earth cation. The minimal value, close to zero, is observed for the GAc sample. Samples based on a mixture of Ac and Af/Ar present intermediate losses, of approximately 2 %, and a loss of 3 % is demonstrated by the $GAf_{0.33}Ar_{0.33}Ac_{0.33}$ sample. The most important losses, approximately 4 %, are related to samples without Ac. Indeed, Ac is quasi-totally decarbonated, and consequently, there is no CO_2 to release. Af and Ar exhibits a high content of carbonate, and, after alkali activation, the same weight loss occurs.

The final weight loss, above 750 °C (III), is linked to the decomposition of the most refractory carbonate, namely, calcite. The losses are very small (~ 0.2 %) for samples based on calcined argillite (using both furnace and flash treatment processes). With the presence of Ar, this loss slightly increases (~ 0.6 %).

At temperatures above 800 °C (data not shown), the low weight loss (approximately 1 %) is due to the formation of SO_2 issued from K_2SO_4, which suggests a reaction between potassium and sulfur [36].

To correlate the different losses to the decomposition of the carbonate species, Fig. 7 displays the evolution of the molar percentage of CO_2 released during the TGA measurement as a function of the molar percentage of the free alkaline earth cation in the sample. Initially, for temperature between 600 and 750 °C, the GAc sample presents the smallest CO_2 loss (~ 1 %), and the GAf sample presents the highest loss (~ 7.5 %). Indeed, in the Ac argillite sample, the carbonate species are mostly decomposed, whereas in Af a higher release rate of the carbonate species is exhibited because the carbonate species did not fully decompose. The loss obtained with $GAf_{0.5}Ac_{0.5}$ (~ 4 %) is between that of the GAf and GAc samples, which suggests a proportionate release of CO_2 and free M^{2+}. The addition of Ar argillite in GAc formed $GAr_{0.5}Ac_{0.5}$, which led to a decrease in the free M^{2+} amount (until 3.5 %) and then an increase in CO_2 formation (~ 4 %), which confirms this proportionality. The $GAr_{0.5}Af_{0.5}$ sample shows the same CO_2 loss compared with that of GAf (7.5 %) but a lower M^{2+} content (0.5 %), probably linked to the high amount of carbonate species in both Ar and Af argillite. Lastly, the $GAf_{0.33}Ar_{0.33}Ac_{0.33}$ sample presents approximately 3 % free M^{2+} and a CO_2 loss close to 6 %, which confirms the linear relation between M^{2+} and the first CO_2 loss.

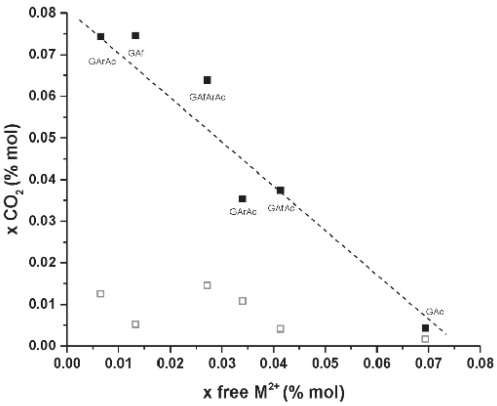


Fig. 7: Evolution of the molar percent of CO_2 release during thermal analysis between (■) 600–750 °C and (□) 750–800 °C according to the molar ratio of free M^{2+} cations (Ca, Mg) in the alkali-activated samples GAf, $GAf_{0.5}Ac_{0.5}$, $GAr_{0.5}Ac_{0.5}$, GAc, $GAf_{0.33}Ar_{0.33}Ac_{0.33}$ and $GAr_{0.5}Af_{0.5}$ samples after seven days.

For the second loss between temperatures of 750 and 800 °C, which corresponds to the decomposition of other types of carbonates, small variations are observed between the samples. GAf, $GAf_{0.5}Ac_{0.5}$ and GAf present similar CO_2 losses under 0.5 %. The addition of Ar argillite leads to a small increase in this loss, up to 1.3 %, for the $GAr_{0.5}Ac_{0.5}$, $GAr_{0.5}Ac_{0.5}$ and $GAf_{0.33}Ar_{0.33}Ac_{0.33}$ samples. These data confirm that this second loss is not related to the M^{2+} content, but to carbonate that is not decomposed with a thermal treatment at 750 °C.

The thermal analysis highlights different types of carbonates, which originate from the used raw materials or newly formed after alkali activation, but did not precisely identify them. Structural analyses using FTIR spectroscopy and XRD will be useful in this case.

(b) ***Evolution of the carbonate species***

To identify the carbonate species in argillite according to different thermal treatments, and their evolution with alkali activation, a focused study on the carbonate contribution using FTIR spectroscopy and X-ray diffraction was performed (Fig. 8). Fig. 8A represents the FTIR spectra of the argillite (Ar, Af, Ac) and alkali-activated samples after seven days.

Compared to Af argillite, the GAf sample shows the appearance of a new band between 1415 and 1380 cm^{-1} related to the formation of a mixed carbonate (with alkali and alkaline earth cations) due to alkali activation [37]. Moreover, the contribution of dolomite (1455 cm^{-1}) and calcite at a higher wavenumber (1510 cm^{-1}) disappears [21, 31]. The same evolution is observed in the $GAf_{0.5}Ac_{0.5}$ sample with a decrease in the intensity due to the low amount of carbonate species in the Ac sample. For the GAc sample, the intensity of the carbonate contributions strongly decreases for the same reason. Indeed, the Ac spectrum displays a very low intensity for all the carbonate bands, and no contribution related to mixed carbonates is exhibited. Then, the progression of the $GAr_{0.5}Ac_{0.5}$ sample is similar to the other alkali-activated samples with the formation of the mixed carbonates. The same behavior is observed with $GAf_{0.5}Ar_{0.5}$ in contrast to raw argillite, Ar, in which there is no indication of a mixed carbonate formation; but clear contributions from calcite (1510 and 1430 cm^{-1}) and dolomite (1455 cm^{-1}) are present. Finally, the $GAf_{0.33}Ar_{0.33}Ac_{0.33}$ sample presents only calcite and mixed carbonate contributions due to the alkali activation of the argillites. The presence of potassium issues from the silicate solution in excess, leading to carbonate mixed compounds or to the formation of K_2SO_4 [36].

To improve the identification of carbonate species, measurement with Raman spectroscopy has been performed but the spectra cannot be used because of the fluorescence due to the iron in the argillite. Therefore, X-ray diffraction is used to complete the FTIR analysis.

Fig. 8B shows the X-ray patterns of the argillite samples (Ar, Af and Ac) and of the alkali-activated samples after seven days. Only the 28 – 33 ° (2θ) range is presented in order to focus on carbonate species and sulfates. Two different large contributions can be distinguished: at approximately 29.5 ° (2θ) that correspond to the

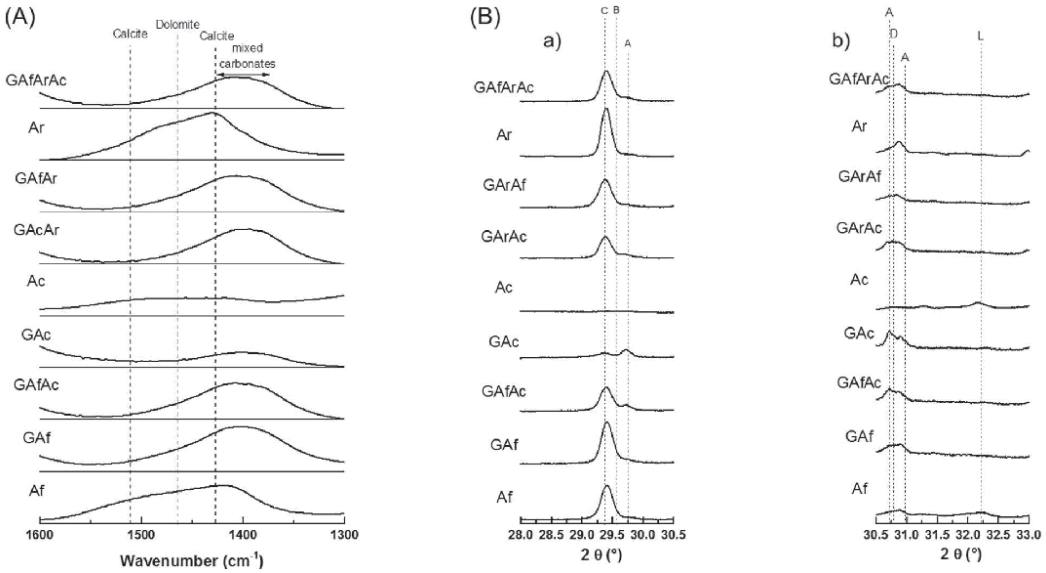


Fig. 8: (A) FTIR spectra and (B) X-ray patterns focus on the carbonate species (28 – 30.5° (a) and 30.5 – 33° (b) ranges with different scale) for raw materials (Ac, Af and Ar) and alkali activated samples after seven days (GAf $GAf_{0.5}Ac_{0.5}$, GAc, $GAr_{0.5}Ac_{0.5}$, $GAr_{0.5}Af_{0.5}$ and $GAf_{0.33}Ar_{0.33}Ac_{0.33}$). JCPDS files: C: $CaCO_3$ (04 – 012 – 0489), B: $K_2Ca(CO_3)_2$ (00 – 025 – 0626), A: K_2SO_4 (04 – 006 – 8317), D: $CaMg(CO_3)_2$ (04 – 011 – 9833) and L: CaO (04 – 002 – 6758).

carbonate species (Fig. 8B (a)) and close to 31 ° (2θ) due to the carbonate species and sulfate contributions (Fig. 8B (b)). These diffraction lines are wide, and their angular ranges are evolving according to the nature of the sample, suggesting different reactions. For the first peak, different possible contributions have been identified as calcite ($CaCO_3$), butschliite ($K_2Ca(CO_3)_2$) and arcanite (K_2SO_4). For the second peak, the middle contribution is identified as dolomite ($CaMg(CO_3)_2$) and is surrounded by two contributions of arcanite. Finally, for the raw materials, Af and Ac, another peak can be seen at approximately 32 ° (2θ) associated with lime.

Compared to the Af sample, GAf does not show a peak that corresponds to lime, which disappears with alkali activation. Additionally, an arcanite peak appears at 31 ° (2θ), which is possibly due to an excess of potassium from the alkali-silicated solution. Moreover, the peak of calcite shifted to a higher angle, probably due to the appearance of new mixed carbonate species (butschliite). The $GAf_{0.5}Ac_{0.5}$ sample presents a smaller peak at 29.5 ° (2θ) due to the lower amount of carbonate species in Ac, and there is also an increase in intensity in the arcanite peak. This behavior is confirmed for the GAc sample, which barely presents the carbonate species and arcanite peaks. Indeed, argillite Ac does not show either a carbonate or sulfate peak but does exhibit a well-defined lime peak at 32.5 ° (2θ). The $GAr_{0.5}Ac_{0.5}$ sample confirms the disappearance of the lime peak and the formation of arcanite, which is consistent with the alkali activation and the modification of the large carbonate peak including calcite and mixed carbonate species. With Af argillite, the $GAr_{0.5}Af_{0.5}$ sample presents the same XRD pattern, but the arcanite peaks are less discernible. Finally, for the $GAf_{0.33}Ar_{0.33}Ac_{0.33}$ sample, there is again a shift and a widening of the calcite peak, which signifies a new carbonate species and the formation of arcanite.

The results indicate that the alkali activation of calcined argillite (or mixture of raw and calcined argillite) leads to the formation of new mixed carbonates based on potassium. Indeed, there are unstable alkali earth cations resulting from the decomposition of the carbonate species during various thermal treatments [8]. Moreover, the high concentration of the alkaline silicate solution probably led to an excess of potassium in the mixture that can react with the carbonate formed by the alkali earth cations and form arcanite. The findings suggest that this sulfate formed during alkali activation with a high potassium concentration and the pyrite decomposition products.

IV. Discussion

All the previous data highlight the structural differences between the synthesized samples. These differences are strongly related to the thermal treatment of the argillite samples that influence essentially the aluminum and alkaline earth cations in the mixture. For this, correlations were established in Fig. 9 between the reactive Al, the free alkaline earth cations and the FTIR shift in the Si-O-M band of the different studied samples. The reactive aluminum was calculated by the amount of Al^{IV} (determined by NMR) multiplied by the amorphous rate, and then this quantity was divided by the amount of Al^{VI} (Table 2).

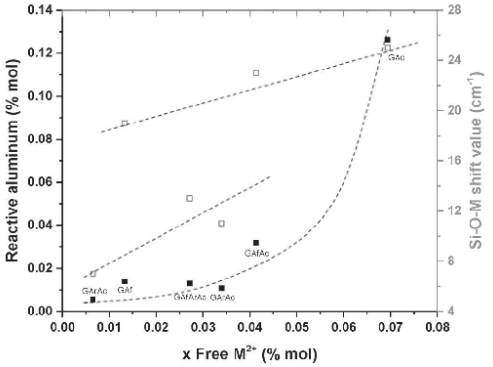


Fig. 9: (■) Rate of reactive aluminum and (□) FTIR shift of the Si-O-M bonds according to the molar percent of free M^{2+} cations (Ca or Mg) in the different samples GAf, $GAf_{0.5}Ac_{0.5}$, $GAr_{0.5}Ac_{0.5}$, GAc, $GAf_{0.33}Ar_{0.33}Ac_{0.33}$ and $GAr_{0.5}Af_{0.5}$ samples after seven days.

On one hand, the increase in the proportion of calcined argillite (with flash and, to a greater degree, with furnace calcination) leads to an increase in the amounts of reactive aluminum from 2 to 12 % and free lime from 0.5 to 7 % for the $GAr_{0.5}Af_{0.5}$ and GAc samples, respectively. This result can be explained by the higher degree of dehydroxylation of the clay minerals using furnace calcination of the Ac sample compared with using flash calcination of the Af sample and non-treated argillite (Ar). Therefore, more aluminum is released from the aluminosilicate source, which enables a polycondensation reaction. Moreover, the degree of carbonate decomposition is also higher using furnace calcination (Ac sample) compared to the decomposition using flash calcination (Af sample and the non-treated argillite (Ar)), inducing more free alkaline earth cations in the mixture.

On the other hand, the FTIR shift increases from 6 to 24 cm^{-1} with an increase in the amount of free M^{2+} from 0.5 to 7 % in $GAr_{0.5}Af_{0.5}$ and GAf. Once again, the importance of thermal treatment and its influence on the structural evolution of the samples is demonstrated. In fact, the two groups of samples can be distinguished: the samples containing raw argillite ($GAr_{0.5}Ac_{0.5}$, $GaR_{0.5}Af_{0.5}$ and $GAf_{0.33}Ar_{0.33}Ac_{0.33}$) exhibit a low amount of M^{2+} and smaller shift values; and the samples containing calcined argillite (the GAf, $GAf_{0.5}Ac_{0.5}$ and GAc samples) exhibit a higher quantity of M^{2+} and higher shift values. The increase in the shift value indicates the formation of a higher number of Si-O-Al bonds from the Si-O-Si bonds, which indicates the formation of an improved geopolymer network [26, 38, 39].

All the previous results prove the suitability of COx argillite after heat treatment to produce alkali-activated materials and aid in the understanding of the evolution of the different constituents of COx argillite after thermal treatment at 750 °C and alkali activation with a potassium alkaline solution, as summarized in Fig. 10:

- The thermal treatment allows the dehydroxylation of the clay minerals (illite, muscovite, smectite, chlorite, and kaolinite) present in COx argillite.

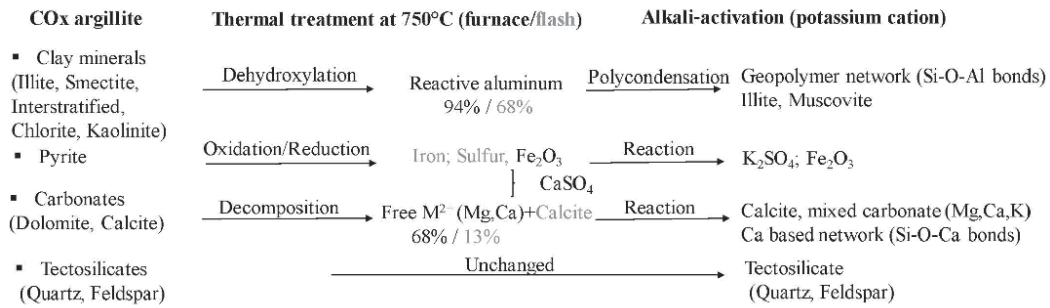


Fig. 10: Summary of the evolutions of the main mineral compounds in the argillite according to the thermal treatment and the alkali-activation.

The dehydroxylation is more complete with furnace calcination compared to flash calcination, leading to an increase in reactive aluminum in the mixture (the Al^{IV} percentages are approximately 68 % and 94 % for flash and furnace calcination, respectively). This reactive aluminum is essential for a polycondensation reaction and the formation of a geopolymer network (Si-O-Al bonds). Some illite and muscovite persist in the final material, which does not depend on the thermal treatment process.

- Whatever the process, thermal treatment induces the reduction of iron and the oxidation of sulfur in pyrite. In furnace-calcined argillite, the formation of hematite is responsible for the orange-reddish color. After alkali activation, the sulfate may interact with potassium to form potassium sulfate (K_2SO_4), which was more abundant in samples based on furnace-calcined argillite.
- In the case of the carbonates, which are essentially calcite and dolomite in COx argillite, their decomposition depends on the calcination temperature/duration and atmospheric conditions. Furnace thermal treatment induces the decomposition of carbonates producing free alkaline earth cations (especially free lime) (M^{2+}, 68 %). Some of the calcium can interact with sulfate resulting from pyrite oxidation to form $CaSO_4$. In the case of flash calcination, the decomposition is not complete, leading to a lower amount of free alkaline earth cations (M^{2+}, 13 %) and the persistence of some calcite. After alkali activation, several interactions occur between free cations to form mixed carbonates and calcite but also other calcium-based network (Si-O-Ca) bonds.
- The tectosilicate present in COx argillite, essentially quartz and feldspar, is resistant to thermal treatment and alkali activation and persists in the final structure.

V. Conclusions

To study a different method for the valorization of Callovo-Oxfordian (COx) argillite, alkali activation has been examined. After a previous study concerning the activation of COx argillite by a thermal treatment [8], this study aims to investigate the formation, structure and mechanical properties of the alkali-activated materials based on COx argillite. For this, the feasibility of consolidated materials containing raw, furnace- and flash-calcined argillite in presence of a potassium alkaline solution was evaluated. It was demonstrated that both furnace and flash treatments, and a mixture of raw and calcined argillite are suitable for the alkali activation of the consolidated samples. FTIR spectroscopy data demonstrate a polycondensation reaction and the formation of a geopolymer network in samples containing calcined argillite. However, the reaction is not favored in the sample containing non-treated argillite. This result agrees with compressive strength measurements, which are higher in samples based on calcined argillite (16 MPa). Thus, it was possible to determine the reactivity of argillite, heated or not, in presence of a potassium alkaline solution:

(i) The non-treated argillite exhibits a very low reactivity or is non-reactive in presence of the alkaline solution due to very small amount of aluminum, which can be dissolved, and the presence of crystalline phases. Therefore, aluminum can be used in alkali-activated materials only as a filler.

(ii) The reactivity of argillite increases with flash calcination at 750 °C due to the partially dehydroxylated clay minerals and decomposed carbonates leading to higher amount of reactive aluminum and free alkaline cations in the mixture. A polycondensation reaction was effective in leading to a relatively sufficient mechanical strength. The presence of free alkaline oxides leads to several interactions and the formation of new carbonates and other networks containing calcium. The remaining or newly formed carbonates do not perturb the reaction. This thermal treatment process seems beneficial from an ecological and economical point of view.

(iii) The furnace calcination of argillite at 750 °C is more efficient in terms of the dehydroxylation of clay minerals and decomposition of carbonates. The polycondensation reaction is favored, leading to good mechanical strength.

(iv) The mixture of flash- and furnace-calcined argillite exhibits a similar reaction rate and mechanical strength compared with furnace-calcined argillite.

(v) The presence of non-calcined argillite in the mixture slows down the polycondensation reaction and weakens the structure.

According to these results, a thermal treatment is essential to increase the chemical reactivity of argillite to develop alkali-activated materials. Therefore, it is possible to valorize COx argillite by using alkali-activation. Depend-

ing on the targeted applications in the Cigéo project and the requested working properties, the flash and/or furnace calcination processes can be varied.

VI. Appendix

Supplementing our results detailed under III. Results (1) Raw Materials, additional data are provided in the following.

Fig. 11 shows the DTA-DTG curves of raw argillite (Ar) and furnace-treated argillite at 750 °C (Ac).

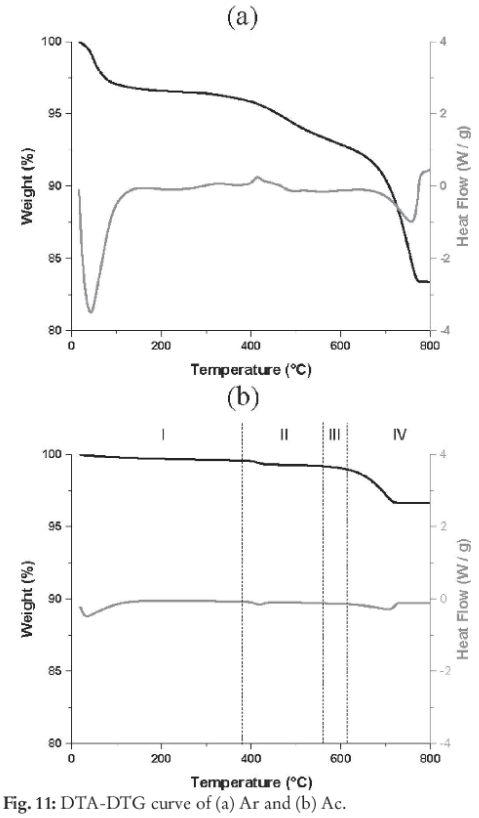


Fig. 11: DTA-DTG curve of (a) Ar and (b) Ac.

Thermal analysis of the raw argillite, Ar sample, (Fig. 11a) shows a weight loss of 15.33 % of CO_2, which is considered as the total decarbonation of argillite. This value is in accordance with the amount of CaO and MgO obtained with X-ray fluorescence analysis. The thermogram of the calcined argillite, Ac sample, (Fig. 11b) displays four weight losses. The first one (I), between 25 and 375 °C, is related to the release of the structural water of the argillite. The second (II), between 375 and 550 °C, corresponds to water loss from the decomposition of the $Mg(OH)_2$ formed during the calcination (Eq. 1). The third loss (III), between 550 and 625 °C, is associated with a first decarbonation related to the calcite formed consecutively to the decomposition of the dolomite (Eq. 2, Eq. 3). Last, above 625 °C (IV) the second decarbonation (discernible by a heat flow variation) is related to the calcite decomposition (Eq. 2). Indeed, the calcite is naturally more stable in temperature than dolomite, which is confirmed by the weight loss (II).

$$Mg(OH)_2 \xrightarrow{O_2} MgO + H_2O \quad (1)$$

$$CaCO_3 \xrightarrow{air} CaO + CO_2 \quad (2)$$

$$MgCa(CO_3)_2 \xrightarrow{air} MgO + CaCO_3 + CO_2 \quad (3)$$

Quantification of the free earth alkaline cations formed during the thermal treatment is performed with the TGA measurements coupled with a mass spectrometer. It appears that the dehydroxylation of clays minerals occurs mainly between 450 and 550 °C, so it was chosen to use the weight losses above 550 °C (and check that they really correspond to decarbonation processes). The different amounts of CO_2 (in molar percent) and water (from dihydroxylation) are compared to the value obtained by means of X-ray fluorescence and the Rietveld data. All these data are collected in Table 4.

The amount of water released during the second weight loss (II) for the samples Ac and Af corresponds to the amount of magnesium present in the dolomite, i.e. 1.6 % (TGA) and 1.8 % (Rietveld). These data confirm the identification of these losses and that the thermal treatment at 750 °C is sufficient to entirely decompose the dolomite.

The available calcium rate is calculated with the other weight losses and the amount of free alkali earth cation is estimated with Eq. 4.

$$\text{rate of free cation} = \frac{n\,CO_2^{1st\ loss} + (n\,CO_2^{2nd\ loss} - n\,CO_2^{Ar})}{n\,(Ca + Mg)^{total\ X\text{-}ray\ fluo}} \quad (4)$$

The flash treatment at 750 °C, Af sample, leads to a rate of 12.8 % of free earth alkali cation, in accordance with the partial decomposition of the different carbonates species. The furnace treatment at 750 °C, Ac sample, leads to 68 % reactive M^{2+} cation. However, some carbonate species are not decomposed.

Table 4: Molar percent of H_2O and CO_2 obtain with TGA measurements

	Mg cation	Ca cation			Free % M^{2+}
Samples	x H_2O	I x CO_2	II x CO_2	Σ x CO_2	± 5
Ar	0	1,6	13,8	15,4	--
Af	1,6	2,2	14,2	16,4	12,8
Ac	1,6	1,3	3,2	4,5	68,3

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Thermal resistance of argillite-based alkali-activated materials. Part 1: effect of calcination processes and alkali cation.

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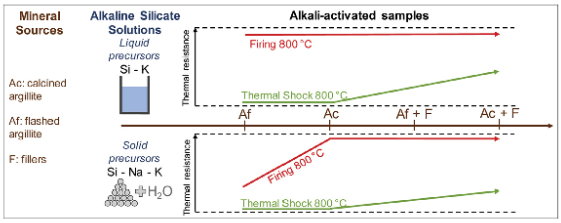
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HIGHLIGHTS

- Samples resist to firing but a lack of resistance to thermal shock is observed.
- The thermal resistance depend of the argillite calcination process.
- Use of filler limits the shrinkage and has no influence on the compressive strength.
- The chemical composition of the samples controls their thermal behaviour.

GRAPHICAL ABSTRACT



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ABSTRACT

Here, the valorization of Callovo-Oxfordian (COx) argillite from the geological layer focused by the Cigéo project (Industrial Center for Geological Disposal of radioactive waste) is studied by Andra. Its reuse by alkali-activation is studied in order to develop thermally resistant binders. The thermal properties of various argillite-based samples are studied at 800 °C, and they present a good resistance to a slow firing environment but a lower resistance to thermal shock. This article discusses the influence of the sample compositions on the thermal resistance. First, the thermal activation of argillite has a significant impact on the thermal resistance of the alkali-activated samples. Indeed, a higher resistance is reached with the use of furnace-calcined argillite due to the complete dehydroxylation of clay minerals and decomposition of carbonates. However, the use of flash-calcined argillite (partial dehydroxylation and decompositions) leads to different species present in the mixture and therefore may be conducive to higher structural evolutions during sample firing. Then, the influence of the nature of the alkaline silicate solution is highlighted. It appears that the use of sodium-potassium silicate powder-based solution (Si-Na-K) is conducive to lower reactivity and more viscous flow than a liquid-based potassium solution (Si-K). Finally, the addition of filler, sand (SiO_2) and calcined clay (Al_2O_3-SiO_2) allows for better thermal resistance but limits the development of mechanical properties.

1. Introduction

Geopolymer materials are amorphous inorganic polymers based on a 3D network of silica and alumina tetrahedrons. They are synthesized without thermal treatment by the alkaline-activation of a mineral source. Glukhovsky [1] introduced the alkali-activated materials in 1957. The term alkali-activation refers to a larger group of materials based on various alkaline solutions and mineral sources. This activation

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usually occurs at room temperature or with a low curing temperature (< 100 °C) [2]. More recently, Davidovits called geopolymers a subgroup of these alkali-activated materials [2]. These materials are commonly obtained by the activation of metakaolin with potassium or sodium silicate solutions. The final structure obtained with these materials is a function of the raw materials and could lead to a pure geopolymer network. These geopolymer materials present interesting properties related to the ease of synthesis and shaping but mainly related to the structure. Indeed, they exhibit good mechanical properties and thermal resistance [3].

These properties can also be obtained in the case of alkali-activated materials containing calcium. Indeed, Bernal et al. [4] focused on the effect of calcium on the thermal behavior of alkali-activated materials. It has been proven that the addition of a low amount of calcium increases the densification temperature and improves the mechanical strength after thermal treatment. Several types of fillers have been added to geopolymer materials in order to improve their mechanical and thermal properties, such as refractory aluminosilicate particles (refractory brick) and fibers (alumina–silica–zirconia fiber), which have been added to metakaolin-based geopolymers [5–7]. These additives exhibit a significant shrinkage reduction and improve the volumetric stability; therefore, they enhance post-exposure strength due to the strong interactions between reinforcements and matrix. Trindade et al. [8] demonstrated that the replacement of natural sand with chamotte in geopolymer materials based on metakaolin and blast furnace slag leads to higher stability above 500 °C, which was confirmed by Krivenko et al. [9].

The formulation of an alkali-activated material is mainly influenced by the alkaline silicate solution. There are two key parameters, i.e., the cation nature and the precursor nature. The main alkali cations used are sodium and potassium. To achieve good thermal resistance, the use of potassium is generally recommended [10]. In fact, the use of sodium leads to the appearance of viscous flow at lower temperatures than potassium, which is not optimal for thermal resistance [3,10]. The solution precursors can be aqueous alkaline-silicate solutions, powder alkaline-silicate or mixtures of silica solution and alkaline powders [11,12]. These different types of activators are conducive to different chemical reactivities and thus to different end-products. Indeed, Essaidi et al. [11] showed that the use of both an aqueous solution and an alkaline-silicate powder leads to similar mechanical properties. However, powdered alkaline-silicates slow down the polycondensation reaction kinetics. Concerning the aluminosilicate source, various mineral sources can be used. Generally, metakaolin is used, but other clays, mineral waste or industrial by-products can also be utilized as the aluminosilicate source [13–15]. Thus alkali-activation is a way to valorize a mineral by-product, such as Callovo-Oxfordian (COx) argillite. COx argillite is a mineral primarily containing clay minerals (mainly illite and interlayered illite/smectite) in addition to a large amount of carbonate species with 22% calcite [16,17]. Among the different applications of alkali-activated binders, the development of thermally resistant materials can be an interesting way to valorize the excavated COx argillite. In previous work [18], it has been demonstrated that raw argillite is not reactive enough to be alkali-activated and needs to be thermally treated. To improve the chemical reactivity, two different thermal treatment processes at 750 °C are used: classic furnace calcination and flash process calcination. These two treatments lead to different reactivities and characteristics. Gharzouni et al. [19] highlighted these discrepancies. Dupuy et al. [18] showed that with at least half-calcined argillite, alkali-activation begins to be possible.

The main goal of the present work is to develop thermally resistant binders based on COx argillite. The influence of the mineral sources in the presence of fillers (sand and calcined clays), with both liquid-based potassium solution and powder-based potassium-sodium solution, is tested. The characterization of the thermal resistance of the argillite-based samples is performed with a slow heat increase or a thermal "shock" both from ambient temperature and up to 800 °C. Then, analyses were carried out before and after thermal treatment (compressive strength, scanning microscopy, density measurement, dilatometric measurements) in order to identify its influence on the chemical formulation of each sample.

2. Material and methods

2.1. Raw materials and sample preparation

This study focuses on the thermal behavior of Callovo-Oxfordian argillite-based alkali-activated materials. Andra provides the raw mineral. It comes from the UA2 geological layer in the broader Callovo-Oxfordian clay layer, which has been studied by Andra [16,17]. This argillite, widely studied by B. Yven et al. [16], is composed of 52% clay minerals (mainly illite and interlayered illite/smectite but also 4% kaolinite and 4% chloride), 26% carbonate species (primarily calcite and a small amount of dolomite), and the other compounds are quartz with trace amounts of plagioclase, feldspar and pyrite. Before alkali-activation, the argillite is calcinated using two different processes, both at 750 °C. The first one, corresponding to Ac-named argillite, is a 4-h-long furnace calcination; the second one, Af-named argillite, is a flash calcination[1] (process described by Gharzouni et al. [19]). Table 1 shows the various data obtained from these argillites. Different alkaline silicate solutions were used. The first one, named S, is based on a commercial potassium silicate solution (Si/H_2O = 0.065) with the addition of potassium hydroxide to reach a 0.58 Si/M *ratio* (M = K and Na). The other solution, named P, is based on powder precursors and presents a 0.60 Si/M *ratio* and a higher water content (Si/H_2O = 0.080). It is prepared with sodium silicate powder, potassium hydroxide and water. To increase the thermal resistance of the samples, two fillers are added (Table 1). The first one is a sand, named Sd, containing a large amount of quartz with a small amount of kaolinite and calcite. The second is a calcined clay, Cc, containing cristobalite and mullite.

The alkali-activation process is described in Fig. 1. The first step is the preparation of the alkaline-silicate solution, S or P, with the stirring of different compounds. Then, the argillites, Ac, Af or a mix of both, are added under strong mixing. If a filler, i.e., Sd or Cc, is used, it is previously mixed with the argillite. Samples are then casted in closed molds and stored at room temperature for seven days. Samples are identified as XA + F, with X representing the alkaline solution used, A the argillite and F the filler.

2.2. Sample characterization

Thermal resistances were investigated with two different thermal treatments: (i) a slow firing of 1 h at 800 °C with a 1 °C/min heating ramp and natural cooling, resulting in a one-day-long treatment (named hereafter "firing"); and (ii) a thermal shock of 10 min at 800 °C with an immediate exposure to the temperature using a lift furnace (named hereafter "thermal shock").

The compressive strengths were tested using a LLOYD EZ20 universal testing machine with a crosshead speed of 0.5 mm/min. The compressive tests were performed on five samples for each composition. The samples were cylindrical in shape, with a diameter of 15 mm and a height of approximately 30 mm, and they were aged for 28 days in a closed mold at room temperature [20]. Concerning the compressive strength measurements of the fired samples, the rectification occurred before the firing, which resulted in the higher error of the measurement. The samples' bulk densities were obtained by measuring the masses and height/diameter ratios of the cylindrical samples used for compressive strength measurements.

Dilatometric measurements were performed under air with a vertical dilatometer Setsys made by Setaram Instrumentation. The

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Table 1
Physicochemical data of the different mineral sources. (*$CaCO_3$ and kaolin traces).

Nomenclature	Si/Al	D(50) ± 25 µm	ρ ± 0.05 g/cm³	S_{BET} ± 2.5 m²/g	Wettability ± 40 µL/g
Ac	3.63	160	2.72	5	536
Af	3.63	21	2.63	29	530
Sd	*	190	2.73	6	323
Cc	1.12	180	2.42	1	327

liquid-based solution, presents proper features, exempt of cracks, after firing in the furnace. However, after the thermal shock, the sample presents major cracks, thus revealing a lack of stability under this treatment. The addition of filler in the mixture will lead to different interactions with the alkali-activated matrix. On one hand, previous work [21,22] have demonstrated that the sand is only coated by the alkaline solutions, without strong interaction with the matrix. On the other hand, the calcined clay presents also a good stability in the reactive mixture and does not interact, except in presence of sodium

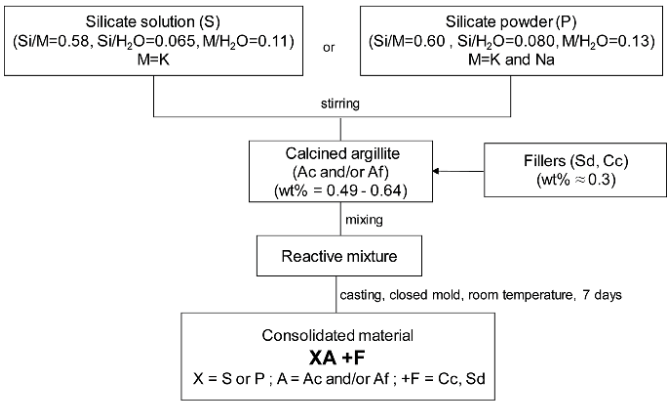


Fig. 1. Experimental procedure of sample preparation based on liquid and powder silicate solutions.

cylindrical samples (6 mm height, 5 mm diameter) were placed between two platinum/alumina holders during the analysis [6], and a correction was applied to remove the contribution of the device/holders. Samples were heated until 1000 °C at 5 °C/min and cooled at 20 °C/min.

The microstructures of the samples were observed on the sample surface using a Jeol IT 300 scanning electron microscope after the carbon coating of the samples.

3. Results and discussion

3.1. Thermal resistance evaluation

Alkali-activated samples were prepared using two alkaline-silicate solutions (S and P), three different aluminosilicate raw materials (Ac, Af and a 50/50 wt% mixture of both) and two fillers (Sd and Cc). Fig. 2 presents the chemical characteristics of the different studied samples. The use of solution S leads to a higher Al/M molar *ratio* and a lower Si/Al molar *ratio* than those obtained with solution P. This difference is related to the use of a lower liquid/solid *ratio* in the case of the liquid-based solution, S, than the powder-based solution P, for feasibility reasons. Moreover, small differences are observed with S-based samples based on the way that argillite is activated. Indeed, to achieve better consolidation, more Af argillite is used than Ac argillite. Finally, the use of filler changes the characteristics of the sample. The addition of calcined clay (Cc), which is rich in aluminum, leads to an increase of the Al/M *ratio* and a decrease of the Si/Al *ratio*. The use of sand only leads to an increase of the silica content and therefore the Si/Al *ratio*.

Pictures of the samples before and after the two different thermal treatments (furnace firing and thermal shock), are shown in Table 2. First, it appears that the thermal shock treatment damages all samples, whereas many samples are resistant to the furnace firing.

The SAc sample, based on the furnace calcination of argillite and the carbonate [23,24]. Despite this different behavior, both Sd and Cc lead to an improvement of the thermal stability with proper features after the furnace firing and the presence of fewer cracks with the thermal shock. This increase of resistance is in accordance with the literature, which has shown that the presence of filler enhances the thermal shock resistance [6,25]. The use of solution P leads to similar results, i.e., a good resistance to firing and a lack of resistance to thermal shock.

The use of flash calcined argillite, Af, leads to the appearance of more cracks due to various chemical decompositions that occur during heating [19]. Indeed, for SAf without filler, the furnace firing leads to the appearance of "medium" cracks. A lower resistance to firing is observed with solution P (PAf sample). This is probably due to the appearance of more viscous flow related to the presence of sodium in solution P [3,10]. The addition of sand, Sd, allows for a slight increase in the resistance to firing with PAf. However, samples based on calcined clay (Cc) show an important enhancement of the thermal resistance. Indeed, the SAf + Cc sample presents a good resistance to firing and a medium resistance to thermal shock. For PAf + Cc, a medium resistance is observed for both thermal treatments.

The samples based on the AcAf mixture display intermediate thermal resistance. S-based samples present similar resistance to Ac-based samples. However, with solution P, the resistances are close to the SAf sample, i.e., good firing resistance only with calcined clay (Cc).

To summarize, the use of Ac argillite leads to optimal resistance to firing and to a lack of resistance to thermal shock with both S and P solutions. The Af based-sample exhibits a lower resistance, i.e., more cracks, and this resistance is slightly better with the S solution. According to the literature, the use of fillers enhances the resistance to firing and thermal shock, especially in the case of the addition of calcined clay [26].

In the following sections, due to the low resistance of different samples to thermal shock, only data relative to the samples before and after firing will be presented.

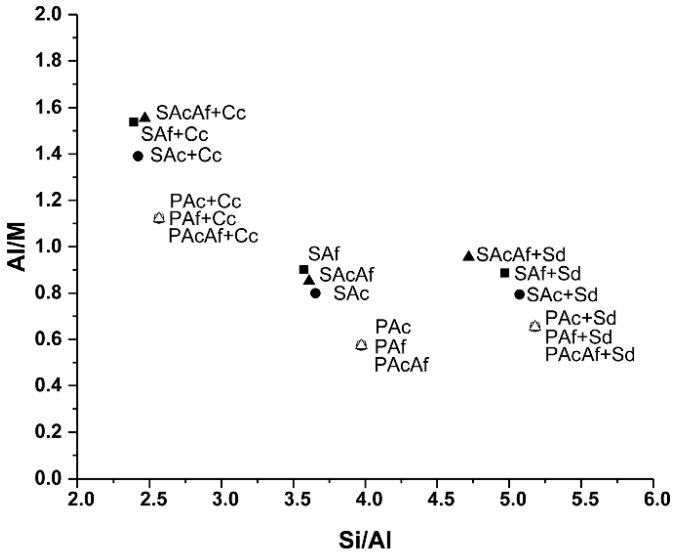


Fig. 2. Al/M molar ratio as a function of Si/Al molar ratio for the ●SAc, ■SAf, ▲ SAcAf, ○ PAc, □ SAf and Δ PAcAf based samples.

3.2. Effect of thermal treatment on mechanical properties

In order to evaluate the thermal resistance of different samples, compressive strength and density measurements were conducted before and after the furnace firing. Table 3 shows the data concerning the compressive strength and density values of the studied samples before and after the firing. Fig. 3 displays an example of the variation of the compressive strength as a function of the strain for SAc samples (with and without filler).

The beginning of the compressive strength curve, until 0.5–1% of strain, corresponds to the loading of the samples and is not directly related to the sample properties. Before the firing (Fig. 3A), the SAc compressive strength curve exhibits linear variations characteristic of an elastic regime. The addition of filler (+Sd, +Cc) to this raw material leads to a decrease in the compressive strength value and plastic deformation, especially in the case of the addition of sand (Sd), which is consistent with the literature regarding alkali-activated materials [27,28]. After the firing (Fig. 3B), the curve profiles are not perfectly linear. This may be due to the presence of cracks induced by the thermal treatment. Fewer variations are observed with the presence of filler, probably due to the refractory properties of the fillers [6,23].

Before the firing, the SAc samples present a compressive strength value of 16 MPa and a density of 1.77 g/cm^3 (Table 3). The addition of fillers, i.e., Sd and Cc, leads to a decrease in the compressive strength (11–13 MPa) and an increase in the density (1.83–1.86 g/cm^3). This decrease in the mechanical properties is probably related to interactions between the filler and the free calcium contained in the Ac-based mixture [18]. Rovnanik et al. [23] observed similar behavior with a calcium-containing mineral source, i.e., lower compressive strength with the presence of filler. After the firing, the compressive strengths slightly increase without filler and remain similar with filler. For the SAc sample, this small increase is probably due to structural evolutions combined with shrinkage. Dombrowski et al. [29] also observed an increase in the compressive strength of fly ash-based alkali-activated materials after thermal treatment, which is due to shrinkage and densification. With the presence of fillers, no compressive strength evolution is noticed, suggesting that there are interactions between the filler and the free-calcium. These evolutions will be discussed in Part 2.

Compared to furnace calcination, the flash-treated argillite, Af, leads to an alkali-activated material with a lower mechanical strength of 12 MPa. This is due to the lower reactivity of Af argillite. Indeed, the flash calcination leads to a partial decomposition of the argillite, resulting in a lower reactivity [19]. In contrast to the Ac-based sample, the addition of fillers is conducive to an increase of the compressive strength values. This result can be explained by the lower chemical reactivity of Af argillite compared to Ac argillite due to a lower amorphous phase [18]. So, Af does not fully react, inducing an excess of silicate solution, which can act as a coating around the filler grains and thus enhancing the mechanical strength [14]. After the firing of the samples, the compressive strengths strongly increase without filler and moderately increase with filler. The very high evolution observed with the SAf sample, from 12 to 27 MPa, may be due to the higher rate of structural evolutions and phase transformations. Indeed, it is supposed that the high amount of silica and calcite in Af argillite leads to the formation of calcium silicate, which is responsible for the enhancement of the mechanical properties after thermal treatment [30–32]. For the other samples, with fillers, the increase of compressive strength can also be explained by structural evolutions in the sample. The use of calcined clay, Cc, leads to a lower increase of compressive strength than that without filler. This is related to the presence of cristobalite in the Cc additive (information from the supplier: Imerys). In effect, the cristobalite exhibits a phase transformation at 220 °C with a volume expansion of 4.5% [33], which may weaken the sample. The density decreases similarly for all samples after firing. Without filler, a different behavior, i.e., a density decrease, is observed compared to the SAc sample. This result can be explained by the appearance of important cracks, as described in Table 2 and observed in Fig. 3, which leads to a decrease of the apparent density.

The sample based on a blend of AcAf exhibits the highest compressive strengths before firing (6, 21 and 22 MPa for SAcAf, SAcAf + Sd and SAcAf + Cc, respectively). It is supposed that the combination of Ac and Af leads to the development of both properties of Ac and Af, i.e., the important reactivity of Ac argillite and the low interactions of Af argillite with the filler. After firing, the compressive

Table 2
Photos before and after the different thermal treatments for samples based on the alkali-activation of Ac, Af and AcAf argillites with the S and P solution and with and without fillers (white: good resistance, hatched: medium resistance and grey: lack of resistance).

Solution		S			P		
Thermal treatment		Without	Furnace	Shock	Without	Furnace	Shock
Samples	Ac						
	Ac + Sd						
	Ac + Cc						
	Af						
	Af + Sd						
	Af + Cc						
	AcAf						
	AcAf +Sd						
	AcAf +Cc						

strength without filler increases up to 24 MPa and decreases with fillers down to 15 MPa. This result once again suggests structural evolutions in the SAcAf sample (related to the partial reactivity of Af argillite) but no interaction with the filler. Last, the densities of the samples with fillers are similar, but without filler, the density slightly decreases to an intermediate value between the densities of the SAc and SAf samples.

Samples based on solution P present lower compressive strengths than those based on solution S. Solution P is based on sodium silicate powder and potassium hydroxide. This mixture results in a lower reactivity solution than a "simple" solution-based silicate. This observation is in accordance with the work of Essaidi et al. [11], who observed a decrease in mechanical strength with the use of powder-based solutions. Before the firing, the compressive strength values are between 7 and 12 MPa, with little influence due to the presence of fillers. The lowest values are observed with Ac argillite, and the highest values are observed with the AcAf mixture. Indeed, the difference in reactivity between Ac and Af seems to be reduced with the use of solution P. After firing, the compressive strengths increase slightly, with better resistance exhibited with fillers. It is supposed that the appearance of viscous flow (more important with solution P, containing sodium [3,10]) allows interactions between the geopolymer phase and the fillers, which are responsible for this evolution. Only the AcAf-based samples leads to different results, i.e., lower compressive strength with filler. Similar to the situation with solution S, this low compressive strength is probably due to the interaction between the free calcium of Ac argillite and the filler [23]. Moreover, with solution P, no significant reinforcement of the sample seems to occur.

The density values are slightly lower with P than with S. Before the firing, they are approximately 1.7 and 1.8 g/cm^3 for samples without and with filler, respectively. After the firing, these values decrease slightly to 1.5–1.6 g/cm^3. These differences are in agreement with the alkali-cation mass and size, which are both lower with sodium.

The compressive strength measurements underline the differences in thermal behavior according to the argillite, alkaline solution and filler used. Higher compressive strength after firing is obtained with the potassium-based solution and flash-calcined argillite (Af). To

Table 3
Compressive strength and density values and of the studied samples before and after the firing.

Silicate solution	Nomenclature	Thermal treatment (800 °C)			
		Before		After	
		Compressive strength ± 1.5 MPa	ρ ± 0.05 g/cm^3	Compressive strength ± 1.5 MPa	ρ ± 0.05 g/cm^3
S	SAc	16	1.77	19	1.76
	SAc + Sd	11	1.83	11	1.65
	SAc + Cc	13	1.86	12	1.67
	SAf	12	1.79	27	1.60
	SAf + Sd	17	1.86	21	1.66
	SAf + Cc	19	1.86	18	1.62
	SAcAf	17	1.78	24	1.69
	SAcAf + Sd	21	1.87	15	1.60
	SAcAf + Cc	22	1.87	15	1.59
P	PAc	7	1.69	12	1.57
	PAc + Sd	8	1.80	14	1.62
	PAc + Cc	8	1.78	12	1.57
	PAf	11	1.69	10	1.63
	PAf + Sd	10	1.81	14	1.64
	PAf + Cc	9	1.77	12	1.54
	PAcAf	11	1.68	14	1.58
	PAcAf + Sd	11	1.77	10	1.52
	PAcAf + Cc	12	1.79	10	1.54

understand these interactions, dilatometric measurements are performed.

3.3. Effect of thermal treatment on dimensional stability

The results of the dilatometric measurements performed on the different alkali-activated samples are shown in Fig. 4. All dilatometric curves present an important dimensional variation until 200 °C, which is due to the loss of the water contained in the porous network and promotion of significant shrinkage related to the increase in capillary forces [10]. Then, there is temperature range of stability until 700 °C. Above 700 °C, thermal expansion is visible. This last phenomenon occurs in the same range of temperature as the decomposition of the carbonate compounds present in the sample (calcite decomposes at 700 and 800 °C for Af-based samples; lower amounts of calcite and mixed potassium-calcium carbonate decompose at 800 °C for Ac-based samples [18]). Depending on the sample, this expansion occurs until 1000 °C, as with SAc without filler (Fig. 4. A.a). The use of Af argillite (Fig. 4A b) leads to a significant expansion (1%) between 700 and 800 °C and a small shrinkage above 800 °C, which is probably related to phase crystallization. The use of solution P (Fig. 4. B) leads to similar curves with a higher initial shrinkage (2–3% more) and the appearance of a second shrinkage due to crystallization above 900 °C. The sample cooling leads to a small linear shrinkage (< 1%) due to the dilatation of the samples.

The Ac-based sample (Fig. 4. A.a) presents a global shrinkage of 6%. The addition of filler, i.e., Sd and Cc, leads to a lower initial shrinkage (< 200 °C) that is approximately 1% less with Sd and 2% less with Cc. This shrinkage mitigation is in accordance with the observation of Buchwald et al. [26] and is probably due to the refractory properties of the fillers and to different reactions in the mixture in presence of filler [23]. Then, the dimensional variations are reduced but similar with the

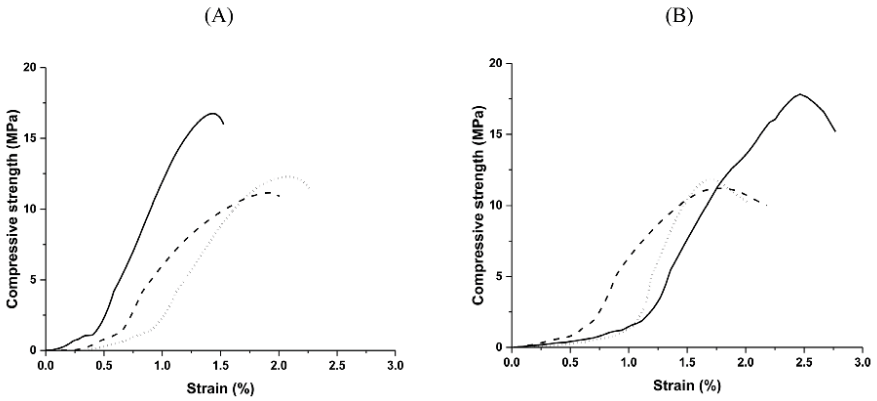


Fig. 3. Curve of compressive strength increase in function of the strain of (–) SAc, (—) SAc + Sd and (····) SAc + Cc samples (A) before and (B) after firing.

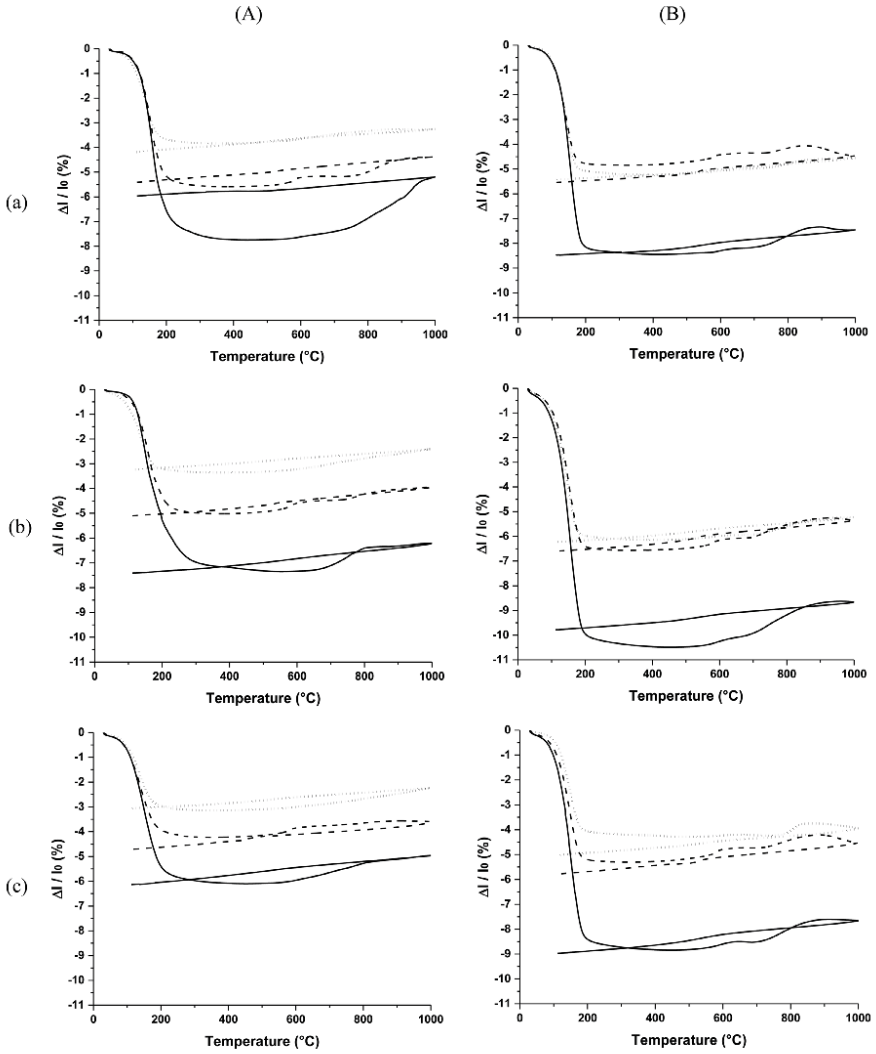


Fig. 4. Dilatometric curves of samples based on (A) S and (B) P solution, (a) Ac, (b) Af and (c) AcAf argillite with (—) Sd, (····) Cc and (–) no filler.

use of Sd and are non-existent with Cc, suggesting different solid state reactions. Moreover, with the addition of sand, Sd, the phase transition of the quartz is visible close to 600 °C [34,35], in agreement with the high amount of silica. The Af-based sample (Fig. 4. A.b) presents a global shrinkage of 7.5%, which is higher than that of the Ac-based sample, which presents a 6% shrinkage. This difference is due to the decomposition of carbonate species [18,19], which probably enhances the formation of viscous flux due to their amorphous structure and freshly formed CaO. With the AcAf mixture (Fig. 4. A.c), alkali-activated samples present a shrinkage of 6.2%, which is an intermediate value between those of SAc and SAf.

The use of solution P (Fig. 4. B) leads to different behavior above 700 °C, i.e., expansion is observed until 900 °C, and then shrinkage occurs until 1000 °C. This is probably due to viscous sintering related to the presence of sodium [36]. The global shrinkages are 8.5, 10 and 9% for Ac-, Af-, and AcAf-based samples, respectively, which confirms the higher shrinkage observed with SAf. These shrinkage values are higher using P than they are using S. The shrinkage difference is detected before 200 °C and is related to the liquid to solid *ratio* and reactivity, which is lower with solution S [11,37]. The presence of sand leads to similar behavior with solution S, i.e., lower initial shrinkage (3–4%) and lower volumetric variations. With the use of calcined clay, the dimensional variations are slightly enhanced due to the higher interactions between the calcined clay and the sodium contained in solution P [23].

Dilatometric measurements evidence a strong relation between shrinkage and the chemical composition of the mixture (argillite and solution nature). To investigate the microstructure, scanning electronic

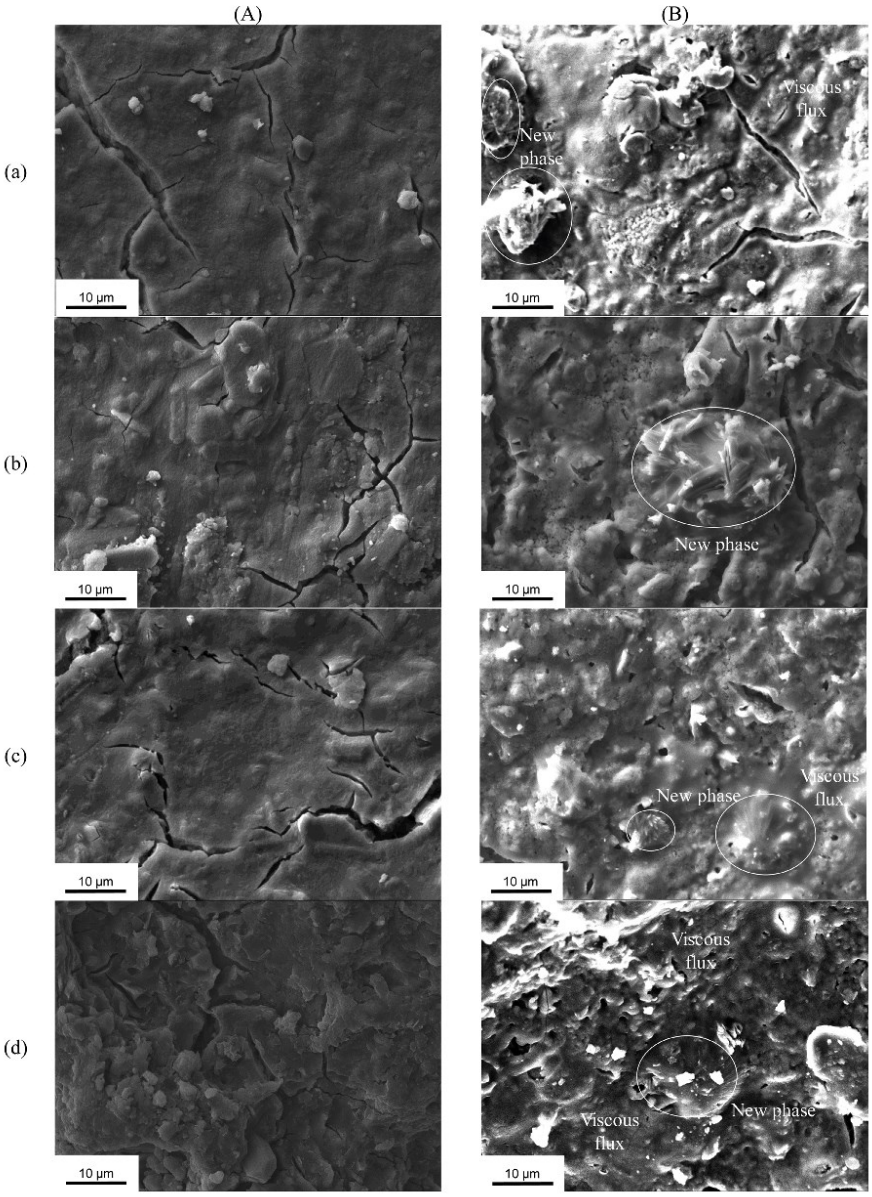


Fig. 5. SEM micrographs (A) before and (B) after furnace thermal treatment for (a) SAf, (b) SAf + Cc, (c) SAcAf and (d) SAcAf + Cc samples.

microscopy is performed.

3.4. Effect of thermal treatment on the microstructure

Fig. 5 displays SEM observations and focuses on only four samples (before and after the firing) for which different mechanical variations have been observed (i.e., a large increase in the compressive strength after the firing without filler and stability (SAf + Cc) or decrease in the compressive strength (SAcAf + Cc) with filler). Observations of P-based samples are available in the supplementary files. Before the firing, the samples present similar aspects, i.e., a smooth surface associated with the geopolymer network with the presence of micro cracks. Some unreacted particles (probably clay minerals) from the raw materials are present, but the filler is not visible on the sample surface [38]. For the

SAf sample (Fig. 5. B. a), the firing leads to the formation of new phases. Evidence of viscous flow is also detectable. The presence of small black dots is noticeable and likely corresponds to surface pores. This porosity is probably related to the decomposition of the carbonate species present in Af during the firing, resulting in the release of CO_2 [19]. This sample presents the greatest increase in compressive strength after firing (12–27 MPa, Table 3), which is probably due to the appearance of a new calcium-based phase. The addition of calcined clay to SAf (Fig. 5. B. b) also leads to the apparition of a new phase, but the calcined clay particles are still not visible on the surface [39]. Fibrous particles are visible on the center-right of the photo and may be associated with this new phase. Due to the large amount of calcium in the argillite (*ratio* of reactive Ca/Si ~ 0.5 [19]), this phase is likely a calcium silicate; according to the literature, it can be attributed to wollastonite [40,41]. This sample presents a lower amount of wollastonite, which can explain the stability of its compressive strength after firing (Table 3).

The micrograph of the SAcAf sample (Fig. 5. B. c) shows fibrous phases dispersed in a large viscous flux. Similar to the SAf sample, it is supposed that the firing of the alkali-activated sample leads to the formation of a calcium silicate, which is responsible for the increase in the compressive strength after the firing (17–24 MPa). With the presence of filler, Cc, the same phases are detectable but with higher heterogeneity and porosity. Indeed, mercury-porosimetry measurements (performed according to the method of Papa et al. [42]) show an increase in porosity of 4–5% based on the addition of calcined clay (from 18 to 23% for SAc and from 17 to 21% for SAf, in accordance with the work of Gharzouni et al. [43]). All these differences are probably responsible for the low compressive strength of this sample.

In consequence, microstructural observations show that thermal treatment leads to structural reorganization and the formation of new phases. Further structural investigations are necessary to validate these observations.

4. Discussion

To correlate the structural evolutions to the chemical compositions of mixtures, the compressive strengths after firing have been plotted based on the molar *ratio* of network-modifying cations (alkali and earth alkali: Ca, Mg, K and Na) divided by the amount of network-forming cations (Si and Al) in the mixture (Fig. 6). The shrinkage values deduced from dilatometry measurements have also been reported.

The compressive strengths of the S-based samples increase with the increase of the *ratio* (network modifying/forming cations) and with the dilatometric shrinkage (Fig. 6,A). This tendency is confirmed by all samples, except SAf + Cc, which presents a low compressive strength compared to other SAf samples, but the difference is lower than the measurement error. The compressive strength decreases with the decrease of the molar *ratio*, which corresponds to the addition of fillers (from 0.51 without filler to 0.42 with Cc and 0.34 with Sd). The same tendency seems to be observed for the shrinkage values. In fact, without filler, the higher amounts of alkalis and earth-alkalis (in the case of SAf followed by SAcAf and SAc samples), due to different carbonate decomposition rates, probably enhance the formation of new phases, improving the mechanical strength after firing. Indeed, Af argillite presents two type of carbonates (dolomite and calcite) that decompose during the firing, releasing higher amounts of calcium and magnesium that were available to react. In the presence of the Ac argillite, only calcium issued from calcite decomposition is available during the thermal treatment [18]. Moreover, the addition of aluminosilicate fillers induces an increase in the silica and alumina content, resulting in a lower molar *ratio*, which lowers the compressive strength.

The use of solution P leads to lower compressive strength than that with solution S (Fig. 6,B), mainly due to the higher amount of water in the mixture [11]. Indeed, the higher amount of water provided by solution P is in excess and leads to a high rate of water in the sample after alkali activation [44]. This water will lead to a higher shrinkage value

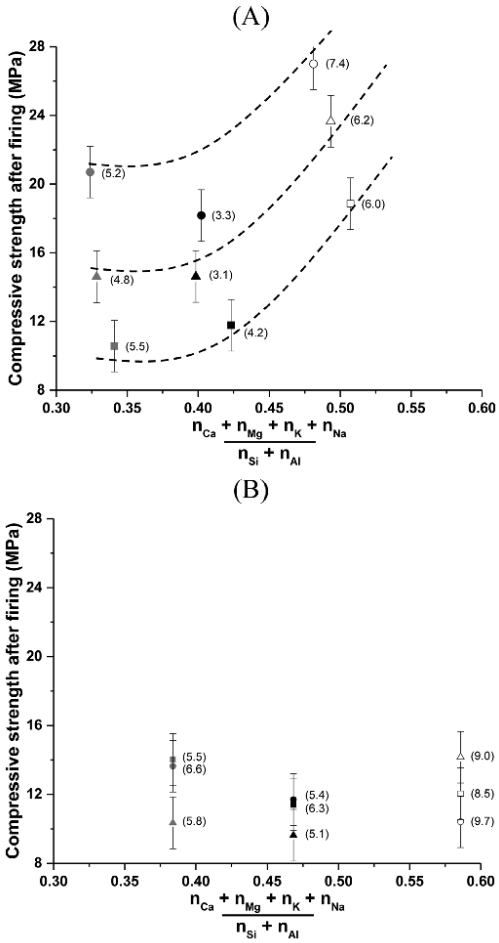


Fig. 6. Evolution of the compressive strength after firing (shrinkage percent in bracket), according to (Ca + Mg + K + Na)/(Si + Al) molar ratio with (A) S and (B) P solutions and ■ Ac, ● Af and ▲ AcAf argillite (grey with Sd, black with Cc and empty chips without filler), dash lines just illustrate the evolution.

and lower compressive strength. Moreover, the presence of sodium leads to lower compressive strength [36] and to the different behavior of the cation at high temperature. The low compressive strengths measured are less significant due to the higher relative error. However, a similar behavior is observed with the AcAf mixture, and no significant behavior is detected with Ac argillite. Only Af argillite leads to a decrease in the compressive strength based on the *ratio* of network modifying/forming cations. This result suggests that different reactions occur between the highly reactive earth-alkali cations and sodium, leading to the appearance of different phases or no new phases.

All these facts highlight that the chemical and mineralogical composition directly controls the mechanical properties of the alkali-activated samples, as observed by Temuujin et al. [45]. For example, the formation of silicate-calcium-hydrate (C-S-H) leads to the decrease in thermal resistance [45]. However, Dupuy et al. [18] showed the absence of C-S-H in alkali-activated samples based on argillite, with the

scattering of earth alkali cations in the geopolymer matrix and the formation of new carbonate species. Walkley et al. [46] highlighted that the calcium present in the aluminosilicate matrix or in unreacted particles can form wollastonite during the firing. This phase is well known to be used as reinforcement in geopolymer matrices [41,47,48] In the case of argillite-based materials, the potential *in situ* formation of wollastonite provides an explanation for their thermal behavior, as observed for the S-based samples and mainly with Af argillite. Moreover, although the argillite has a high Si/Al (~3.6) value and the CaO content is 10%, which are not optimum to develop fire-resistant binders [45,49], the structural evolutions in the argillite during thermal treatment allow it to achieve the correct thermal resistance.

5. Conclusion

This study focuses on the development of thermally resistant alkali-activated samples based on two calcinations of COx argillite with a flash (Af) and a furnace (Ac) process. The alkali-activation is performed with two alkaline silicate solutions: S (K-Si solution) and P (powder K + Na-Si solution). To reinforce the samples, two fillers are used: sand (Sd) and calcined clay (Cc). The evaluation and characterization of the thermal resistance underline that:

- The use of argillite can lead to optimal resistance to firing and a lack of resistance to thermal shock. The resistances are better with the use of S-solution, and Af based-samples present more cracks after thermal treatment. The addition of fillers enhances the resistance to firing and thermal shock.
- The compressive strength measurements show various evolutions of the different samples after firing. Better compressive strengths are obtained with the Af argillite and solution S. The presence of filler does not lead to higher mechanical resistance.
- Dilatometric measurements display a direct relation between shrinkage and the composition of the mixture (argillite and solution nature). Global shrinkages are higher with solution P and the use of argillite. The use of filler is conducive to lower shrinkage.
- Microstructural observations show reorganization in the solid state with microstructure evolutions and new phase formation. Indeed, with solution S, an acicular phase appears; with solution P, the surface aspect begins to coarsen.

Last, a relation has been found between the compressive strength after firing and the molar *ratio* of network modifying/forming cations in the mixture. This information confirms that the chemical composition, mainly the amount of alkali and earth alkali cations, directly controls the mechanical properties of the alkali-activated samples during firing.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.matchemphys.2018.06.079.

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Publication 4 (ACL4)

C. Dupuy, A. Gharzouni, I. Sobrados, N. Texier-Mandoki, X. Bourbon, S. Rossignol

Thermal resistance of argillite-based alkali-activated materials. Part 2: identification of the formed crystalline phases.

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Thermal resistance of argillite based alkali-activated materials. Part 2: Identification of the formed crystalline phases

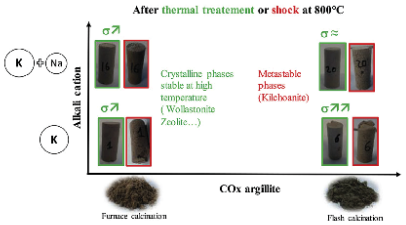
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HIGHLIGHTS

- The thermal behaviour of argillite based alkali-activated materials has been studied.
- Formed crystalline phases like wollastonite enhance the compressive strength.
- Metastable phases such as kilchoanite weaken the material.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Argillite
Thermal treatment
Thermal shock
Carbonate species
Alkaline earth
Crystalline phases

ABSTRACT

This study aims to understand the thermal behaviour of argillite based alkali-activated materials. Thermally heated argillites with different processes (furnace and flash process) and two alkaline solutions based on potassium or on a mix of potassium and sodium were used to synthesize consolidated materials. Then, the thermal resistance of the synthesized samples was evaluated by thermal treatment and to thermal shock at 800 °C. Whatever the sample, a good resistance to thermal treatment with an increase of the compressive strength after thermal treatment was noticed. Indeed, the compressive strength ratio ($\sigma_{after}/\sigma_{before}$) varies between 1 and 2.2. However, all samples do not resist to thermal shock. In order to understand these behaviours, structural investigations by ^{27}Al MAS-NMR, XRD, FTIR spectroscopy and DTA-DTG were performed. As the temperature increases, the nature of formed phases, strongly depends on the chemical composition of the geopolymer materials (type of carbonates, nature of alkali cation and alkaline earth) and on the thermal treatment conditions (heating rate and exposure time). The formation of crystalline phases such as wollastonite and zeolite result from the reaction between the available species like Ca^{2+} and Mg^{2+} from carbonate compounds decomposition and K^+, Na^+, Si^{4+} and Al^{3+} from the amorphous geopolymer network. These phases seem to improve the resistance to thermal treatment (ramp of 1 °C/min, 800 °C, 1 h). However, the formation of metastable phases such as kilchoanite during a rapid thermal treatment (800 °C, 10 min) decreases the mechanical resistance (σ/10). In conclusion, the use of potassium alkaline solution (Si/K = 0.58) and flash calcined argillite induce better thermal resistance.

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1. Introduction

Currently, fire resistant materials are required for various applications and domains (aerospace, construction and building materials, refractory materials, foundry, etc.). Geopolymer or more generally alkali activated materials are known to have good thermal stability [1–3]. However, due to the variety of the potential used raw materials (metakaolin, fly ash, blast furnace slags, industrial co-products, etc) and the variability of their chemical compositions, the thermal resistance may change considerably from one material to another. The used alkali cation influences also the thermal behaviour. It was demonstrated that the viscous sintering onset temperature, regardless of the Si/Al ratio, decreases when using sodium or mixed alkali cation (sodium and potassium) compared to potassium [2,4]. Indeed, the thermal behaviour is linked to structural variation and phase transformation, which are controlled by thermodynamics, ie, the most thermodynamically stable phases will be formed with the increase of the temperature [2]. For example, Buchwald et al. [5], have demonstrated that the thermal behaviour of sodium-based geopolymer is controlled by the dehydration at a temperature below 400 °C and the transformation of the geopolymer network to nepheline between 850 and 950 °C. In the case of potassium based geopolymers, the thermal behaviour is related to their recrystallisation to feldspars, leucite and kalsilite at a temperature of 1000 °C [4].

Other authors [6] have studied the thermal behaviour of fly ash based geopolymers using sodium and potassium based alkaline solutions. Sodium-based materials exhibit a drastic decrease of strength at 800 °C in relation to an increase of the average pore size. The amorphous structure is transformed to crystalline Na-feldspars. However, for potassium-based materials an increase of strength until 1000 °C was evidenced. These facts were explained by the decomposition of the geopolymer leading to the presence of free Na, K, Si and Al. This decomposition is favored using Na cation which lower the melting temperature. Moreover, it has been proven that in a multicomponent melt, silicium will complex in preference with K > Na > Ca > Mg [7]. The thermal behaviour also depends on the thermal treatment conditions such as the reached temperature, heating rate and exposure time. A rapid rise of the temperature was evidenced to induce an important thermal gradient between the surface and the core of the sample leading to stresses, cracks and deterioration of the material [8]. That is why, many authors [9] focused on the resistance to thermal shock. For instance, Nazari et al. [10], have studied fly ash based alkali-activated materials after thermal shock at 1000 °C. They prove the formation of zeolite.

The existing literature generally focusses on the evaluation of the thermal resistance and mechanical behaviour after temperature exposure but there is a lack of knowledge concerning the structural variation understanding, which is responsible of this behaviour especially in complex systems (raw materials composition, mixed alkali cations, etc). In previous work [11], alkali activated materials based on COx argillite which conserve or even increase their mechanical properties after heat treatment were successfully obtained. In the present work, the motivation of this study is not only the valorization of argillite and the obtaining of fire resistant materials, but, also a further understanding of the structural evolution leading to this thermal behaviour. For this, the structural changes in argillite based alkali activated materials under different thermal treatment conditions will be examined. Thus, this study will contribute to the transition to the industrial scale and the widespread of these materials as fire resistant binders.

2. Material and methods

2.1. Raw materials and sample preparation

The samples are prepared using two aluminosilicate sources and two different alkaline silicate solutions. The aluminosilicate sources are argillite calcined with furnace (Ac) or flash process (Af) [12]. The first alkaline solution, denoted as S, is based on an aqueous solution of potassium silicate and potassium hydroxide (63 wt % of water and Si/K molar ratio = 0.58). The second alkaline solution, P, is based on a sodium silicate powder, water and potassium hydroxide (58 wt % of water and Si/M molar ratio = 0.60, where M = K and Na) with a Na/K ratio of ~1.3. The samples are cast in closed polystyrene mold and kept at room temperature. They are denoted as XA with X the alkaline silicate solution (X = S or P) and A the argillite nature (A = Ac or Af). The chemical compositions of the studied samples are reported in Table 1.

Table 1
Nomenclature and chemical compositions of the different studied samples.

Nomenclature	Solution		Reactive mixture		
	Si/M (M = K and/or Na)	Alkali cation	Si/Al molar ratio	Si/M molar ratio	Liquid/Solid mass ratio
SAc	0.58	K	3.7	2.9	0.78
SAf			3.6	3.2	0.67
PAc	0.60	K, Na	4.0	2.3	1.07
PAf					

The thermal resistance was tested with two different treatments: a classic calcination at 800 °C (ramp of 1 °C/min, step of 1 h and natural cooling) and with a thermal shock (at 800 °C during 10 min with a lift-furnace) [11].

2.2. Sample characterization

Compressive strengths were tested with a LLOYD EZ20 universal testing machine with a crosshead speed of 0.5 mm/min for the studied alkali-activated materials before and after thermal treatment. For each composition, measurements were done on five cylindrical samples (15 mm diameter and 30 mm height). The compressive strengths were expressed in MPa and represent the average of the five measurements.

High-resolution NMR experiments were performed at room temperature using a Bruker AVANCE-400 spectrometer, operating at 104.26 MHz for ^{27}Al signals. ^{27}Al MAS-NMR experiments were carried out for the studied alkali-activated materials before and after thermal treatments. The powder samples were compacted inside ZrO_2 rotors and were spun at 10 KHz. The number of scans was 400. In order to record the central transitions of aluminum (^{27}Al) (I = 5/2), a π/8 (1.5 µs) pulse was applied and 1 MHz filter was used. Chemical shift values were given with respect to an external aqueous $AlCl_3$ solution. In all cases, ^{27}Al MAS-NMR spectra are formed by a central (1/2, −1/2) transition and satellite (± 3/2, ± 1/2) and (± 5/2, ± 3/2) transitions that were modulated by spinning side bands covering a large region. Second-order quadrupolar interactions are not significant. The relative areas of the components were determined using DMFIT program considering first-order quadrupolar interactions [13].

Fourier-Transform Infrared (FTIR) spectra were obtained with a ThermoFisher Scientific Nicolet 380 spectrometer for the studied alkali-activated materials before and after thermal treatments. Spectra were acquired in transmission mode using KBr pressed discs (0.6 mg of sample and 100 mg of KBr). The spectra were recording between 400 and 4000 cm^{-1} with a 4 cm^{-1} resolution and composed of 64 scans. The atmospheric CO_2 contribution was removed between 2280 and 2400 cm^{-1} and replaced by a straight line [14].

X-ray diffraction patterns were acquired via X-ray diffraction (XRD) experiments on a Bruker D8 advance powder diffractometer using CuK α radiation (λKα = 0.154186 nm). The analytical range is between 10° and 50° (2θ), with a step of 0.02° and an acquisition time of 1 s for alkali activated materials powder materials before and after thermal treatments. JCPDS (Joint Committee Powder Diffraction Standard) files were used for phase identification. The amorphous phase for each

Table 2
Thermal resistance evaluation (++ high, +medium, - low) according to visual aspect and compressive strength ratio before and after thermal treatment ($\sigma_{after}/\sigma_{before}$) for the different samples.

Samples	Resistance to thermal treatment (800 °C)	Resistance to thermal shock (800 °C)	Compressive strength ratio ($\sigma_{after}/\sigma_{before}$)
SAc	++	–	1.2
SAf	+	–	2.2
PAc	++	–	1.7
PAf	+	–	1.0

sample was determined using the Rietveld method [13,14]. For this quantification, 30% of ZnO was added to the sample powder and the analysis was performed with the Topas software.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on an SDT Q600 apparatus from TA Instruments in an atmosphere of flowing dry air (100 mL/min) in platinum crucibles. The signals were measured with Pt/Pt–10%Rh thermocouples. The samples were heated up to 1300 °C with a rate of 5 °C/min.

3. Results and discussion

3.1. Structural changes after thermal treatments

It has been previously shown that the alkali activated samples based on various aluminosilicate sources (Ac and Af) and alkaline solutions (S and P) present different resistances to thermal treatment and to thermal shock at 800 °C [12]. The physical behaviour of the different samples to the thermal treatments (slow or fast increase of the temperature) are reported in Table 2. On one hand, all samples exhibit good thermal resistance to calcination at 800 °C (dimensional stability and no or small cracks detectable by visual observation). Moreover, for all samples, except of PAf sample, the compressive strength values increase after the thermal treatment ($\sigma_{after}/\sigma_{before} > 1$). SAf sample presents the highest compressive strength ratio ($\sigma_{after}/\sigma_{before}$). On the other hand, all samples do not resist to thermal shock. A high amount of crack limits the mechanical resistance and the samples just resist to the handling. As a consequence, compressive strength tests cannot be performed after this thermal treatment. These different physical behaviours suggest structural variations as the temperature increases, which depend on the raw material and the thermal treatment conditions. The kinetic of increase as well as the maximum temperature reached are key parameters.

In order to identify the structural changes after thermal treatment and shock, ^{27}Al MAS-NMR and FTIR measurements were undertaken. The obtained spectra before and after thermal treatments are shown in Figs. 1 and 2 for all studied samples. The detailed data concerning the chemical shifts, the FWHM and the percentages of the curve area of the various contributions are given in Table 3. Only the results of SAc sample will be further discussed. For the other samples, more informations are given in supplementary file. Before calcination (Fig. 1. A. a), two environments of aluminum were distinguished in the case of SAc sample: a major contribution of tetrahedral aluminum (% Al^{IV} = 87.6), relatively broad and overlaps several components at 72, 64, 56 and 50 ppm due to muscovite, feldspar and geopolymer network, respectively [13,15,16]. A minor contribution of octahedral aluminum (% Al^{VI} = 12.4) located at 2.4 and −6 ppm is also observed and can be due to muscovite which is not fully altered after heat treatment and alkali activation of argillite [17]. After calcination, the contribution related to tetrahedral aluminum seems to be slightly thinner and composed of only two components slightly shifted to lower ppm, at 62 and 56.5 ppm. After thermal shock, quite similar changes are observed. The contribution related to octahedral aluminum disappears reflecting the dehydroxylation of muscovite as the temperature increases.

Concerning FTIR data, SAc sample before thermal treatment (Fig. 2.A.a) shows a large band overlapping contributions of different carbonates such as calcite (at 1510 and 1430 cm^{-1}) and mixed carbonates based on calcium and potassium (at 1380 cm^{-1}) [18]. A broad Si-O-Si band centered at 1015 cm^{-1} [19] is observed overlapping a contribution around 930 cm^{-1}, related to Si-O-Ca bonds [20]. A shoulder at 867 cm^{-1} is observed and is attributed to calcite [21]. The doublet at 797 and 778 cm^{-1} and the peak at 694 cm^{-1} are related to quartz [22]. The band at 611 cm^{-1} reveals the presence of sulfate [23]. After calcination at 800 °C, the intensity of the band relative to the different carbonates decreases drastically revealing their decomposition. Small changes can be detected for the Si-O-Si band. Regarding the broadness of the peak, it is difficult to distinguish if it overlaps other contributions due to formed crystalline phases. However, a shoulder at 900 cm^{-1} is observed in addition to the disappearance of the one at 867 cm^{-1} suggesting the formation of a new phase which is probably wollastonite [24]. The intensity of peaks relative to the doublet of quartz decreases indicating either α to β transformation or a modification of quartz crystallinity [25]. Moreover, peaks at 708, 683 and 644 cm^{-1} appear and can be attributed to wollastonite [24]. After thermal shock, another crystalline phase characterized by contributions at 1044, 978, 930, 890, 855 and 708 cm^{-1} instead of wollastonite seems to be formed and can be associated to kilchoanite [26]. Moreover, the contribution of mixed carbonates at 1380 cm^{-1} is more defined compared to furnace-calcined samples suggesting a different kinetic of carbonate decomposition related to the kinetic of thermal treatment. The results obtained by ^{27}Al MAS-NMR and FTIR spectroscopies indicate a structural rearrangement leading to more crystalline structure after calcination and thermal shock [27]. In order to more precisely identify the formed phases, X-ray diffraction was performed. The X-ray patterns of Ac and Af based samples with S and P solutions are displayed in Fig. 2, before and after calcination and shock at 800 °C. The identified mineral phases and associated chemical formula and JCPDS files are reported in Table 4. Moreover, X-ray patterns of SAc and PAc samples after calcination at 600 °C and 700 °C and phase quantification using Rietveld method are reported in supplementary file. The X-ray patterns (Fig. 3. A. a) display different peaks relative to quartz, muscovite, $KAl_3Si_3O_{11}$ (from the dehydroxylation of muscovite [28]), arcanite, hematite and orthoclase are observed [18]. After the thermal treatment, $KAl_3Si_3O_{11}$ contributions intensity decreases drastically, and a zeolite phase (anorthic potassium aluminum silicate, $KAlSiO_4$) appears. This phase was named according to literature $KAlSiO_4$ O1 [29,30] and is probably formed from $KAl_3Si_3O_{11}$ and potassium present in the amorphous phase of the geopolymer network. Moreover, peaks related to calcium silicate, wollastonite, appear and quartz peaks intensity decreases, which is in accordance with FTIR results and suggests a reaction between silica and calcium oxide released from the carbonate species decomposition. According to literature, this phase is formed at about 780 °C [31]. This result was validated by XRD at 600 and 700 °C (see supplementary file) where wollastonite was not yet formed. Diopside ($CaMgSi_2O_6$) was also detected suggesting a reaction between free alkali-earth cations (Ca and Mg) from carbonates decomposition and geopolymer network former (Al and Si). After thermal shock, similar variations are observed. However, wollastonite is not formed and quartz intensity remains similar, but another crystalline calcium silicate appears, named kilchoanite ($Ca_6Si_3(SiO_4)O_{10}$). This phase is generally formed under hydrothermal conditions [32]. Thus, its formation in this case can be explained by the different thermal treatment conditions, i.e. the rapid exposure at 800 °C. According to phase quantification, reported in supplementary file, the amorphous phase decreases from 63 to 54 and 53% for SAc sample before and after thermal treatment and shock, respectively.

Fig. 3. A. b, gathers the X-ray patterns of SAf sample and few variations with SAc sample are observed. Before the thermal treatment of the alkali-activated sample, the presence of calcite is noticed, which can be explained by the partial decomposition of calcite in Af argillite raw

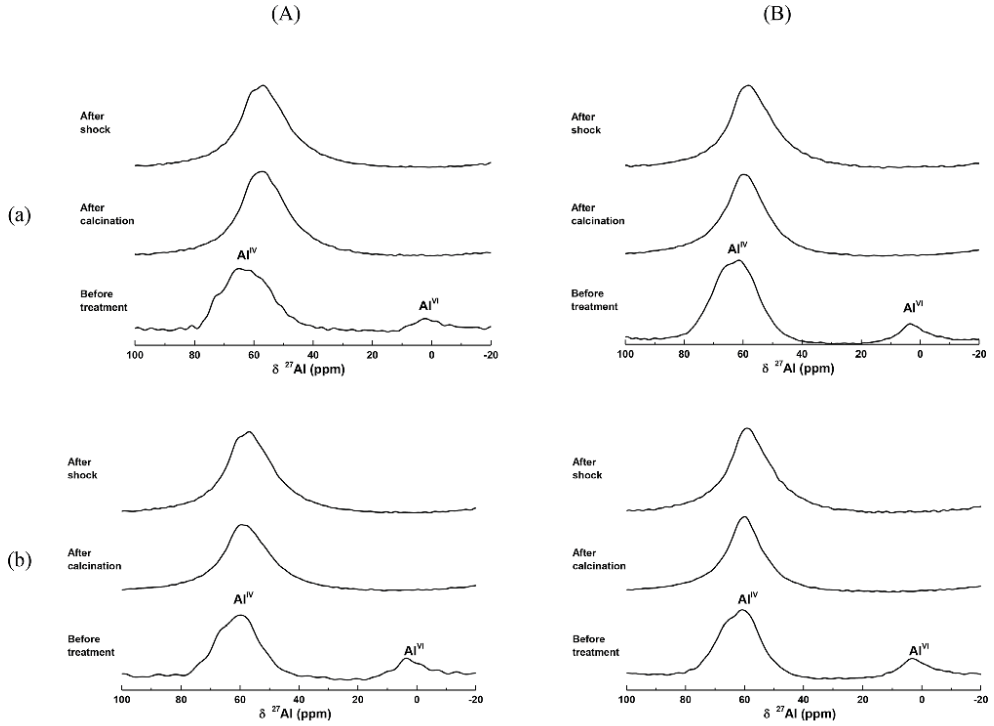


Fig. 1. ^{27}Al MAS-NMR spectra before and after thermal treatments (furnace and thermal shock) of samples with (A) S and (B) P alkaline solutions and (a) Ac and (b) Af argillites.

material as previously demonstrated [11]. After the thermal treatment of the sample, the peaks related to calcite disappear and the same transformations as SAc sample occur. The only difference is an increase of the intensity of the peaks related to the formed phases during the heating.

The use of P solution with different argillite samples (Ac and Af) leads to similar X-ray patterns before the thermal treatment of the alkali-activated samples (Fig. 3. B). However, after thermal treatment there is formation of more new crystalline phases. Indeed, in addition to wollastonite, there is formation of combeite ($Na_{4.8}Ca_3Si_6O_{18}$) and nepheline type phase ($Na_{2.8}K_{0.6}Ca_{0.2}Al_{3.8}Si_{4.2}O_{16}$) in a smaller amount due to the presence of sodium provided by P solution [33]. Moreover, peaks attributed to leucite ($KAlSi_2O_6$) and kalsilite ($KAlSiO_4$) are observed. These phases were formed at a temperature above 700 °C because they were not visible on PAc diffractogarm at 700 °C (see supplementary file). Kalsilite was not observed using S solution which is may be due to the difference in terms of potassium and silicium availability in the alkaline solution (see Table 1). Indeed, Si/M (M = K and or Na) is higher using S solution (3 and 2.3 for S and P based materials, respectively). This fact is in agreement with literature [34] evidencing that in presence of a little amount of sodium, kalsilite is preferentially formed than zeolite. Diopside was also detected in PAc and PAf samples. Last, with thermal shock, whatever the sample, neither wollastonite nor kilchoanite are formed. Calcium reacts preferentially with sodium to form combeite or nepheline. Leucite was not formed. Only kalsilite in low amount is detected. The amorphous phase slightly decreases from 65 to 61% for PAc sample before and after thermal shock, respectively (see supplementary file).

In summary, FTIR spectroscopy corroborates ^{27}Al MAS-NMR results and evidence structural variations after thermal treatment for the different sample in function of the different phases initially present in alkali activated materials. This fact suggests different interactions between the available species leading to crystallization of different phases. The X-ray diffraction analysis permit to confirm the identification proposed by FTIR and NMR. All these data give an evidence of the structural changes and the formation of different phases according to the used raw materials and the thermal treatment conditions. Thus, it will be interesting to establish a reactional model in order to understand the origin of the formed phases.

3.2. Thermal analysis and reaction model

Once the formed phases are identified, it is interesting to understand how they were formed.

For this, the synthesized materials were investigated using thermal analysis DTA-DTG. The obtained weight loss and first derivative of weight loss curves for the different samples are given in Fig. 4. Whatever the studied sample, endothermic peaks accompanied with weight losses are observed as the temperature increases.

For SAc sample (Fig. 4A), a major weight loss (I) of 28.7% is observed between 30 and 200 °C and attributed to the dehydration of the sample i.e. the release of free and adsorbed water [35]. After a temperature of 200 °C, it is difficult to clearly distinguish the other weight losses. However, according to the first derivative of weight loss (Fig. 4A b), a second weight loss (II) of 1.9%, between 200 and 450 °C, can be attributed to the decomposition of $Ca(OH)_2$ (equation (1) [37]).

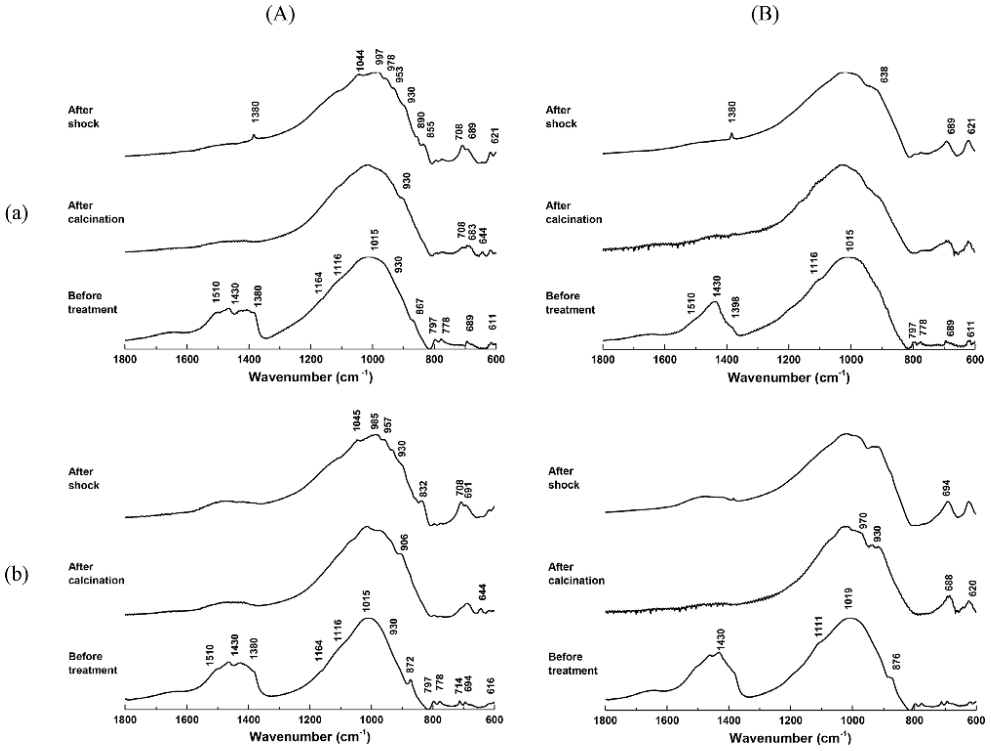


Fig. 2. FTIR spectra before and after thermal treatments (furnace and thermal shock) of samples with (A) S and (B) P alkaline solutions and (a) Ac and (b) Af argillites.

Another minor weight loss (IV) of 0.4% at about 800 °C is associated to the decomposition of calcite (equation (2) [38]) which is remained in Ac raw material or formed after alkali activation [18]. Furthermore, weight losses at 1100 and 1150 °C of 0.3 and 0.7% respectively can be attributed to the decomposition of different sulfate compounds [36].

$$Ca(OH)_2 \rightarrow CaO + H_2O \quad (1)$$

$$CaCO_3 \rightarrow CaO + CO_2 \quad (2)$$

$$Mg(OH)_2 \rightarrow MgO + H_2O \quad (3)$$

For SAf sample (Fig. 4.A) similar thermal behaviour is observed as SAc sample with a lower weight loss due to dehydration (I) of 21.5%. A weight loss of 1.3% at about 380 °C is also observed revealing the decomposition of $Mg(OH)_2$ (equation (3) [39]). An additional weight loss (III), between 450 and 650 °C, is due the dehydroxylation of clay minerals not fully dehydroxylated after a flash calcination in Af raw material [11]. A higher weight loss (IV) of 4.1%, between 650 and 800 °C can be associated to the decomposition of carbonate compounds with different crystallinity such as dolomite, mixed carbonates and calcite [18,40]. At 1150 °C, a weight loss is observed and attributed to the decomposition of sulfate compound as demonstrated by thermal analysis coupled to mass spectrometry reported in the supplementary file.

Using P solution (Fig. 4.B), containing both potassium and sodium, slight differences are observed such as a higher first weight loss (I) (39.8 and 28.1% for PAc and PAf samples, respectively). This fact can be explained by a higher initial liquid to solid mass ratio as mentioned in Table 1 (The liquid/solid mass ratios are 0.78, 0.67, 1.07 and 1.07 for SAc, SAf, PAc and PAf samples, respectively). Moreover, only weight losses (II and IV), attributed to the decomposition of $Mg(OH)_2$ and mixed carbonates (sodium and magnesium mixed carbonates), were observed.

To summarize, the different released species which will be available to react in function of temperature for the studied samples determined from thermal analysis are reported in Fig. 5.

For SAc sample, Al^{3+}, Si^{4+} and K^+ ions available from clay minerals dehydroxylation ($KAl_3Si_3O_{11}$) and geopolymer amorphous phase will crystallize to form a zeolite phase (Equation (4)) named $KAlSiO_4$ O1 by Smith et al. [29]. This phase is based on aluminosilicate tetrahedral sheets with insertion of potassium between the sheets [41]. This phase is usually formed at 1200 °C [30] but it is supposed that the mixed effect of the clay mineral alteration, the alkaline activation and the potassium ions allows the formation of this phase at 800 °C, as observed by Steenari et al. [42] with metakaolin and potassium.

Moreover, two calcium based phases, wollastonite and kilchoanite, with different Ca/Si molar ratios are formed after thermal treatment and shock, respectively. Indeed, Ca^{2+} ions issued from $Ca(OH)_2$ and $CaCO_3$ decompositions can react with silica (Equations (5) and (6)). These data are in agreement with the literature of wollastonite formation (at 780 °C [31,43]) and also its formation in alkali-activated materials with similar calcium amount, evidenced by Walkley et al. [44]. Furthermore kilchoanite phase is formed at about 600–800 °C or even less, at 220 °C under hydrothermal conditions [45,46], which can explain its formation only with thermal shock (very rapid heating).

The difference of Ca/Si molar ratio (1 and 1.5 for wollastonite and

Table 3
The detailed data concerning the chemical shifts, FWHM and the percentages of the curve area of the various contributions.

			Alkaline solutions					
			S			P		
			Chemical shift (± 0.2 ppm)	FWHM (ppm)	Percentage (%)	Chemical shift (± 0.2 ppm)	FWHM (ppm)	Percentage (%)
Argillites	Ac	Before treatment	72	4.9	3.8			
			64	10	32.7	68	10	32.7
			58	10	49.4	60	13	53.3
			50	10	1.7			
			2.4	8	8.3	2.5	10	11.7
			−6	10	4.1	−6	10	2.2
		After calcination	62	12	8.6	67	10	11.0
			56.5	17	91.4	59.2	13	82.7
						52	10	6.3
		After shock	62	12	9.1	65	10	10.3
			56.5	16.8	90.9	58	13	74.0
						50	10	15.7
	Af	Before treatment	72.6	4.9	3.4			
			66	8	13.0	68	10	25.2
			58.9	12	62.1	60	13	56.8
			50	10	2.4			
			2.9	10	14.1	2.5	10	15.2
			−6	10	5.0	−6	10	2.8
		After calcination	62.5	10	11.6	65	10	8.5
			57.4	17.2	88.4	59.6	13	88.7
						50	8	8.0
		After shock	65	12	25.8	64	10	11.1
			56.5	16.5	74.2	58.5	13	75.2
						50	12	13.7

Table 4
Mineral phases and associated chemical formula and JCPDS files determined by XRD.

Mineral phase	Chemical formula	JCPDS files
Aphthitalite	$K_3Na(SO_4)_2$	00-020-0928
Arcanite	K_2SO_4	04-006-8317
Calcite	$CaCO_3$	04-012-0489
Combeite	$Na_{4.8}Ca_3Si_6O_{18}$	04-007-5453
Diopside	$CaMgSi_2O_6$	00-041-1370
Hematite	Fe_2O_3	00-033-0664
Hydrated muscovite	$KAl_2AlSi_3O_{10}H_2O$	01-082-3733
Kalsilite	$KAlSiO_4$	00-011-0579
Kilchoanite	$Ca_6Si_3(SiO_4)O_{10}$	04-009-7055
Leucite	$KAlSi_2O_6$	01-071-1147
Muscovite	$KAl_3Si_3O_{11}$	00-046-0741
Nepheline type	$Na_{2.8}K_{0.6}Ca_{0.2}Al_{3.8}Si_{4.2}O_{16}$	00-052-0320
Orthoclase	$KAl_{0.98}Si_{3.02}O_8$	01-076-0742
Quartz	SiO_2	01-086-1630
Wollastonite	$CaSiO_3$	00-027-0088
Zeolite	$KAlSiO_4$	00-048-1028

kilchoanite, respectively) can be explained by the difference of available silica after the two thermal treatments. In fact, for slow thermal treatment the available silica can be issued not only from the geopolymer amorphous phase but also from the quartz disseminated in the viscous flow. This hypothesis was validated by the decrease of quartz amount after thermal treatment according to rietveld quantification (supplementary file). Nevertheless, this is not the case for thermal shock, since the lower reaction time induces a better stability of quartz conducing to a lower amount of available silica. No reaction of Mg^{2+} is observed because it is probably in the form of $MgSO_4$ which decomposes at high temperature as previously shown by DTA-DTG and validated with mass spectrometry presented in the supplementary file.

$$KAl_3Si_3O_{11} + K_2O \rightarrow 3\ KAlSiO_4 \quad (4)$$

$$CaO + SiO_2 \rightarrow CaSiO_3 \quad (5)$$

$$6\ CaO + 4\ SiO_2 \rightarrow Ca_6Si_3(SiO_4)O_{10} \quad (6)$$

For SAf sample, the released species are Mg^{2+} and Ca^{2+} from $Mg(OH)_2$, $Ca(OH)_2$, mixed carbonates and $CaCO_3$ decomposition. Thus, higher amount of alkaline earth cations are available in addition to more Al^{3+}, Si^{4+} and K^+ from clay minerals dehydroxylation which is in accordance with the increase of the intensity of peaks related to formed crystalline phases observed by XRD. This phenomenon is mainly visible with the wollastonite formation, which is enhanced in presence of calcite ($CaCO_3$) [47].

In the case of PAc sample, the released species are Mg^{2+} and Ca^{2+} from $Mg(OH)_2$ and $CaCO_3$ decomposition, respectively. The released Ca^{2+} reacts with silica, alumina, sodium and potassium of the geopolymer amorphous phase to form wollastonite (Equation (4)), combeite (Equation (7)) and nepheline type phase (equation (8)) after thermal treatment or shock. The combeite is obtained from the crystallization, at 700 °C [48], of a CaO-SiO_2-Na_2O glass or silicate gel [49]. In the presence of sodium, the amorphous network of P-based sample presents similar structure, i.e. an amorphous phase with calcium, silicon and sodium species leading to combeite formation. The presence of sodium ion can also conduce to nepheline formation. Indeed, this compound is well known to be formed in geopolymer materials [50]. This crystallization occurs close to 600 °C for pure geopolymer and close to 800 °C with fly ash based one [51]. Moreover, in presence of nepheline the Al^{3+}, Si^{4+} and K^+ ions from geopolymer amorphous phase and muscovite will not form $KAlSiO_4$ O1 phase [52,53] but leucite (Equation (9)) and kalsilite (Equation (4)). Indeed, Tuttle et al. [53] have evidenced that at 800 °C and with 10% of nepheline the orthorhombic $KAlSiO_4$ O1 forms hexagonal $KAlSiO_4$ (kalsilite) and leucite. Last, the

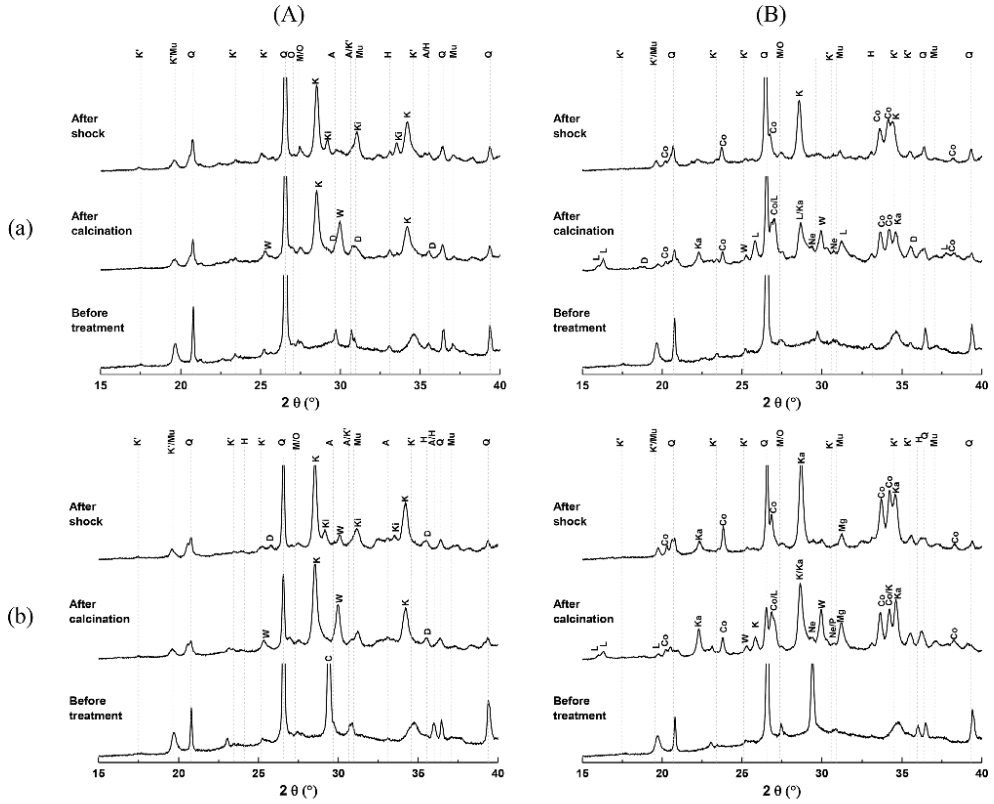


Fig. 3. XRD patterns of samples before and after calcination and thermal shock of samples with (A) S and (B) P alkaline solutions and (a) Ac and (b) Af argillites. (K: zeolite, L: leucite, K': muscovite, Q: quartz, Ki: kilchoanite, C: calcite, Co: combeite, Ne: nepheline type, Ka: kalsilite, W: wollastonite, A: arcanite, Mu: hydrated muscovite, O: orthoclase, D: diopside, H: hematite and Ap: aphthitalite).

availability of Mg^{2+} explains the formation of diopside (Equation (10)) after thermal treatment as determined by XRD [54,55].

$$3\,CaO + 6\,SiO_2 + 2.4\,Na_2O \xrightarrow{O_2} Na_{4.8}Ca_3Si_6O_{18} \quad (7)$$

$$0.6\,KAl_3Si_3O_{11} + 0.2\,CaO + 1.4\,Na_2O + Al_2O_3 + 2.4SiO_2 \rightarrow Na_{2.8}K_{0.6}Ca_{0.2}Al_{3.8}Si_{4.2}O_{16} \quad (8)$$

$$K_2O + Al_2O_3 + 4\,SiO_2 \rightarrow 2\,KAlSi_2O_6 \quad (9)$$

$$CaO + MgO + 2\,SiO_2 \rightarrow CaMgSi_2O_6 \quad (10)$$

PAf samples exhibit the same chemical behaviour as the PAc. The same species are released in both cases, in relation to the release of Si, Al and K from dehydroxylated clay minerals inducing the formation of leucite and kalsilite after thermal treatments.

In order to correlate the formed phases with the chemical composition of each sample, the percentage of the main formed phases after thermal treatment, determined by Rietveld, was plotted in function of different molar ratios in Fig. 6. The percentages of wollastonite and combeite were plotted in function of $(n_{Ca} + n_{Na})/n_{Si}$ molar ratio (Fig. 6 A). It was shown that for lower $(n_{Ca} + n_{Na})/n_{Si}$ molar ratios, which corresponds to S solution based samples (0.5 and 0.6 for SAc and SAf samples respectively), wollastonite was the main formed phase. However, no combeite was formed. For higher $(n_{Ca} + n_{Na})/n_{Si}$ molar ratios which is related to P solution based samples (0.9 and 1.1 for PAc and PAf samples, respectively), combeite is formed in detriment of wollastonite. Therefore, in presence of potassium alkaline solution, wollastonite is in preferentially formed, which improves the thermal resistance (the increase of the compressive strength after thermal treatment, see Table 2). However, in presence of mixed cations (Na/K ~1.3), sodium favors the formation of combeite. The presence of combeite seems not to enhance the thermal resistance (stabilization or small increase of the compressive strength, see Table 2). So, it would be better to use pure potassium alkaline solution rather than mixed alkali cations (sodium and potassium).

The variation of the percentages of leucite, kalsilite and zeolite were plotted in function of $(n_K + n_{Na})/(n_{Si} + n_{Al})$ molar ratio (Fig. 6 B). It is observed that for lower $(n_K + n_{Na})/(n_{Si} + n_{Al})$ molar ratio (0.6 and 0.7 for SAc and SAf samples, respectively), there is only formation of zeolite phase. Nevertheless, for higher $(n_K + n_{Na})/(n_{Si+}n_{Al})$ molar ratio (0.8 and 0.9 for PAc and PAf samples, respectively), there is only formation of leucite ad kalsilite. This finding corroborates the previous data and confirm once again that the use of potassium is recommended in order to improve the thermal resistance.

Finally, the percentage of diopside is presented in function of $(n_K + n_{Na} + n_{Mg})/n_{Si}$ in Fig. 6C. Higher molar ratios $(n_K + n_{Na} + n_{Mg})/n_{Si}$ induce higher percentage of diopside. The

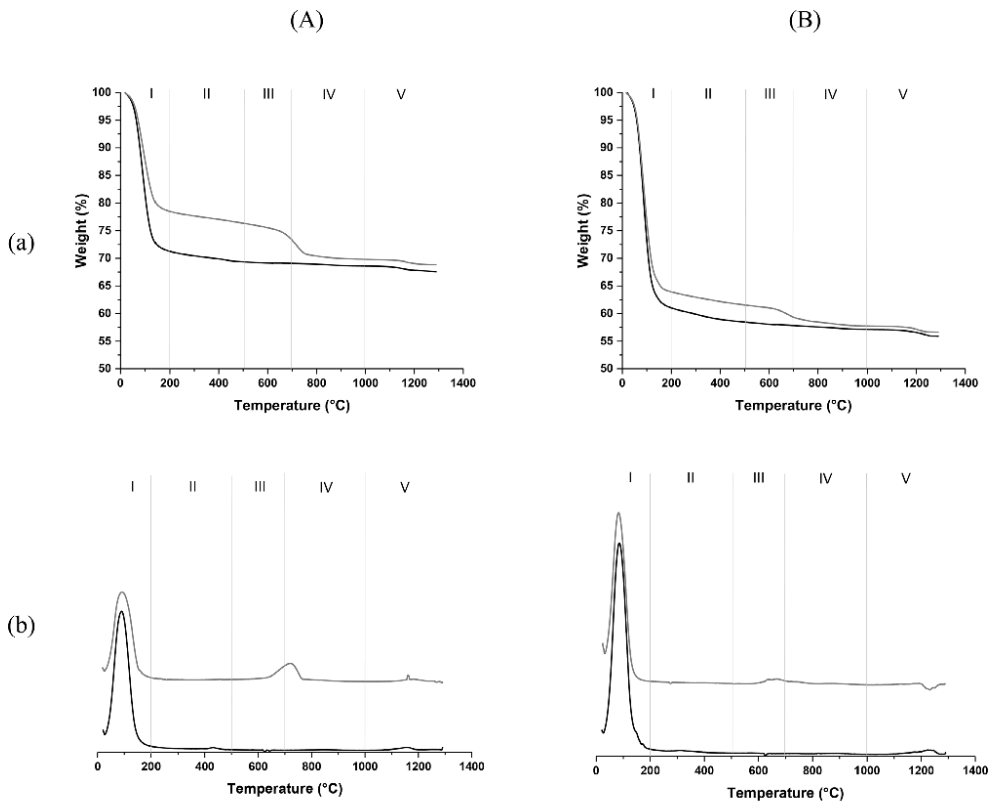


Fig. 4. (a) Weight loss and (b) first derivative of weight loss curves for samples based on (A) S and (B) P solutions with Ac (black) and Af (grey) argillites.

formation of this phase is closely related to the availability of Mg provided by Af argillite as demonstrated previously.

Finally, the chemical composition controls the thermal behaviour and the formed phases after thermal treatment. In order to obtain thermally resistant argillite based materials at 800 °C, calcined argillite with flash or furnace processes can be used. The use of flash calcined

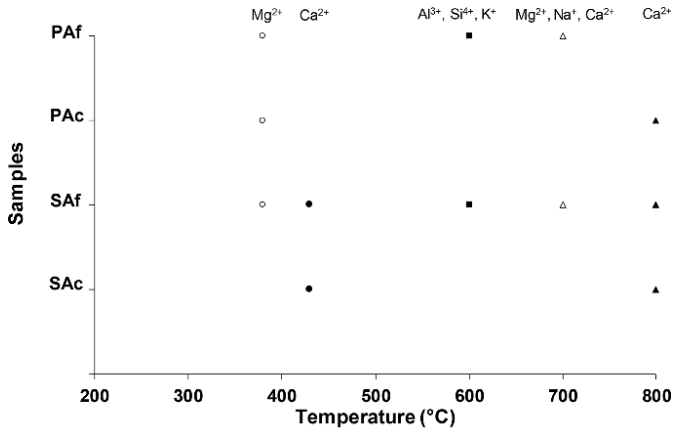


Fig. 5. Temperature of decomposition and nature of the released species of the (•) hydroxide, (■) clay and (▲) carbonate species.

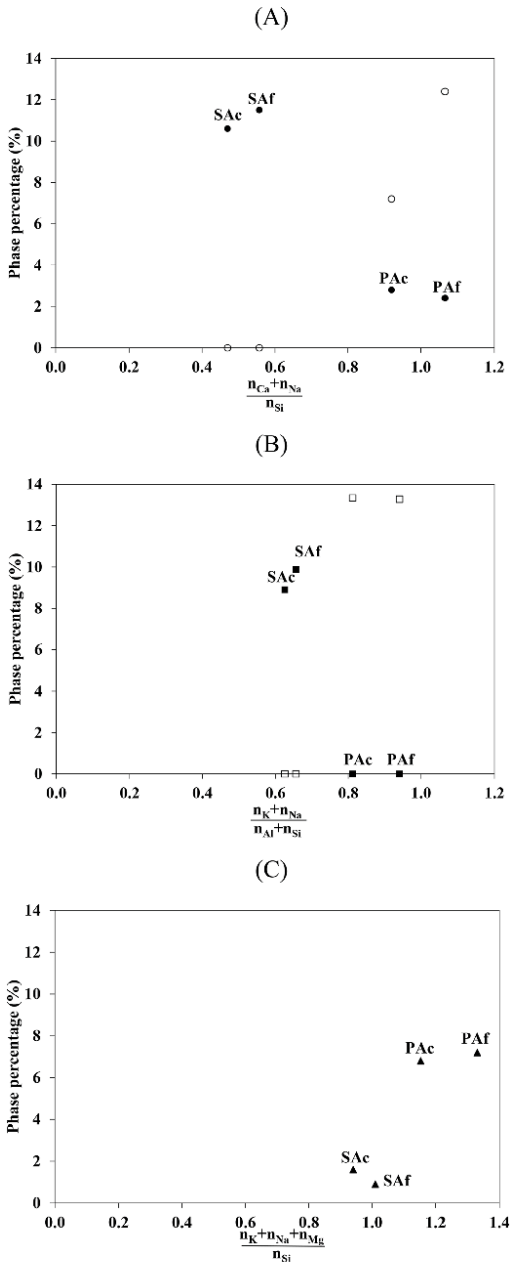


Fig. 6. Variation of phase percentages formed after thermal treatment (A) • wollastonite, ○ combeite, (B) ■ zeolite, □ leucite and kalsilite and (C) ▲ diopside in function of the chemical composition of the different mixtures.

argillite leads to higher increase of the compressive strength after thermal treatment. Moreover, this process is more economically profitable since the calcination time is reduced.

4. Conclusion

Thermal behaviour of argillite based alkali-activated materials was investigated. The studied samples were synthesized using thermally heated argillites with furnace or flash processes at 750 °C and two alkaline solutions based on potassium or on a mix of potassium and sodium. Regardless of the sample, a good resistance to thermal treatment at 800 °C (ramp 1 °C/min) was obtained ($1 \leq \sigma_{after}/\sigma_{before} \leq 2.2$). However, all samples exhibit low resistance ($\sigma_{before}/10$) to thermal shock (800 °C, 10 min). These different behaviours can be explained by different structural variations depending on the used argillite and alkaline solution and the thermal treatment conditions. Indeed, it was demonstrated that for potassium based samples, the carbonates, present in the raw materials, decompose during thermal treatment leading to available calcium which may react with silica from geopolymer amorphous phase to form wollastonite after thermal treatment or kilchoanite after thermal shock. Aluminum, silicon and potassium available from argillite clay minerals dehydroxylation and geopolymer amorphous phase crystallize to form a zeolite phase. In presence of a mix K-Na alkaline cations, combeite and nepheline type are preferentially formed regarding to wollastonite. Moreover, leucite and kalsilite are formed.

In consequence, the nature of formed phases, as the temperature increases, is controlled by the chemical composition of the geopolymer materials such as the type of carbonates, the nature and availability of alkali cations and alkaline earth and the thermal treatment conditions such as the heating rate and the exposure time. For slow heating rate, the formation of wollastonite seems to improve the thermal resistance. However, for a rapid heating rate, the formation of metastable phases such as kilchoanite decreases the thermal resistance. In order to obtain thermally resistant argillite based materials at 800 °C, it would be better to use potassium alkaline solution and flash calcined argillite. Thus, these results will permit to choose the adequate raw materials for the targeted application.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.matchemphys.2018.07.036.

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Publication 5 (ACL5)

C. Dupuy, J. Havette, A. Gharzouni, N. Texier-Mandoki, X. Bourbon, S. Rossignol

Metakaolin-based geopolymer: formation of new phases influencing the setting time with the use of additives.

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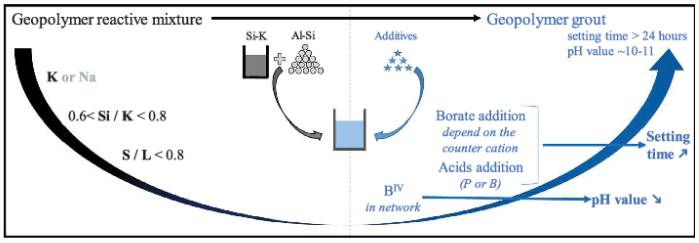
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HIGHLIGHTS

- Setting time of geopolymer samples has been controlled with the use of additives.
- The addition of boron-based compound can decrease the pH value of geopolymer sample.
- Boron coordination seems to be the key parameter to control the geopolymer pH value.
- The phosphate species perturb the polycondensation reactions.

GRAPHICAL ABSTRACT



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ABSTRACT

The aim of this investigation was the development of a geopolymer grout. To achieve this goal, it is necessary to control the characteristics of the reactive mixture (i.e., between the dissolution of the mineral source and the consolidation of the binder) and its setting time. The targeted application (geological radioactive waste disposal) requires a grout with a setting time greater than 24 h, a viscosity in the range from 1 to 5 Pa·s and a moderate pH value between 10 and 11. To reach these values, a metakaolin-based geopolymer was used with the addition of mineral additives. The viscosity measurements reveal that a focused viscosity is reached and that the setting time can be easily controlled and extended above 24 h with the addition of 2.8%$_{weight}$ of acids (boric and phosphoric) or 10%$_{weight}$ of borax. The acids reduce the reactivity of the mixtures by decreasing the alkalinity and inducing slow silica/alumina dissolution. The borax extends the setting time by increasing the water content and by modifying the polycondensation reactions to form huge structural entities. The decrease in the pH value to the target (10–11) can only be reached using 10%$_{weight}$ of borax or 7.5%$_{weight}$ of lithium tetraborate due to the insertion of $B^{[IV]}$ in the geopolymer network.

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1. Introduction

Geopolymer materials are shaped through an alkaline silicate solution and an aluminosilicate source [1]. After the dissolution of the aluminosilicate source in the alkaline silicate solution, polycondensation reactions occur, and the binder is a liquid reactive mixture until the end of amorphous network formation and its solidification [2]. Some applications may require controlling this reactive mixture by regulating the setting time, viscosity or stress rate [3]. The high alkalinity of geopolymer materials can also be a restrictive parameter that can be controlled. These investigations

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are part of a larger study, which consists of the development of an injectable grout to be used in future deep geological radioactive waste disposal. This binder necessitates a reactive mixture with a long setting time (>1400 min, i.e., more than 24 h), a moderate viscosity (1–5 Pa·s, for comparison, water presents a viscosity of 1.10^{-3} Pa·s) and a pH value between 10 and 11.

To reach these objectives, it is necessary to adapt the geopolymer mixture with different parameters. El Idrissi et al. underlined the major impact of the water amount in the mixture to control the setting time and viscosity of the binder [3]. These parameters are directly related to the L/S (liquid/solid) *ratio*, and Lee et al. showed that an increase in the L/S from 0.44 to 0.64 leads to a 100% increase in the setting time [4]. Another key parameter for the geopolymer formulation is the Si/M (M = Li(+I), Na(+I) or K(+I) or) *ratio*, which is a characteristic of the alkaline silicate solution. A decrease in this *ratio* induces stronger reactivity, resulting in a lower setting time and a higher pH value for the binder [5,6]. Both of these parameters allow wide control, but can be limited to reach the focused grout. Indeed, the increase in the water content and the decrease in the alkali species amount induce a lower pH value, which can limit the reactivity of the mixture and compromise its consolidation [7]. To favor the polycondensation reactions, the water amount needs to be limited, with less water in the mixture than metakaolin [8]. Moreover, siliceous species are strongly influenced by the decrease in the alkali amount in the solution, which can result in its polymerization and limit the polycondensation reactions [4].

The use of external compounds is indicated to promote the focused properties without strongly degrading the geopolymer network. Carbon-based surfactants and superplasticizers can be used to adapt the viscosity and/or the setting time of the mixture [9,10] but are inadequate for focused applications (geological radioactive waste disposal). For this reason, only inorganic additives are used for focused applications. Among them, the use of phosphate has been studied, and Lee et al. [11,12] demonstrated delayed behaviors with the addition of orthophosphoric acid and dipotassium phosphate. With the orthophosphoric acid, Chang et al. showed an 800% increase in the setting time [13]. This triple acid probably strongly influences the pH value of the mixtures. Another way to attain focused properties is the use of boron-based compounds. Borax is well-known for its ability to delay properties and can easily increase the setting time by a factor two [14]. Liu et al. [15] demonstrated that this effect disappears at approximately 90 °C. Zajac et al. also showed that borax induces a decrease in the pH value in cement materials [16]. This effect can be extended to borosilicate inorganic polymer, which presents moderate pH value [17]. Rakhimova also showed that the use of boric acid can be used to increase the setting time [18], and it is supposed that other borate compounds, such as calcium and lithium tetraborate, can also have significant effects. Therefore, many studies have focused on the use of inorganic additives, all of which contain glass-forming cations, but there are very few studies in the literature comparing different additives with various insertion rates.

The main objective of this work was to develop geopolymer grouts with a controlled viscosity, setting time and pH value. To accomplish this goal, the behavior (viscosity) of the reactive mixture was studied according to the addition of various inorganic compounds at different insertion rates. Then, the optimal additive amount, which resulted in a low pH value and a high setting time, was established for each compound. Last, a structural study (XRD) was performed to understand the various impacts and interactions induced by the use of additive on the geopolymer polycondensation reaction and the resulting mechanical properties.

2. Material and methods

2.1. Raw materials and sample preparation

The geopolymers use for this study are based on metakaolin (M1000 – Imerys) and on a commercial potassium silicate solution with the addition of potassium or sodium hydroxide. Various Solid/Liquid (S/L) and Si/M (M = Na and K) *ratios* were used and the addition of six additives (dipotassium phosphate, orthophosphoric acid, boric acid, borax, colemanite and lithium tetraborate) was studied. In this paper, the geopolymer samples are named $G_lC^r+^{\%}L$ and the explanations are presented in Table 1.

The sample preparation protocol is described in Fig. 1. The alkaline silicate solution was prepared for the first time. The metakaolin was added followed by additive addition during mixing. The additive amounts ranged from 0 and 20%$_{weight}$ of the total reactive mixture. Finally, the mixture was caste in a closed mold and stored at room temperature.

2.2. Sample characterization

The viscosity and setting time values were obtained from several viscosity measurements during the consolidation time. Data acquisitions were performed punctually with a Brookfield DV-2T viscometer and samples were stored in a closed vessel on a lab roller (60 round/min). The measurements were stopped when a limit value of 600 Pa·s was reached and the sample was considered consolidated.

The pH values of the consolidated samples were measured after seven days of immersion in water with an m/V *ratio* of approximately 0.5. The measurements were performed with a WTW 3310 pH-meter and a specific sensor for extreme pH values (calibrated in the range from 10 to 13). The water resistance was evaluated by visual observation of the external aspects after seven days in water (seven day-aged samples, m/V~0.2).

The compressive strengths were tested using an Instron 5969 universal testing machine with a crosshead speed of 0.5 mm/min and a 50 kN sensor. The compressive tests were performed on five samples for each composition. The samples were cylindrical in shape with a diameter of 15 mm and a height of approximately 30 mm. They were aged for 28 days in a closed mold at room temperature and cured for 12 h at 70 °C before rectification.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed with a TA Instruments SDT Q600. Measurements were performed under dry airflow (100 mL/min) in a platinum crucible. Samples were store in a climatic chamber (20 °C and 80% of relative humidity) for seven days before the analysis and then heated up to 300 °C at a rate of 5 °C/min.

X-ray diffraction (XRD) patterns were obtained with a Brucker-D8 Advance with a Bragg-Brentano geometry and a Cu Kα1α2 detector. The analytical range is between 10° and 50° (2 θ) with a resolution of 0.02° (2θ) and a dwell time of 1.5 s. Phase identification was performed with reference to a Joint Committee Powder Diffraction Standard (JCPDS). Before analysis, the samples were heated to 70 °C to dry the powders.

3. Results

3.1. Study of the reactive mixture

3.1.1. Influence of the mixture composition

To develop the focused binders (setting time >24 h, viscosity >10 Pa·s and pH value in the range from 10 to 11) and to study the additive influence, the first step was the selection of the

Table 1
Description of the used nomenclature.

Letter	Description
l	S/L ratio
C	Nature of the alkali cation: K or KNa for the mixture of both
r	Si/M *ratio*
%	Weight percent of additive (in comparison to the reactive mixture)
L	Name of the used additive: "KP" for dipotassium phosphate "P" for orthophosphorique acid "B" for boric acid "NaB" for borax decahydrate ($Na_2B_4O_7(H_2O)_{10}$) "LiB" for litium tetraborate "CaB" for colemanite ($Ca_2B_6O_{11}(H_2O)_5$)

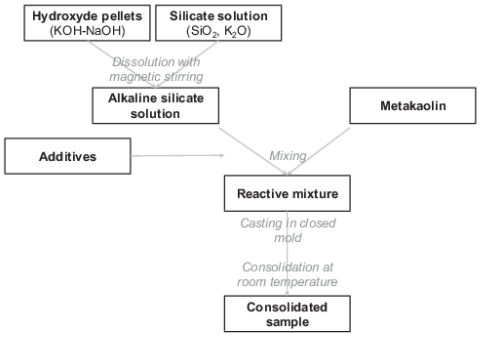


Fig. 1. Protocol for the preparation of the geopolymer samples.

geopolymer mixtures. Thus, the evolution of the viscosity with respect to time for the various mixtures was studied (Fig. 2). For this aim, the influence of the silicate solution alkali-cation (GK and GKNa samples), the Si/M *ratio* (between 0.58 and 0.8) and the S/L *ratio* (from 0.64 to 1.17) were studied.

The influence of the alkaline silicate solution is presented in Fig. 2A. Using a similar Si/M *ratio*, the use of a pure potassium silicate solution (GK samples) led to a lower viscosity than with the presence of sodium (GKNa samples). For example, the $GKNa^{0.7}$ sample presented an initial viscosity close to 12 Pa·s and the $GK^{0.7}$ sample had a viscosity of 6 Pa·s. For this Si/M *ratio*, the viscosity was twice as high in the presence of sodium. This is in accordance with the literature [5,19] and can be explained by the higher hydration sphere of the sodium cation than the potassium cation. The viscosities of the GKNa samples were too high for the requirements of the focused grout (>10 Pa·s) and their setting times were shorter than the GK samples; thus, we chose to use GK samples for the study.

Regarding the variation in the Si/M *ratio*, the $GK^{0.58}$ sample showed a setting time close to 250 min, while the $GK^{0.7}$ sample was close to 350 min and the $GK^{0.8}$ sample was close to 360 min. Similar behaviors were observed with the GKNa samples. This increase in the setting time is associated with the increase in the Si/M molar *ratio* of the alkaline silicate solution, but appears to be limited above 0.7; this corresponds to the lower reactivity of the alkaline silicate solution, which leads to slower dissolution and polycondensation reactions [4]. With a 0.8Si/M *ratio*, the increase in the setting time is probably related to the incomplete dissolution of the metakaolin, which limited the polycondensation duration [20]. Moreover, the initial viscosity was lower with a Si/M *ratio* of 0.7 than with a ratio of 0.58 or 0.8, which is probably related to the lower reactivity for the $GK^{0.58}$ sample and the slower dissolution for the $GK^{0.8}$ sample. Finally, the use of a higher Si/M *ratio* induced to a lower pH value; thus, we aimed to develop the grout using an alkaline silicate solution with a Si/M molar *ratio* of 0.7 in this study.

The second parameter for the geopolymer mixture is the loading in metakaolin, which is described by the S/L *ratio* (Fig. 2B). The smallest S/L *ratio* displayed a viscosity of 0.1 Pa·s and a setting time close to 500 min, whereas the highest S/L *ratio* presented a 6 Pa·s viscosity and a 275 min setting time. Thus, the decrease in the S/L *ratio* directly led to a decrease in the viscosity and an increase in the setting time; this behavior was linear with an increasing S/L *ratio*. This observation confirmed that the viscosity and setting time directly depend on the amount of water in the geopolymer mixture, as is described in the literature [21,22]. Indeed, the use of a high amount of water increases the workability

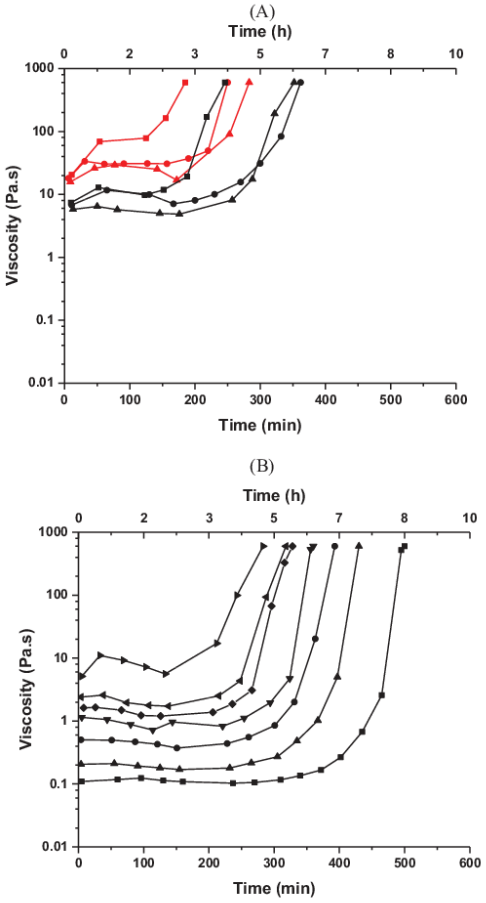


Fig. 2. Evolution of the viscosity in function of time of a basic reactive mixture with (A) different alkaline silicate solutions (in red GKNa and in black GK, with Si/M molar ratio of ■ 0.58, ▲ 0.7 and ● 0.8) (B) different S/L weight ratio (■ 0.64, ▲ 0.75, ● 0.85, ▼ 0.9, ◆ 1.07 and ◄1.17). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of the mixture but also results in a lower reactivity of the alkaline silicate solution, which limits the dissolution of the metakaolin and delays the consolidation. However, the use of the lowest S/L *ratio* is not the best choice for the grout because it leads to the formation of a weak network and a very low viscosity [23]. Moreover, in the next section, we inserted additives into the reactive mixture. As it is known that the use of additives in the mixture can have a negative effect on the network properties and may induce to a very low viscosity [24], we used the $G_{1.01}K^{0.7}$ sample as a compromise between the viscosity, setting time and mechanical properties.

3.1.2. Influence of the additive on the viscosity

The influence of mineral additive insertion in the reactive mixture has been studied using the viscosity evolution on the function of time with different amounts of additive. Fig. 3 displays two examples of curves with phosphate-based additives, with the summary for all data in Fig. 4.

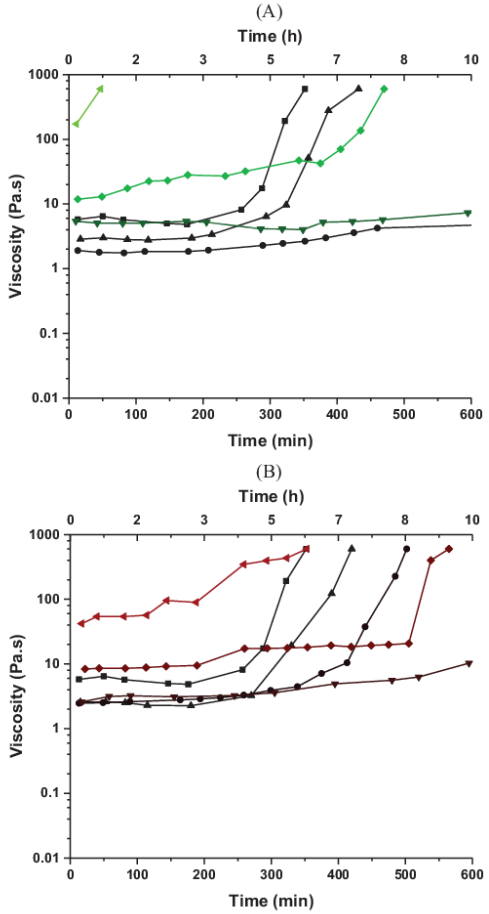


Fig. 3. Evolution of the viscosity in function of time for $G_{1.01}K^{0.7}$ reactive mixture with (A) phosphoric acid (■ GK, ▲ $^{0.9}$P, ● $^{1.8}$P, ▼ $^{2.8}$P, ♦ $^{3.7}$P and ◀ $^{4.7}$P) and (B) dipotassium phosphate (■ ^{0}GK, ▲ $^{1.8}$KP, ● $^{5.4}$KP, ▼ $^{9.3}$KP, ♦ $^{13.6}$KP and ◀ $^{17.0}$KP).

Fig. 3A displays the viscosity evolution with the addition of orthophosphoric acid in the range from 0.9 to 4.7%$_{weight}$. With the addition of less than 2.8% of acid (samples $^{0.9}$P and $^{1.8}$P), the viscosity decreased from 6 to 2 Pa·s and the setting time increased to 1300 min. For 2.8% of orthophosphoric acid, the setting time was the maximum (1850 min) and the viscosity began to increase and reach the 6 Pa·s viscosity associated with the GK sample. Above 2.8%, the viscosity strongly increased (up to 100 Pa·s with $^{4.7}$P) and the setting time decreased (until 50 min with $^{4.7}$P). Thus, we believe that the addition of 2.8% of orthophosphoric acid corresponds to the insertion limit, above which the delaying effect is reversed. This delaying effect is probably related to the high acidity of P (Fig. 5), which leads to the partial neutralization of the siliceous species, resulting in solution polymerization and to a decrease in its reactivity [25]. The phosphate also has an important effect on the setting time. Indeed, PO_4(-III) anions delay aluminosilicate-gel formation by limiting the formation of silica-based oligomers [11]. The observed delay is in accordance with the observations observed in Lee et al. and Chang et al. [12,13].

The viscosity curves for the $G_{1.01}K^{0.7}$ sample with the addition of dipotassium phosphate (KP) have been plot in Fig. 3B. The insertion of dipotassium phosphate led to a similar evolution as orthophosphoric acid, i.e., a decrease in the viscosity from 6 to 2 Pa·s and an increase in the setting time to 650 min at which a time a limit is reached where the trend reversed and the sample properties deteriorate. This limit appears to be between 5.4 and 9.3 percent, which is superior to the amount of orthophosphoric acid used. It can be explained by the lower concentration in phosphor in the dipotassium phosphate (18%$_{weight}$) than in the orthophosphoric acid (32%$_{weight}$) and to the high amount of potassium available in the dipotassium phosphate (45%$_{weight}$), which can counterbalance the effect of the phosphor compounds by increasing the alkalinity. Indeed, KP addition leads to an increase of 60%$_{weight}$ of potassium in the reactive mixture. The increase in the setting time is lower than that observed by Nugteren on a fly ash-based geopolymer [24] and those obtained with orthophosphoric acid, but leads to a 100% increase in the setting time. This is due to the use of metakaolin displaying a higher reactivity than fly ash.

The viscosity and setting time data with other additives are shown in Fig. 4. Both the amount and the nature of the anion/cation due to the additive influence the setting time. The addition of boric acid (B) leads to a similar behavior as P and KP, i.e., the existence of a maximal limit of insertion over which the positive impact of the additive on the viscosity and setting time reverses. This limit is in the range from 2.5 to 4 percent, and boric acid induces a significant decrease in the viscosity to 2 Pa·s and an increase of the setting time to 1400 min. The delaying effect has not been studied in the literature and is supposed to be linked to the acidity and to interactions between the geopolymer network and boron. For boric acid, the boron is 3-cordinated, but boron can also be 4-cordinated and be inserted into the geopolymer network [26]. The use of borax (NaB) induces to a strong increase in the setting time (to 1600 min) regardless of the amount added and to a decrease in the viscosity. This phenomenon is related to the decrease in the S/L *ratio*, which is related to the high amount of water in the borax ($Na_2B_4O_7$, 10 H_2O) [22]. Experiments have also been performed with dehydrated borax, and the resulting setting time increase was very limited, confirming the major influence of the water on the setting time delay. Bore the boron oxide is a glass-forming compound that can also create a network within silica [27]. For example, with the use of other borate compounds, such as LiB and CaB, few variations are observed with less than 5% of additive. A decrease in the properties is observed above 4%, i.e., an increase in the viscosity and a decrease in the setting time. This is probably related to the formation of new phases based on the addition of lithium and calcium.

Thus, the addition of acid to the $G_{1.01}K^{0.7}$ mixture mainly influences the alkaline silicate solution by promoting solution polymerization. This leads to the appearance of a maximal additive insertion rate, as was observed with KP insertion where the Si/M *ratio* increased to a limit value [4]. For the borate compounds, the effect is directly related to the nature of the counter cation (Li, Na, and Ca) and its electronic charge. The cations have different influences on the anions in the reactive mixture, which can be observed by studying the pH of the various samples in the following section.

3.1.3. Influence of the additive on the pH and water resistance

After focusing on the setting time and viscosity, the pH of the $G_{1.01}K^{0.7}$ samples with the different amounts of additive was studied (Fig. 5). Indeed, the initial pH value of the geopolymer without additive was 12.35, suggesting that the addition of additive is indispensable to reach the targeted pH value of 10–11. Among the tested additive panel, some induced a strong decrease in the

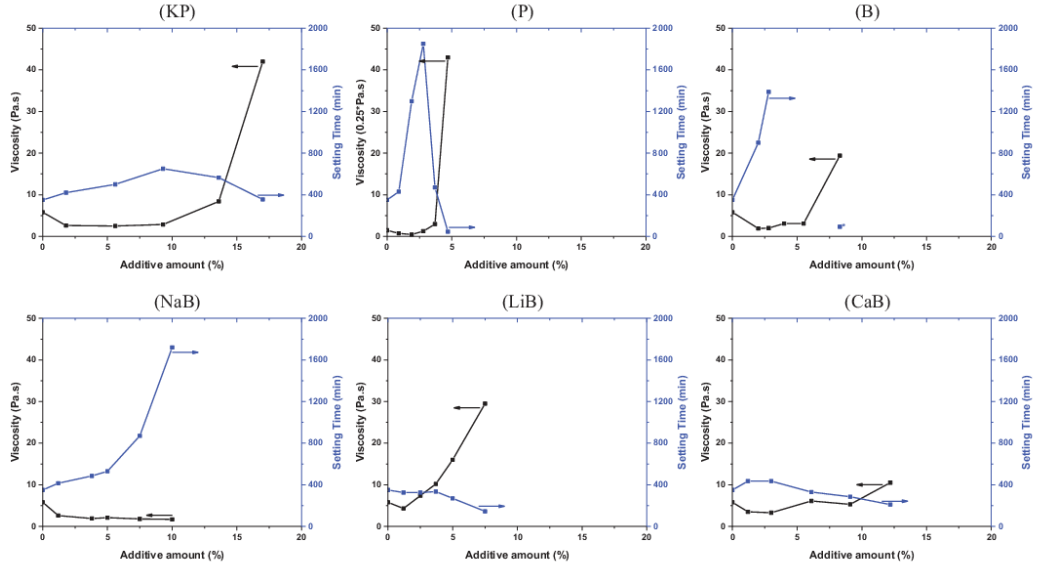


Fig. 4. Evolution of the initial viscosity and setting for the $G_{1.01}K^{0.7}$ samples with the addition of different additives (*consolidation obtained above the non-consolidation area due to very high amount of additive).

pH value while other appeared to have no influence and even a negative influence, i.e., an increase in the pH value.

The insertion of dipotassium phosphate (Fig. 5A) in the geopolymer mixture induced an increase in the pH value to 13.5 for the $G_{1.1}K^{0.7}$ $^{13.6}$KP sample. This increase is directly related to the high amount of potassium (45%$_{weight}$) compared to phosphor (18%$_{weight}$) in the dipotassium phosphate. Despite its positive influence on the geopolymer mixture setting time, the use of KP appears to be limited by its high alkalinity due to its Si/M *ratio* of approximately 0.4. The use of an acidic additive allows a significant decrease in the pH value to 11.5 with P and 11 with B. However, the addition of both orthophosphoric and boric acids induced a decrease in the pH value to the insertion limit (observed on Fig. 4) where their beneficial effects were reversed. At this limit, the pH value increased above 12, and over this limit, the pH still decreased but the samples did not resist water. We believe that the high acidity strongly disturbed the polycondensation close to the insertion limit, which limited the consumption of the alkaline species and counteracted the decrease in the pH value. Above this additive amount, the acidity was sufficient to induce a decrease in the pH despite the high alkalinity, though the geopolymer network did not form and the consolidation only corresponded to the formation of a physical gel (which explained the lack of water resistance) [25]. This gel formation also corresponded to the observed increase in the viscosity above the insertion limit (Fig. 4). Thus, the lower pH values obtained with water-resistant samples were 12 with P and 11.5 with B.

The influence of borate compound addition on the $G_{1.01}K^{0.7}$ sample pH values is described by Fig. 5B. The three compounds allowed a decrease in the pH values, but different behaviors were observed. With the use of colemanite (CaB) and lithium tetraborate (LiB), the decreases are limited close to 4% of additive, similar to the setting time evolutions (Fig. 4). Indeed, with the addition of colemanite, the pH of $G_{1.1}K^{0.7}$ ^{3}CaB was 11.75, and the pH value slightly increased for a higher CaB concentration. The formation of calcium oxide or hydroxide is supposed to be responsible for this increase [28]. The use of lithium tetraborate led to a strong continuous decrease in the pH value to 10.60. However, above ~4% of LiB, which displayed a pH value of 11, the samples are not water-resistant and present a very high fragility (impossible to unmold the sample without breaching). The addition of borax (NaB) allowed a continuous decrease in the pH value regardless of the amount of borax and this behavior was similar to the one observed with the setting time. Despite the presence of sodium, a pH value of 11.2 could be reached for the $G_{1.1}K^{0.7}$ ^{10}NaB sample. This is due to the moderate pH value of the borax (pH = 9), which was inserted to 30%$_{weight}$ [29] and to the large amount of water in the borax [30]. More, it is supposed that the potential presence of boron in the geopolymer network could induce a decrease in the pH value [26].

Consequently, the focused pH value of the geopolymer samples can be reached with the use of an additive. The influence of the additive on the decrease in the pH value is related to the increase in setting time, with the same limit values of additive reached for the beneficial behavior. Thus, it is important to study the structural evolution. For these structural studies, only one sample additive will be presented. These studies will be related to the composition close to the additive limit in the $G_{1.01}K^{0.7}$ samples.

3.2. Properties of the consolidated samples

3.2.1. Structural data

The X-ray patterns of the different samples were gathered in Fig. 6. The reference sample, $G_{1.01}K^{0.7}$, presented a large dome centered a 29° (2θ) corresponding to the amorphous geopolymer network [31]. A few peaks are visible, corresponding to the presence of quartz, kaolinite, muscovite and anatase, which are the different crystalline phases initially present in the metakaolin. With the insertion of additive, the main impact is the decrease in the dome centered at 29° (2θ), which is associated with the lower amount of

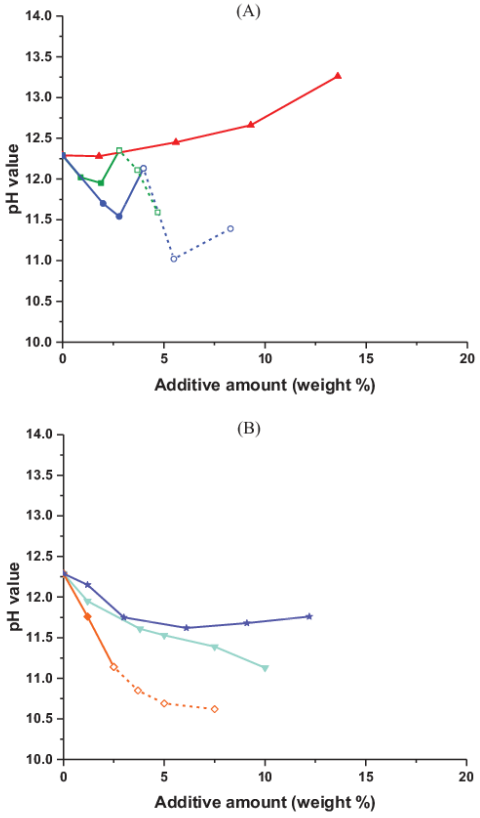


Fig. 5. Evolution of the pH values after consolidation for $G_{1.01}K^{0.7}$ samples with different amount of (A) ■ P, ▲ KP and ● B and (B) ▼ NaB, ♦ LiB, and ✱ CaB (empty bullet point correspond to no water resistant samples).

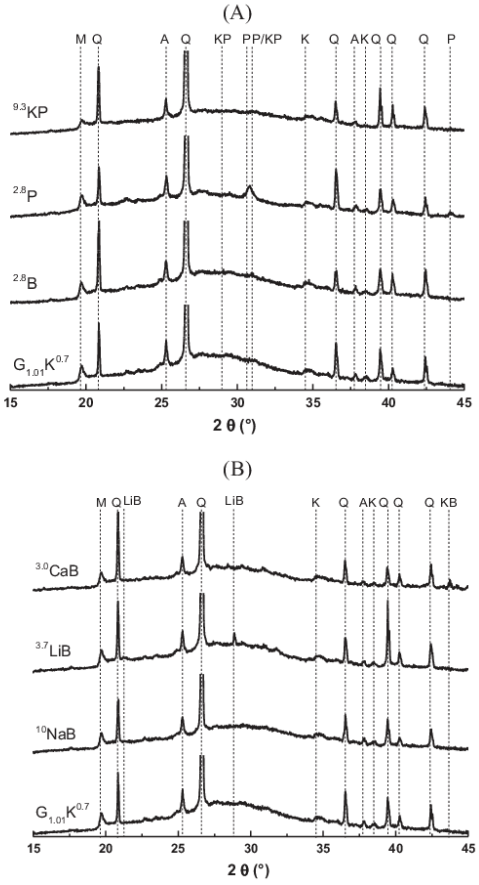


Fig. 6. X-ray patterns of $G_{1.01}K^{0.7}$ samples with (A) KP, P and B and (B) NaB, LiB and CaB additives (JCPDS files: K-kaolinite 00-001-0527, M-muscovite 04-019-1573, A-anatase 01-086-1157, Q-quartz 00-046-1045, P-potassium aluminium phosphate 00-034-1370, KP-potassium phosphate hydrate 00-026-1457, LiB-lithium borate hydrate 00-051-0514, KB-potassium borate hydroxyde hydrate 00-048-0106).

geopolymer network formed in the samples. The appearance of crystalline phases can also be detected with the use of additive. More precisely, the addition of phosphate compounds leads to the formation of new phosphate-based phases in the mixture (Fig. 6A). The addition of $KAlP_2O_7$ shows the clear appearance of the orthophosphoric acid P. The potassium cation and the phosphor entities can potentially react with the aluminum species present in the solution. Effectively, the low reactivity of the metakaolin has the possibility to release aluminum and silica species very slowly, which favors the availability of aluminum species able to react with the phosphor element [32]. The formation of potassium phosphate with the dipotassium phosphate is proposed to occur due to the interaction between the potassium and the phosphate from KP. In contrast, with the addition of boric acid (B), no phase formation can be detected by the X-ray diffraction, which appears to confirm that the boron is inserted into the amorphous network.

The X-ray patterns of samples with borate compounds are displayed in Fig. 6B. The use of colemanite, CaB, induced the appearance of a new phase identified as a potassium borate hydroxide hydrate. It is believed that this phase, which is usually synthesized under mild hydrothermal conditions, is formed by the reaction between the boron and the potassium (in excess from the alkaline silicate solution) in the reactive mixture [33]. In parallel, the calcium is presumed to react with the silica and form calcium silicate [34]. With the use of LiB, lithium tetraborate, the appearance of lithium borate hydrate is observed. Its poor crystalline structure is usually synthesized in solution in the reaction between lithium hydroxide and boric acid [35]. The formation of this structure releases half of the boron cations, which probably react with the silica and integrate into the geopolymer network. The addition of borax (NaB) does not induce a phase evolution, which supposes that all the species are in an amorphous phase.

Therefore, the use of additive leads to a decrease in the amorphous contribution in the sample and the crystallization of new phases can also be observed. The addition of phosphate compounds to the mixture induces the formation of a new phase in the sample based on the potassium phosphate. With the addition of boron, the structure modifications depend on the nature of the additive. The colemanite and lithium tetraborate insertion lead to

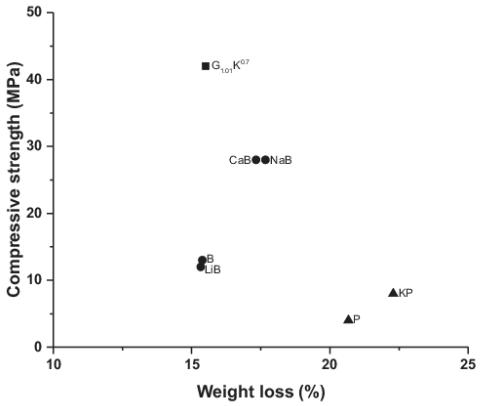


Fig. 7. Compressive strength according to the weight loss of the samples with (■) $G_{1.01}K^{0.7}$, (●) borate-based additive and (▲) phosphate-based additives.

the formation of a hydrated phase, whereas borax and boric acid addition do not lead to the appearance of new phases.

3.2.2. Mechanical properties

The compressive strengths of the different samples are displayed as a function of the weight loss (to 300 °C) in Fig. 7. Specific studies focused on the water loss (after curing at 80% relative humidity) have been performed and are available in the supplementary file.

The compressive strength of the $G_{1.01}K^{0.7}$ sample is 42 MPa for a weight loss of 15%. Usually, the compressive strength of geopolymer materials is related to the amount of water in the sample and an increase in the water induces a decrease in the mechanical properties [36]. According to this, samples synthesized with additives can be gathered in three different groups, i.e., phosphates, borax/colemanite and boric acid/lithium tetraborate.

(i) The sample with phosphate-based additives present very important water losses that are probably due to the perturbation of the polycondensation reaction due to the PO_4(-III) groups according to the formation of new phase (XRD results). The various polycondensation reactions lead to a high amount of water, resulting in very low compressive strength that is close to 5 MPa, which is in accordance with the study by Dupuy et al. focused on orthophosphoric acid addition [37].

(ii) The borax and colemanite present a moderate increase in water loss, which can be explained by their initial hydration. This increase in the amount of water induces a lower compressive strength close to 28 MPa [36]. Nevertheless, this decrease is limited by the fact that the water that is initially present in the additive acts as a diluting factor that favors the formation of silicate species rings, which was determined by Raman investigation, and thus leads to the polymerization of the solution [38]. In this case, the boron is able to be trapped in these structural entities, which limits the formation of a metastable phase and enhances the polycondensation reaction. Moreover, with the insertion of colemanite, these mechanical properties could be probably be related to the formation of calcium-silica bonds in the network, as is shown in the work by Gharzouni et al. [39]. Indeed, the XRD data showed interactions between boron and potassium leading to the $K_2B_5O_8(OH)\,2(H_2O)$ compound. In this case, the reactions between silica and calcium can occur. With the addition of borax, the Si/M *ratio* decreased to very low value (~0.5), which can explain the decrease in the compressive strength [40].

(iii) The last group, which was composed by the boric acid and the lithium tetraborate, did not correspond to the classic correlation between compressive strength and water loss. Both samples presented a 15% water loss, similar to the $G_{1.01}K^{0.7}$ sample, but a low compressive strength of 13 MPa. These lower water losses can be explained by the higher polarizing effect of the H(+I) and Li(+I) cations than the Ca(+II), K(+I) and Na(+I) cations [39]. This results in strong interactions between the cations and the water with higher bonds. This induces higher stability for the bonded water and limits it decomposition under 300 °C [41]. For the lithium tetraborate, the lithium cation can act as an alkaline activator, which can explain the low compressive strength modifying the Si/M ratio to 0.55. With the boric acid, the insertion of boron induces disorder in the mixture, which decreases the compressive strength. Indeed, the boron is probably partially inserted in the geopolymer network (for the 4-coordinated) [42] and acts as an inhibitor for the polycondensation reactions (for the 3-coordinated).

The mechanical properties are therefore related to the amount of water in the samples and decreases with the insertion of additives. To understand the relationship between the working properties and the structural evolution, it is necessary to focus on the molar amount of P(+V), B(+III), Ca(+II), Li(+I) and Na(+I).

4. Discussion

To understand the mechanisms involved in controlling the setting time, the influence of the anionic group of the used additive was studied. To study this parameter, the composition of the various amounts of additive were studied here. Fig. 8 displays the setting time of the different mixtures according to the (P + B)/(K + Na + Li + Ca) molar *ratio*, which corresponds to the amount of glass-forming cation provided by the additive divided by the amount of alkali/earth alkali cation in the mixture acting as modifiers. This *ratio* describes the balance between the positive charges provided by the alkali/earth alkali species and the negative charges associated with the forming cation groups (PO_4(-III), BO_3(-III) or BO_4(-IV).

Similar behaviors are observed with the addition of orthophosphoric acid, P, and dipotassium phosphate, KP, i.e., the optimum a delaying effect of the forming/alkali *ratio* of 0.2 (Fig. 8A). Regardless of the additive nature, the forming/alkali *ratio* has a direct influence on the setting time. Even if the delay is not the same, the optimum is reached similarly, and it turns out that the presence of PO_4 groups directly influences the setting time. Lee et al. [10] showed that phosphate groups limit the silica dissolution in the mixture. This fact suggests that the PO_4(-III)-delaying effect is due to the delay in the formation of the aluminosilicate gel from the lack of available silica [11]. This effect appears to be limited when the phosphate, which is in excess, reacts and forms a new phase (potassium phosphate with KP and alumino-potassium phosphate), which leads to the inversion of the curve. The addition of boric acid, B, also induces an increase in the setting time with the existence of a limited value of insertion between 0.4 and 0.9 forming/alkali. In this range, the samples do not present a real consolidation and the formation of various physical gels is suggested. The boric acid effect is also related to its interactions with the geopolymer network, as evidenced by the compressive strength measurements. Above a 0.4 *ratio*, the interaction between the boron and the network become dominant, which limits the material consolidation.

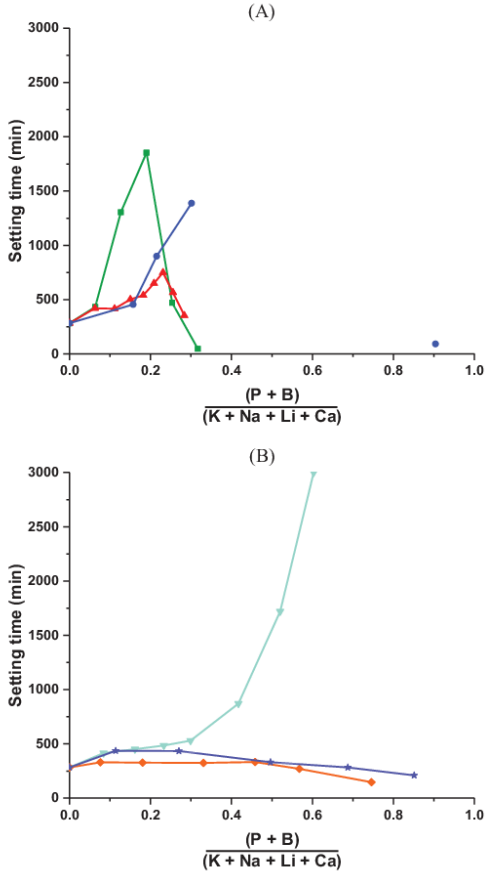


Fig. 8. Evolution of the setting time according the A (P + B)/M (K + Na) molar *ratio* in $G_{1.01}K^{0.7}$ samples with addition of (A) ■ P, ▲ KP and ● B (B) ▼ NaB, ♦ LiB, and ✶ CaB.

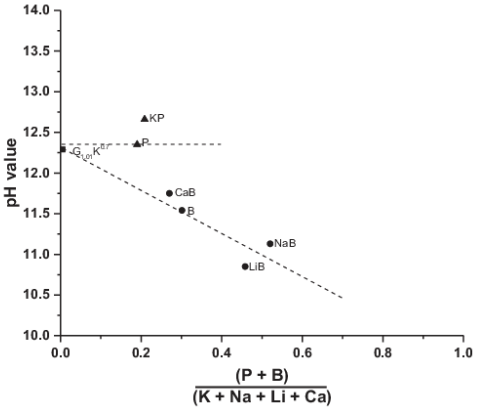


Fig. 9. Evolution of the pH value according the A (P + B)/M (K + Na) molar *ratio* with (■) G1.01 K0.7, (●) borate-based additive and (▲) phosphate-based additives.

The insertion of LiB and CaB in the geopolymer mixture (Fig. 8B) induces few variations in the setting time, regardless of the forming/alkali *ratio*. With LiB, the increase in the *ratio* leads to the formation of hydrated lithium borate but does not induce significant perturbation of the geopolymerization kinetics. Colemanite insertion also leads to small variations. The decrease observed above a *ratio* of 0.3 is supposed to be linked to the formation of calcium silicate in the network. Indeed, the presence of calcium in geopolymer materials can form Ca-Si bonds, resulting in a decrease in the setting time [39,43]. The addition of borax induces a strong increase in the setting time above a *ratio of* 0.4. This lack of a limit is probably related to the addition of water, which increases the workability of the mixture. Indeed, experiments have been performed with dehydrated borax; when borax displays a ratio of 0.41, its use induces a setting time increase lower than 100%, whereas decahydrated borax induces an increase over 200%.

Therefore, with the phosphate-based compounds, the setting time variations appear to be related to the amount of the PO_4(-III) group, with an optimal value of the P/K *ratio* close to 0.2. With the boron-based species, the effect depends of the nature of the counter cation. The addition of boric acid induces an increase in the setting time to a 0.3 forming/alkali *ratio*, whereas the addition of borax induces a strong increase between a *ratio* of 0.3 to more than 0.6 and no variations are observed with lithium and calcium borate.

The forming alkali/earth-alkali cation *ratio* also allowed for the study of the impact of the additive on the pH value (Fig. 9). For this study, only the 6-optimal compositions were studied (one per additive) to avoid the over-limit samples for which the pH values were not significant.

Without any additive, the $G_{1.01}K^{0.7}$ sample presented a pH value of 12.30. The addition of the optimum amount of phosphate-based compound (0.2 *ratio*) did not lead to a significant variation in the pH, which appeared to be limited approximately 12.3 ± 0.3. The P (+V) counter balance from the Al(+III) in the aluminosilicate chains resulted in chain termination during the polycondensation. Thus, the P(+V) induced aluminosilicate chain shortening, resulting in limited polycondensation.

This restricted polycondensation limits the alkaline species consumption, leading to more available K(+I). This high alkali concentration restricts the decrease in the pH value.

The addition of various boron-based compounds induces a stronger pH value decrease. This decrease appears to be proportional to the forming/alkali *ratio*. The lower values obtained, 10.8 and 11.2, correspond to the higher *ratio* close to 0.5. This *ratio* can be related to the boron coordination. Effectively, Bray et al. [44] showed that the amount of four-coordinated boron increased (to the detriment of three-coordinated boron) with the insertion of alkali cations (until 50% of alkali cations) in glasses [45]. In the case of geopolymer materials, similar behaviors could occur and will be confirmed by NMR measurements in further work. According to this supposition, when the forming/alkali *ratio* increases, the rate of $B^{[IV]}$ extends. This means that the borax and lithium tetraborate samples present an amount of $B^{[IV]}$ higher than with the boric acid and colemanite. The higher amount of $B^{[IV]}$ facilitates insertion of the boron in the geopolymer network [42,46]. In contrast to $B^{[III]}$, which can only interfere with the polycondensation reaction, the presence of $B^{[IV]}$ in the mixture can directly participate in the geopolymerization. This results in enhanced polycondensation, leading to a higher consumption of alkali species and a lower pH value. According to Bray et al. [44], the use of boric acid and colemanite induces a lower amount of $B^{[III]}$. This results in a limited

geopolymer network and to the lack of alkali-consumption, which is responsible for the higher pH value.

Finally, the chemical composition of the various samples can be correlated to the setting time evolution and the pH value of the sample. Indeed, the forming/alkali cation *ratio* allows for the description of the delaying effect of the additive by underlining the optimum insertion rate (close to 0.2 with the insertion of phosphate, 0.3 with boric acid and more than 0.5 with borax). With the use of boron-based additives, this same *ratio* is correlated to the pH value of the sample, which can probably be explained by the evolution of the boron coordination. The addition of phosphate-based compounds to the mixture does not induce a decrease in the pH value due to the effect of the P(+V) cations, which restrict the polycondensation reactions.

5. Conclusion

The aim of this work was to develop a geopolymer with a controlled setting time and a moderate pH value. The use of inorganic additive is necessary to reach the target, i.e., a setting time greater than 24 h and a pH value between 10 and 11. In this study, six additives based on phosphor and boron (glass-forming cations) have been tested at different rates and the following results have been demonstrated.

(i) The addition of dipotassium phosphate (9.3%$_{weight}$) induced an increase in the setting time (close to 100%) due to a slower polycondensation reaction (from the effect of the P(+V) on the aluminosilicate chain in the mixture). It results in a higher amount of water in the samples and to the degradation of the mechanical properties (~5 MPa). The pH value is increased by the high amount of potassium provided by the additive.

(ii) The use of orthophosphoric acid (2.8%$_{weight}$) induced a high increase in the setting time (~500%) related to both the effect of the P(+V) on the polycondensation reaction and the decrease in the mixture reactivity. It results in a slower dissolution of silica/alumina. The limited polycondensation leads to a very low compressive strength (~5 MPa) and limits the decrease in the pH value.

(iii) The insertion of 2.8%$_{weight}$ of boric acid induced similar variation in the setting time (+400%), which is due to the low reactivity of the mixture, leading to a slow dissolution of silica/alumina and to a slow polycondensation reaction. The pH value moderately decreased (11.5) and is purportedly related to the presence of $B^{[IV]}$ in the network, which induces disorder and results in a 12 MPa compressive strength.

(iv) The pH value of the reactive mixture is not significantly affected by the addition of 5.1%$_{weight}$ of colemanite. A low decrease in the pH (to 11.7) can be observed due to the presence of water among the colemanite and calcium cations. Moreover, the calcium may react with the silica, resulting in a lower setting time and can act as a mechanical reinforcement in the mixture (σ~28 MPa).

(v) Samples with 3.7%$_{weight}$ of lithium tetraborate presented no variations in the setting time but the higher pH value decreased (to 10.8). The low pH value appears to be related to the presence of $B^{[IV]}$ in the mixture, which is inserted in the geopolymer network and enhanced the alkali-consumption. However, the resulting compressive strength is limited (~12 MPa) due to the low Si/M ratio (~0.55).

(vi) The addition of decahydrated borax (10%$_{weight}$) increased the setting time due to the addition of water in the mixture and by the various kinetics of the reaction related to the $B^{[IV]}$ insertion into the mixture. It also led to a decrease in the pH value to 11.2. Similar to lithium tetraborate, this decrease appears to be related to the presence of $B^{[IV]}$ in the mixture. The resulting mechanical resistance of 28 MPa can be explained by the amount of water provided by the borax, which limits the effect of the high amount of sodium in the mixture (Si/M = 0.5).

Therefore, the setting time can be controlled by the insertion of phosphorous compounds, which promote the polycondensation. A similar result can be obtained by the use of hydrated or acidic compounds. The pH value is efficiently reduced with the use of boron-based additives containing $B^{[IV]}$, which can be inserted into the geopolymer network.

Conflict of interest

None.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.conbuildmat.2018.12.114.

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^{29}Si, ^{27}Al, ^{31}P and ^{11}B magic angle spinning nuclear magnetic resonance study of the structural evolutions induced by the use of phosphor- and boron–based additives in geopolymer mixtures.

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^{29}Si, ^{27}Al, ^{31}P and ^{11}B magic angle spinning nuclear magnetic resonance study of the structural evolutions induced by the use of phosphor- and boron–based additives in geopolymer mixtures

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ABSTRACT

This study aims to develop a geopolymer binder, which requires a control of the reactive mixture setting time, viscosity and pH value. A previous study underlines the possibility of controlling the setting time, viscosity and pH value of geopolymer binders by the addition of phosphate- or boron–based compounds. To understand the structural evolutions responsible for these operating property changes, magic angle spinning (MAS) nuclear magnetic resonance (NMR) analysis were performed on the different binders. A batch of ten specific samples was studied by ^{11}B or ^{31}P (depending on the additive nature), ^{27}Al and ^{29}Si MAS NMR. The NMR spectral decomposition results were correlated with the operating properties of the different binders. The setting time increase was associated with the formation of a secondary phase based on boron or phosphorous. The pH variation is connected with both the modified Si/Al ratio and the asymmetric B^{III} species associated with one non-bridging oxygen (NBO) atom. Thus, determination of the various NMR environments is a useful tool to predict the setting time and pH value evolutions.

1. Introduction

Geopolymers are inorganic binders synthesized by the dissolution of an aluminosilicate source in an alkaline silicate solution with the following formula: $M_n [(SiO_2)_z (AlO_2)]_n wH_2O$ (M is the alkaline cation, n is the polymerization degree, z is the Si/Al ratio and w is the water amount) [1,2]. The synthesis of geopolymers results in the formation of a reactive mixture that remains liquid until geopolymer consolidation. This colloid solution step in geopolymer elaboration allows easy handling, shaping and a broad application area. Indeed, the reactive mixture characteristics, such as viscosity or setting time, can be controlled and adjusted by either the geopolymer formulation or the use of additives [3,4]. With the development of very workable binders presenting a low viscosity and a delayed setting time, the formulation of geopolymer grout is thus possible [5,6]. The main difficulty is controlling the rheological properties, for which the use of external compounds such as organic plasticizers [7] or inorganic compounds [8] is necessary. A previous study focused on the insertion of inorganic compounds into metakaolin-based geopolymers to increase the setting time and decrease the binder pH value [9]. The insertion of dipotassium hydrogen phosphate, orthophosphoric acid, boric acid, sodium tetraborate, colemanite (calcium borate) and lithium tetraborate has been studied. Their influence on both setting time and pH value has also been extensively discussed. The results indicate that the use of phosphate-based additives induces a large increase of the setting time but limits the pH value decrease. Boron-based additives present various behaviours according to their counter cations, inducing an important pH value decrease.

These compounds are based on boron or phosphate, which correspond to the most studied inorganic additives [4,8,10,11]. Both phosphorous and boron are glass-forming cations and can be four-coordinated [12]. It is assumed that these characteristics can enhance the interaction between the cation and the geopolymer network. NMR investigations have provided information about the atomic environment and polymerization reactions [13]. NMR has been widely used on glassy materials, which are similar to the amorphous structure of geopolymers. ^{27}Al and ^{29}Si MAS NMR can describe the geopolymer network. ^{27}Al MAS NMR provides information concerning the amount of four-coordinated aluminum and can identify the amount of Al^{IV} incorporated in the network [14]. ^{29}Si MAS NMR data also provide

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information on the geopolymer network nature, with estimations of the number of Si-O-Al bonds amount and the estimation of the number of aluminum atoms bridged per silicon atom [15]. Some properties of geopolymers have been explained by Si-Al species by Fletcher et al. [16]. The evolution of the Si/Al and P/B *ratios* has also been studied on alkali borosilicate glasses [17] and alkali phospho-alumino-silicate glasses [18]. ^{11}B MAS NMR data provide information about 3- or 4-fold coordinated boron [19]. In alkali-based boron glasses, a relation between an increase in the alkali amount and an increase in 4-coordinated boron has been observed [20–22]. This increase of the amount of B^{IV}, usually referred as N_4 *ratio* (amount of $B^{IV}/(B^{IV} + B^{III})$, also induces an increase in both boron and silica nonbridging oxygen (NBO) [23]. The atomic size of the alkali used leads to major structural differences. An increase in the alkali radius leads to a lower polymerization rate and to weaker binding forces between NBO and alkali [24]. It was also demonstrated that the use of lithium strongly limits the formation of BO_4 units and their interaction with the silicate network [19]. These interactions have been characterized by NMR studies by L.S. Du [25,26], who identified the chemical shift associated with B-O-Si bonds according to the number of silicon atoms related to each boron. This work focused on sodium borosilicate glasses with SiO_2/B_2O_3 ratios ranging from 0.5 to 8.0 and Na_2O/B_2O_3 ratios ranging from 0.1 to 1.0. For example, the chemical shifts of several B^{IV} environments (2B,2Si; 1B,3Si; and 0B,4Si) were determined (at 1.5, −0.3 and − 2.2 ppm, respectively) for glasses with $SiO_2/B_2O_3 = 2.0$ and $Na_2O/B_2O_3 = 0.5$. Phosphate glass is composed of phosphate species, which are phosphor-based tetrahedrons with one double oxygen bond [27]. Thus, phosphate can feature up to three bonding oxygen. In phosphate glassy networks, the addition of Al^{3+} ions induces a modification of P-O-P bonds that are partly replaced by Al-O-P bonds, leading to the formation of Q^1(1Al) [28,29]. In phospho-alumino-silicate glasses, phosphorous preferentially forms a glassy network with alumina, which does not interact with silica. Alkali insertion allows the formation of Si-O-Al bonds, but the formation of Si-O-P bonds remains very limited [30]. In these glasses the addition of phosphate leads to polymerization of the silica network [18]. Indeed, the phosphate groups required a large amount of alkali for charge compensation. These alkali species come from the silica network, which induced an increase in the Si Q^4 species to the detriment of the Si Q^3 species. For glassy materials, ^{31}P NMR usually presents phosphorous atoms that are bonded to a different number of aluminum atoms, but these atoms can also be associated with silica or alkaline species, mainly in crystalline compounds [16,13,31]. Thus, the ^{31}P spectra of glasses are usually decomposed into Q^0, Q [1], Q^2 and Q^3 bonds (in the ranges of 12 −to -7, 4 to −20, −18 to −25 and −32 to −47 ppm, respectively [13]). Moreover, if these phosphorous atoms are bonded to aluminum atoms, it leads to a major shift in the ^{27}Al contributions compared to silica-bonded aluminum [32]. Al^{IV} is located at approximately 47 ppm; Al^{V}, at approximately 14 ppm; and Al^{VI}, at approximately −13 ppm. Acid geopolymers, based on phosphorous, also present a large number of Al-O-P bonds in their amorphous network along with the presence of residual orthophosphate groups [33,34].

Therefore, a NMR study of ^{11}B, ^{27}Al, ^{29}Si and ^{31}P nuclei in geopolymer samples should provide valuable information on the influence of additives. The aim of this work is to perform NMR analysis on a selected batch of samples that all contain additives with one or two insertion rates per additive to identify the structural data. Then, the influence of these variations on the geopolymerization reactions is discussed and correlated with both pH value and setting time evolutions.

2. Experimental part

2.1. Sample preparation and identification

The geopolymers studied in this paper are based on a commercial potassium silicate solution with the addition of potassium hydroxide pellets until a 0.7 Si/K *ratio* is reached. The mineral source used is metakaolin M1000 supplied by Imerys (liquid/solid *ratio* ~1) [9]. After the synthesis, as described in Fig. 1, the samples are stored in a closed mold at room temperature for seven days. Six additives based on phosphorous or boron are added to the samples. The description of these samples is available in Table 1. For lithium tetraborate, two different additives are used: amorphous and crystalline. All the six additives are fully dissolved in the reactive mixture, resulting in homogeneous geopolymer samples. The samples are named GK for the reference geopolymer, and additive-containing samples are named $Ab^{\%}$, where Ab and % correspond to their name abbreviation and their insertion rate (in mass percent), respectively. For example, NaB^{10} corresponds to a geopolymer elaborated by the addition of ten weight percent of sodium tetraborate decahydrate.

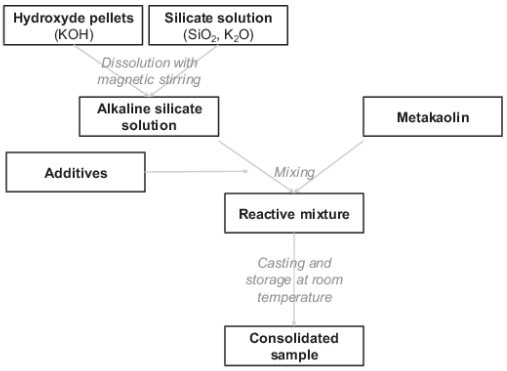


Fig. 1. Geopolymer preparation protocols.

The data set is composed of ten samples, namely, the reference geopolymer (GK), samples with the optimal rate of insertion (evidenced by a previous study [9]) of the six additives ($P^{2.8}$, $KP^{9.3}$, $LiBam^{3.7}$, NaB^{10}, $CaB^{6.1}$ and $B^{2.8}$) and three more samples ($LiBcr^{3.7}$, NaB^{5} and $B^{1.4}$) based on different amounts of boron. In the results section, only the results for the GK, $P^{2.8}$, $KP^{9.3}$, $LiBam^{3.7}$, NaB^{10}, $CaB^{6.1}$ and $B^{2.8}$ samples will be discussed to provide the clearest graphs. However, all the data will be used in the discussion to obtain better correlation. The chemical composition of the ten samples (nominal values) is available in the Table 2.

2.2. Experiments

The pH value measurements were performed on consolidated samples (aged of seven days) after seven days immersion in water with a sample/water weight *ratio* of approximately 0.5. Then, the pH value of the water is measured with a WTW 3310 pH meter and a specific sensor for extreme pH values calibrated in the range of 10–13. The measurement error, related to the measurement devices and buffing solutions, was around ± 0.1 pH units.

The setting time value was evaluated by viscosity follow-up over

Table 1
Additive description.

Abbreviation	Compound name and composition
P	Orthophosphoric acid (H_3PO_4)
KP	Dipotassium hydrogen phosphate (K_2HPO_4)
B	Boric acid (H_3BO_3)
LiBam	Amorphous lithium tetraborate ($Li_2B_4O_7$)
LiBcr	Crystalline lithium tetraborate ($Li_2B_4O_7$)
NaB	Decahydrate sodium tetraborate ($Na_2B_4O_7(H_2O)_{10}$)
CaB	Colemanite ($Ca_2B_6O_{11}(H_2O)_5$)

Table 2
Samples chemical composition ($\%_{mol}$).

Sample	Si ($\%_{mol}$)	Al ($\%_{mol}$)	Ca ($\%_{mol}$)	Na ($\%_{mol}$)	K ($\%_{mol}$)	Li ($\%_{mol}$)	P ($\%_{mol}$)	B ($\%_{mol}$)
GK	50.7	35.0	0.0	0.0	14.3	0.0	0.0	0.0
$LiBam^{3.7}$	45.4	31.2	0.0	0.0	12.8	3.5	0.0	7.1
$LiBcr^{3.7}$	45.4	31.2	0.0	0.0	12.8	3.5	0.0	7.1
$NaB^{10.0}$	44.5	30.6	0.0	4.1	12.6	0.0	0.0	8.2
$NaB^{5.0}$	47.4	32.6	0.0	2.2	13.4	0.0	0.0	4.4
$CaB^{6.1}$	48.2	33.1	1.3	0.0	13.6	0.0	0.0	3.8
$B^{2.8}$	48.7	33.6	0.0	0.0	13.8	0.0	0.0	3.9
$B^{1.4}$	49.8	34.2	0.0	0.0	14.0	0.0	0.0	2.0
$P^{2.8}$	49.7	34.2	0.0	0.0	14.0	0.0	2.1	0.0
$KP^{9.3}$	44.5	30.6	0.0	0.0	20.8	0.0	4.1	0.0

time. In these experiments, several viscosity measurements were performed punctually with a Brookfield DV-2 T during sample consolidation until the viscosity reached 600 Pa.s (the value at which the sample was considered as consolidated). Between each viscosity measurement, the samples were maintained under stirring with a lab roller (60 round/min). The setting time evaluation was performed by the tangent lines method, with an error of ± 40 min [35].

Raman spectroscopy was performed on silicate solutions (with additives) by an In Via Reflex Renishaw spectrophotometer with a 532 nm and 40 mW laser. The spectral range was from 200 to 1400 cm^{-1} with an acquisition time of 5 s.

Magic angle spinning nuclear magnetic resonance analysis (MAS-NMR) was conducted with a Bruker AVANCE 400 and a 9.4 T magnetic field [36] at 79.49 MHz for ^{29}Si, 104.26 MHz for ^{27}Al, 161.97 MHz for ^{31}P and 128.38 MHz for ^{11}B. ^{11}B, ^{27}Al, ^{29}Si and ^{31}P spectra were obtained after single pulse irradiation of 3, 2, 5 and 2 µs, respectively, with a recycling time of 5 s for ^{11}B, ^{27}Al and 10 s in the case of ^{29}Si and ^{31}P. The samples were ground to a fine powder and dried at 40 °C. Samples were spun in 4 mm ZrO_2 rotors at 10 kHz around an axis inclined at 54°44′ with respect to the magnetic field (magic-angle spinning technique, MAS). The number of scans was chosen to get signal/noise ratios higher than 10 (200, 400, 800 and 120 respectively). ^{11}B, ^{27}Al and ^{31}P chemical shifts values were reported in ppm relative to 0.3 M H_3BO_3, 1 M $AlCl_3$ and 85% H_3PO_4 aqueous solutions and tetramethylsilane (TMS) for ^{29}Si.

Spectral decomposition was performed with Dmfit software [37], taken into account only the central part of the spectrum in all cases. Relative intensities, positions and line widths of different components were determined with a non-linear least square iterative method. Spectral decompositions present an accuracy estimated at ± 0.2 ppm for chemical shift values and at ± 3% for the area quantification. A summary of the various contributions is gathered in Table 3.

Table 3
Summary of the ^{27}Al, ^{29}SI, ^{31}P and ^{11}B NMR contributions.

NMR nucleus	Chemical shift range (ppm)	Contribution identification	References
^{27}Al	68 — 52	Al^{IV}	[13]
	38 — 28	Al^{V}	[13]
	15 — −5	Al^{VI}	[13]
	49 — 45	Al^{IV} – P	[29,47]
	18 — 15	Al^{V} – P	[29,47]
	−11 — −14	Al^{VI} – P	[29,47]
^{29}Si	−82 — −90	Q^4 – 4Al	[39]
	−85 — −94	Q^4 – 3Al	[39]
	−92 — −98	Q^4 – 2Al	[39]
	−96 — −107	Q^4 – 1Al	[39]
	−102 — −115	Q^4 – 0Al	[39]
	−107.0	Quartz	[41]
	−110 — −112	Amorphous silica	[42,41]
	−112.0	Silicic acid	[43,41]
^{31}P	6.5	PO_4 with alkali	[32]
	5.5	Q^1 – Al	[48]
	4.0	Q^1 – Si	[32]
	1.1	Q^1 – P ($K_4P_2O_7$)	[13,31]
^{11}B	13.0	B^{III} – asymmetric nonring	[25]
	6.0	B^{III} – alkali media	[13,53]
	2.5	B^{IV} – 2Si	[25,26]
	0.5	B^{IV} – 3Si	[25,26]

3. Results

3.1. Reference geopolymer study (^{27}Al and ^{29}Si)

The ^{27}Al MAS NMR spectrum of the GK sample (reference geopolymer) is plotted in Fig. 2.A. This spectrum presents two different contributions. The main one, located at 58.0 ppm, is associated with four-coordinated aluminum [13] and accounts for more than 90% of the spectrum area (Table 4). The second one, at 1.8 ppm, corresponds to six-coordinated aluminum [13]. In the aluminosilicate system, as with raw metakaolin, another alumina species (five-coordinated) can be observed at 29 ppm, but its contribution is very low [38].

Fig. 2.B displays the ^{29}Si NMR spectrum of the reference geopolymer (GK sample). The spectrum presents a large band in which many contributions can be identified. The three-dimensional structure of geopolymers is considered to be composed of only four-coordinated silicon (Q [4]), which can be bridged with silicon or aluminum [39]. According to this, the spectrum is decomposed into five contributions of Q^4 silicon: bridged with four aluminum atoms (Q^4 4Al, −82.5 ppm), with three aluminum atoms (Q^4 3Al, −87.5 ppm), with two aluminum atoms (Q^4 2Al, −92.4 ppm), to one aluminum atoms (Q^4 1Al, −98.0 ppm) and with only silicon (Q^4 0Al, −103.0 ppm) [40]. The small shoulder at lower chemical shift (< −105 ppm) can be associated with the contribution of quartz (−107.0 ppm [41]), and another with silicic acid (−112 ppm, called “SiH” on the spectrum [42–44]). All these data are in agreement with the work of Gharznouni et al. based on various metakaolins [45].

3.2. Phosphate-based samples study (^{27}Al, ^{29}Si and ^{31}P)

Fig. 3.A presents the NMR spectra of GK samples with the addition of phosphate-based additives (orthophosphoric acid and potassium hydrogen phosphate), and the results of the NMR spectral decomposition are reported in Table 4.

The ^{27}Al curves of the geopolymers display three contributions related to Al^{IV}, Al^{V} and Al^{VI} at 58.0, 29.2 and 1.3 ppm, respectively. The variations related to the Al^{IV} amount with the addition of phosphates are gathered in Fig. 3.A. The addition of orthophosphoric acid led to a significant decrease of the amount of Al^{IV} (58.0 ppm) from 94% to 48% (Table 4). This decrease is due to the effect of Al^{VI} (2.0 ppm) and Al^{V} (29.2 ppm). The four-coordinated aluminum is associated with the geopolymer network, whereas the six and penta-coordinated aluminum corresponds to unreacted metakaolin [36]. Consequently, the higher rate of Al^{VI} and Al^{V} is associated with a limitation of the geopolymerization reaction. The presence of Al^{V}, which is a very reactive fraction

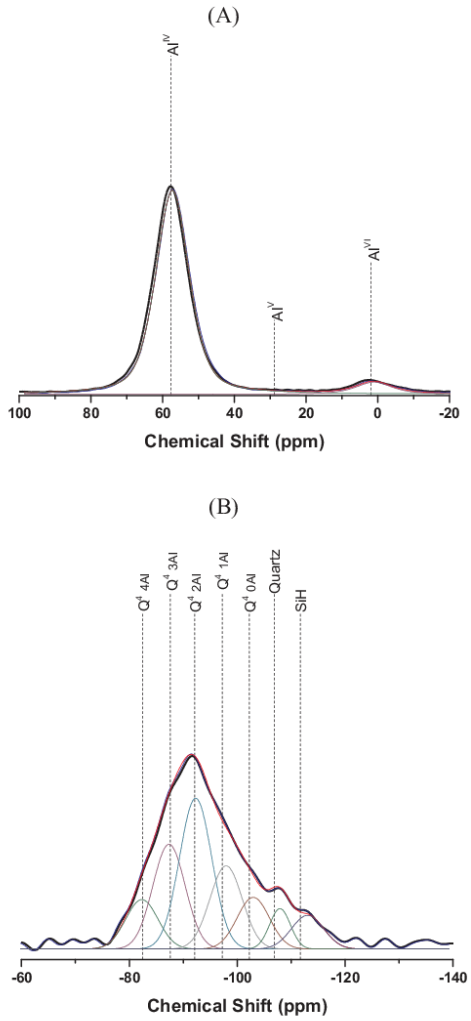


Fig. 2. MAS NMR spectra, with decomposition, of (A) ^{27}Al and (B) ^{29}Si nuclei in the GK sample.

of the metakaolin, emphasizes the large limitation of geopolymerization due to the use of orthophosphoric acid.

The addition of dipotassium hydrogen phosphate induces limited variations compared to the reference geopolymer. A decrease of only 4% in the Al^{IV} contribution is observed, leading to 4% more of Al^{VI} and no Al^{V} contribution. Moreover, a very limited shift in the four-coordinated aluminum contribution (~ −1.2 ppm) attributed to phosphor-bridging aluminum bonds is observed [46]. According to the literature, the formation of Al-O-P bonds leads to an important negative shift in the aluminum contributions [28,47]. Thus, the geopolymerization reactions are more markedly decreased by the addition of orthophosphoric acid than the addition of dipotassium hydrogen phosphate.

The ^{29}Si spectrum shown in Fig. 3.B mainly presents an intensity increase from −92.0 to 115.0 ppm with the insertion of phosphate-based additives. The silicon coordination is evolving to more Si Q^4 0Al (and other low-aluminum bonded silica). The insertion of orthophosphoric acid induces a strong increase (+ 15%) in the contributions associated with Q^4 1Al, Q^4 0Al, quartz and silicic acid (−98, −103, −108 and −113 ppm, respectively) (Table 4). This diminution in Si-O-Al bonds corresponds to a decrease in the geopolymerization reactions. The insertion of dipotassium hydrogen phosphate leads to similar variations, i.e., more low-aluminum-bonded silicon. The extent of this low bonding variation is, however, limited to 7% versus 18% with orthophosphoric acid. Therefore, the use of dipotassium hydrogen phosphate seems to lead to a better geopolymer network, which is in agreement with the data obtained from the ^{27}Al spectrum.

The ^{31}P NMR spectra (Fig. 3.C) present several contributions: one major contribution surrounded by three small other contributions is centered at approximately 5.0 ppm. These contributions can be due to several environments, such as PO_4^{3-} species (~6.5 ppm) and Q^1 (5.0 to −10.0 ppm) bonds with different bonding atoms (~5.0 ppm for Al, ~4.0 ppm for Si and ~1.0 ppm for P) [30,31,48]. For the studied samples, the spectrum with decomposition is available in the supplementary file. More precisely, samples containing orthophosphoric acid present a first contribution at 5.6 ppm with two shoulders at 6.5 and 5.3 ppm. The main contribution and the second shoulder, at 5.6 and 5.3 ppm, respectively, are related to Q^1 phosphorous with a bridging oxygen to tetrahedral alumina (P-O-Al) [47]. The first shoulder, which is a small shoulder, can be attributed to orthophosphate groups (PO_4^{3-}) equilibrated with potassium cations [31] and is probably related to excess phosphate in the solution. With the use of dipotassium hydrogen phosphate, the first two contributions, PO_4^{3-} at 6.5 ppm and P Q^1 1Al at 5.1 ppm, are observed. The P-O-Al bonds at 5.1 ppm present a lower spectrum area (50% with KP versus 81% with P). However, two other contributions can be distinguished at lower shifts. At ~ 4.0 ppm, a Q^1 phosphorous contribution is observed, and it is postulated that this Q^1 corresponds to phosphorous bridged with silica, which results in a lower chemical shift [31]. The last broad peak located at 1.1 ppm is associated with Q^1 (P-O-P) of $K_4P_2O_7$ [13,30], which has been observed in the $KP^{9.3}$ sample [9]. With both phosphate-based additives, the main contribution is associated with Q^4 1Al, which is considered related to bonding between the phosphorous and aluminum atoms in the terminal chain, in agreement with the lower polycondensation reactions (as observed in the ^{27}Al and ^{29}Si spectra).

3.3. Boron-based sample study (^{27}Al, ^{29}Si and ^{11}B)

The spectra from various NMR measurements on boron-based additives are collected in Fig. 4, and all the spectral decomposition results are gathered in Table 5.

^{27}Al NMR spectra of boron-based samples (Fig. 4.A) display a similar contribution to the spectrum of the reference geopolymer (GK). Few variations are observed, such as a decrease of less than 3% in the four-coordinated aluminum amount (Table 5). This result could indicate that boron addition weakly disturbs the Al environment.

Boron-based samples present similar ^{29}Si contributions to the reference and phosphor-based samples. However, the intensity of the contributions below −92.0 ppm is higher for the boron-based samples than for the reference geopolymer (Fig. 4.B). These contributions are associated with low-aluminum-bonded silicon atoms. The addition of lithium tetraborate induces very limited variations. The increase in the low-aluminum-bonded silicon atom contributions (Q^4 1Al, Q^4 0Al, quartz and silicic acid) is limited to ~3.0%. Similar behaviour is observed with the insertion of colemanite ($Ca_2B_6O_{11}(H_2O)_5$), with an increase in the low-aluminum-bonded silicon contributions of close to 3.5%. With the use of boric acid and sodium tetraborate, a strong increase in the Q^4 1Al, Q^4 0Al, quartz and silicic acid contributions of approximately 10% is observed (Table 5). The addition of boron-based additives increases the number of low-aluminum-bonded silicon atoms.

Table 4
NMR spectral decomposition data for (A) the reference geopolymer and (B) samples with phosphor-based additives.

(A)

Sample		^{27}Al			^{29}Si						
		Al^{IV}	Al^{V}	Al^{VI}	Q^4 4Al	Q^4 3Al	Q^4 2Al	Q^4 1Al	Q^4 0Al	quartz	SiH
GK	*Position (± 0.2 ppm)*	58.0		1.8	−82.5	−87.5	−92.4	−98.0	−103.0	−107.9	−113.5
	FWMH (± 0.2 ppm)	11.0		12.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0
	Area (± 3%)	93.7		6.3	9.8	20.9	30.0	16.6	8.9	8.4	5.4

(B)

Sample		^{27}Al			^{29}Si							^{31}P				
		Al^{IV}	Al^{V}	Al^{VI}	Q^4 4Al	Q^4 3Al	Q^4 2Al	Q^4 1Al	Q^4 0Al	quartz	SiH	PO4	Q^1 Al	Q^1 Al	Q^1 Si	Q^1 P
$P^{2.8}$	*Position (± 0.2 ppm)*	56.7	29.2	1.9	−80.5	−86.9	−92.2	−97.3	−102.7	−108.4	−114.5	6.1	5.6	5.3		
	FWMH (± 0.2 ppm)	11.3	31.0	16.0	6.8	6.8	7.0	6.8	6.8	7.0	7.0	0.8	0.4	0.7		
	Area (± 3%)	48.3	22.2	29.5	7.6	14.6	20.7	19.6	15.8	14.2	7.5	18.7	50.4	30.9		
$KP^{9.3}$	*Position (± 0.2 ppm)*	56.8		1.8	−81.2	−87.2	−92.2	−97.3	−102.4	−107.8	−114	6.4		5.1	4	1.1
	FWMH (± 0.2 ppm)	11.2		13.0	7.0	7.0	6.8	7.0	7.0	7.0	7.0	1.5		1.0	1.5	3.8
	Area (± 3%)	90.0		10.0	8.3	18.9	26.1	20.1	12.1	9.7	4.8	19.4		50.6	10.1	19.9

This result can be explained by either (i) a weakness of geopolymerization because the boron atoms induce a lower consumption of metakaolin, resulting in a lower amount of high-aluminum-bonded silica or (ii) the formation of different networks in the presence of boron (mainly boric acid and sodium tetraborate) inducing a change in the number of aluminum-bonded atoms per silicon atom.

Boron atoms can be three-coordinated (20–5 ppm in NMR) or four-coordinated (5–0 ppm in NMR) according to the oxygen atom. Boric acid initially presents three-coordinated boron, and the alkaline tetraborate compounds and colemanite have both three- and four-coordinated boron atoms [17,49–52]. The study of the ^{11}B spectra (Fig. 4) displays a main contribution close to 0.0 ppm, with the presence of a shift and shoulders associated with various boron contributions (the spectrum with decomposition is available in the supplementary file). The main peak seems to be associated with two B^{IV} fourfold-coordinated boron contributions (2.5 and 0.5 ppm). They can be related to silicon-bonded boron with B^{IV} 2Si at 2.5 ppm and B^{IV} 3Si at 0.5 ppm [24,25]. Two small contributions, at 13.0 and 6.0 ppm, can be associated with B^{III} threefold-coordinated boron. The contribution at 13.0 ppm corresponds to basic non-ring asymmetric three-coordinated boron atoms and is mainly observed only with the use of sodium tetraborate [24]. The contribution located at 6 ppm can be associated with three-coordinated boron with all bridging oxygen atoms. Indeed, in alkali glasses, three-coordinated boron has been observed to have a very low chemical shift (below 5 ppm) [13,53], and it is supposed that geopolymers could reproduce similar alkali amorphous environments.

To validate the transformation of B^{III} into B^{IV} observed in Fig. 4.C, the N_4 *ratio* was calculated as for the glassy materials [24,54]. Values of 2.2, 2.7 and 1.2 were obtained at 1.5, 1.6, 0.5 and 0.4 M contents for lithium tetraborate, sodium tetraborate and colemanite, respectively. These data show that the N_4 value variation can be related to the addition of alkali and earth alkali cations to the mixture. This result is in accordance with the glass literature and confirms the similarity between glass and geopolymer materials [24,55]. Moreover, this increase in B^{IV} could be associated with the insertion of four-fold coordinated boron inside the geopolymer network. Indeed, William et al. [56] have demonstrated the possibility of forming a geopolymer network containing boron from the alkali activation mixture of borax and fly ash. According to this supposition, the nature of the B^{IV} species could provide information on the network composition. Indeed, depending on the additive nature, the amount of each B^{IV} 2Si and B^{IV} 3Si contribution evolves, resulting in a shift in the main contribution (from 2.5 to 0.5 ppm when the number of silicon atoms bonded to boron increases).

For all samples, three possibilities can be distinguished: the formation of a large majority of B^{IV} 2B (lithium tetraborate), the formation of both B^{IV} 2Si and B^{IV} 3Si (colemanite) and the formation of a large majority of B^{IV} 3Si (sodium tetraborate and boric acid) (Table 5). Samples displaying a higher level of B^{IV} 3Si are characteristic of a network where boron is very well incorporated in the tetrahedral position. Consequently, it allows a better insertion of the boron into the geopolymer network with the use of sodium tetraborate and boric acid.

The N_4 *ratio* provides information not only about the B^{IV} amount that can be inserted in the network but also on the amount of residual B^{III}. Among B^{III} species, only asymmetric B^{III} located at 13.0 ppm associated with disorder is considered. Indeed, these B^{III} species can present NBO atoms, which can induce the appearance of negative charges [52,57]. More specifically, in the literature, these asymmetric B^{III} species have been associated with boron with one NBO atom [13,24]. Fig. 5 displays the evolution of the asymmetric B^{III} amount for the different samples. Both lithium and sodium tetraborate present a high content of asymmetric B^{III} that is twice those of colemanite and boric acid. This asymmetric B^{III} induces interactions between boron and the geopolymer network. It is supposed that the presence of a negative charge, due to the NBO atom of asymmetric B^{III}, can lead to interaction with the alkali cations, resulting in an “alkali-boron” interaction to compensate for the charges modifying the geopolymer network.

Thus, depending on the additive nature, boron can be inserted into the geopolymer network in tetrahedral sites and/or can induce the appearance of charge defects along with the presence of asymmetric trigonal boron.

4. Discussion

4.1. Summary of the NMR observations

The reference geopolymer GK presents a large majority of Al^{IV} (90%), which corresponds to the aluminum inserted inside the geopolymer network. For ^{29}Si, various contributions can be associated with Q^4 xAl (x ranging from 0 to 4), quartz and silicic acid. The GK sample presents a large majority of high-aluminum-bonded silica associated with the geopolymer network.

The incorporation of orthophosphoric acid in the mixture leads to the appearance of a large amount of phosphorous Q^1 bridged with alumina at the terminal of the aluminosilicate chains, resulting in a low polycondensation reaction [9]. The insertion of dipotassium hydrogen phosphate induces a lower amount of phosphorous Q [1], leading to

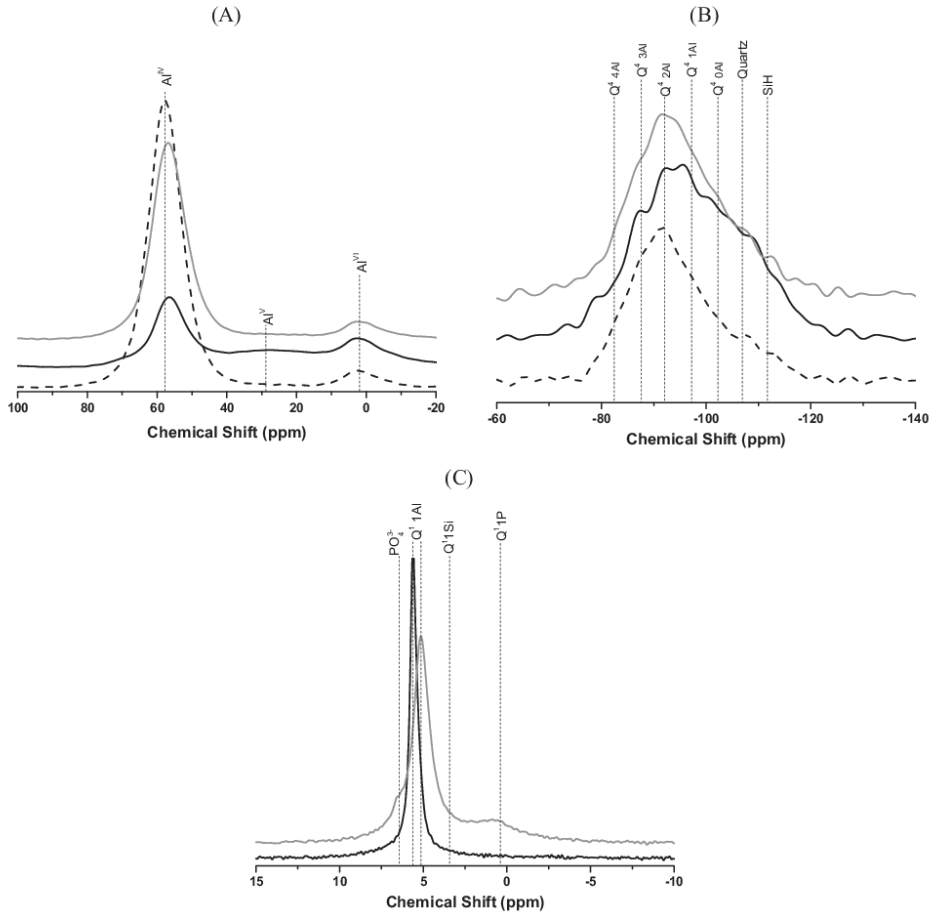


Fig. 3. MAS NMR spectra of (A) ^{27}Al, (B) ^{29}Si and (C) ^{31}P nuclei in the (—) GK, (—) $P^{2.8}$ and (—) $KP^{9.3}$ samples.

better polycondensation along with the presence of $K_4P_2O_7$ (as observed in XRD data [9]) or orthophosphate groups equilibrated by the excess of potassium.

The addition of a boron-based sample induces a change in the geopolymer network, along with a decrease in the aluminum-silicon bridge amount visible in both the ^{27}Al and ^{29}Si spectra. The study of ^{11}B NMR data indicates the insertion of boron in the network, which is responsible for the decrease in aluminum-silicon bonds. The formation of asymmetric B^{III} is also observed in the samples, which leads to the appearance of NBO, resulting in charge defects in the structure [24]. The use of both sodium and lithium tetraborate leads to more charge defects in the samples.

4.2. Relation between setting time and structural evolution

The setting time evolutions of the various samples were correlated with the NMR spectral decomposition results. Fig. 6 displays the evolution of the setting time according to the relative geopolymer network amount. These data are based on the hypothesis that the network amount can be calculated from the amount of Al^{IV}, Si Q^4 4Al, Q^4 3Al and Q^4 2Al (associated with the aluminum and silicon molar percent), representing the molar percent of the geopolymer network. In the presence of additives, this geopolymer network amount was modified by the interaction of phosphorous or boron atoms. The previous value was subtracted by the amount of network formed with the forming cation (molar percent of B^{IV}, P Q^1 1Si, Q^1 1Al and Q^1 1K). For example, with the use of sodium tetraborate, the amount of 17.4%$_{mol}$ was calculated by subtracting 2.7%$_{mol}$ of the secondary phase from 20.1%$_{mol}$ of the geopolymeric network. As a result, there is a smaller amount of relative network (after subtraction) with the use of sodium tetraborate, which presents a higher setting time. Essentially, this decrease in the relative network amount corresponds to an increase in the secondary network based on P or B. Indeed, decreasing this relative network leads to an increase in the setting time. The formation of these secondary networks is thus responsible for the setting time increase. This finding is in accordance with the NMR results, i.e., less Al^{IV} and high-bonded silica combined with the appearance of B-O-Si and P-O-Al bonds.

Only two samples did not present this correlation between relative network amount and setting time, the two lithium tetraborate-based samples. This behaviour can be explained by the behaviour of the

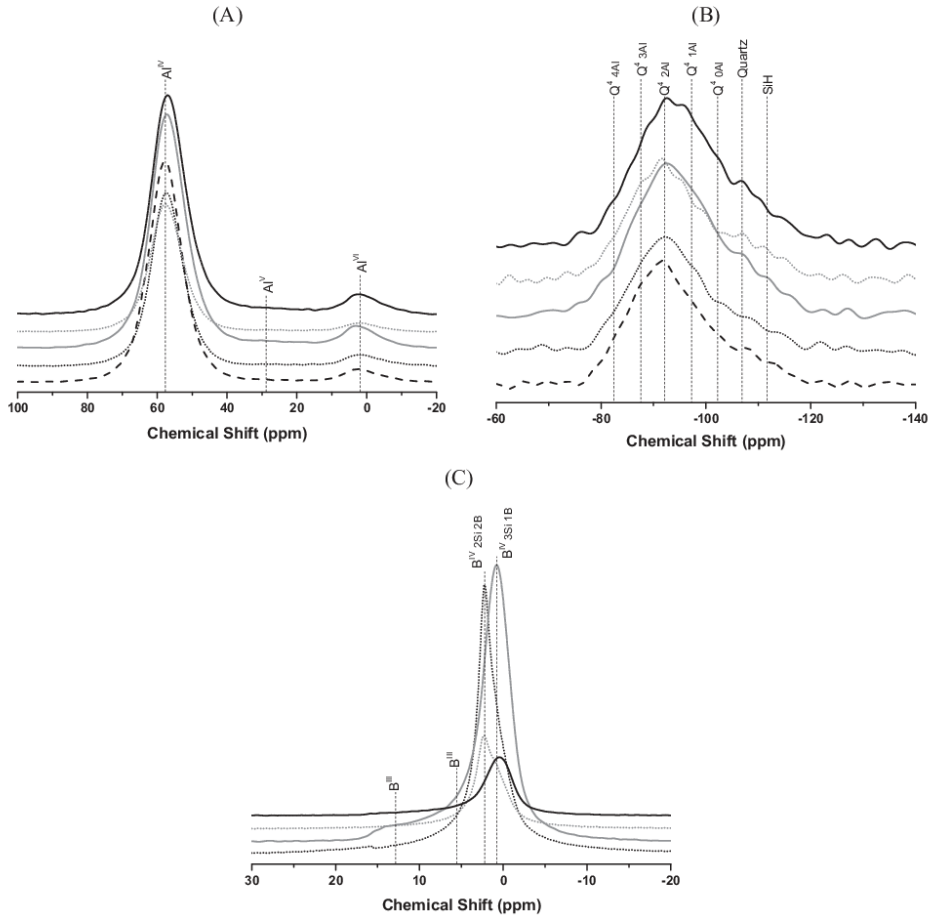


Fig. 4. MAS NMR spectra of (A) ^{27}Al, (B) ^{29}Si and (C) ^{11}B nuclei in the (– –) GK, (····) LiB$^{3.7}$, (——) NaB$^{10.0}$, (·–·–) CaB$^{6.1}$ and (—) B$^{2.8}$ samples.

alkaline ions in silicate solutions. Raman spectroscopy was performed on alkaline silicate solution in the presence of the different additives (Fig. 7) to observe the polymerization evolution of the silicate solution. The reference silicate solution used for the GK sample preparation presents two large contributions. The first one, at 900 cm^{-1}, is associated with Q^2 Si species [58,59], and the second one, between 1000 and 1050 cm^{-1}, is associated with Q^3 and Q^{3c} contributions (Q^{3c} correspond to Q^3 species with a cyclic geometry) [60,61]. The ratio between the Q^2 and Q^3 species defines the reactivity of the solution [62]. Compared to the reference solution of the GK sample, the solution to which sodium tetraborate was added exhibited an increase in the Q^3 and Q^{3c} contributions associated with extensive polymerization of the siliceous species. This result is in agreement with the lower reactivity of the sodium tetraborate solution than the reference solutions. With the use of lithium tetraborate, the amount of Q^2 species is similar, leading to the same reactivity. Consequently, the use of lithium tetraborate does not change the solution reactivity, and the setting time remains similar to that of the GK sample. Furthermore, with sodium tetraborate, the lower reactivity of solution induces lower geopolymerization and an increase in setting time.

The formation of a secondary network in the presence of an additive can explain the variation in the setting time of the various mixtures. The phosphate-based additives lead to the appearance of disorder as well as a crystalline compound previously identified as $KAlP_2O_7$ [9]. The boron-based additives induce the formation of some boron atoms in the geopolymer network and generates other NBO atoms.

4.3. Relation between the pH value and the structural evolution

According to research by J. Davidovits [2], the geopolymer elementary formula can be described as $M_n[(SiO_2)_z(AlO_2)]_n wH_2O$ (M the alkaline cation, n the polymerization degree, z the Si/Al ratio and w the water amount). The polymerization rate, n, strongly depends on the Si/Al *ratio*, z, due to the lack of charge induced by the presence of aluminum in the structure. It is therefore supposed that the pH value is related not only to the available alkali content but also to the Si/Al ratio. In this study, it was demonstrated that four-coordinated boron can act as a network-forming cation and is thus assimilated to the geopolymer network, which does not need charge equilibrium. However, phosphorous has been mainly associated with the Q^1 1Al position,

Table 5
NMR spectral decomposition data for samples with boron-based additives.

Sample		^{27}Al			^{29}Si							^{11}B			
		Al^{IV}	Al^{V}	Al^{VI}	Q^4 4Al	Q^4 3Al	Q^4 2Al	Q^4 1Al	Q^4 0Al	quartz	SiH	B^{III}	B^{III}	B^{IV} 2Si	B^{IV} 3Si
$LiBam^{3.7}$	*Position (± 0.2 ppm)*	57.5		1.7	−82.5	−87.5	−92.4	−98.0	−103.7	−108.7	−114.4	13.0	5.5	2.5	0.4
	FWMH (± 0.2 ppm)	11.0		12.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	6.0	6.0	2.4	3.9
	Area (± 3%)	93.3		6.7	9.6	18.7	29.6	19.7	9.6	7.7	5.1	4.8	21.5	45.1	28.6
$LiBcr^{3.7}$	*Position (± 0.2 ppm)*	57.3		1.3	−82.5	−87.5	−92.4	−97.6	−102.7	−107.6	−113.5	13.0	5.4	2.3	0.3
	FWMH (± 0.2 ppm)	10.8		11.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	6.0	6.0	2.0	3.4
	Area (± 3%)	92.8		7.2	7.7	16.3	26.6	20.4	10.9	10.5	7.6	3.7	14.4	50.6	31.3
$NaB^{10.0}$	*Position (± 0.2 ppm)*	57.0		2.3	−81.7	−87.5	−92.4	−97.6	−102.4	−107.5	−113.6	13.0	5.7	2.3	0.4
	FWMH (± 0.2 ppm)	12.0		12.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	5.6	6.0	2.0	3.4
	Area (± 3%)	91.8		8.2	8.0	17.7	26.5	20.7	11.2	9.9	6.0	4.1	10.6	15.3	70.0
$NaB^{5.0}$	*Position (± 0.2 ppm)*	57.6		1.6	−81.7	−87.4	−92.6	−97.6	−102.6	−107.7	−114.2	13.0	5.4	2.5	0.5
	FWMH (± 0.2 ppm)	11.1		11.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	6.0	5.8	2.0	3.4
	Area (± 3%)	94.4		5.6	8.9	21.2	28.0	16.5	11.0	9.1	5.3	4.3	20.6	49.0	26.1
$CaB^{6.1}$	*Position (± 0.2 ppm)*	57.6		1.8	−81.7	−87.5	−92.5	−97.8	−102.6	−107.5	−113.8	13.0	5.4	2.5	0.5
	FWMH (± 0.2 ppm)	11.0		11.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	5.6	6.0	2.0	3.4
	Area (± 3%)	94.1		5.9	9.5	20.5	27.2	17.1	8.4	10.8	6.5	2.6	16.7	40.4	40.3
$B^{2.8}$	*Position (± 0.2 ppm)*	56.9		1.8	−81.7	−87.5	−92.2	−97.6	−102.4	−107.5	−114	13.0	5.7	2.3	0.4
	FWMH (± 0.2 ppm)	11.5		12.3	7.0	7.0	7.0	7.0	7.0	7.0	7.0	6.0	6.0	2.0	3.4
	Area (± 3%)	90.9		9.1	7.5	16.3	25.2	23.5	10.4	11.0	6.1	3.2	13.6	10.4	72.8
$B^{1.4}$	*Position (± 0.2 ppm)*	57.1		1.3	−81.7	−87.5	−92.2	−97.3	−102.4	−107.8	−114	13.0	5.4	2.7	0.5
	FWMH (± 0.2 ppm)	11.2		12.3	7.0	7.0	7.0	7.0	7.0	7.0	7.0	6.0	5.8	2.0	3.4
	Area (± 3%)	90.9		9.1	9.2	18.4	25.7	20.2	10.1	10.6	5.8	3.9	20.2	37.3	38.6

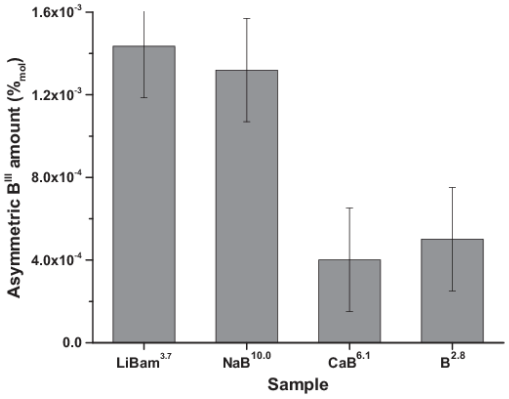


Fig. 5. Evolution of the B^{III} asymmetric boron amount, in molar percent, for the different boron-containing samples.

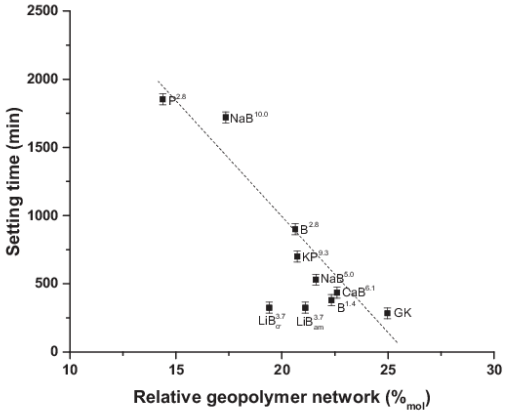


Fig. 6. Evolution of the setting time according to the difference between the geopolymer network amount and the amount of network formed by the forming cation.

which balances a negative charge induced by aluminum. To explain the pH value variation, the Si/Al ratio was calculated based on the following hypothesis: the boron atoms were added to the silicon, and the contribution of phosphorous was subtracted. The (Si + B^{IV} – P-1Al)/Al *ratio* (hereafter named charge balance) was plotted as a function of pH value (Fig. 8.A).

The reference geopolymer, GK, presents a charge balance of 1.45. The addition of phosphate-based additives resulted in a decrease in this charge balance to close to 1.38 and a decrease in pH. This evolution perfectly underlines the phosphate effect on pH value. The addition of boron simultaneously involves an increase in this charge balance up to 1.68 and a decrease in pH value. Nevertheless, the pH value is directly linked to the (Si + B^{IV} – P-1Al)/Al *ratio*, implying the free alkali amount. Only the two samples containing the lithium tetraborate do not seem to be directly influenced by this charge balance but still induce a pH value decrease. This fact could be explained by the small size of lithium ions, which could be randomly distributed in tetrahedral or interstitial positions within the [SiO_4] environment [63]. If lithium is located inside the network, it should equilibrate the tetrahedral charges, resulting in a lower amount of negative charges and consequently a higher charge balance value. With amorphous lithium tetraborate, the difference observed in the pH value decrease/charge balance relation can be explained by these interactions with lithium ions. Indeed, if the hypothesis that half of the lithium ions truly compensate for an aluminum charge defect is made, it will lead to a charge balance of 1.71 (calculated by subtracting the amount of supposed compensating lithium from the aluminum amount in the charge balance calculation). However, crystalline lithium tetraborate displays a higher pH value than amorphous lithium tetraborate. This difference should be associated with the behaviour of the crystalline lithium tetraborate in solution. Indeed, Raman spectroscopy (not given) shows that the crystalline lithium tetraborate is not dissolved in the alkaline silicate solution, which can explain the lower impact of the lithium ions from the crystalline tetraborate compound.

To describe the pH value evolution in these samples, the asymmetric

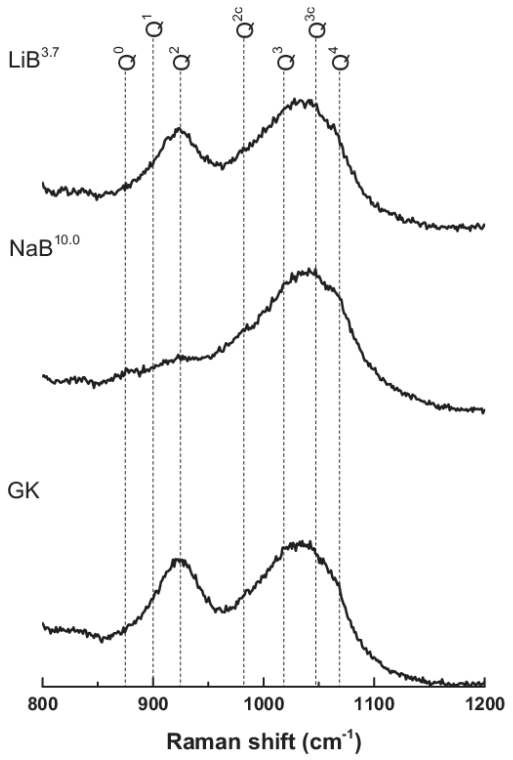


Fig. 7. Raman spectra of the silicate solutions associated with the GK, NaB^{10} and $LiB^{3.7}$ samples.

B^{III} amount was also plotted in Fig. 8.B. A linear relation between the pH value evolution and the amount of these B^{III} atoms is observed (**Part.III.3.**). Indeed, asymmetric B^{III} provides NBO atoms associated with a negative charge, which should be compensated by an alkaline cation. Thus, the increase in the content of asymmetric B^{III} atoms and the resulting interactions cause the pH value decrease observed in the boron-based samples. Crystalline lithium tetraborate does not present the same relation between pH value and asymmetric B^{III}. As described in the previous paragraph, this difference is considered associated with the low solubility of crystalline lithium tetraborate in the mixtures.

The pH value evolution is thus related to the tetrahedral network based on Si-O/Al/P/B, where Si, Al, and B^{IV} act as network-forming cations. In parallel, the asymmetric B^{III} and P Q^1 1Al defined the charge balance by bridging or not bridging the alkali cation.

5. Conclusion

The addition of phosphate- and boron-based compounds to a geopolymer reference material induced structural changes that were studied by NMR. These modifications are correlated to the setting time and pH value of the various binders. The main NMR data (^{29}Si, ^{27}Al, ^{31}P and ^{11}B) are reported below:

(i) The Al^{IV} environment decreases in the presence of the mineral additives, supposing a lower amount of geopolymer network. This effect is enhanced with the use of orthophosphoric acid, leading to the presence of residual Al^{V}. All the ^{29}Si NMR spectra indicate a slight decrease in the number of alumina-silica bonds to the benefit of silica-silica bonds. This finding confirms that the geopolymer network amount is reduced in the presence of additives.

(ii) ^{31}P analysis shows the presence of phosphate groups (PO_4^{3-}) and P Q^1 (bonds to Al and/or Si and/or K) in the samples. More precisely, the P Q^1 1Al species are supposed to be at the terminal of the aluminosilicate chains, resulting in partial geopolymerization. This amount induces the formation of a secondary network, involving an increase in setting time.

(iii) The main environments of the ^{11}B spectra are characteristics of boron atoms in a tetrahedral environment (B^{IV}) connected to silicon tetrahedrons. The differences between the geopolymer network and the secondary network, related to the B^{IV} amount, were identified as responsible for the setting time increase. Among the residual B^{III} species, the presence of asymmetric B^{III} with one nonbridging oxygen is distinguished in relation to the pH value decrease.

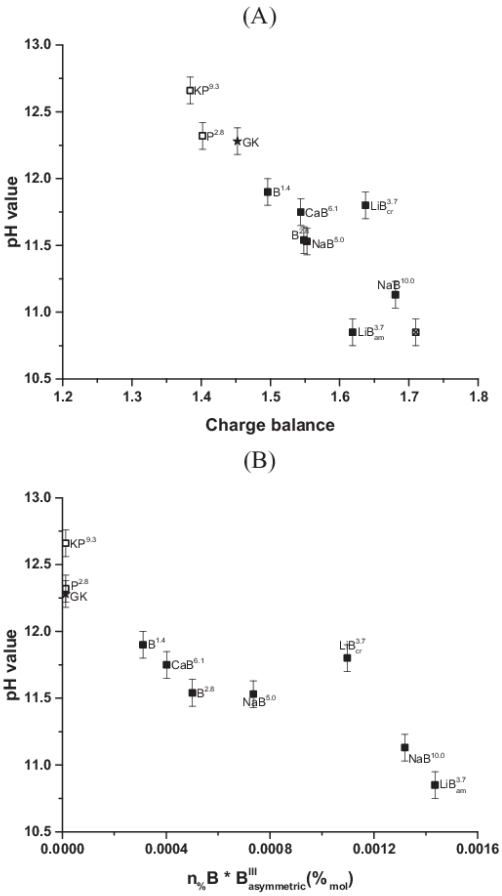


Fig. 8. Evolution of both (A) charge balance and (B) the amount of asymmetric B^{III} with the pH value for the ⋆ GK sample, (□) phosphate-based samples and (■) boron-based samples (error +/− 0.1 pH unit). ⊠ corresponds to the pH calculated for $LiBam^{3.7}$.

The various environments of the various additives are able to predict the setting time and the pH value.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jnoncrysol.2019.119541.

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Determination of the reactivity degree of various alkaline solutions: chemometric investigation.

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Determination of the reactivity degree of various alkaline solutions: a chemometric investigation

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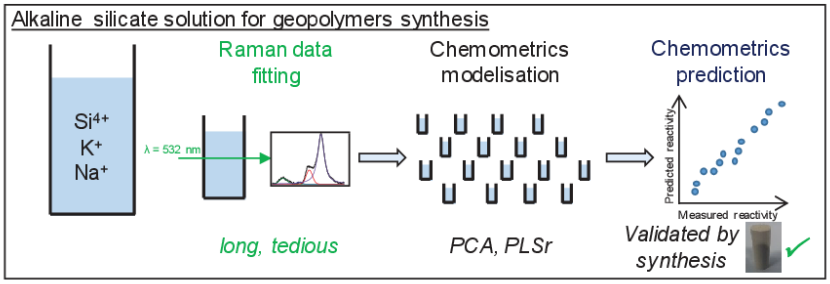
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Alkaline silicate solution *Reactivity* *Raman spectroscopy*

PLS regression *Chemometrics* *Geopolymer*

Graphical abstract



Abstract

Knowledge of alkaline silicate solutions is crucial in order to optimize geopolymer properties. Geopolymers are new binders resulting from the activation of an aluminosilicate by an alkaline solution. It is well established that the solution reactivity strongly affects the geopolymerization and therefore the geopolymer working properties. As a consequence, an evaluation of the reactivity degree of alkaline silicate solutions prior synthesis is of the utmost interest. However, the determination of the solution reactivity is currently tedious, and for geopolymer commercialization, it would be necessary to find an easy way to determine it. Therefore, Raman spectroscopy combined with chemometric techniques is proposed as a solution to easily determine the alkaline silicate solution reactivity. To conduct this investigation, 65 silicate solutions were characterized by Raman spectroscopy, and reference values of their reactivity degree were determined. Finally, principal component analysis (PCA) and partial least squares regression (PLSr) were performed to build a statistical model able to predict the alkaline silicate solution reactivity from Raman spectra.

I. Introduction

Alkaline silicate solutions are used in various industrial applications, including binder gel formers, coatings, deflocculants and corrosion inhibitors [1, 2, 3]. Recently, alkaline silicate solutions have also emerged as precursors for geopolymer synthesis. Geopolymers, which are innovative materials, result from the alkaline activation of an aluminosilicate source at room temperature [4]. Its formation implies the dissolution of aluminosilicate species in an alkaline environment to form an amorphous network by polycondensation reactions [5]. Therefore, alkaline silicate solution reactivity is one of the most important parameters for geopolymer formation. Thus, the impact of alkaline silicate solutions (nature of the alkali cation, Si/M ratio (given M=K or Na), alkali molar concentration, etc.) on geopolymer working properties has been highly demonstrated [6, 7]. The nature of the alkali cation affects the geopolymerization reaction and therefore the geopolymer working properties. For example, the large size of the potassium cation enhances the polycondensation reaction, leading to a stronger network. Moreover, the Si/M ratio of the solution modifies the alumina incorporation into the matrix [6]. Several studies on silicate solutions have demonstrated that the reactivity degree can be estimated using Raman spectroscopy and a fitting procedure [8, 9, 10]. Indeed, this spectroscopic characterization of siliceous species provides information about monomers and oligomers [11]—more specifically, those having 3-, 4- or 5-membered rings [10]. The alkaline silicate solution reactivity degree (depending on the nature of siliceous species) is impacted by various parameters, such as the Si/M molar ratio, the dilution level and the alkaline cation [12, 13]. Vidal et al. [12] have demonstrated that highly depolymerized solutions are highly reactive, which leads to the formation of different geopolymer microstructures. The amount of rings and chains of the alkaline silicate solution is affected by the preparation method and the alkali cation [13]. In addition, previous studies have highlighted the effect of siliceous species, especially the chain and ring ratio on geopolymer setting time [14]. Therefore, the chain and ring concentrations can be associated with alkaline silicate solution reactivity for geopolymer preparation. The estimation of the reactivity degree of an alkaline silicate solution being mainly based on a spectral fitting is a long and tedious operation. However, to commercialize geopolymers, it is necessary to find an easy way to determine the solution reactivity and monitor the solution evolution to predict the resulting properties of the geopolymers.

Chemometric methods, introduced by Svante Wold in 1972 [15], are useful to extract relevant information associated with the samples and variables of a dataset. Chemometric analyses are combinations of mathematical and statistical methods that permit to extract maximal chemical information from data sets. These methods also allow the prediction of a parameter from spectroscopic data. Principal component analysis (PCA), the most classical approach for treating multivariate data, can be used as an exploratory data analysis tool. Indeed, it is a good method to visualize distributions of samples and variables in a multivariate space [16, 17]. Chemometric methods have been widely applied as explorative approaches and predictive ones in infrared (IR) or Raman spectroscopy [18, 19, 20].

Chalmers and Wilton [21] have demonstrated that the conjunction between vibrational spectroscopy, such as Fourier transform infrared (FTIR) and Raman spectroscopies, and chemometrics is a powerful tool for the chemical and physical characterization of polymers. Partial least squares regressions (PLSr) attempt to relate instrumental signals, such as Raman spectra, to dependent variables, such as the reactivity degree, using a score matrix [16, 17]. PLSr allows modeling the relation between an acquired spectral data matrix **X** and a property of interest ***y***.

PLS regressions have also been used in the pharmaceutical industry to determine the amount of active compound in tablets from near infrared and Raman spectra [22, 23]. Chemometrics has also been extensively developed in the agrofood industry. For example, Raman spectroscopy coupled with chemometrics enabled discrimination between chemically strongly related oils [24]. Similarly, Raman spectroscopy with chemometric methods allowed the discrimination and quantification of the sugar contents in honey samples [25].

The aims of this study were to explore the complexity of alkaline silicate solutions containing additives using PCA and predict their reactivity with PLS regression methods.

II. Material and methods

1. Raw materials and sample preparation

The present work involved six commercial alkaline silicate solutions based on potassium and/or sodium, supplied by Woellner (Woellner GmbH, Wöllnerstraße 26, D-67065 Ludwigshafen, Germany) (**Table 1)**. These solutions were described by their Si/M molar ratio (given M=K or Na), which were initially between 1.68-0.66 depending on the solution. From the six commercial solutions, 65 solutions were prepared by adjusting the Si/M ratio from 1.68 to 0.50 (by dissolving hydroxide pellets, KOH or NaOH into the solution). Three replicates of the 65 solutions were prepared leading to a total number of 195 solutions which were spectrally analyzed and then used to develop a reactivity prediction model. Moreover, an independent test set, composed of 65 other solutions, was prepared separately and used to estimate the accuracy of the PLSr model. Therefore, several parameters were varied, including the nature of the cation, the Si/M molar ratio and the alkali molar concentration.

The nomenclature used is $S_{X,Y}^{m}$, where S_X is the silicate solution type (S_1, S_2, S_3 or S_4), Y is the introduced alkaline cation (K or Na) and m is the Si/M molar ratio.

Table 1. Data of **(A)** the raw alkaline silicate solutions used and **(B)** the solution with adjusted Si/M molar ratio.

(A)

Name	Cation in solution	Density ($g.cm^{-3} \pm 0.02$)	Water content (%)	*m* (Si/M)
$S_{1.K}$	K	1.18	0.79	1.68
$S_{1.Na}$	Na.K	1.18	0.79	1.68
$S_{2.K}$	Na.K	1.36	0.64	1.71
$S_{3.K}$	K	1.51	0.59	0.66
$S_{4.K}$	Na.K	1.34	0.62	1.68
$S_{4.Na}$	Na.K	1.34	0.62	1.68

(B)

Name	Number of solutions	Density range ($g.cm^{-3} \pm 0.02$)	Si/M range
$S_{1.K}^{m}$	13	1.18 - 1.37	0.50 - 1.68
$S_{1.Na}^{m}$	13	1.18 - 1.37	0.50 - 1.68
$S_{2.K}^{m}$	13	1.36 - 1.59	0.50 - 1.71
$S_{3.K}^{m}$	3	1.51 - 1.56	0.50 - 0.66
$S_{4.K}^{m}$	12	1.34 - 1.50	0.58 - 1.68
$S_{4.Na}^{m}$	12	1.34 - 1.53	0.58 - 1.68

2. Technical characterization

Spectral acquisition

Raman spectroscopy was performed on the silicate solutions using an In Via Reflex Renishaw spectrophotometer with a 532-nm laser operating on the sample at a power of 40 mW. Scattered light was collected in backscattering mode using a triple monochromator equipped with a 2400-lines/mm diffraction grating. The spectral range was 200 to 1400 cm^{-1}, and the acquisition time was 5 s. The analysis cells were changed after 30 analyses. For a given solution, Raman acquisition was performed on three independently prepared samples.

Raman spectra of pure silicate solutions ($S_{1.K}^{1.68}$ and $S_{1.K}^{0.50}$) are presented in **Figure 1**. According to the literature, the contribution located at 325 cm^{-1} is attributed to the M-O- bonds **(Table 2.)** [26]. The bands observed near 440, 550, 600, 500 and 645 cm^{-1} are assigned to the ring breathing mode of a ring with 5 or more tetrahedral bonds (denoted R_5 or more), R_3, R_4 [27, 23, 15, 28], the ν(Si-O-Si) stretching mode of the chains ($C_{5,6,7}$) [29] and monomer contribution (ν(Si-O)) [30], respectively.

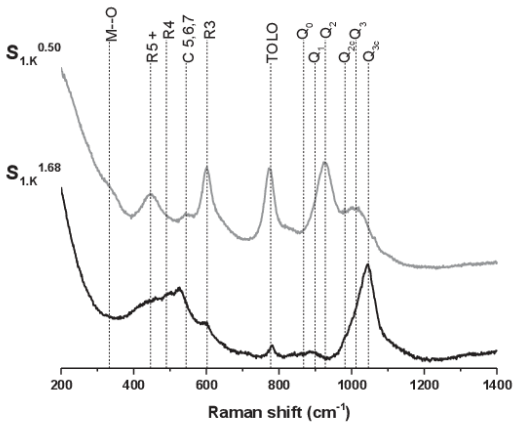


Figure 1. Raman spectra of pure silicate solutions with different Si/M ratios.

Table 2. Raman contributions of the alkaline silicate solutions used.

Contribution	Position (cm^{-1})	References
M-O (–M^+ O^-–) (network modifiers)	340–360	[30]
$\delta[R_{5\text{ and more}}]$	400–490	[31]
D_1 ($\delta[R_4]$)	453–550	[31]
υ_s (Si-O-Si) $C_{5.6.7}$	515–535	[32]
D_2 ($\delta[R_3]$)	587–606	[11, 33]
υ_s (Si-O) Monomers	639–649	[32]
υ Si-O-Si (TO-LO)	650–850	[34]

Spectral fitting procedure and reactivity degree calculation

In geopolymer science, the chain and ring concentrations can be linked to the alkaline silicate solution reactivity [14]. Therefore, to estimate the reactivity degree, the $\frac{R_3+R_4+R_5}{C_{5,6,7}}$ ratio is calculated with the areas of the R_3, R_4, R_5 and $C_{5,6,7}$ spectral contributions. The various spectra were decomposed using Wire software (Renishaw inc., version 4.3) [13]. First, spectra were corrected by subtracting the baseline modeled by a 5-degree polynomial curve. Second, spectra were decomposed considering various pseudo Voight functions arising from several contributions, as described in the literature [35]. To compare the solutions after decomposition, the different contributions were normalized by the total area in the 250-800 cm^{-1} spectral range. An example of a Raman spectrum decomposition of a silicate solution ($S_{N.K}^{0.9}$) is presented in **Figure 2**, where the black curve corresponds to the recorded spectrum. The decomposition data is composed of the six blue curves (the fit of the six contributions), and the red curve

is the reconstructed spectrum from the addition of the six fitted contributions. This tedious decomposition has been applied on each spectrum of the whole dataset to obtain the reference value of reactivity for all solutions.

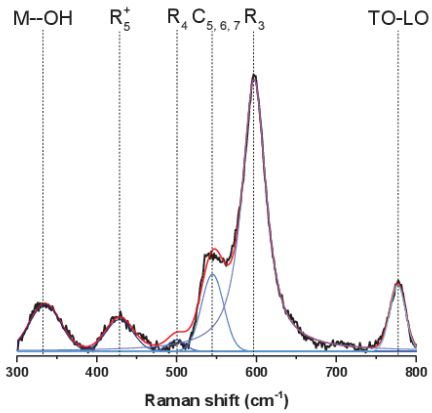


Figure 2. Example of Raman decomposition used for the determination of the reactivity degree ($S_{N.K}^{0.9}$).

2. Data analysis

In this study, chemometric methods were employed for data analysis using the SOLO chemometric software (Eigenvector Research, version 8.6.1) [36]. Raman spectral data of all samples were collected and organized in a matrix **X**. This matrix gathers all the spectral information, i.e., input data related to each sample. A second matrix **y** contains reference values associated with each raw of **X**. As explained previously, reference values have been obtained from the calculation of the $\frac{R_3+R_4+R_5}{C_{5,6,7}}$ ratio.

Spectral data preprocessing

In general, Raman spectra have to be preprocessed prior chemometric analysis in order to keep only chemical variances [37]. **Figure 3** displays spectra before and after this pretreatment. This preprocessing has been selected in order to suppress the baseline shift of the spectra, mainly due to fluorescence effect (**Figure 3.a)**. Moreover, only the 300-1200 cm^{-1} spectral range has been considered in order to only focus on the silica and alkaline contributions. Then a Savitzky-Golay second derivative (second order polynomial, 21 points window) has been applied [37, 38, 39]. Finally, a mean centering has been applied on spectra (**Figure 3.b**) [39].

Principal component analysis

The first step of this study was to determine the correct parameter to distinguish all the samples and, more specifically, the solution reactivity. PCA is usually used as an exploratory analysis tool permitting the visualization of the sample distribution in the multivariate space [40, 41]. In this study, the Raman

spectra initially described by 1015 spectral variables (Raman intensity values for 1015 wavenumbers), are reduced using PCA into *p* scores considering the new hyperplane defined by the *p* selected principal components. In other words, these scores are the new coordinates of each spectrum along these *p* dimensions defined by the *p* principal components. The distribution of these scores along principal components allows us to potentially observe groups of spectra in so-called scores plots. Lastly, a spectral interpretation of the extracted principal components makes it possible to link groupings to physical or chemical properties.

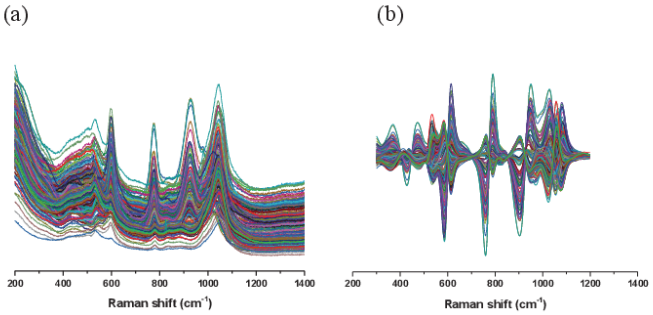


Figure 3. Evolution of the data preprocessing according to the treatment with (a) the original data and (b) the data after the preprocess treatment (truncating, first derivative, mean centering).

Partial least squares regression

In this work a PLS regression method is developed in order to predict the reactivity of unknown solutions or to check the reactivity of old solutions. It consists of developing a mathematical model, i.e. a function predicting the studied property **y** from the spectral matrix **X** of a calibration data set. After the validation of the model by a cross-validation, an independent test set is used to check the possibility to predict the reactivity of the solutions.

The efficiency of this type of model can be evaluated by different methods and figures of merit. During the model elaboration, various parameters are calculated to evaluate its predictive capacity. Three parameters are mainly used: the coefficient of determination (R^2), the root mean square error of calibration (RMSEC) and the root mean squared error of cross validation (RMSECV) [42]. The coefficient of determination corresponds to ratio between the variance explained by the model and the total variance in the data.

III. Results

1. PCA on the dataset

To observe the relation between the Raman spectra and the solution reactivity, a PCA model has been developed (**Figure 4.**). The number of PCs to be considered has been determined considering the captured cumulative variance and the RMSE values (**Figure 4.a**). More specifically, an increase of the PC number from one to four leads simultaneously to a strong increase of the captured variance and to a major decrease in the RMSEC/RMSECV values. Only limited variations of these parameters were observed for additional PCs. As a consequence, an optimal number of four PCs were selected, explaining 98 % of the total variance. Readers interested in the disclosure of more detailed information about the use of root mean square errors for the selection of the optimal number of components should refer to the paper of R. Bro *et al* [43].

Q residuals and Hotelling T^2 values of the PCA model are gathered in **Figure 4.b** with their confidence limits. A large part of the data points (i.e. spectra) is gathered in the confident limits, and the majority of the solution located outside these limits display only a small residual (< 2 %) or a small Hotelling value (< 2.5 %). Outliers presenting both residuals and Hotelling values over the limits (only 5 spectra) were removed before the model calculation.

In this study, only the most useful and interesting PCs to describe the solution reactivity (PC1 and PC3) were exploited. The first PC loading (**Figure 4.c**) presents four significant spectral contributions (in positive and negative due to the derivative) at 600, 780, 920 and 1050 cm^{-1}. These contributions are related to the R_3 ring, the TO/LO, the Q_1/Q_{2c} and Q_3/Q_{3c} contributions respectively [12]. These species describe both the species related to reactive solution (R_3, TO/LO, and Q_1/Q_{2c}) and to weakly reactive solution (Q_3/Q_{3c}) [12]. The third PC exhibits two main contributions (**Figure 4.d**). The first intense peak at 530 cm^{-1} corresponds to the chain, which is the key parameter of the ring/chain *ratio*. The second main peak is composed of two successive variations at 1030 and 1070 cm^{-1}, related to both Q_{3c} and Q_3 contributions. The Q_{3c} species appears when the reactivity increases, so PC3 seems to present a high sensitivity to the solution reactivity [12].

To highlight the chemical information carried by the two PCs, spectra represented as points in the score plot (**Figure 4.e**) are colored according to their reactivity degree calculated with the $\frac{R_3+R_4+R_5}{C_{5,6,7}}$ ratio. More precisely, logarithmic values have been considered in order to take into account a very large range of ratios and ease the interpretation. The first PC is correlated with the reactivity of solutions. However, a small contribution of PC3 is also detected. These PCA results allow confirmation of the ability of the chemometric techniques to discriminate the solution reactivity with Raman spectroscopy measurements. This statistical model provides qualitative information, with a high dependence of chain and ring concentration, on the reactivity. However, in the industry, it is necessary to provide in an automatic away a quantitative or semiquantitative value of the solution reactivity to optimize their use. This first PCA exploration suggests that the $\log(\frac{R_3+R_4+R_5}{C_{5,6,7}})$ value is a way to discriminate the solution reactivity and therefore can be used to construct a PLSr predictive model to easily determine the solution reactivity.

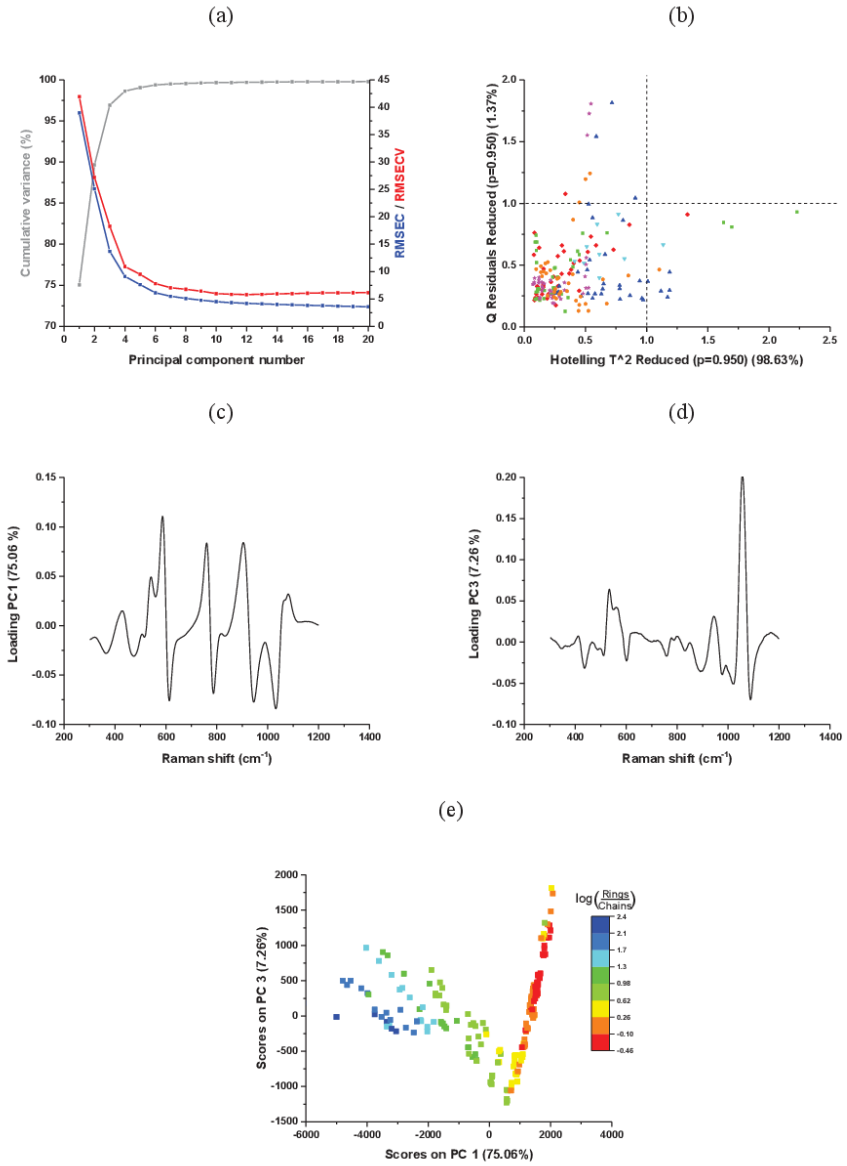


Figure 4. Data relative to the PCA analysis with **(a)** an evolution of the cumulative variance and root mean square errors (RMSEC, RMSECV) according to the number of principal components used, **(b)** the repartition of the sample Q residual vs Hotelling values, (--) confidence limit, (♦) $S_{1.K}$, (■) $S_{1.Na}$, (▲) $S_{2.K}$, (▼) $S_{3.K}$, (★) $S_{4.Na}$, (●) $S_{4.K}$, **(c)** the loading of PC1, **(d)** the loading of PC3 and **(e)** the score plot of PC1 vs. PC3.

2. PLSr on the dataset

A multivariate regression has been used to predict the solution reactivity. The PLSr model has been developed considering a cross validation procedure (Venetian blind technique, 10 data splits and a maximum of 20 latent variables). As a consequence, the calibration set of 195 samples has been used to construct the regression model and the cross-validation step. An independent test set of 65 samples (i.e. unknown from the model) has been used to evaluate its accuracy (**Figure 5**).

Figure 5.a gathers the cumulative variances for **X** and **y** and RMSE values as a function of the number of latent variables (LVs) used. The RMSECV value strongly decreases until seven LVs. Cumulative variances of 99 and 93 % for **X** and **y** are respectively observed in this case. However, experimentally the use of six LVs leads to better hotelling and residuals distributions, with a very small increase of the RMSE (and R^2 / bias values). According to these experimental results, an optimal number of six latent variables has been selected for the predictive model.

Q residual and Hotelling's values of the model are shown in **Figure 5.b**. The large majority of the samples are located in the confident limits. Approximately five percent of the samples present a high Hotelling value ($T^2 > 1$) and less than 10 % present high Q residuals ($Q > 1$). Only two samples present both Hotelling values and residuals out of the confident limits. These outliers (already observed during PCA analysis) have been naturally removed from the calibration set corresponding to less than 5% of the spectra.

Figure5.c,d present prediction results of the constructed PLSr model considering the calibration and the test sets. A very good relation is observed between reference $\mathbf{log}(\frac{R_3+R_4+R_5}{C_{5,6,7}})$ values and predicted ones. During the calibration step, a R^2 value of 0.93 and a RMSEC value of 0.175 have been obtained. For the validation step, a R^2 value of 0.92 and a RMSECV value of 0.187 have been observed. Finally, the test step has allowed us to obtain R^2 and RMSEP values of 0.85 and 0.246 respectively which are very good figures of merit considering the range of the reactivity parameter. This prediction error is analytically acceptable for the estimation of the reactivity degree from Raman spectra. It should be also noted that during calibration, validation and test, observed biases were 0, 2.10^{-4} and -5.10^{-2} respectively and considered as non-significant from a statistical point of view. These results demonstrate that a PLSr model based on Raman spectra can be used for the estimation of the reactivity degree.

After demonstrating that the PLSr model can significantly predict a reactivity value from a Raman spectrum, it is interesting to focus on the spectral data involved by this model. In this aim, the VIP (Very Important Parameter) scores, available in **supplemental material**, have been studied and evidenced that the model is mainly ruled by four main spectral contributions (VIP score > 1) [44]. These contributions are related to silicate chains $C_{5,6,7}$, R_3 rings, TO/LO contribution, Q_1/Q_2 silicon atoms and Q_{3c}/Q_3 silicon atoms.

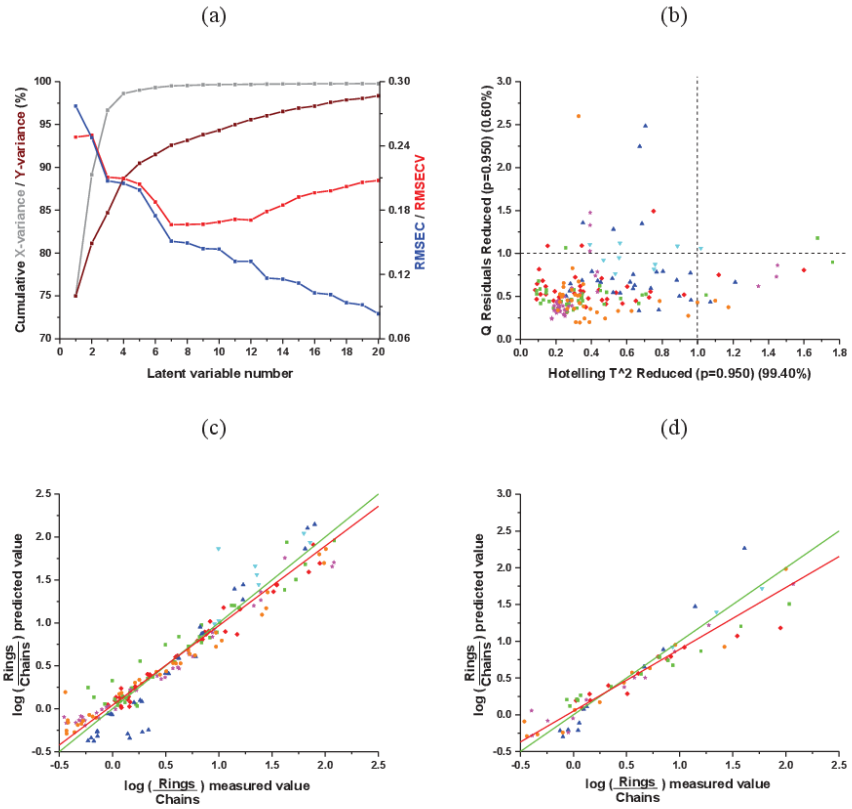


Figure 5. Data relative to the PLSr analysis with **(a)** the evolution of the cumulative variance according to the number of PLS factors, **(b)** the repartition of the sample Q residual vs Hotelling values, **(c)** the predicted vs reference values during the calibration step and **(d)** the validation step. (♦) $S_{1.K}$, (■) $S_{1.Na}$, (▲) $S_{2.K}$, (▼) $S_{3.K}$, (★) $S_{4.Na}$, (●) $S_{4.K}$.

IV. Discussion

A chemometric model based on PLSr has been developed and can potentially predict the ability of a solution to form a consolidated geopolymer. The greatest interest of this model is its ability to predict the geopolymer feasibility as a function of the alkali silicate solution used. Indeed, as observed in the literature, geopolymer formation is highly dependent on silicate solution properties. To link this statistical model to geopolymer formation, six silicate solutions in the range of -0.5 to 2.0 log(rings/chains) have been used to synthetize geopolymers. Therefore, to demonstrate the usefulness of this model, these unknown solutions have also been analyzed by Raman spectroscopy. The prediction of their reactivity degrees is presented in **Figure 6**. It appears that the reactivity degree is well predicted

with the chemometric model. The solutions B, C, E and F present a low value of the log(rings/chains) factor. However, solutions D and A seem to exhibit higher reactivity because the log(rings/chains) factor is approximately 1.7.

The associated geopolymers have been also prepared from these six unknown solutions. **Figure 6.B** presents the consolidation state versus the log(rings/chains) factor. The solutions presenting a log(rings/chains) value from 0.9 to 1.8 are optimal for geopolymer consolidation with optimized working properties. The unconsolidated materials correspond to the results obtained with the predictive PLSr model. Indeed, only the synthetized geopolymers with the A and D solutions have presented a consolidation. Therefore, this chemometric model provides relevant information regarding solution reactivity for geopolymer formation.

(A) (B)

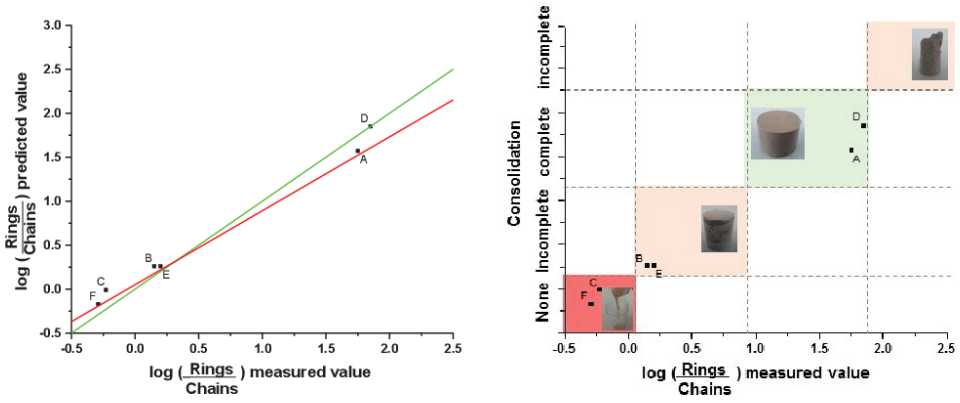


Figure 6. Application of the PLSr model **(A)** predicted vs reference values of the unknown solutions and **(B)** results of the reactivity test by geopolymerization.

Conclusion

Raman spectroscopy combined with chemometric analysis have been used in this study to predict the reactivity of alkaline silicate solutions. To conduct this investigation, 65 silicate solutions were characterized by Raman spectroscopy, and the reactivity degree was first estimated using the spectral fitting method which is the reference one. PCA was first performed to observe all spectral contributions that can be linked to the reactivity degree of the solution. This analysis confirms the discriminatory power of log(rings/chains) value for the chemometric analyses. Then, a PLSr model was developed to determine the reactivity degree of unknown solutions. Based on the good prediction results, six randomly selected solutions were finally analyzed with the same PLSr model. The resulting predicted

reactivities were in total agreement with the feasibility of the geopolymer synthesis from corresponding solutions, which confirmed the PLSr model validity.

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Publication 8 (ACL8)

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Formulation of an alkali-activated grout based on Callovo-Oxfordian argillite for an application in geological radioactive waste disposal.

Construction and Building Materials, submitted

Formulation of an alkali-activated grout based on Callovo-Oxfordian argillite for an application in geological radioactive waste disposal.

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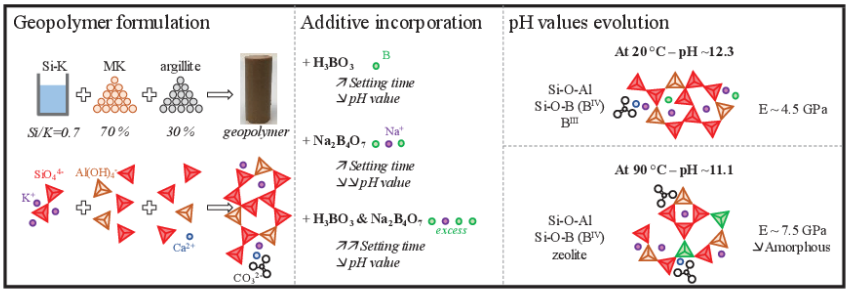
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Geopolymer *Grout* *COx argillite*

Bore *pH value* *Setting time*

Graphical abstract



Abstract

Cigéo is a French disposal project for long-term radioactive waste management in a geological medium composed of Callovo-Oxfordian (COx) argillite. If accepted, the construction of this facility will lead to the excavation of millions of tons of COx argillite, the valorization of which is of interest. In this study, the formulation of alkali-activated grouts based on COx argillite, with a long setting time (up to 24 hours) and a moderate pH value (10-11), is investigated. The first step was to select the reference mixture based on calcined argillite (650 °C) and metakaolin. The selected binder presented an initial setting time of 11 hours and a pH value of 12.7. In this mixture, the addition of 2.5 $\%_{weight}$ boric acid produced a 24-hour setting time. The pH value decreased to 12.4 and 12.3 with the incorporation of boric acid and sodium tetraborate, respectively. Finally, samples cured at 90 °C (the high-level waste disposal cell temperature under operating conditions) are studied. The high temperature leads to a decrease in the pH value down to a minimal value of 11.1. Analysis of the cured samples reveals a reorganization of the geopolymer network during the treatment. The formation of zeolite phases in the network, which can trap alkaline cations, is considered and can explain the pH value decrease.

I. Introduction

Cigéo is the geological disposal facility project for radioactive waste managed by the French National Radioactive Waste Management Agency (Andra) for high-level and long-lived intermediate-level radioactive wastes. This disposal is planned to take place 500 m below ground level in a specific geological layer composed of the Callovo-Oxfordian (COx) argillites [1]. If the French authorities accept the project, construction of the facility will lead to the excavation of an enormous amount of COx argillite. This study investigates the valorization of this argillite and presents the formulation of an alkali-activated grout based on COx argillite. Previous works have already studied COx argillite to elaborate on alkali-activated materials. First, Gharzouni *et al.* focused on the thermal treatment of raw argillite to increase the chemical reactivity of these argillites [2]. This thermal treatment (up to 700 °C) contributes to the decomposition of the carbonate species available in argillite and to the formation of calcium oxide. Additionally, the alkali activation of calcined argillite is possible [3]. However, a flash setting time for the alkali-activated argillite samples occurs due to the large amount of calcium oxide in the mixture [4, 5].

The studied grout is planned to be located at the boundary between the geological argillite and the lining of the high-level radioactive waste disposal cell, which features a temperature of 90 °C. This application requires the use of only inorganic compounds and a binder with a low pH value after consolidation (10-11). Moreover, for the injection, the grout needs to possess a moderate viscosity (0.5-5.0 Pa.s) and a high setting time (~24 hours). To achieve these requirements, it is necessary to optimize the binder formulation. First, several studies have assessed the benefit of using a potassium silicate solution to limit the viscosity and increase the setting time of the reactive mixture [6, 7]. The alkalinity also needs to be controlled, and Vance *et al.* have demonstrated that the optimal Si/K *ratio* is between 0.5 and 1.0 [8]. The amount and nature of the aluminosilicate source also present a major influence. The amount of aluminosilicate source is usually expressed by comparison with the amount of silicate solution with the l/s weight *ratio* (liquid/solid). Thus, an increase in the l/s *ratio* leads to a viscosity decrease and a setting time increase. Concerning the nature of the aluminosilicate, Hemra *et al.* and Perna *et al.* provided evidence that the incorporation of 50 $\%_{weight}$ fly ash reduced the setting time from 190 to 25 min and that the incorporation of 33 $\%_{weight}$ ground granulated blast furnace slag reduced the setting time from 720 to 120 min [9, 10]. These changes are mainly due to the large amount of available calcium in these sources, as in the argillite-based samples [5]. The presence of calcium can lead to the formation of calcium-silicon bonds or to the precipitation of secondary phases [4, 11]. Controlling the binder pH value is more complicated. To decrease the alkalinity, it is necessary to reduce the amount of alkaline species, which are mainly provided by the silicate solution. The decrease in the solution alkalinity is limited by its reactivity, which requires a minimal value to dissolve the mineral source [12]. The use of metakaolin, i.e., acid clay, is preferred to limit the mixture alkalinity [13]. Indeed, the use of a high calcium content mineral source usually leads to an increase in the pH value [5, 14].

Thus, the use of additives is required to reach the desired properties. In this study, analyses have been performed to control these parameters in a metakaolin-based geopolymer. The use of boron-based additives, mainly boric acid and sodium tetraborate, has been demonstrated to efficiently increase the setting time and limit the pH value [15]. This study confirms the results of Antoni *et al.*, who demonstrated that in fly ash-based geopolymers, the addition of 5 $\%_{weight}$ sodium tetraborate can increase the setting time by 100 % [16]. Zajac *et al.* also demonstrated that in cementitious materials, the use of sodium tetraborate can decrease the pH value [17]. Alternatively, different authors have studied the incorporation of borate species in reactive mixtures, not as additives but as mineral sources [18]. Those study showed that the resulting materials usually present a higher setting time due to the low reactivity of the boron-based species [19]. The pH value of the silicate solution can also be limited because a large amount of sodium is provided by the sodium tetraborate [20].

To understand the mechanisms related to the geopolymer setting time increase and pH value decrease in the presence of boron, Dupuy *et al.* studied the structural evolution of samples in the presence of boron [21]. NMR analysis of geopolymers containing lithium tetraborate, sodium tetraborate, boric acid or calcium borate has been performed. Inside the geopolymer network, the boron atoms can exhibit a coordination number of IV inside the geopolymer network or III with a lower connectivity and non-bridging-oxygen atoms (NBO) [18, 21, 22]. From these data, the setting time increase has been related to the formation of a secondary network, based on the Si-O-B bonds, to the detriment of the pure Si-O-Al geopolymer network [21]. The pH value decrease is directly related to the charge balance of the geopolymer, corresponding to the $(Si+B^{[4]})/Al$ *ratio* [21]. Davidovits defined a geopolymer by the following equation: $M_n [(SiO_2)_z (AlO_2)]_n wH_2O$ (where M is the alkaline cation, n is the polymerization degree, z is the Si/Al *ratio* and w is the water amount) [23]. In this equation, z is the Si/Al *ratio,* and the alkali amount, n, is directly associated with the aluminum amount. Thus, in a defined system, an increase in z or the charge balance in the presence of boron limit the amount of alkali in the sample, resulting in a lower pH value.

Therefore, the aim of this work is the development of an alkali-activated grout based on COx argillite and presenting a setting time close to 24 hours and a pH value close to 11. This development starts by the selection of the optimal binder containing metakaolin to limit the flash setting time and high pH value. Then, the incorporation of boric acid and/or sodium tetraborate is studied, and the resulting setting time and pH value evolution are characterized. Finally, the pH value after exposure to 90 °C, which is close to the temperature of the intended final use of the binder, is characterized and discussed.

II. Experimental part

1. Raw materials and sample preparation

This study focuses on the alkaline activation of calcined argillite (650 °C). This argillite, provided by Andra[1], is composed of 52 % clay minerals (interlayered illite/smectite, illite, kaolinite and chlorite), 26 % carbonate species (calcite and dolomite), 20 % quartz and some traces of pyrite, feldspar and hematite [1]. Gharzouni *et al.* studied the thermal evolution of this argillite during calcination. [2]. Moreover, previous work has demonstrated that this argillite is chemically very reactive, so to counter this high reactivity, different percentages of metakaolin (M1000 – Imerys[2]), from 40 to 100 $\%_{weight}$, are substituted for the argillite [3].

The alkaline activation is performed with a potassium silicate solution, which presents a Si/K *ratio* of 0.70 (*ratios* of 0.64 and 0.58 can also be used, as specified). In the reactive mixture, two additives can be added: sodium tetraborate ($Na_2B_4O_7$), referred to as NaB, and boric acid (H_3BO_3), referred to as B.

The synthesis starts with the preparation of the silicate solution by the dissolution of potassium hydroxide in a commercial silicate solution (supplied by Woellner[3]). Then, while mixing, the two aluminosilicate sources (argillite and metakaolin) are added to the silicate solution to obtain the reactive mixture. If a mineral additive is required, it is added to the reactive mixture during mixing. Then, the samples are named $GM1_xA650_y B_a NaB_b$, with x and y represents the percentages of metakaolin (M1) and argillite (A650), respectively. In the presence of additives, a and b correspond to the additions (in $\%_{weight}$) of boric acid and sodium tetraborate, respectively.

2. Sample characterization

All the pH values of consolidated samples were measured at 20 °C after seven days of immersion in water with a sample/water mass *ratio* of approximately 0.5. Measurements were performed on samples subjected to two treatments: at 20 °C and after treatment at 90 °C. At 20 °C, seven-day-old samples were directly placed in water for the measurement. For the treatment at 90 °C, seven-day-old samples were placed in an oven (90 °C) for 12 hours and then immersed in water at 20 °C. All the measurements were performed with a pH-meter WTW 3310 and a specific sensor for extreme pH values (calibrated to the 10-13 range).

The setting time values were obtained with several viscosity measurements throughout the consolidation time. Acquisitions were performed punctually with a Brookfield DV-2T viscometer, and between each measurement, samples were stored in closed vessels on a lab roller (60 round/min). The analysis was stopped when the limit value of 600 Pa.s was reached. Then, viscosity curves as a function

[1] Andra, 92298 Châtenay-Malabry, France.
[2] Imerys-AGS, F*17270 Clérac, France.
[3] Woellner GmbH, D-67065 Ludwigshafen, Germany.

of time were drawn, and the setting time was measured by the tangent evaluation method (**Figure 1**) [24].

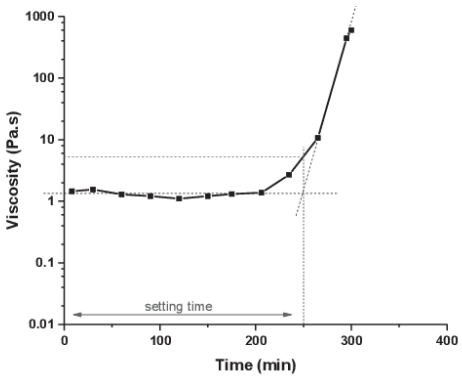


Figure 1. Example of viscosity curve of GM1 sample over time, for the setting time evaluation (viscosity error +/- 1 %).

Magic-angle spinning nuclear magnetic resonance analysis (MAS-NMR) was conducted with a Bruker AVANCE 400 and a 9.4 T magnetic field at frequencies of 128.38 MHz, 79.49 MHz and 104.26 MHz for ^{11}B, ^{27}Al and ^{29}Si, respectively [2]. ^{11}B, ^{27}Al and ^{29}Si spectra were obtained after single pulse irradiation of 3, 2, and 5 µs, respectively, with a recycling times of 5 s for ^{11}B and ^{27}Al and 10 s for ^{29}Si. Before analysis, samples were ground to a fine powder and dried at 40 °C. Samples were placed in 4 mm ZrO_2 rotors at 10 kHz around an axis inclined at 54°44' with respect to the magnetic field (the MAS technique). The number of scans was chosen to obtain a signal/noise *ratio* higher than 10 (200, 400 and 800 for ^{11}B, ^{27}Al and ^{29}Si, respectively). ^{11}B and ^{27}Al chemical shift values are reported in ppm relative to 0.3 M H_3BO_3 and 1.0 M $AlCl_3$ aqueous solutions, respectively, and ^{29}Si chemical shift values are reported relative to tetramethylsilane (TMS).

Spectral decomposition was performed with Dmfit software [25], taking into account only the central part of the spectrum in all cases. Relative intensities, positions and line widths of different components were determined with a nonlinear least square iterative method.

Compressive strength was measured by an Instron 5969 universal testing machine with a crosshead speed of 0.5 mm/min and a 50 kN sensor. For each composition, five samples with a cylindrical shape ($\Phi/H = 0.5$) were tested. The samples were aged for 28 days in a closed mold at room temperature. The thermally cured samples were exposed to 90 °C for 12 hours before rectification. The ultrasonic contact echography technique was used to determine the Young's modulus of the samples [26]. In this process, samples with various thicknesses (from 5 to 8 mm) were placed successively between two couples of transducers (longitudinal and transverse) operating at 600 kHz. The time delay of the waves based on

the thickness of the studied specimen was measured, and the Young's modulus was calculated from the longitudinal and transverse velocities and bulk density.

A Bruker-D8 Advance presenting a Bragg-Brentano geometry and Cu $K_{\alpha1\alpha2}$ detector was used to obtain the X-ray patterns. The analytical range was between 10° and 50° (2θ) with a step of 0.02 ° (2θ) and a dwell time of 1.5 s. Phase identification was performed with Powder Diffraction File (PDF) data from the International Center for Diffraction Data (ICDD).

Fourier transform infrared (FTIR) spectra were obtained with a Nicolet i10 with a transmission modulus and KBr pellets. The spectra were recorded between 400 and 4000 cm^{-1} by 128 scans with a 4 cm^{-1} resolution. *In situ* FTIR measurements were performed on a Nicolet 380 spectrometer equipped with an attenuated total reflectance module. The following of the structural evolution during the first hours of polycondensation were performed with spectra acquisition every 10 min for 13 hours (64 scans per acquisition). The atmospheric CO_2 contribution was removed between 2280 and 2400 cm^{-1} and replaced by a straight line [27].

III. Results

1. Binder formulation without additives

To develop the proposed grout, the first step is to formulate the binder without additives. To achieve the high setting time, low pH value and highest possible amount of argillite, several binders based on different Si/M ratios and argillite amounts were tested. The resulting setting times and pH values are reported in **Figure 2** as functions of the aluminum and potassium concentrations, respectively.

In terms of setting time (**Figure 2. A**), an increase in the Si/K *ratio*, from 0.58 to 0.70, induced a limited increase in the setting time, from 500 to 600 min. Larger variations are observed with the increase in the metakaolin content (40 to 80 $\%_{weight}$), resulting in an increase from 540 to 650 min. However, for all samples, the increase in setting time is proportional to the increase in the aluminum concentration in the reactive mixture. This change is not only related to the aluminum content but also to the presence of some alkaline earth elements, which should be taken into account to explain this behavior. In effect, the setting time should decrease with increasing aluminum content [28]. In the case of the Si/M increase (M = alkali ion), the increase in aluminum concentration is due to the decrease in potassium concentration, which reduces the reactivity of the alkaline solution [25, 29]. For samples with different metakaolin percentages, the increase in aluminum concentration in the sample is related to the decrease in the argillite amount. Indeed, argillite presents a low aluminum content (~13 $\%_{weight}$) but a high alkaline earth cation content (~13 $\%_{weight}$) [1]. The presence of calcium and magnesium induces kinetic changes during geopolymerization, resulting in faster setting times. **Figure 3** presents *in situ* FTIR spectroscopy results with the initial and final spectra. The first broad peak, from 3200 to 3400 cm^{-1}, is associated with –OH stretching, and another –OH contribution, related to water molecule bending, is visible at 1650 cm^{-1}

[30]. These two contributions decrease in intensity during the polycondensation reactions due to water consumption. Carbonate species at approximately 1400 cm^{-1} are detected due to the interaction between atmospheric CO_2 and alkali cations. The main variation observed over time is related to the position of the Si-O-Si bonds (Q^2 silicone), initially located close to 992 cm^{-1}. The formation of the geopolymer network leads to the formation of Si-O-Al bonds, which results in a shift in the Si-O-Si bonds [31]. The evolution of the Si-O-Si bond position over time is plotted in **Figure 3. B** and allows estimation of the rate (shift value) and kinetics (slope value) of the polycondensation reaction. The $GM1_{0.8}A650_{0.2}$ sample displays both low values for the shift (21 cm^{-1}) and kinetic reaction (slope 0.03 cm^{-1}/min). This behavior is in agreement with previous work on the effect of precursor reactivity [32]. The weak difference in the shift value between $GM1_{0.4}A650_{0.6}$ (26 cm^{-1}) and $GM1_{0.6}A650_{0.4}$ 5 (21 cm^{-1}) samples could be attributed to the decrease in the A650 content. The addition of argillite induces an increase in the magnesium amount, leading to the formation of some magnesium silicate compounds and reducing the shift of the polycondensation reactions [33]. The variation in the slope (from 0.18 to 0.03 cm^{-1}/min) with increasing argillite content illustrates that the kinetic reactions are improved due to the content of rare earth cations. In fact, the setting time is controlled by both the metakaolin and argillite contents.

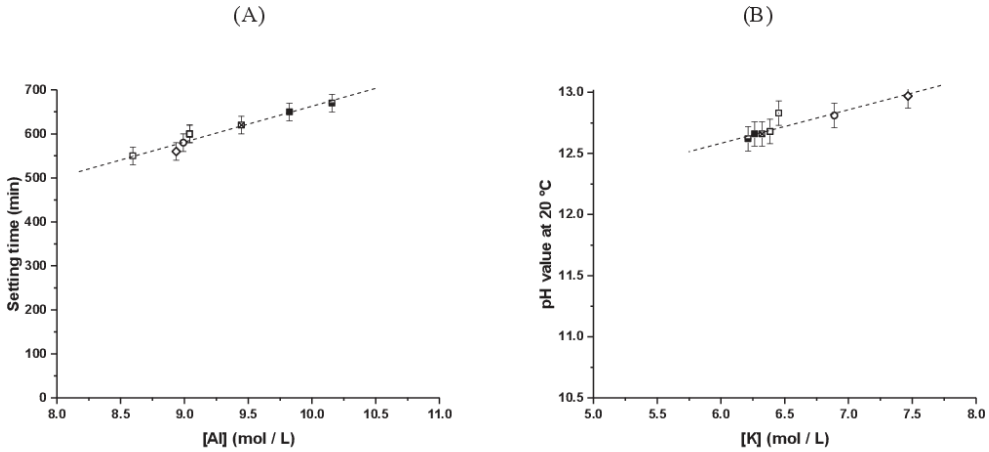


Figure 2. Evolution of **(A)** the setting time in function of the aluminum concentration and **(B)** of the pH value at 20 °C in function of the potassium concentration for $GM1_xA650_y$ samples presenting a Si/K ratio of (◆) 0.58, (●) 0.64 and (■) 0.70 with a rate of metakaolin, x, of (▣) 40 %, (□) 50 %, (▩) 60 %, (▀) 70 % and 80 % (▬).

The evolution of the pH value is described in **Figure 2.B**. The increase of the Si/K *ratio* is the main parameter limiting the pH value, with a decrease from 13.0 to 12.6. The increase in the metakaolin rate also leads to a decrease in the pH value (from 12.8 to 12.6), which is mainly visible between a rate of

40 and 50 $\%_{weight}$ metakaolin. These variations can be related to the potassium concentration in the reactive mixture [25, 34]. Indeed, a decrease in the alkaline concentration leads to a lower pH value. This pattern is limited by the silicate solution reactivity: a too-large decrease in the alkalinity induces weak polycondensation reactions, leading to a partial geopolymerization mechanism, thus resulting in a higher pH value [35]. Therefore, without additives, the setting time is controlled by the aluminum concentrations of the various binders. The pH value can be limited by decreasing the potassium concentration. In this study and according to the previous data, a Si/M *ratio* of 0.70 is selected for the alkaline silicate solution. Concerning the metakaolin amount, a higher content will lead to both a higher setting time and a lower pH value. However, there is no significant difference between 80 and 70 % metakaolin, so the $GM1_{0.7}A650_{0.3}$ sample is selected. To optimize the argillite valorization, sample $GM1_{0.5}A650_{0.5}$ is also studied.

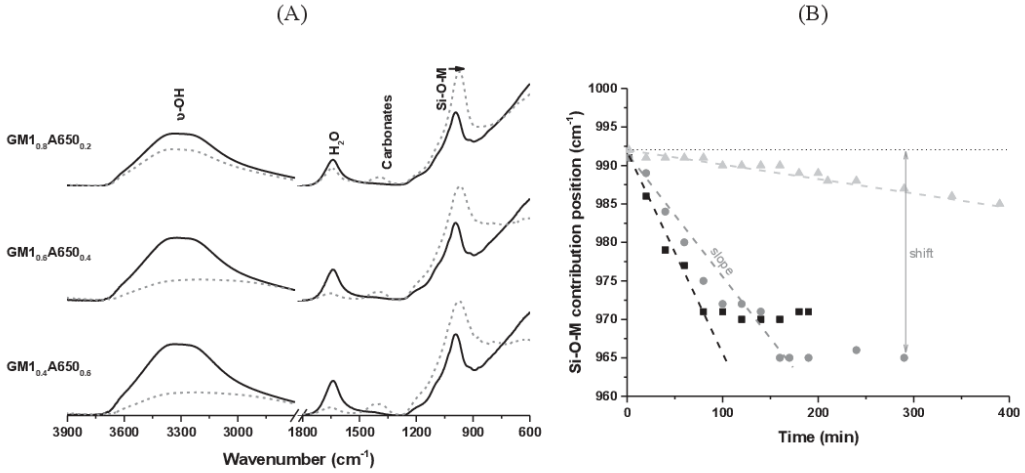


Figure 3. (A) *in situ* FTIR spectroscopy spectra at (——) initial and (- - -) final time and **(B)** evolution of the Si-O-M band value in function of the time for (■) $GM1_{0.4}A650_{0.6}$, (●) $GM1_{0.6}A650_{0.4}$ and (▲) $GM1_{0.8}A650_{0.2}$ samples.

2. Use of additive in the mixtures

To reach both the pH value and the setting time targets, boric acid and/or sodium tetraborate were added to the two selected reactive mixtures ($GM1_{0.7}A650_{0.3}$ and $GM1_{0.5}A650_{0.5}$).

The results are gathered in **Table 1**. Furthermore, to show results of samples subject to conditions similar to closed of the using conditions, pH values are also measured after exposure at 90 °C (12 hours).

Table 1. pH values recorded at 20 and after 90 °C and setting time of $GM1_{0.5}A650_{0.5}$ and $GM1_{0.7}A650_{0.3}$ samples in presence of boric acid and sodium tetraborate.

	pH value (+/- 0.05)				Setting time (+/- 30 min)	
Samples	**$GM1_{0.5}A650_{0.5}$**		**$GM1_{0.7}A650_{0.3}$**		**$GM1_{0.5}A650_{0.5}$**	**$GM1_{0.7}A650_{0.3}$**
Temperature (°C)	*20*	*90*	*20*	*90*	*20*	*20*
Reference	12.74	12.40	12.66	12.12	600	650
$B^{2.0}$	12.41	11.60	12.37	11.34	720	940
$B^{2.5}$	12.48	11.66	12.36	11.28	720	1220
$NaB^{5.5}$	12.27	11.49	12.24	11.19	650	860
$NaB^{7.0}$	12.27	11.41	12.18	11.10	700	940
$NaB^{8.5}$	12.37	11.26	12.25	11.14	680	1080
$B^{1.2}$ $NaB^{7.0}$	12.44	11.41	12.43	11.05	890	970
$B^{1.2}$ $NaB^{8.5}$	12.46	11.34	12.73	11.03	980	2350
$B^{2.0}$ $NaB^{7.0}$	15.54	11.35	12.55	11.13	980	2800
$B^{2.0}$ $NaB^{8.5}$	12.50	11.27	12.46	11.12	1420	4000

Setting time evolution

The setting times of the two reference mixtures $GM1_{0.7}A650_{0.3}$ and $GM1_{0.5}A650_{0.5}$ are 600 and 650 min, respectively. The addition of boric acid or sodium tetraborate increases the setting time proportional to the amount of additive and especially to the amount of argillite in the reactive mixture. In the presence of one additive, $GM1_{0.5}A650_{0.5}$ mixtures present a moderate setting time increase limited to 20 %. With the addition of both boric acid and sodium tetraborate, a larger setting time increase is observed, with a value of over 900 min. The use of the maximal additive amount ($GM1_{0.5}A650_{0.5}$ $B^{2.0}$ $NaB^{8.5}$) results in a setting time of 1420 min (exceeding the target value). The $GM1_{0.7}A650_{0.3}$ samples show a larger setting time increase than the other samples. With the addition of 2.5 $\%_{weight}$ boric acid, a setting time of 1220 min, close to the target value, can be obtained. The $GM1_{0.7}A650_{0.3}$ samples with both additives present far more significant setting time increases, with a maximal setting time of 4000 min for the $GM1_{0.5}A650_{0.5}$ $B^{2.0}$ $NaB^{8.5}$ sample. All the setting times are plotted in **Figure 4** (data from **Table 1**) according to the aluminum and boron molar amounts. The increase in setting time is directly related to the amount of aluminum and boron. Thus, as demonstrated previously, an increase in the aluminum amount results in the geopolymerization thermodynamic effect [36]. Meanwhile, the boron content exerts a major influence on the setting time increase due to the incorporation of boron during oligomer formation. The use of both additives produces a large increase in the boron amount, resulting in a higher setting time. This effect is thought to be linked to the formation of different networks in the sample.

Indeed, the formation of an amorphous boron-based network, mainly connected to silica, has already been demonstrated by several authors [18, 21]. Thus, the use of one additive leads to a significant increase in the setting time, but only one sample, $GM1_{0.7}A650_{0.3}B^{2.5}$, presents an acceptable setting time for the intended application. Nevertheless, for samples containing 50 $\%_{weight}$ argillite, the use of two additives is necessary to reach the target setting time.

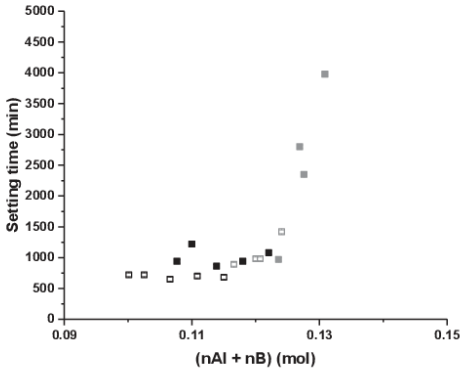


Figure 4. Evolution of setting time according to the aluminum and boron molar amount for (□) $GKM1_{0.5}A650_{0.5}$ and (■) $GKM1_{0.7}A650_{0.3}$ samples in presence of (■) one additive or (■) two additives (error +/- 30 min).

pH value evolution

The incorporation of additives also led to a decrease in the pH value at 20 °C (**Table 1**). Initially, the $GM1_{0.5}A650_{0.5}$ binder presents a pH value of 12.75. The pH values shift to 12.40 and 12.25 with the addition of boric acid and sodium tetraborate, respectively. The $GM1_{0.7}A650_{0.3}$ samples presented an initial pH value of 12.65, decreasing to 12.35 with the addition of boric acid and to 12.20 with the addition of sodium tetraborate. Thus, the use of sodium tetraborate leads to a greater decrease in the pH value. The variation related to the additive amount is not very significant, but lower pH values do not seem to be associated with larger additive amounts. The combination of both additives leads to high pH values, possibly due to a large boron excess in the mixtures. The pH values are lower after the treatment at 90 °C. Without additives, the measured pH values are 12.40 and 12.10 for $GM1_{0.7}A650_{0.3}$ and $GM1_{0.5}A650_{0.5}$ samples, respectively. These samples present a significant decrease (0.3-0.5 pH units). However, in the presence of one additive, a greater pH value decrease occurs. The average decreases observed for the $GM1_{0.5}A650_{0.5}$ and $GM1_{0.7}A650_{0.3}$ samples are approximately 0.8 and 1.0 pH units, respectively. A minimal value close to 11.10 is measured for the $GM1_{0.7}A650_{0.3}$ $NaB^{7.0}$ sample. The mixture of both additives does not lead to a significant pH value decrease. However, the $GM1_{0.7}A650_{0.3}$

$B^{1.2}$ $NaB^{8.5}$ sample exhibits a pH value of 11.05. These pH value variations seem to be related to the B / (K + Na) molar *ratio*, as plotted in **Figure 5**. Two groups of pH values, at 20 and 90 °C, can be easily distinguished and display similar behavior, *i.e.,* a decrease in the pH value with an increase in the B / (K + Na) molar *ratio*. This *ratio* describes the amount of glass-forming cation present in the mixture as a function of the glass-modifying cation available in the mixture. This *ratio* is linked to the ability of the formed network to be equilibrated by the available alkaline species. The increase in this value suggests that the boron atoms are able to react during the polycondensation reactions. Thus, the boron atoms need to be compensated by alkaline cations, which are thus not available to increase the pH value. The decrease in the pH value as a function of this *ratio* is confirmed only with the use of one additive. Samples containing both boric acid and sodium tetraborate do not present lower pH values, despite a higher B / (K + Na) molar *ratio*; instead, the pH values of these samples remain stable.

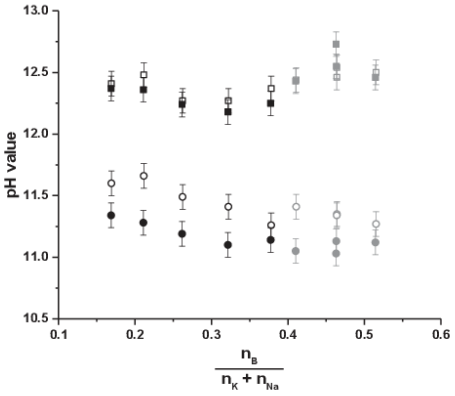


Figure 5. Evolution of the pH value at (■) 20 °C and (●) 90 °C according to the molar *ratio* boron/alkali for (□) $GKM1_{0.5}A650_{0.5}$ and (■) $GKM1_{0.7}A650_{0.3}$ samples in presence of (■) one additive or (■) two additives.

This phenomenon is thought to be related to the change in the reactive mixture due to the presence of a very large amount of boron, alkali and hydrogen cations. To understand these variations, the X-ray patterns of the various samples are shown in **Figure 6**. The sample without additives, $GM1_{0.7}A650_{0.3}$, displays contributions of quartz, illite, microcline, calcite, dolomite and arcanite (K_2SO_4). These phases correspond to the nonreactive components of argillite, with the exception of arcanite, which is formed during geopolymerization [2, 3]. A large amorphous contribution, in the form of the large dome centered at 29° (2θ), is visible [27]. The addition of boric acid, sodium tetraborate or both does not lead to the formation of a new crystalline phase but rather a decrease in the amorphous contribution. This phenomenon is most obvious in the samples with both additives (illustrated here by $GM1_{0.7}A650_{0.3}$ $B^{2.0}$

$NaB^{8,5}$ sample). The amorphous contribution corresponds to the geopolymer network amount. Its decrease is related to a limited geopolymerization reaction, which seems to be related to an excess of the two additives in the mixtures. This difference could be due to exchange between the two additives and, notably, the counter cation that interacts in opposition (Na and H), promoting the availability of potassium and an increase in the pH value. In fact, the addition of boric acid leads to a lower reactivity of the solution by polymerization [21]. The addition of sodium (tetraborate) once again depolymerizes the solution by modifying the silicate species distribution (chains and rings, observed by Raman spectroscopy) in the solution [25]. In this case, the benefit of the incorporation of both additives is limited.

Thus, the addition of boric acid or sodium tetraborate induces a strong pH value decrease in the various samples. Nevertheless, it is necessary to investigate the strong pH value decrease observed after thermal curing at 90 °C.

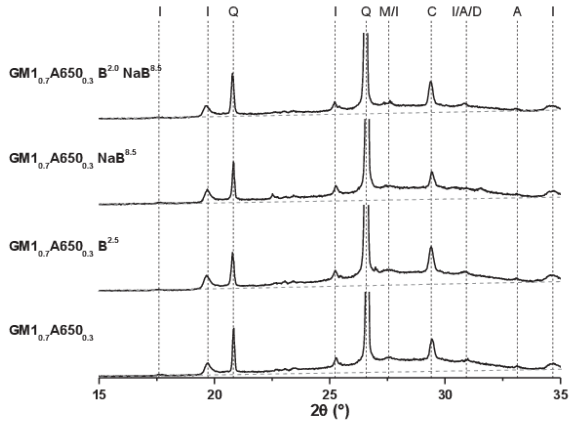


Figure 6. X-ray pattern of $GM1_{0.3}A650_{0.7}$, $GM1_{0.3}A650_{0.7}$ $B^{2.5}$, $GM1_{0.3}A650_{0.7}$ $NaB^{8.5}$ and $GM1_{0.3}A650_{0.7}$ $B^{2.0}$ $NaB^{8.5}$ samples (PDF files: I: illite 04-019-1573, Q: quartz 00-046-1045, C: calcite 04-012-0489, M: microcline 04-011-0523, A: arcanite 04-006-8317 and D: dolomite 04-011-9833).

3. Study of the sample evolution from 20 to 90 °C

To understand the evolution of the pH value and mainly the difference between the values at 20 and 90 °C, further studies have been performed. For these characterizations, five reference samples were selected: GM1, $GM1_{0.5}A650_{0.5}$, $GM1_{0.7}A650_{0.3}$, $GM1_{0.7}A650_{0.3}$ $B^{2.0}$ and $GM1_{0.7}A650_{0.3}$ $NaB^{8.5}$.

Mechanical and density measurements

To characterize the mechanical behavior of the various samples at 20 and 90 °C, the density, compressive strength resistance (σ), Young's modulus (E) and ultrasonic speed (longitudinal and

transverse) were measured (**Figure 7**). The density values of all samples are displayed in **Figure 7.A**. Initially, densities are close to 1.7 g.cm^3 with no significant variation. After curing, these values decrease to values close to 1.2 g.cm^3. Thus, all samples display similar behavior, *i.e.,* considerable water loss and limited dimensional variations.

The compressive strength values are plotted in **Figure 7.A**. At 20 °C, the pure metakaolin geopolymer has a higher compressive strength (42 MPa). The addition of 30 and 50 $\%_{weight}$ argillite induces a strong decrease to 28 and 23 MPa, respectively. These variations are related to the fact that the amount of reactive species in the argillite is less than the amount of Al and Si available in metakaolin, which leads to a weaker network [2, 3]. The incorporation of an additive also leads to a loss of mechanical properties, with a compressive strength close to 17 MPa. The decrease detected in the presence of argillite is due to the small amount of available aluminum, limiting the sample polycondensation [2]. With the addition of boron, the compressive strength decreases. This process is related to the modification of the polycondensation reaction by the boron species, in accordance with the X-ray diffraction results (**Figure 6**) [18, 22]. After treatment at 90 °C, the mechanical strength values increased significantly. These variations, associated with the density values, indicate network reorganization during the curing process, related to the loss of water (11-15 $\%_{weight}$ – data available in **supplementary files**). These results are in accordance with the work of Li *et al.*, who demonstrated that the evaporation of the pore water leads to greater strength in metakaolin-based geopolymers [37].

At 20 °C, samples present Young's modulus values close to 4.5 GPa, with few significant variations (**Figure 7.C**). These values are in accordance with the usual Young's modulus values of geopolymers (4.0-6.0 GPa) [38, 39]. After thermal curing, the values of the argillite-containing samples increase slightly to 5.4 or to 6.5-7.0 GPa without and with additives, respectively. These variations represent a significant increase in the sample rigidity after the treatment. Furthermore, this increase is significantly larger with the incorporation of additives and can attributed to a different network evolution in the presence of both argillite and additives. The longitudinal and transverse ultrasonic speeds in the samples are displayed in **Figure 7.D**. At 20 °C, the longitudinal speeds are close to 1700 m/s and greater than 1850 m/s for samples without and with additives, respectively. The transverse speeds are lower, close to 1050 m/s in samples without additives and 950 m/s in samples with additives. Longitudinal speeds are commonly higher than transverse speeds, and for each type of material, a *ratio* transverse/longitudinal speed can be defined [40, 41]. However, the samples with additives are significantly different from the samples with a higher longitudinal speed and a lower transverse speed. The difference in speeds in these samples reveals the presence of anisotropy [40]. After the 90 °C treatment, the speeds increase significantly to approximately 300 m/s for the longitudinal speed and to 150-550 m/s for the transverse speed. The samples with additives present different behaviors, with a very large increase in the transverse speed. This increase results in the disappearance of the anisotropy observed at 20 °C, possibly indicating a network reorganization during the thermal curing [40].

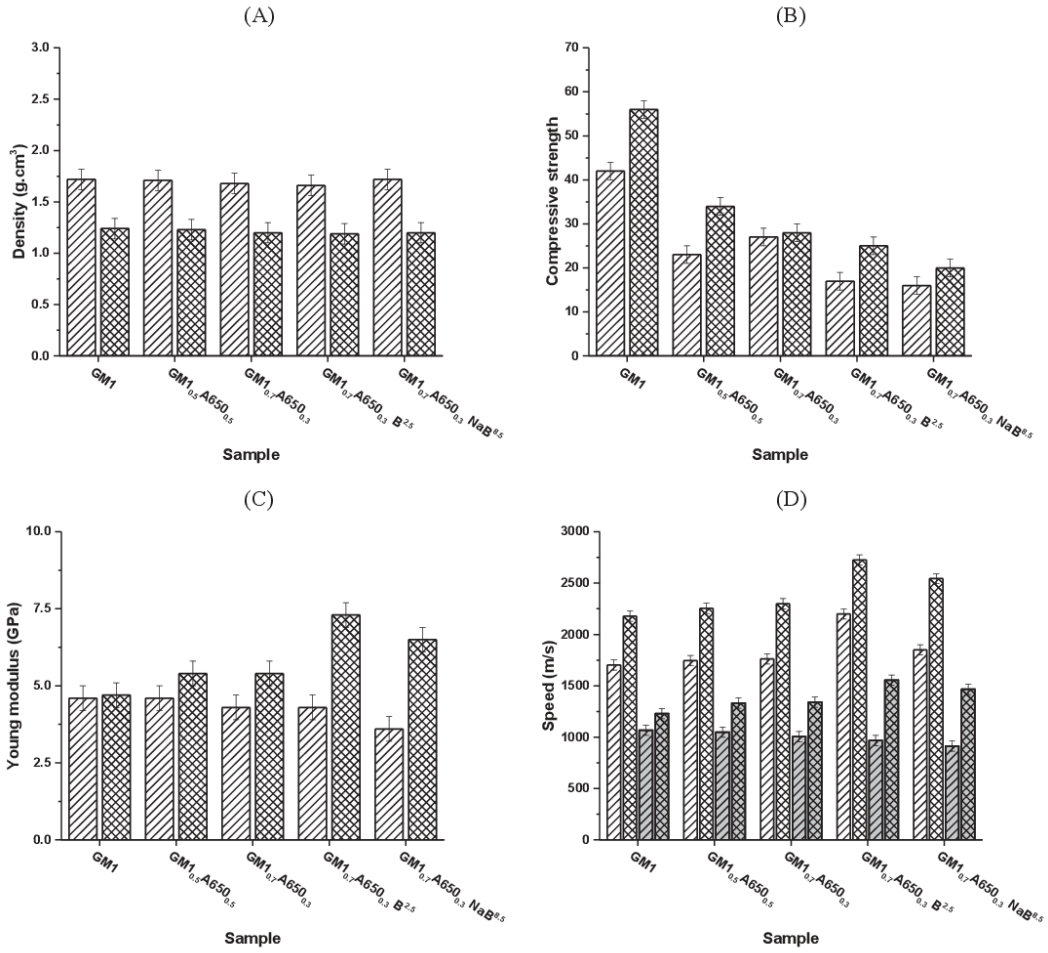


Figure 7. Evolution of **(A)** the density, **(B)** the compressive strength, **(C)** the Young Modulus and **(D)** the (□) longitudinal and (▒) transversal ultrasonic speed for GM1, GM1$_{0.5}$A650$_{0.5}$, GM1$_{0.7}$A650$_{0.3}$, GM1$_{0.7}$A650$_{0.3}$ B$^{2.5}$ and GM1$_{0.7}$A650$_{0.3}$ NaB$^{8.5}$ samples at (▨) 20 °C and (▩) 90 °C.

NMR analysis

MAS-NMR analysis was performed on the five samples at 20 °C, and measurements after exposure to 90 °C were also performed on the GM1 and GM1$_{0.7}$A650$_{0.3}$ NaB$^{8.5}$ samples. **Figure 8** displays examples of the ^{11}B, ^{27}Al and ^{29}Si NMR spectra of GM1$_{0.7}$A650$_{0.3}$ NaB$^{8.5}$ with and without curing at 90 °C.

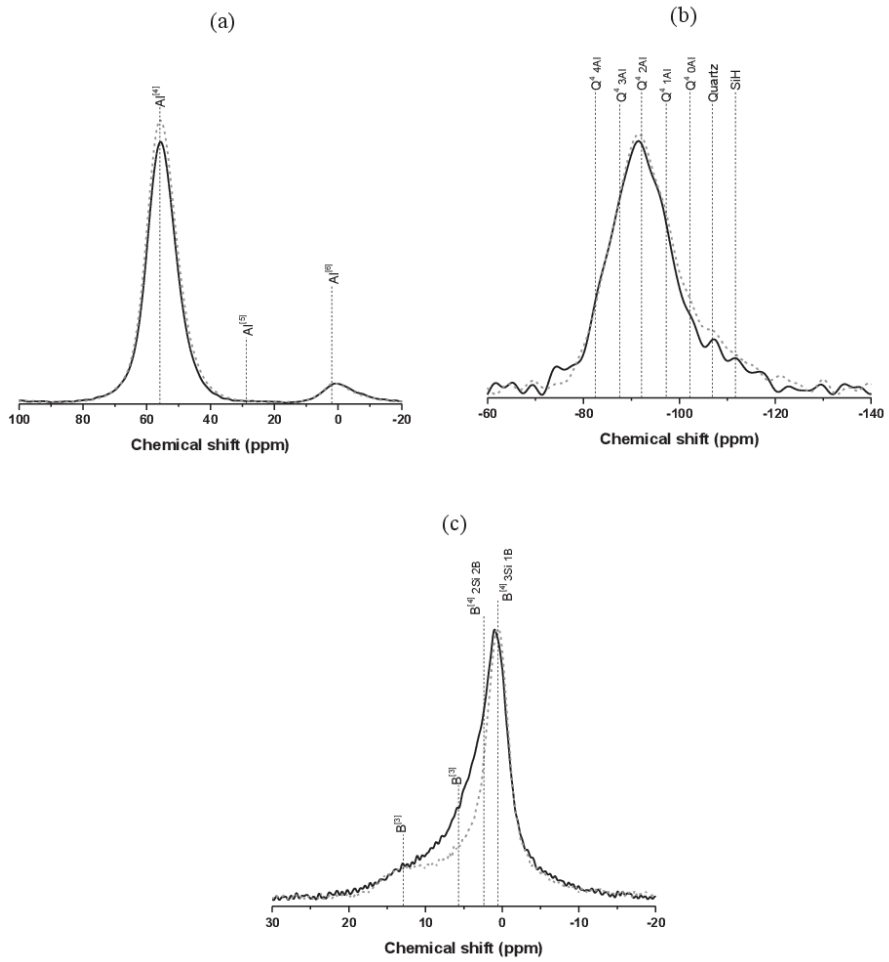


Figure 8. NMR spectra of **(a)** ^{27}Al, **(b)** ^{29}Si and **(c)** ^{11}B of samples exposed to (——) 20 and (- - -) 90 °C (^{11}B boron spectra have been normalized for a better reading).

The ^{27}Al spectra (**Figure 8. A)** present two contributions at 57 and 4 ppm associated with $Al^{[4]}$ and $Al^{[6]}$, respectively [50]. No $Al^{[5]}$ contribution is visible [2]. The chemical shift associated with $Al^{[4]}$ is typical for geopolymer samples, and the $Al^{[6]}$ chemical shift corresponds to unreacted clay minerals [42, 43]. No significant variation is observed between the sample cured at 90 °C and the other samples. Spectra of ^{29}Si present a unique large and broad contribution from -75 to -120 ppm (**Figure 8.B**). These spectra are decomposed with the hypothesis that the three-dimensional geopolymer network is composed of only four-coordinated silicon (Q^4), which can be connected to silicon or aluminum atoms [44]. From

this hypothesis, the spectra are decomposed into five contributions of Q^4 silicon based on the connecting atoms: four aluminum atoms (Q^4 4Al, -82.5 ppm), three aluminum atoms (Q^4 3Al, -87.5 ppm), two aluminum atoms (Q^4 2Al, -92.5 ppm), one aluminum atom (Q^4 1Al, -97.5 ppm) and purely silicon (Q^4 0Al, -102.5 ppm) [45]. Two other contributions, at -107.0 and -112.0 ppm, can be associated with quartz and silicic acid (referred to as SiH), respectively [46, 47]. The treatment at 90 °C does not induce major variation. The area of contributions related to silicon connected to large numbers of aluminum atoms (Q^4 4Al and Q^4 3Al) decreases slightly, benefitting Q^4 0Al. This change is significant for producing a lower degree of silicon-aluminum connectivity in the network, resulting in a more disordered network. The ^{11}B spectra (**Figure 8.C)** display two contributions of four-coordinated boron at 2 and 0 ppm associated with boron bridging 2 and 3 silicon atoms, respectively [48, 49]. Two contributions of three-coordinated boron are also visible at 13 and 7 ppm, associated with symmetric and asymmetric boron [50]. After the thermal curing at 90 °C, the spectrum is well resolved, and the number of $B^{[4]}$ atoms increases significantly to the detriment of the $B^{[3]}_{asymmetric}$, indicating an increase in the silicon-boron connectivity.

The results of the ^{29}Si contribution decompositions are shown in **Figure 9**, and the decomposition data of the ^{11}B spectra are available in **Table 2** and are discussed later. For each sample, the seven contribution areas were normalized by the areas of the GM1 sample contribution and plotted on the chart. Thus, it is possible to observe a decrease in the Q^4 0Al, quartz and silicic acid contributions associated with an increase in the amount of Q^4 4Al and Q^4 3Al silicon atoms. The incorporation of argillite in the mixture ($GM1_{0.5}A650_{0.5}$ and $GM1_{0.7}A650_{0.3}$ samples) leads to major variations. The amount of Q^4 4Al, 3Al and 2Al silicon atoms strongly increased at the expense of the amount of Q^4 0Al, quartz and silicic acid. These variations reach a maximum with the incorporation of 50 $\%_{weight}$ argillite. This increase in the silicon-aluminum connectivity is probably related to the presence of unreacted clay minerals. Indeed, argillite presents a high rate of illite and interlayered illite-smectite, which present limited reactivity and high silicon-aluminum connectivity [2, 51]. The addition of boric acid or sodium tetraborate in the $GM1_{0.7}A650_{0.3}$ mixture leads to similar behavior, *i.e.,* silicon atoms display a lower connectivity with aluminum, resulting in a lower amount of Q^4 4Al and Q^4 3Al atoms. These variations are related to the incorporation of boron into the geopolymer network (**Table 2**), which limits the presence of high aluminum-bonded silicon atoms. The thermal curing of $GM1_{0.7}A650_{0.3}$ $NaB^{8.5}$ at 90 °C leads to a decrease in the aluminum-silicon connectivity (more Q^4 0Al and less Q^4 4Al and Q^4 3Al), indicating a reorganization of the network during curing. These changes result in better boron incorporation into the network and to more Q^4 0Al silicon atoms (**Table 2**). After curing at 90 °C, the GM1 sample also presents strong variations. However, in this sample, the amount of Q^4 4Al silicon atoms increased to the detriment of low aluminum-bonded silicon contributions. This increase suggests some modification during the thermal curing. This finding is in accordance with those of Tsai *et al.*, who demonstrated that the geopolymer network can still evolve several days after consolidation via

thermal curing [52]. This observation confirms the results of the Young's modulus measurements (**Figure 7.C**).

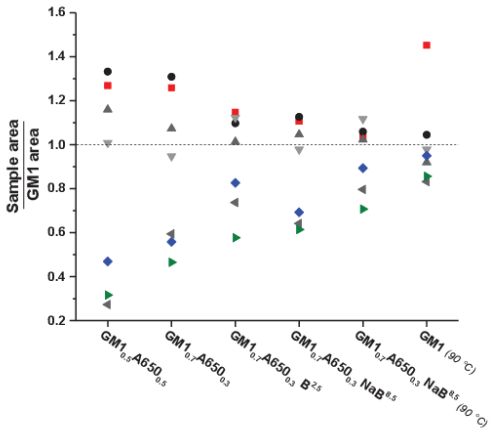


Figure 9. ^{29}Si NMR data of the various samples, expressed by the sample/GM1 area *ratio* for each contribution: (■) Si Q^4 4Al, (●) Si Q^4 3Al, (▲) Si Q^4 2Al, (▼) Si Q^4 1Al, (◆) Si Q^4 0Al, (◀) quartz and (▶) silicic acid.

Data associated with the ^{11}B NMR spectra decompositions are available in **Table 2**. The NMR spectrum of the GM1$_{0.7}$A650$_{0.3}$ B$^{2.5}$ sample shows that a large majority of the B$^{[4]}$ atoms, 90 %, are incorporated in the geopolymer network and are bonded to 2 or 3 silicon atoms. The residual B$^{[3]}$ atoms are mainly asymmetric and are associated with the pH decrease in the samples [21]. The addition of sodium tetraborate in the GM1$_{0.7}$A650$_{0.3}$ NaB$^{8.5}$ sample produced to a smaller amount of boron inside the network. This difference results in a larger number of asymmetric B$^{[3]}$ atoms. After curing at 90 °C, the B$^{[3]}$ atoms become B$^{[4]}$ atoms inside the geopolymer network. This behavior can be linked to boron-based glasses, which can contain a significant amount of water in the form of H_2O or -OH [53]. The heating of these glasses induces water decomposition, resulting in higher boron coordination with more B$^{[4]}$ atoms [54]. This increase in B$^{[4]}$ explains the decrease in the silicon-aluminum connectivity observed in the Si^{29} spectra. Moreover, this finding confirms that the geopolymer network rigidity and connectivity are increased by the 90 °C treatment.

Table 2. ^{11}B decomposition data for $GM1_{0.7}A650_{0.3}$ $B^{2.5}$, $GM1_{0.7}A650_{0.3}$ $NaB^{8.5}$ and $GM1_{0.7}A650_{0.3}$ $NaB^{8.5}$ 90 °C samples.

Sample	$B^{[3]}_{symmetric}$ amount (%)	$B^{[3]}_{asymmetric}$ amount (%)	$B^{[4]}$ 2Si amount (%)	$B^{[4]}$ 3Si amount (%)
$GM1_{0.7}A650_{0.3}$ $B^{2.5}$	3.8	5.8	57.7	32.7
$GM1_{0.7}A650_{0.3}$ $NaB^{8.5}$	9.7	27.6	8.1	54.7
$GM1_{0.7}A650_{0.3}$ $NaB^{8.5}$ (90 °C)	12.3	15.4	8.9	63.4

IV. Discussion

To explain the pH value variations during thermal curing, the mechanical properties and the atomic environment have been studied, and it seems that the curing leads to network modifications. In the samples presenting a pH value decrease (argillite-based samples with and without additives), the network rigidity increases (Young's modulus and Q^4 0Al increase). Thus, the network rigidity can be examined by plotting the rate of increase in the Young's modulus values ($(E_{90°C}-E_{20°C})/E_{90°C}$) and the change in transverse ultrasonic speed ($(S_{90°C}-S_{20°C})/S_{90°C}$) as a function of the pH value variation from 20 to 90 °C (**Figure 10**). First, the Young's modulus evolution seems to be related to the pH value decrease. Hence, the network reorganization, responsible for the increase in Young's modulus, is related to the pH decrease. Moreover, the increases in the transverse speed are also proportional to the pH value decrease. A hypothesis, supported by the use of additives by the modification of the isotropic properties, could be that the alkali cations are trapped inside the network and cannot induce a high pH value.

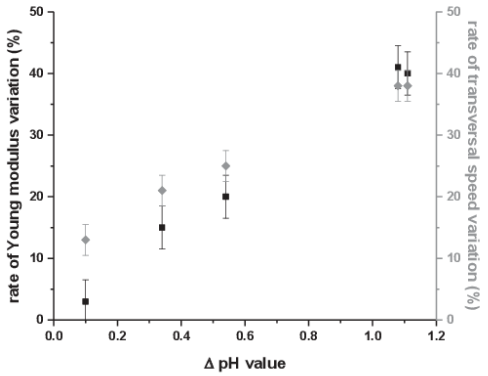


Figure 10. Evolution of the (■) Young modulus ($(E_{90°C}-E_{20°C})/E_{90°C}$) and (◆) transversal ultrasonic speed ($(S_{90°C}-S_{20°C})/S_{90°C}$) of sample exposed at 20 and 90 °C, in function of pH value variation measured from 20 to 90 °C.

Structural analysis based on X-ray diffraction did not provide evidence regarding the formation of a crystalline phase or significant variation in the amorphous network. Thus, FTIR spectroscopy was performed on the G1M1 and G1M1$_{0.7}$A650$_{0.3}$ NaB$^{8.5}$ samples with and without 90 °C curing (**Figure 11).** The FTIR spectra, based on KBr pellets, of the 4000 – 2000 cm^3 range are plotted in **Figure 11.A**. In this range, no differences were detected in the GM1 sample regardless of the temperature. After exposure to 90 °C, the G1M1$_{0.7}$A650$_{0.3}$ NaB$^{8.5}$ sample presents two bands at approximately 3735 cm^{-1} (1) and 2340 cm^{-1} (2) corresponding to hydroxyl bonds and -CO_3 bonds, respectively [55, 56]. The first contribution could be attributed to the Si-OH bonds of zeolites or to Mg-OH bonds [57, 58, 59]. The second is linked to the presence of physisorbed CO_2 on zeolite, located in the range 2380 – 2290 cm^{-1}, with a main contribution at 2340 – 2350 cm^{-1} with K-zeolite [60, 61]. In the second part of the FTIR spectra, from 2000 to 500 cm^{-1} (**Figure 11. B**), the appearance of three new contributions can be detected after curing. For the G1M1 sample, the band at 1550 cm^{-1} (3) probably corresponds to adsorbed carbonates on the sample surface [62, 63, 64]. For the G1M1$_{0.7}$A650$_{0.3}$ NaB$^{8.5}$ sample, this contribution is located at a higher wavenumber, 1570 cm^{-1}. This band is considered to be associated with the vibration mode of Mg-OH deformation, which can correspond to magnesium hydroxide formed with the highly available magnesium in the argillite [59, 65, 2]. Another contribution is observed at 1380 cm^{-1} (4) and can also be associated with two types of carbonate species, either K_2CO_3 or CO_2, adsorbed on zeolite phases [60, 61, 66, 67]. For the GM1 sample, no indication of the presence of zeolite is observed, so the formation of K_2CO_3 is assumed, with the potassium provided by the alkaline silicate solution. For the G1M1$_{0.7}$A650$_{0.3}$ NaB$^{8.5}$ sample, this contribution seems to correspond to carbonate adsorbed on zeolite phases, which confirms the presence of the zeolite phases associated with contributions (1) and (2). Moreover, for both samples, the contribution of Si-O-Si and Si-O-Al bonds (5), centered close to 1000 cm^{-1}, displays a narrow peak due to the reorganization of the network [68]. As demonstrated by NMR (**Figure 9**), the GM1 sample presents a high rate of Si-O-Al bonds after the thermal curing, and the G1M1$_{0.7}$A650$_{0.3}$ NaB$^{8.5}$ sample exhibits the formation of Si-O-B bonds. These variations are confirmed by the infrared spectra, with a limited shift to a lower wavenumber due to the incorporation of aluminum or boron in the network [27, 69].

Thus, the variation observed between samples before and after 90 °C curing is mainly related to the formation of carbonate species in the GM1 sample and to the formation of an amorphous zeolitic precursor in the G1M1$_{0.7}$A650$_{0.3}$ NaB$^{8.5}$ sample. It is supposed that these weakly crystallized zeolites (not visible in X-ray diffractometry, XRD) are formed during curing with the appearance, locally, of hydrothermal conditions [70]. A strong pH decrease is only observed in the argillite-based sample. This pattern suggests that zeolite phase formation is responsible for the trapping of alkaline cations inside the network, limiting the pH value of the sample [71]. On the other hand, in the GM1 sample, the potassium cation formed carbonate species during the curing, which were dissolved during the sample immersion, resulting in a similar pH value with and without the 90 °C treatment [72].

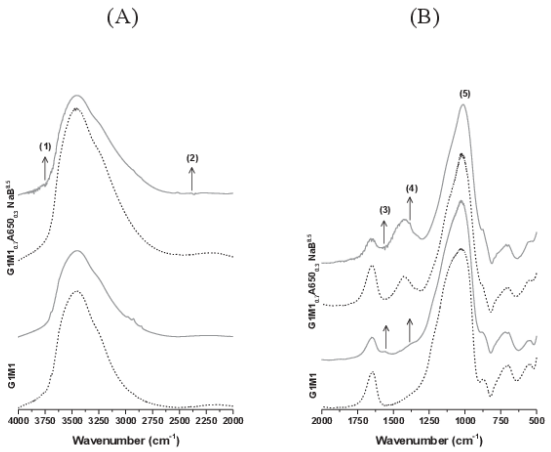


Figure 11. FTIR spectra **(A)** from 4000 to 2000 cm^{-1} and **(B)** from 2000 to 400 cm^{-1} of GM1 and $GM1_{0.7}A650_{0.3}$ $NaB^{8.5}$ samples at **(- - -)** 20 °C and **(—)** after a 90 °C curing.

V. Conclusion

This work demonstrated the possibility of formulating a geopolymer binder containing COx argillite. Optimization of the mixture allowed us to reach the focused setting time (approximately 24 hours) and pH value after exposure to 90 °C (close to 11). The main results are as follows:

(i) To limit the sample pH value and the geopolymerization kinetics of argillite (due to the large amount of available earth alkali cations), the use of a mixture composed of both argillite and metakaolin is essential.

(ii) Then, to reach the desired properties, the incorporation of additives, boric acid or sodium tetraborate, has been studied. This addition allowed us to reach both the setting time and pH value targets. The combination of boric acid and sodium tetraborate has been shown to lead to an excess of the additives in the mixture, limiting their usefulness.

(iii) To study the pH value variations observed in argillite-based samples after a 90 °C curing process, mechanical characterizations were investigated by Young's modulus measurements. An increase in the Young's modulus after thermal treatment has been observed and is associated with the growth of the sample rigidity. Combined with isotropic variation, network reorganization in argillite-containing samples is evident.

The control of the pH value at 90 °C was possible by the formation of a supposed zeolite phase, detectable by FTIR spectroscopy, that is able to trap the alkaline cations, thereby limiting the sample pH value.

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Thermal resistant alkali-activated materials using argillite and two types of solution.

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THERMAL RESISTANT ALKALI-ACTIVATED MATERIALS USING ARGILLITE AND TWO TYPES OF SOLUTION

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ABSTRACT

The French national radioactive waste management agency (Andra) is studying the building of a deep geological disposal for High and Intermediate Level radioactive waste. If accepted, the disposal will lead all along the operating period to the excavation of a large amount of host rock, mainly constituted by argillite. With the aim of using this by-product, alkali-activated materials have been prepared and studied, involving two different alkaline silicate sources (solution and powder). In order to increase the thermal resistance, the addition of sand, as filler, has been studied. A standard test and a thermal shock, both up to 800 °C, are used to study the physical stability of the samples under these thermal constraints. Analyses by XRD and SEM allow correlating the thermal resistance to the structural evolution occurring during the thermal tests.
It was shown that the alkaline-silicate solution composition is the main parameter to control the reactions during the thermal treatment. The use of the powder-based solution, containing sodium, leads to the formation of more viscous flow and less crystalline phases, which reduces the thermal resistance and the mechanical properties. The addition of filler in the samples increases the resistance to thermal sudden increase, but is not sufficient to obtain a correct resistance to shock. The utilization of flash-calcined argillite, containing carbonate species, gives a better crystallization during the thermal treatment and leads to more cracks but an increase of the mechanical properties. Using, these different compositions, a value of 20 MPa can be reached after thermal treatment.

INTRODUCTION

Widely accepted by several countries, the actual plan for a long term management of the high and intermediate level radioactive waste is a deep geological disposal. The French national radioactive waste management agency (Andra) project is called Cigéo (Industrial waste disposal facility). It is predicted to receive the High-Level and Intermediate-Level Long-Lived waste in a specific geological layer: the argillite of the Callovo-Oxfordian (COx argillite), close to 500 m under the ground level. If the authorities validate the project, the construction of the disposal will lead to the excavation of a considerable quantity of argillite. Thus, the -use of the COx argillite is a major issue for the Cigéo operating period.

In order to develop new fire resistant and durable construction materials in geological disposal conditions, alkali-activated materials appear as promising candidates. These binders

have shown increasing interest over the last decades because of their high working performances, wide range of applications and low environmental impact due to their preparation conditions. In this regard, the issue of the synthesis of thermally-resistant, alkali-activated binders based on argillite has been examined. The alkali-activation of the argillite (after a thermal activation of the argillite at 750 °C in a furnace or flash process) has already been studied. It results that the thermally activated argillite can be used as mineral source (Si-Al) to produce alkali-activated materials by polycondensation reactions [1]. These studies underline the importance of the thermal activation (temperature and process) and the subsequent decompositions. The alteration of the clay minerals is closely linked to the argillite reactivity and the carbonate species decomposition leads to the formation of alkaline oxides, which generate new phases during the alkali-activation.

Alkali-activated materials exhibit generally a "correct" thermal resistance but it is necessary to adapt the formulation. First, the nature of the alkaline-silicate solution is a key parameter. The use of sodium-based solution leads to an appearance of viscous flow at a lower temperature than potassium-based solutions and results in a final product with lower mechanical resistance to high temperature [2]. The use of mineral sources with a high Si/Al molar ratio, i.e. > 1.65, also presents a tendency to quickly form viscous flow during heating [2]. Then, it is important to identify the formation of new phases (nature and amount) at high temperature [3]. Indeed, raw materials for alkali-activated binders treated close to 800 °C, show generally crystallization of amorphous phases in new compounds [4]. For metakaolin-based geopolymer, Duxson et al. [5] have demonstrated that there is formation of kaliophilite, leucite or nepheline after a thermal treatment. In the presence of calcium, the calcination leads to the formation of other compounds. For example, with fly ash as shown by Wattanasiriwech et al. [4], a thermal treatment up to 800°C induces the formation of wollastonite, gehlenite (commonly found in cement) and andradite (a calcium-iron silicate). These compounds, which have an important impact on the thermal resistance, need to be identified in order to favor or limit their formation [6]. The use of filler (a chemically non-reactive phase in the mixture) can enhance the thermal properties of the binders with a mechanical role. Various authors studied the addition of quartz, sand, mullite or cordierite in the mixture and observed significant enhancement of the physical properties under temperature [7,8]. This increase is generally related to the amount of filler. Indeed, Wattanasiriwech et al. [9] have determined an optimal rate of 40 % of the mineral source, with the use of mullite-cordierite as fillers in fly-ash alkali-activated materials. More, it has been demonstrated that the addition of filler is essential to obtain samples which can resist thermal shocks [9,10]. To summarize, in order to develop thermally resistant alkali-activated binders, it is necessary to use an aluminosilicate source with a high aluminum content, potassium silicate solution and significant amount of filler, and to control the mineralogical evolution during the calcination (maximum temperature and duration). Moreover, there is not a full understanding of the reaction occurring with alkaline powder solution and mineral sources containing carbonate species.

The aim of this work was to understand the chemical composition effect on the thermal resistance of calcined argillite in the presence of two alkaline silicate solutions (powder or liquid) and the influence of filler. For that, the thermal resistance was evaluated by visual observation (on samples after calcination and thermal shock at 800 °C) and compressive strength measurement (only on samples after a classic calcination). The identification of phase, before and after thermal treatment, was performed by XRD analysis and the morphology of the samples was observed by SEM.

EXPERIMENTAL

Raw materials

The COx Argillite, supplied by Andra, was half composed by clay minerals (interlayed illite/smectite, illite, chloride and kaolinite). It was also composed of 26 wt % of carbonate species (calcite and dolomite), 19 wt % of tectosilicate (quartz and traces of feldspar and plagioclase) and some other compounds like pyrite. In order to increase its reactivity, the argillite was ground and thermally treated at 750 °C with a furnace treatment (Ac) and a flash treatment (Af) [1]. Siliceous sand (Sd) containing traces of kaolin and calcite [8] was used as filler. Table 1 gathers various physico-chemical characteristics about the different mineral sources.

Table 1: Physico-chemical data of the different mineral sources. (* calcite and kaolin traces)

Nomenclature	Si/Al	D50 (µm)	ρ (g/cm^3)	S_{BET} (m^2/g)
Ac	3.63	160	2.72	5
Af	3.63	21	2.63	29
Sd	*	190	2.73	6

Sample preparation

The reactive mixtures were prepared using two aluminosilicate sources and two different alkaline silicate solutions as shown in Figure 1. The first alkaline solution, S, was based on a blend of potassium silicate solution and potassium hydroxide (63 % water and Si / K molar ratio = 0.58). The second alkaline solution, P, was based on a mix of sodium silicate powder, water and potassium hydroxide (58 wt % water and Si/M molar ratio = 0.60, where M = K and Na).

The aluminosilicate sources were calcined argillite and the sand (Sd), representing 38% weight percent of the aluminosilicate source [8]. The mixtures are casted in a closed polystyrene mold and kept at room temperature.

Consolidated samples are named XA + F. X was the alkaline silicate solution and was abbreviated S (K-liquid-based solution) or P (Na-K solid-based solution). Then the argillite nature was specified with A = Ac (furnace calcination) or Af (flash calcination) and if a filler was used, it is noted as +F with F = Sd (sand). For example, PAf + Sd corresponds to Af argillite (flash calcination) alkali-activated by the P solution with the addition of sand as filler.

Sample characterization

The thermal resistance was tested with two different treatments:

- a slow temperature increase up to 800 °C (ramp at 1 °C/min, step of 1 hour and natural cooling), named hereafter as “calcination”;
- a thermal shock (at 800 °C during 10 minutes with a lift-furnace – immediate temperature increase and decrease), named hereafter as “thermal shock”.

The thermal resistance was evaluated according to the visual aspect of the samples (the occurrence and size of cracks, the presence of melted area) and the mechanical resistance by compressive strength measurements, before and after thermal tests. Compressive strength measurements were performed with a LLOYD EZ20 Universal Testing Machine with a crosshead speed of 0.5 mm / min. For each composition, measurements were done five times on cylindrical samples (15 mm in diameter and 30 mm in height) aged of 28 days (stored at room temperature, in a closed mold). The compressive strength value (MPa) represents the average of the five measurements. X-Ray Diffraction (XRD) patterns were obtained with a Brucker-D8 Advance instrument with Bragg-Brentano geometry and a Cu $K_{\alpha1,\alpha2}$ detector. The analytical

range was between 10 ° and 50 ° (2 θ) with a resolution of 0.02 ° (2θ) and a dwell time of 1.5 s. Phase identification was performed with reference to the Joint Committee Powder Diffraction Standard (JCPDS). The microstructure of the powders was observed using a Jeol IT 300 scanning electron microscope, after a carbon coating of the samples.

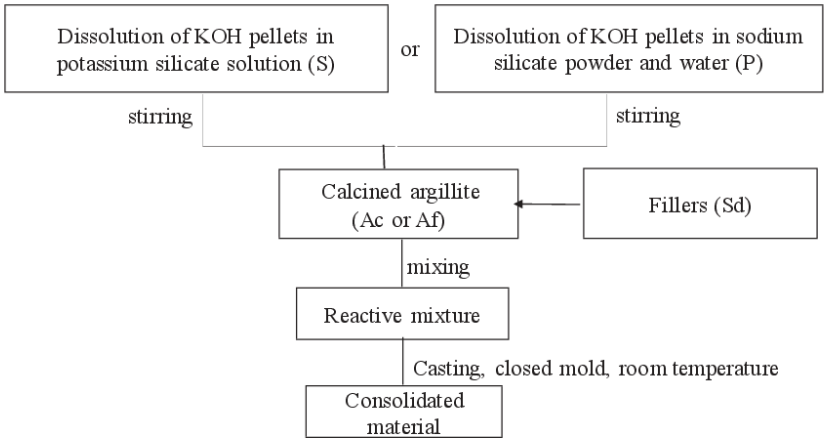


Figure 1. Experimental protocol of sample preparation

RESULTS AND DISCUSSION

Thermal resistance tests

The result of the visual observation after both calcination and thermal shock for the alkali-activated samples are gathered in Table 2.

For the SAc sample, calcined samples exhibited small cracks since the thermal shock generated high degradations of the samples, i.e. large cracks and the loss of the mechanical strength. Consequently, this sample presented good resistance to slow temperature increase and a lack of resistance to thermal shock, due to the difference of the thermal kinetic. The use of silicate solution, P led to similar behavior.

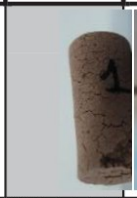
The addition of sand to the Ac-based sample (SAc + Sd and PAc + Sd) induced a similar resistance to the calcination treatment but increased the thermal shock resistance. In fact, the use of filler led to a medium resistance to the thermal shock, resulting in smaller cracks and better mechanical properties. It is supposed that this result may be related to the formation of a granular skeleton based on the filler [11,12]. The better thermal resistance then could be related to a solid-state reaction of the different compounds in relation to the chemical composition of sand (kaolinite, calcite).

The use of thermally activated argillite made with a flash process (Af) was conducive to lower resistance than the use of calcined argillite in a furnace (Ac). Indeed, a medium resistance to the calcination test was obtained with the SAf samples and a lack of resistance with the PAf sample. However, both presented a lack of resistance to thermal shock. This difference between Ac and Af based samples could be explained with the thermal decompositions occurring in the argillite during the thermal tests. Indeed, the thermal activation of the argillite with the flash process led to a partial decomposition of the carbonate species and a partial dehydroxylation of the clay minerals [1]. Consequently, these decompositions occurred during the calcination of the

alkali-activated sample, and were probably responsible of the lack of thermal resistance. In addition, the difference between the two solutions S and P, could be related to the presence of sodium or potassium, which lead to different structures and therefore different thermal behaviors.

The addition of sand to Af-based sample led to an increase in the thermal resistance. As in the case of Ac-based samples, it could be supposed that this was related to the formation of a granular skeleton with the sand as rigid inclusion in the material.

Table 2: Photographs of samples based on Ac and Af before and after thermal treatment with and without filler (Sd) (white: good resistance, hatched: medium resistance and grey: lack of resistance)

Solution		S			P		
Thermal treatment		Without	Furnace	Shock	Without	Furnace	Shock
Samples	Ac						
	Ac + Sd						
	Af						
	Af + Sd						

In order to complete these visual observations, compressive strength measurements were performed on both alkali-activated samples before and after classic calcination (the compressive strength of samples after the thermal shock were too low to be significantly measured). The curves of the compressive strength tests associated with the different samples are displayed on Figure 2

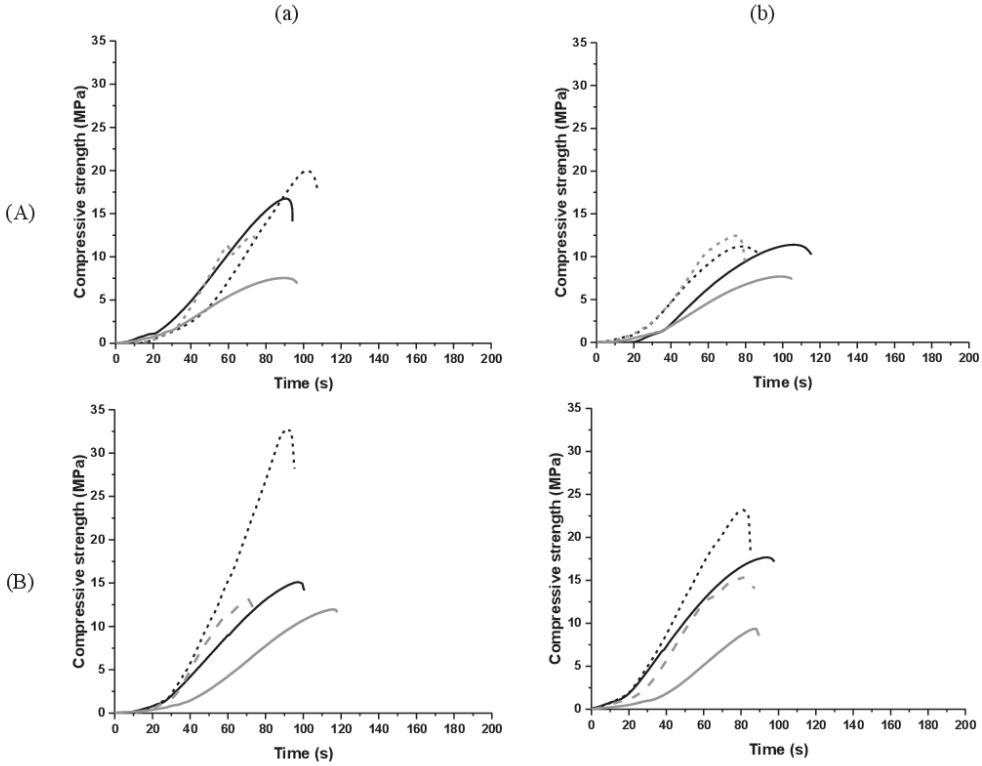


Figure 2. Examples of compressive strength measurement curves of (A) Ac and (B) Af based samples without (a) and with (b) sand, using (in black) silicate and (in grey) powder solutions before (—) and after (- - -) the thermal treatment

. Figure 2,A,a shows the compressive strengths of the Ac-based samples with S and P solutions. For SAc sample, the initial compressive strength was around 16 MPa and after the calcination, this value increased slightly to around 18.5 MPa. This increase revealed that this sample was stable in temperature without major modification. The PAc sample presents a lower initial compressive strength, close to 7 MPa. In comparison with SAc sample, this decrease could be explained by two facts. First, the solid/liquid ratio was smaller using S solution (0.78 versus 1.07 with P solution) [13]. Moreover, the powder-based solution, P, presented a lower reactivity than the S solution, according to previous work [14]. After thermal treatment in a furnace, this compressive strength increased significantly to 12 MPa. In this case, the silicate species present in the P solution could favor the formation of intermediate silicate compounds acting as reinforcements in the sample during the heating [15]. The addition of sand to Ac samples (Figure 2,A,b) led to a decrease in the initial compressive strength using the S solution (Sac sample) but did not impact the PAc sample. This decrease could be explained by interference between the sand and the reactive S solution, inducing a weaker polycondensation reaction and therefore lower compressive strength. In fact, it has been demonstrated that the potassium cation in presence of sand led to better mechanical properties than sodium [16]. The calcination of these

samples with sand led to similar results as those without filler, i.e. a few modifications with the S solution and an increase using the P solution. With both S and P solutions, the use of Af argillite (Figure 2,B) did not lead to significant variation in the initial compressive strength. After the thermal treatment, with P solution there was not a significant increase in the compressive strength, but the major difference could be observed with S solution that presented a remarkable increase in the compressive strength, from 15 to 32 MPa. These differences can be explained by free alkaline-earth cation (Ca^{2+} and Mg^{2+}) issued from carbonate species decomposition contained in the flash-calcined argillite (Af) [17]. These cations may react with silicate to form secondary phases, acting once again as reinforcements in the samples [18,19]. The addition of filler, Sd, to these samples induced similar compressive strength except with S solution which presented a lower value after thermal treatment. This behavior was similar to the SAc + Sd sample, for which it was supposed that the sand limited the polycondensation reactions by reacting with alkaline solutions [20]. All these data underlined the possibility of the formation of several phases during thermal treatment permitting to reach a minimal compressive strength value of 20 MPa.

Structural and morphological evolutions

The Figure 3 gathers the XRD patterns of the different samples before and after the thermal treatment in the furnace. For the Ac-based samples, with both S and P solutions, the patterns are displayed on the Figure 3,A,a. These patterns display some phases present in all the patterns and not impacted by the different thermal treatments. This is why, these phases, i.e. the quartz and muscovite both initially present in the argillite and the arcanite and microcline both formed with the alkali activation, will not be discussed here. Before thermal treatment, SAc sample presented contributions of potassium aluminum silicate ($KAl_3Si_3O_{11}$) formed during the alkali-activation of the argillite [21] and an important amorphous dome due the geopolymer network [22]. After the calcination cycle, there was disappearance of this potassium aluminum silicate, which probably decomposed to the benefit of the formation of a zeolite phase ($KAlSiO_4$) [23,24]. The amorphous dome of the sample decreased in relation to the crystallization of new phases due to the thermal treatment. Indeed, there was also a reaction between the silica and the calcite/calcium above 700 °C, which led to the formation of wollastonite ($CaSiO_3$) [25]. It is supposed that the wollastonite, which formed during the thermal treatment, could act as a mechanical reinforcement due to its fibrous structure [26]. This fact may explain the improvement in compressive strength of the samples after thermal treatment. The use of P solution (containing Na and K) led to the same phases (before and after thermal treatment) as S solution (containing only K). However the formation of additional phases after thermal treatment was observed. Indeed, the heating at 800 °C in the presence of sodium induces the formation of combeite ($Na_{4.8}Ca_3Si_6O_{18}$) [19,27]. Furthermore, the formation of this new phase led to a modification of the amount of available SiO_2, K_2O, Al_2O_3 and MgO, which conduced to the appearance of another polymorph of $KAlSiO_4$, kalsilite and to the formation of a potassium magnesium silicate ($K_2MgSi_5O_{12}$) [23,28]. The use of sand as filler with Ac-based samples (Figure 3,A,b) led to similar structural evolutions. The formation of the new phases, such as the wollastonite, can be correlated to the increase in compressive strengths.

(a) (b)

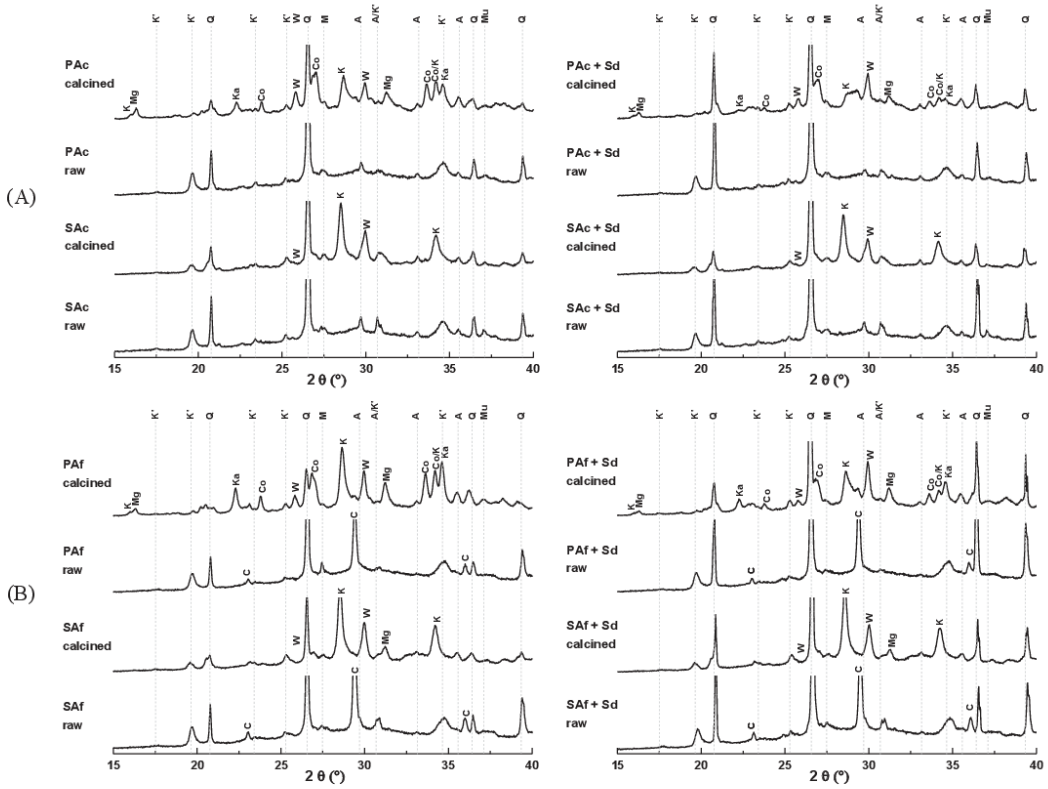


Figure 3. XRD pattern of samples based on (A) Ac and (B) Af argillite without (a) and with (b) sand (JCPDS files: K, $KAlSiO_4$, zeolite (00-048-1028); Mg, $K_2MgSi_5O_{12}$ (00-044-1492); K', $KAl_3Si_3O_{11}$ (00-046-0721); Q, SiO_2, quartz (00-046-1045); C, $CaCO_3$, calcite (04-012-0489); Co, $Na_{4.8}Ca_3Si6O_{18}$, combeite (04-007-5453); Ka, $KAlSiO_4$, kalsilite (04-013-2103); W, $Ca_{0.96}Mn_{0.03}Fe_{0.01}SiO_3$, wollastonite (04-016-8857); M, $KAlSi_3O_8$, microcline (00-019-0932); A, K_2SO_4, arcanite (04-006-8317); Mu, $KAl_2AlSi_3O_{10}(OH)_2$, muscovite (04-019-1573))

The Figure 3,B, displays the X-ray patterns with Af-based samples. The thermal activation of the argillite with the flash process induced a partial decomposition of calcite and dolomite. The calcite contributions were discernible on the patterns of samples before thermal treatment [1]. No other differences could be detected with Ac-based samples. After the furnace calcination at 800 °C of the alkali-activated samples, the decomposition of the residual carbonates occurred and the calcite contribution disappeared. These decompositions led to an intensity increase of wollastonite and potassium magnesium silicate contributions, for both S and P solutions. The formation of these new phases resulted in solid-state reaction consuming silica. In addition, the formation of these phases can still be related to the increase in mechanical strength, which explained the improvement of the mechanical properties of the SAf sample. The lower increase of compressive strength with the PAf sample than the SAf could be explained by the formation

of a higher amount of combeite, which was preferentially formed than wollastonite [29] and resulted in lower reinforcement of the sample.

The addition of filler to the samples based on the flash-calcined argillite did not change the nature of the formed phases and the intensities of the different contributions seemed to be similar. It was supposed that the variations observed in compressive strength were mainly due to the presence of a granular skeleton and/or to the formation of an amorphous phase undetectable in X-ray diffraction. These hypotheses need to be confirmed by dilatometric analyzes.

In order to complete the structural analysis, scanning electron microscopy observations have been performed on samples after thermal treatment in a furnace (Figure 4). The SAc sample (Figure 4, Aa) presents a microstructure characteristic of the presence of viscous flow, due to the melting of the amorphous phase, surrounding the different crystalized particles. The use of P solution, with Na and K, (Figure 4,A,b) leads to a viscous flow encapsulating all the particles.

Samples based on the flash-calcined argillite (Af), Figure 4,B, presented various microstructures with a lower viscous flow, which confirmed the X-ray diffraction analysis, i.e. the presence of a better crystallization with Af. SAf sample showed different particles which probably corresponded to the newly formed phases, responsible for the increase in compressive strength (Figure 4.B,a). The PAf sample presented various phases and a large amount of microcrystalline grains visible which could be attributed to combeite or silicate compounds [30]. The difference between P and S solutions could be also related to the alkaline nature responsible for the melt temperature differences as in the silicate glass compounds [31].

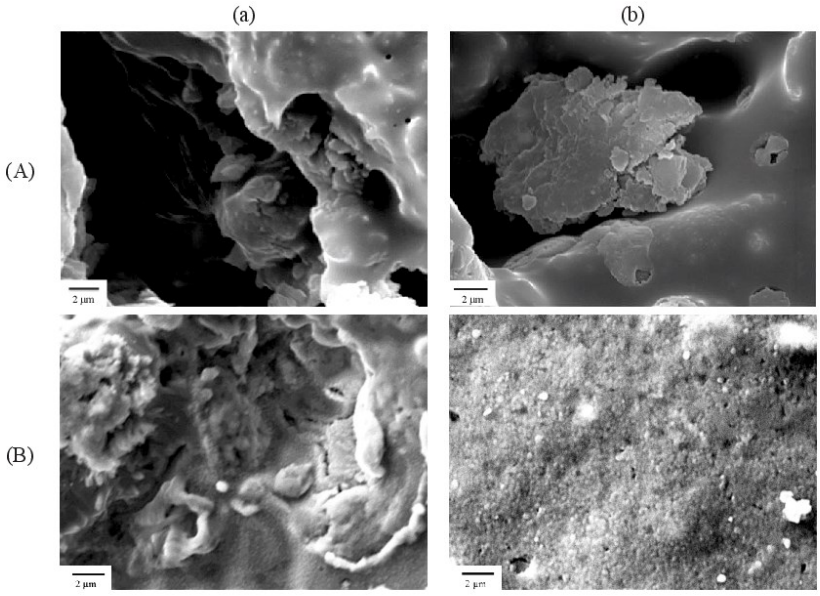


Figure 4. SEM micrographs of calcined samples based on (A) Ac and (B) Af using (a) S solution and (b) P solution.

CONCLUSION

In this paper, the thermal resistance of alkali-activated materials based on COx argillite has been investigated using two alkaline silicate solutions, two aluminosilicate sources and one filler. It has been demonstrated that the majority of the samples resist classic calcination until 800 °C, but they present a weaker resistance to thermal shock (sudden temperature increase).

The nature of the alkaline silicate solution used led to different reactions during the heating, and thus the formation of different phases. The presence of sodium in the powder-based solution favored the formation of combeite and viscous flow instead of wollastonite, which was mainly formed with the potassium-based solution. These differences led to lower compressive strengths with the powder-based solution and weakly impacted the thermal resistance. The use of sand as filler induced a better resistance to thermal shock which still, however, not optimal. This filler probably leads to a better macroscopic structure but slightly limited the formation of new phases during the treatment. Lastly, in alkali-activated samples the use of argillite thermally activated with a flash process, in which the carbonate species were not fully decomposed, led to a different behavior during the thermal treatment. The carbonate species induced solid-state reactions leading to a high amount of new phases. They, consequently, presented a greater compressive strength but more cracks due to the decomposition of the carbonate species during the heating. The use of solution or powder alkaline activators and a calcined argillite permitted to obtain alkali-activated materials with a compressive strength of at least 20 MPa after thermal treatment.

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Acte de congrès 2 (ACLN 2)

C. Dupuy, J. Havette, N. Texier-Mandoki, X. Bourbon, S. Rossignol

Géopolymères à base de métakaolin : impact de l'addition d'acide orthophosphorique dans le mélange réactif.

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GEOPOLYMERES A BASE DE METAKAOLIN : IMPACT DE L'ADDITION D'ACIDE ORTHOPHOSPHORIQUE DANS LE MELANGE REACTIF

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RESUMÉ:

Certaines applications relatives aux liants géopolymères peuvent nécessiter d'adapter les propriétés du mélange réactif. Cette étude porte sur le développement d'un coulis injectable pour lequel il est nécessaire d'avoir une viscosité faible (< 5 Pa.s) ainsi que d'une durée pratique d'utilisation (DPU) très élevée (~24 heures). Pour l'application visée du liant, il est aussi nécessaire de limiter l'alcalinité et donc de diminuer la valeur du pH finale de ce liant (objectif de 10-11).
Afin de respecter ce cahier des charges, l'addition d'acide orthophosphorique dans des mélanges réactifs géopolymères est étudiée. Des suivis de la viscosité des mélanges réactifs dans le temps ont révélé que l'ajout d'acide permet une augmentation de la DPU pouvant atteindre 500 %. La caractérisation (structurale, microstructurale et la résistance mécanique) de différents échantillons a permis d'identifier un taux limite de 5,6 % d'acide au-delà duquel l'effet positif sur la DPU s'inverse. Cette valeur correspond aussi à la limite au-delà de laquelle il n'y a plus formation d'un réseau géopolymère mais uniquement la formation d'un gel physique.

MOTS CLES : géopolymère ; viscosité ; durée pratique d'utilisation ; additif ; phosphore

1. INTRODUCTION

Les géopolymères sont des matériaux qui résultent de l'activation alcaline d'une source aluminosilicate minérale (usuellement du métakaolin) par une solution alcaline silicatée (Davidovits, 2008). Le mécanisme réactionnel se décompose en deux étapes, une dissolution de la source minérale dans la solution conduisant à la formation d'oligomères de silice et d'alumine, puis la polycondensation et la géopolymérisation de ces oligomères (Davidovits, 2008). Lors des différentes réactions de polycondensation, le matériau est dans l'état liquide jusqu'à la prise du matériau. En fonction de l'application visée, il peut être utile de contrôler la viscosité de ce mélange réactif et aussi sa cinétique de consolidation. Parmi les différentes applications relatives aux géopolymères, peu d'études traitent du développement de coulis injectables (El Idrissi et al., 2016), pour lesquels les viscosités et les valeurs de pH des mélanges réactifs sont adaptables, et leur durée pratique d'utilisation (DPU) contrôlable.
La DPU dépend principalement des deux composants majeurs du mélange, la solution alcaline silicatée et la source minérale. En effet, Poulesquen et al. ont montré que l'utilisation d'une solution de silicate potassique conduit à une viscosité plus faible qu'une solution sodique et que l'utilisation d'une solution de faible rapport Si/M (M= K ou Na) à une DPU et une valeur de pH plus faible (Poulesquen et al., 2011) (Duxson et al., 2005). La nature de la source aluminosilicate a aussi un impact majeur sur la viscosité et la DPU. Par exemple, la présence de calcium dans la source minérale peut conduire à la précipitation de phases calciques (silicate de calcium, aluminosilicate de calcium…) et entrainer une diminution brusque de la DPU (Yip et al., 2005). Le rapport solide sur liquide (S / L) du mélange réactif est directement corrélé à la viscosité (augmentant avec le rapport S / L) et à la DPU (diminuant avec l'augmentation de la charge du milieu réactionnel) (El Idrissi et al., 2016). Il est aussi possible de modifier la température pour retarder (faible température) ou accélérer la consolidation (augmentation de température) (Romagnoli et al., 2011).
D'autre part, plusieurs études ont montré l'intérêt de l'ajout d'additifs afin de contrôler la DPU, dans des liants alcalinement-activés proches des matériaux cimentaires. Rattanasak et al. a pu mettre en évidence, que l'utilisation de sulfate ou de di-chlorure de calcium conduit à une importante diminution de la DPU en entrainant la formation de silicate de calcium hydraté (Rattanasak et al., 2010). A l'inverse, l'utilisation de phosphate (sous forme d'acide ou dipotassique) permet de favoriser une augmentation de la DPU pouvant atteindre les 100% (Nugteren et al., 2009) (Lee et al., 2005). De plus, J.Wang et al. ont récemment montré l'intérêt de l'utilisation de zéolites au sein de mélanges réactifs afin de diminuer la valeur de pH de 13 à 11 (Wang et al., 2018). Dans le but d'associer une modification de la DPU et une diminution de la valeur de pH du liant, l'acide orthophosphorique semble être un candidat prometteur.
Ce travail a pour objectif d'obtenir un mélange réactif présentant une valeur de pH comprise entre 10 et 11, ainsi qu'une DPU supérieure à 12 heures et une viscosité comprise entre 0,5 et 5 Pa.s. Pour cela, différentes quantités d'acide orthophosphorique sont ajoutées à un mélange réactif de référence (Gharzouni et al., 2017), et la consolidation du matériau est suivie par des mesures de viscosité dans le temps. Les propriétés d'usages de ces échantillons sont ensuite évaluées, à l'aide de mesures de résistance en compression et de tests de tenue à l'eau. Enfin les évolutions structurales et microstructurales en relation avec la teneur en eau sont confrontées à partir des études par diffraction des rayons X, par microscopie électronique à balayage et par analyses thermiques.

2. PARTIE EXPERIMENTALE

2.1 Matières premières et protocole de synthèse

Cette étude porte sur l'étude de géopolymères synthétisés à base de métakaolin (M1000 - Imerys) et d'une solution de silicate de potassium (Si / K = 0,7 après ajout d'hydroxyde de potassium). Afin de d'optimiser la DPU des échantillons, de l'acide orthophosphorique (85 % massique d'H_3PO_4) est ajouté au mélange réactif, lors du malaxage. La Figure 1 décrit le mode opératoire utilisé pour la préparation des échantillons. Pour les échantillons présentant un fort taux d'acide orthophosphorique, une cure thermale de 24 heures à 70 °C est effectuée afin d'obtenir un échantillon suffisamment consolidé.

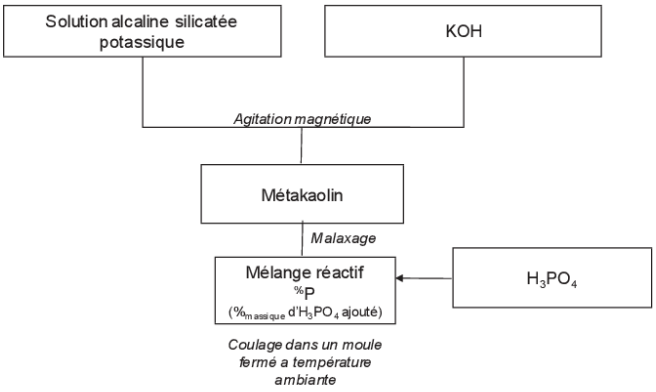


Figure 1. Protocole de synthèse des échantillons géopolymères.

2.2 Techniques de caractérisation

Les valeurs de viscosité et de DPU sont obtenues à l'aide de mesures de viscosité durant toute la durée de consolidation. Ces mesures sont effectuées ponctuellement à l'aide d'un viscosimètre Brookfield DV-2T. Entre chaque mesure, les échantillons sont stockés dans des récipients fermés et maintenus sous agitation sur un mélangeur à rouleaux (60 tours / minute). Une fois la valeur limite de 600 Pa.s atteinte, les mesures sont stoppées et l'échantillon est considéré consolidé.
Les diffractogrammes sont obtenus à partir d'un appareil D8-advance (Brucker) présentant un montage Bragg-Brentano avec détecteur Cu Kα1α2. Les acquisitions sont effectuées entre 10 et 50 ° (2 θ) avec une résolution de 0,02 ° (2 θ) et un temps de pallier de 1,5 s. Les observations microstructurales sont effectuées par un microscope électronique à balayage Quanta 450 (canon à effet de champ), après un dépôt de platine en surface.
Les analyses thermiques différentielles et thermogravimétriques (ATD-TG) sont effectuées sous air sur un SDT Q600 fourni par TA Instrument. La rampe utilisée est de 5 °C / min jusqu'à 800 °C en utilisant des creusets en platine. Avant l'analyse les échantillons sont stockés 12 heures à 80 % d'humidité et 20 °C.
Les valeurs de pH des échantillons consolidés sont obtenues après sept jours d'immersion d'un échantillon âgé de sept jours (m / V ~ 0,5). La valeur de pH est ensuite mesurée à l'aide d'un pH-mètre WTW 3310 et d'une électrode spécifique aux valeurs de pH extrêmes (calibrée dans la gamme 10-13). La tenue à l'eau est estimée après sept jours d'immersion du géopolymère (âgé de sept jours, m / V ~ 0,2).
La résistance mécanique en compression des échantillons est mesurée à l'aide d'un équipement LLOYD EZ20 et d'un asservissement en vitesse de 0,5 mm / min. Les mesures sont effectuées sur des lots de cinq éprouvettes cylindriques rectifiées (Ø/h = 2). La valeur exprimée (MPa) correspond à la moyenne de ces cinq essais.

3. RESULTATS

3.1 Influence sur la cinétique de consolidation

La cinétique de consolidation des mélanges réactifs est suivi par des mesures de viscosité ponctuels pour différents mélanges réactifs présentant des concentrations croissantes en acide orthophosphorique (Figure 2).
Le géopolymère de référence, ^{0}P, présente une viscosité initiale de l'ordre de 6 Pa.s qui reste stable durant environ 250 min. Au-delà, la viscosité croît rapidement et atteint la valeur limite de 600 Pa.s après 350 min. Cette augmentation est due aux réactions de polycondensation au sein du mélange réactif conduisant à sa consolidation. L'ajout d'une faible quantité d'acide orthophosphorique (^{0,9}P et ^{1,9}P) conduit à une forte diminution de de la viscosité initiale (jusqu'à ~2 Pa.s) alors que pour des quantités supérieures

à 2,8 % la viscosité augmente. Cette augmentation peut être due à la précipitation de nouvelles phases au sein du mélange réactif où à l'apparition d'une prise physique (Tognonvi, 2009). Les mélanges ^{1,9}P et ^{2,8}P présentent respectivement des temps de prise de l'ordre de 1300 et 1800 min. Pour des taux d'insertion supérieurs à 2,8 % la DPU diminue très fortement. Les taux d'insertions permettant une augmentation de la DPU sont donc similaires à ceux observés par N.K Lee sur des mélanges contenant des cendres volantes (Lee et al., 2013). Ces variations de DPU sont liées à la présence d'ion H^+ qui perturbent les réactions de polycondensation et de géopolymérisation. Le phosphore peut aussi être présent en quantité suffisante pour réagir avec les atomes d'aluminium ou potassium pour former des phosphates d'aluminium ou de potassium (Tchakouté et al., 2017)(Taher et al., 2015). Ceci aurait pour effet de diminuer la DPU en augmentant les valeurs de viscosité.
La suite de cette étude se focalisera sur la caractérisation de quatre échantillons représentatifs des différents comportements : ^{0}P (géopolymère de référence), ^{0,9}P (faible taux d'acide orthophosphorique), ^{2,8}P (taux optimal pour la DPU maximale) et ^{4,7}P (large excès d'acide).

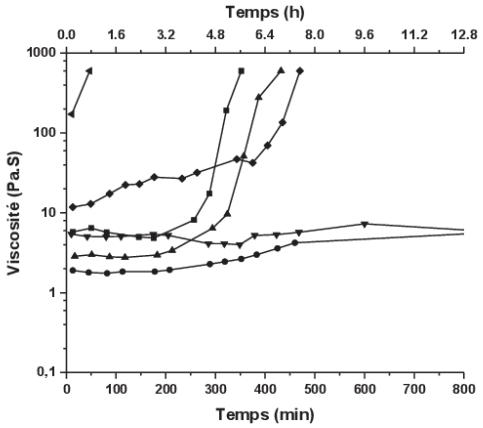


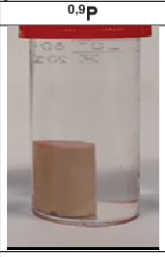
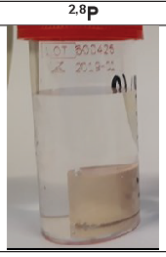
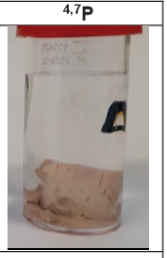
Figure 2. Evolution de la viscosité en fonction du temps pour les mélanges ■ ^{o}P, ▲ ^{0,9}P, ● ^{1,9}P, ▼ ^{2,8}P, ♦ ^{3,7}P et ◄ ^{4,7}P.

3.2 Caractérisation des échantillons

Afin d'évaluer les caractéristiques des géopolymères synthétisés avec de l'acide orthophosphorique des tests de tenue à l'eau, de résistance mécanique en compression et des mesures de valeurs de pH sont effectuées sur les différents échantillons (Tableau 1).
Après 7 jours d'immersion dans l'eau, le géopolymère de référence (^{0}P) ne présente visuellement aucun signe de dégradation. Pour des concentrations en acide inférieures à 3 %, aucun signe de détérioration physique n'est observé. Pour une concentration supérieure, l'échantillon ^{4,7}P se délite fortement au contact de l'eau. Par conséquent, au-delà de 3 % d'acide orthophosphorique, l'échantillon est simplement obtenu par un silicatage/collage sans réaction de polycondensation (Gharzouni et al., 2016a).
La valeur de résistance mécanique en compression de l'échantillon de référence (^{0}P) est de 42 MPa. Dès l'ajout d'une faible quantité d'acide orthophosphorique (^{0,9}P) la valeur de contrainte passe à 7 MPa, puis à 4 MPa pour l'échantillon ^{2,8}P et aucun seuil de résistance pour l'échantillon ^{4,7}P. L'ajout de 2,8 % d'acide orthophosphorique permet donc d'obtenir un échantillon résistant à l'eau mais ne développant pas de réelle tenue mécanique.
L'échantillon de référence sans acide, ^{0}P, a une valeur de pH de 12,30. L'ajout d'acide permet une légère diminution de la valeur de pH, jusqu'à 12,00 avec l'ajout de 0,9 % d'acide mais augmente très faiblement, à 12,35, pour 2,8 %. Une diminution de la valeur de pH jusqu'à 11,60 est cependant observée avec

l'insertion de 4,7 % d'acide, bien que l'échantillon soit faiblement consolidé. L'augmentation de la valeur de pH observée sur l'échantillon ^{2,8}P peut correspondre à la formation d'un réseau géopolymère partiel, avec un excès de cation alcalin.
Ces données révèlent que l'addition de 2,8 % d'acide orthophosphorique au mélange réactif correspond à la limite d'insertion. Pour confirmer ces observations, des analyses structurales et microstructurales sont menées.

Tableau 1. Données relatives au test de tenue à l'eau, aux valeurs de résistance mécanique et aux valeurs de pH des différents échantillons géopolymères.

	^{0}P	^{0,9}P	^{2,8}P	^{4,7}P
Photographie des échantillons après 7 jours d'immersion dans l'eau				
Résistance mécanique en compression (MPa)	42	7	4	~0
Valeur de pH	12,30	12,00	12,35	11,60

3.3 Evolutions structurales et microstructurales

Afin de suivre les évolutions structurales entrainées par l'ajout d'acide orthophosphorique, les diffractogrammes des échantillons ^{0}P, ^{0,9}P, ^{2,8}P et ^{4,7}P sont représentés sur la Figure 3.
Tout d'abord l'échantillon de référence, ^{0}P, présente une déformation de la ligne base, centrée aux alentours de 29 ° (2 θ), révélateur de la formation d'une structure silicatée amorphe ainsi que des contributions associées à du quartz, à de l'anatase et à des minéraux argileux (muscovite et kaolinite) correspondant aux impuretés contenues dans la matière première initiale (Gharzouni et al., 2017). L'ajout d'une faible quantité d'acide orthophosphorique, échantillon ^{0,9}P, ne conduit pas à des modifications structurales notables. L'ajout d'une quantité plus importantes (^{2,8}P et ^{4,7}P) se traduit par l'apparition d'une nouvelle phase associée à un phosphate potassique d'aluminium ($KAlP_2O_7$). L'intensité de ce pic est faible pour l'échantillon ^{2,8}P mais devient plus importante avec l'échantillon ^{4,7}P. Cette phase se forme quand l'acide est présent en fort excès soit une valeur limite de 2,8 %. Ceci correspond à la zone où l'effet retardateur de l'acide orthophosphorique s'inverse.
La Figure 4 regroupe les micrographies MEB des surfaces des différents échantillons. Le géopolymère ^{0}P présente un réseau homogène. Pour des taux d'additifs intermédiaires (^{0,9}P et ^{2,8}P), les microstructures deviennent hétérogènes avec de la porosité soulignant une géopolymérisation partielle en relation avec la dégradation des propriétés mécaniques (Tableau 2). Enfin, la surface de l'échantillon ^{4,7}P est recouverte d'une phase minérale sous forme de plaquettes peu altérées et faiblement liées, caractéristiques des réactions entres les espèces réactives (aluminium, potassium et phosphore). Afin de compléter ces hypothèses, une étude relative à la détermination du taux d'eau contenue dans l'échantillon est réalisée.

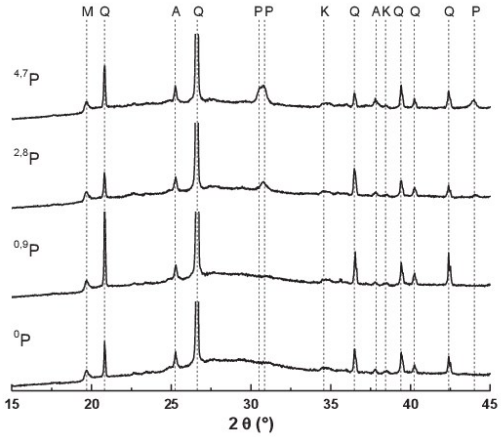


Figure 3. Diffractogrammes des échantillons ^{0}P, ^{0,9}P, ^{2,8}P et ^{4,7}P avec (M - muscovite (04-019-1573), Q - quartz (00-046-1045), A - anatase (01-086-1157), P - phosphate potassique d'aluminium (00-034-1370) et K - kaolinite (00-001-0527).

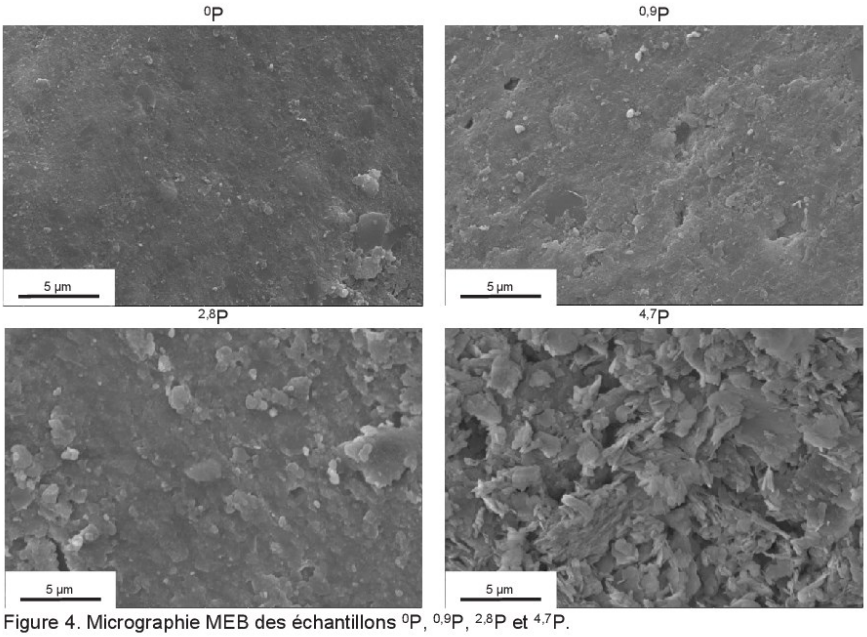


Figure 4. Micrographie MEB des échantillons ^{0}P, ^{0,9}P, ^{2,8}P et ^{4,7}P.

3.4 Comportement thermique

Les différentes analyses thermiques des quatre échantillons présentent toutes une allure similaire, avec une importante perte de masse initiale (< 200 °C) puis une stabilité jusqu'à 800 °C. La Figure 5 présente l'évolution des dérivées des pertes de masse entre 25 et 250 °C pour les échantillons ^{0}P, ^{0,9}P, ^{2,8}P et ^{4,7}P.
Le géopolymère de référence, ^{0}P, a une perte de masse totale de 14 % qui peut se décomposer en deux pertes, une (de 5 %) à une température de 45 °C et une seconde (9 %) à 55 °C. La première perte correspond à l'eau physisorbée et la seconde à une partie de l'eau liée. L'ajout d'une faible quantité d'acide (^{0,9}P) entraine une augmentation de la seconde perte de masse (10 %) pour une perte finale de 15 %. Cette dernière est liée à la présence, plus importante, d'eau dans le réseau géopolymère. La différence observée peut être à l'origine de la diminution des propriétés mécaniques de cet échantillon (Gharzouni et a., 2016b). Pour l'échantillon ^{2,8}P, la perte d'eau totale est de 19 % et la température de décomposition de l'eau liée se décale à une température de 65 °C. Ceci pourrait être lié à la présence de différentes phases, de type hydratées à base de potassium et de phosphore formées lors de réactions secondaires (Xu et al., 2017). Enfin, pour un fort ajout d'acide orthophosphorique (^{4,7}P), la seconde perte de masse (65 °C), devenant largement majoritaire (12 %), est caractéristique de l'absence de consolidation pour cet échantillon, pour lequel la formation d'un gel physique peut être supposée (Tognonvi, 2009).

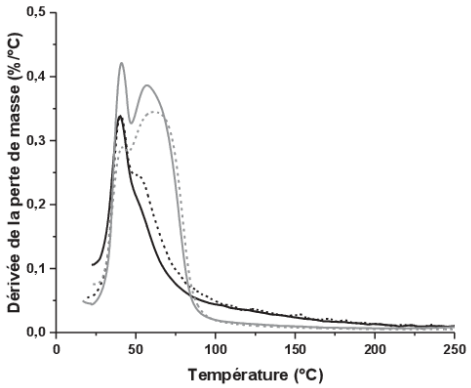


Figure 5. Evolution des dérivées des pertes de masses inférieures à 250 °C pour les échantillons (——) ^{0}P, (- - -) ^{0,9}P, (——) ^{2,8}P et (- - -) ^{4,7}P.

5. CONCLUSION

Dans le but de développer des coulis géopolymères injectables atteignant une durée pratique d'utilisation (DPU) supérieures à 24 heures et présentant une valeur de pH de l'ordre de 10-11, l'ajout d'acide orthophosphorique dans des mélanges géopolymères de références est étudié. Des suivis de viscosité au cours du temps ont mis en évidence deux comportements du mélange réactif en fonction de la quantité d'acide insérée. Jusqu'à ~2,8 % massique d'acide orthophosphorique (valeur seuil entre les deux comportements) un contrôle de la DPU est possible (facteur 5) ainsi qu'une diminution limitée de la valeur de pH (< 0,4). Pour des concentrations en acide supérieures, la DPU diminue très fortement (- 80 %), la viscosité augmente (facteur 10) et les valeurs de pH diminuent de près de 7 %.
La caractérisation des différents types d'échantillons ont permis de mettre en évidence qu'en dessous de la valeur seuil de 2,8 % la formation d'un réseau géopolymère est privilégiée et que la résistance mécanique diminue jusqu'à quelques MPa. Au-delà de cette valeur, les échantillons ont une consolidation physique, sans réseau géopolymère.
L'acide orthophosphorique est donc un additif permettant de réguler le temps de prise par formation de différentes phases plus ou moins hydratées qui conditionnent les propriétés d'usage.

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CONCLUSION GENERALE

Ce travail a été effectué dans le but de développer un coulis injectable à base des argilites du Callovo-Oxfordien. Les spécificités du matériau visé étaient une viscosité modérée (0,5-5,0 Pa.s), une durée pratique d'utilisation importante (jusqu'à 24 heures) et une valeur de pH après consolidation comprise entre 10 et 11. Afin de répondre à cette problématique, l'activation alcaline de l'argilite puis la formulation d'un coulis ont été initiées. Cette étude a donc été réalisée en plusieurs étapes, débutant par le traitement thermique des argilites pour les rendre réactives, et la compréhension des transformations associées, jusqu'à l'activation alcaline des argilites. Pour comprendre ces différentes étapes, une étude systématique de la structure locale a été menée à l'aide de différentes techniques spectroscopiques. La corrélation de ces évolutions structurales, avec la composition des mélanges réactifs ainsi que leurs propriétés d'usage, a permis la réalisation d'un coulis ayant les spécificités requises.

Afin d'activer alcalinement l'argilite, il a tout d'abord été nécessaire de l'activer thermiquement, de comprendre les évolutions induites par ce traitement, puis d'étudier la faisabilité de matériaux alcali-activés à partir de différentes solutions alcalines silicatées. Dans le but de comprendre les transformations chimiques liées aux traitements thermiques, trois types de calcination ont été réalisés, à l'aide d'un four statique, d'un four rotatif et d'un procédé industriel de type flash. Quel que soit le type de calcination utilisé, la déshydroxylation des minéraux argileux et la décomposition des espèces carbonatées interviennent respectivement avant et après 650 °C. Ces transformations sont totales lors de l'utilisation d'un four statique, plus limitées avec un four rotatif et faibles dans un four flash, conséquence de la faible durée d'exposition. Les transformations totales identifiées lors de l'utilisation d'un four statique conduisent à une forte densification, et à la présence de particules de taille élevée (ce qui n'est pas observée avec les autres procédés).

Afin d'évaluer la faisabilité d'échantillons alcali-activés, des argilites calcinées à 750 °C dans des fours statique et flash ont été sélectionnées (ces échantillons présentent respectivement 68 et 94 % d'aluminium, dit réactif, en coordinence IV contre 30 % dans les argilites non calcinées). Les essais de faisabilité d'activation alcaline ont révélé que l'utilisation d'une solution potassique de réactivité modérée ([K] ~5 mol/L), permettait d'obtenir une consolidation optimale, la plus proche des spécificités visées. Les matériaux consolidés ainsi obtenus présentaient différents réseaux géopolymères ainsi que des phases secondaires. Le comportement de ces matériaux en température (800 °C) a également été étudié, et il a pu être mis en évidence la formation de phases cristallisées, telles que des silicates de calcium. La formation de ces silicates de calcium a aussi été observée lors du vieillissement des échantillons,

supposant une relation entre les évolutions temps/température. Il a ainsi été possible de synthétiser des échantillons à base d'argilite présentant un réseau géopolymère et une tenue mécanique correcte ($\sigma_{compression}$ ~15 MPa), répondant à l'application visée (coulis d'injection). En revanche, ces premiers liants ont présenté des valeurs de durée pratique d'utilisation trop faibles (< 30 min) et des valeurs de pH trop élevées (> 13) vis-à-vis des valeurs ciblées.

L'optimisation des liants vis-à-vis de ces deux paramètres a, dans un premier temps, été effectuée sur un géopolymère de référence à base métakaolin, présentant des rapports Si/K = 0,70 et s/l = 1,01. Afin d'accroître la durée pratique d'utilisation et de diminuer la valeur de pH de ce liant, différents additifs minéraux à base de phosphore et de bore ont été sélectionnés. En fonction du type d'additif, les valeurs cibles ont pu être atteintes, notamment avec le tétraborate de sodium (durée pratique d'utilisation jusqu'à 27 h avec une valeur de pH de ~11,2). Des études structurales ont été menées, par spectroscopie RMN, afin de comprendre les réactions mises en jeu. Il a été démontré que l'incorporation d'additifs dans ce mélange réactif de référence, conduit à un réseau géopolymère présentant une plus faible connectivité des atomes de silicium avec les atomes d'aluminium. Lors de l'utilisation d'additifs à base de bore, il a été mis en évidence que les atomes de bore étaient majoritairement en coordinence IV ($B^{[4]}$), incorporés au réseau silicaté. La présence d'une fraction d'atomes de bore en coordinence III ($B^{[3]}$), introduisant des atomes d'oxygène non-pontants, a aussi été notée et associée à la baisse des valeurs de pH. L'utilisation d'additifs à base de phosphore, a conduit à la formation de groupements phosphates connectés (Q^1) ou isolés. Ces groupements ont fortement limité les réactions de polycondensation et conduit à des échantillons dont les propriétés mécaniques sont très limitées ($\sigma_{compression}$ ~5 MPa).

L'ajout d'additifs minéraux a ensuite été réalisé au sein des mélanges réactifs à base d'argilite. Afin d'optimiser les valeurs de pH et les durées pratiques d'utilisation, une source aluminosilicatée composée de 70 $\%_{mass}$ de métakaolin et de 30 $\%_{mass}$ d'argilite calcinée en four rotatif à 650 °C a été sélectionnée. Des valeurs de pH de l'ordre de 11,1 et des durées pratiques d'utilisation proches de 17 h, ont pu être atteintes avec l'incorporation de tétraborate de sodium ou d'acide borique. Ces échantillons ont aussi été étudiés dans des conditions proches des conditions de fonctionnement dans Cigéo (température de 90 °C et coulage en contact avec des argilites du Callovo-Oxfordien). Les premières données ont révélé une réorganisation du réseau géopolymère avec la formation supposée de phases de type zéolite. Enfin, l'étude d'interfaces coulis/argilites géologiques a mis en évidence qu'une diffusion de l'élément potassium, du coulis vers les argilites, pouvait avoir lieu.

Toutes ces caractérisations du réseau local permettent de dire que :

(i) La durée pratique d'utilisation des liants a pu être maitrisée grâce à la connaissance du réseau secondaire, à base de cations formateurs de verre (P ou B), se formant au détriment du réseau géopolymère.

(ii) La valeur de pH a été contrôlée par la présence d'atomes de bore en coordinence III asymétriques.

(iii) Un traitement à 90°C des échantillons consolidés à base d'argilite conduit à une diminution des valeurs de pH (0,3-0,8).

Les perspectives de ce travail pourraient être :

(i) D'optimiser la formulation du liant à base d'argilite et de métakaolin. Effectivement, il pourrait être envisagé de changer la nature du métakaolin, d'utiliser d'autres mélanges de sources minérales ou de modifier le mode de calcination (calcination des mélanges minéraux -mélangés ou co-broyés- et non des minéraux individuels). Cela compléterait le contrôle de la réactivité des cations alcalino-terreux ainsi que le taux de transformation en aluminium IV.

(ii) D'étudier le mode d'introduction des additifs minéraux. En effet, afin de réduire le taux d'incorporation ou d'augmenter leur effet, un co-broyage des additifs et de la source minérale pourrait être investigué. De même, l'étude de l'impact de la dissolution des additifs au sein des solutions alcalines silicatées, permettrait de comprendre l'attaque des sources aluminosilicatées. Cela pourrait permettre d'identifier la formation de germes métastables comme par exemple une zéolite.

(iii) De comprendre les mécanismes de diffusion entre les argilites géologiques et le liant dans les conditions de stockage (90 °C). Pour cela, il serait nécessaire d'identifier les différentes évolutions intervenant lors de l'augmentation de température jusqu'à 90°C. De même, il faudrait mener des études modèles avec un métakaolin pur et différents cations alcalins afin d'expliquer les mécanismes de diffusion intervenant à l'interface liant/argilites géologiques.

ANNEXES

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Annexe II – A. Liste des différentes contributions détectées sur les spectres IRTF.

Nombre d'onde (cm^{-1})	Attribution	Phase/minéral associé	Références
3696	ν O-H	Kaolinite	[1]
3640-3620	ν O-H	Illite, smectite, interstratifié	[2]
3400	ν H-O-H	H- liée à l'eau	[3]
2977, 2939	ν C-H	bandes C-H	[4]
1630	δ OH	Eau de cristallisation	[3]
1550	ν CO_3	-CO_3 lié à du MgO ou CaO	[5]
1510	ν CO_3	Calcite	[6]
1454	ν CO_3	Dolomite	[7]
1432	ν CO_3	Calcite	[7]
1378	ν CO_3	K_2CO_3	[8]
1160	ν SO_4	Sulfites	[9]
1033	ν Si-O-Si	Minéraux argileux	[10]
930	ν Si-O-Ca	Silicate de calcium	[11]
910	δ Al-O	Kaolinite	[12]
870	δ CO_3	Calcite	[4]
796, 774	δ Si-O	Quartz	[10]
710	δ CO_3	Calcite	[4]
691	δ Si-O	Quartz	[10]
613	δ -SO_4	Sulfate de calcium	[9]

Annexe II – B. Liste des contributions détectées par spectroscopie Raman.

Contribution	Position (cm^{-1})	Références
M-O	340–360	[13]
$\delta[R_{5\ et\ plus}]$	400–490	[14]
D_1 ($\delta[R_4]$)	453–550	[14]
υ_s (Si-O-Si) $C_{5,6,7}$	515–535	[15]
D_2 ($\delta[R_3]$)	587–606	[16, 17]
υ_s (Si-O) Monomères	639–649	[15]
υ Si-O-Si (TO-LO)	650–850	[18]
υ_s Si Q^0	800–875	[19]
υ_s Si Q^1	850–900	[18]
υ_s Si Q^{2c}	900–950	[20]
υ_s Si Q^2	950–1000	[20]
υ_s Si Q^{3c}	1000–1050	[17]
υ_s Si Q^3	1050–1100	[17]
υ_s Si Q^4	1120–1130	[21]

Annexe II – C. Liste des contributions détectées par RMN MAS (^{11}B, ^{27}Al, ^{29}Si et ^{31}P).

Noyau	Zone de déplacement chimique (ppm)	Identification de la contribution	Références
^{27}Al	68 — 52	$Al^{[4]}$	[22]
	38 — 28	$Al^{[5]}$	[22]
	15 — -5	$Al^{[6]}$	[22]
	49 –45	$Al^{[4]}$ – P	[23, 24]
	18 – 15	$Al^{[5]}$ – P	[23, 24]
	-11 – -14	$Al^{[6]}$ – P	[23, 24]
^{29}Si	-82 – -90	Q^4 – 4Al	[25]
	-85 – -94	Q^4 – 3Al	[25]
	-92 – -98	Q^4 – 2Al	[25]
	-96 – -107	Q^4 – 1Al	[25]
	-102 – -115	Q^4 – 0Al	[25]
	-107.0	Quartz	[27]
	-110 – -112	Silice amorphe	[26, 27]
	-112,0	Acide silicique	[28, 29]
^{31}P	6,5	PO_4 en présence d'alcalins	[30]
	5,5	Q^1 – Al	[31]
	4,0	Q^1 – Si	[30]
	1,1	Q^1 – P ($K_2P_2O_7$)	[22, 32]
^{11}B	13,0	$B^{[3]}$ – asymétrique (non anneaux)	[33]
	6,0	$B^{[3]}$ – en milieu alcalin	[22, 34]
	2,5	$B^{[4]}$ – 2Si	[33, 35]
	0,5	$B^{[4]}$ – 3Si	[33, 35]

Annexe II – D. Liste des fiches PDF associées aux différents composés analysés sur les diffractogrammes.

Nom du composé	Formule élémentaire	Fiche JCPDS
Anatase	TiO_2	00-021-1272
Arcanite	K_2SO_4	04-006-8317
Aphthitalite	$K_3Na(SO_4)_2$	00-020-0928
Arcanite	K_2SO_4	04-006-8317
Borate de lithium hydraté	$LiBO_2$, 8 H_2O	00-051-0514
Butschliite	$K_2Ca(CO_3)_2$	00-025-0626
Calcite	$CaCO_3$	04-012-0489
Chaux	CaO	04-002-6758
Combeite	$Na_{4,8}Ca_3Si_6O_{18}$	04-007-5453
Diopside	$CaMgSi_2O_6$	00-041-1370
Dolomite	$CaMg(CO_3)_2$	04-011-9833
Hématite	Fe_2O_3	00-033-0664
Hydroxyde de borate de potassium hydraté	$K_2B_5O_8(OH)$, $2H_2O$	00-048-0106
Illite/muscovite	$KAl_3Si_3O_{10}(OH)_2$	04-019-1573
Kaolinite	$Al_2Si_2O_5(OH)_4$	00-001-0527
Kalsilite	$KAlSiO_4$	00-011-0579
Kilchoanite	$Ca_6Si_3(SiO_4)O_{10}$	04-009-7055
Leucite	$KAlSi_2O_6$	01-071-1147
Muscovite déhydroxylée	$KAl_3Si_3O_{11}$	00-046-0741
Néphéline	$Na_{2,8}K_{0,6}Ca_{0,2}Al_{3,8}Si_{4,2}O_{16}$	00-052-0320
Orthoclase	$KAl_{0,98}Si_{3,02}O_8$	01-076-0742
Phosphate de potassium hydraté	$K_4P_2O_7$, 3 H_2O	00-026-1457
Pyrite	FeS_2	04-011-7328
Quartz	SiO_2	00-046-1045
Wollastonite	$CaSiO_3$	00-027-0088
Zéolite	$KAlSiO_4$	00-048-1028

Annexe II – E. Energie des rayons X associée aux éléments chimiques étudiés par analyse chimique.

Elément chimique	Energie de la raie K_α (keV)
B	0,183
O	0,525
Na	1,041
Mg	1,253
Al	1,486
Si	1,739
P	2,013
S	2,307
K	3,312
Ca	3,960
Fe	0,705

Annexe II – F. Détails des différentes solutions alcalines silicatées utilisées dans le modèle de chimiomètrie.

Le jeu de données utilisé pour la chimiométrie est basé sur quatre solutions alcalines silicatées commerciales (**Tableau 1**). Lors de leur préparation, elles sont associées à un hydroxyde alcalin (KOH ou NaOH). Deux des quatre solutions commerciales, S1 et S4, sont étudiées avec l'ajout de KOH et de NaOH, ce qui conduit à l'étude de six solutions. Pour chacune des solutions, plusieurs échantillons (entre 3 et 13), présentant des réactivités différentes, sont préparés. La réactivité est modifiée par variation de la quantité d'hydroxyde introduite dans la solution commerciale, ce qui induit une évolution du rapport Si/M, de la solution.

Le lot de solution ainsi défini comporte 65 solutions alcalines silicatées différentes. Celles-ci ont été préparées quatre fois, afin d'obtenir trois spectres par solution pour la construction du modèle et un spectre pour tester le modèle.

Tableau 1. Détail du jeu de données utilisé pour la chimiométrie.

Solution de base	Solution commerciale	Hydroxyde alcalin	Nombre de solutions	Gamme de Si/M
$S1_K$	S1	KOH	13	0,50 – 1,68
$S1_{Na}$	S1	NaOH	13	0,50 – 1,68
$S2_K$	S2	KOH	12	0,58 – 1,71
$S3_K$	S3	KOH	3	0,50 – 0,66
$S4_K$	S4	KOH	12	0,58 – 1,68
$S4_{Na}$	S4	NaOH	12	0,58 – 1,68

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Annexe III – A. Tableau récapitulatif des pertes de masse mesurées lors du traitement thermique des différents types d'argilites.

Échantillon	Perte de masse (%) dans les gammes :				
	25-350 °C	**350-500 °C**	**500-620 °C**	**620-750 °C**	**750-900 °C**
A25	3,82	1,92	1,64	6,89	2,48
A650	1,20	0,58	0,42	6,57	0,39
A750	0,40	0,33	0,34	2,29	0,05
AR650	1,07	0,23	0,34	8,27	0,66
AR750	0,71	0,10	0,29	4,97	0,21
AF650	1,23	0,50	1,18	12,26	0,98
AF750	0,94	0,34	1,14	8,37	0,23

Annexe III – B. Données relatives à l'étude des spectres de RMN MAS de l'aluminium 27 des différents types d'argilites.

La **Figure 1** présente les spectres RMN de l'Al^{27} des différents types d'argilite et le **Tableau 1** les résultats de décomposition associés.

Initialement l'argilite crue, A25, présente majoritairement (70 %) deux contributions associées aux atomes d'aluminium en coordinence VI, à 2 et -6 ppm (respectivement associées aux illites/smectites et à la kaolinite [1, 2]). Les 30 % d'atomes d'aluminium restant sont en coordinence IV, identifiables par deux contributions, à 67 et 56 ppm, correspondant à des contributions d'illite et d'illites/smectites [3, 4]. Les différents traitements thermiques conduisent à une augmentation de la fraction des atomes d'aluminium en coordinence IV, au détriment des atomes d'aluminium en coordinence VI. Cette augmentation s'accompagne d'une nouvelle contribution d'aluminium en coordinence IV, à 61 ppm, associée à la kaolinite déhydroxylée [5].

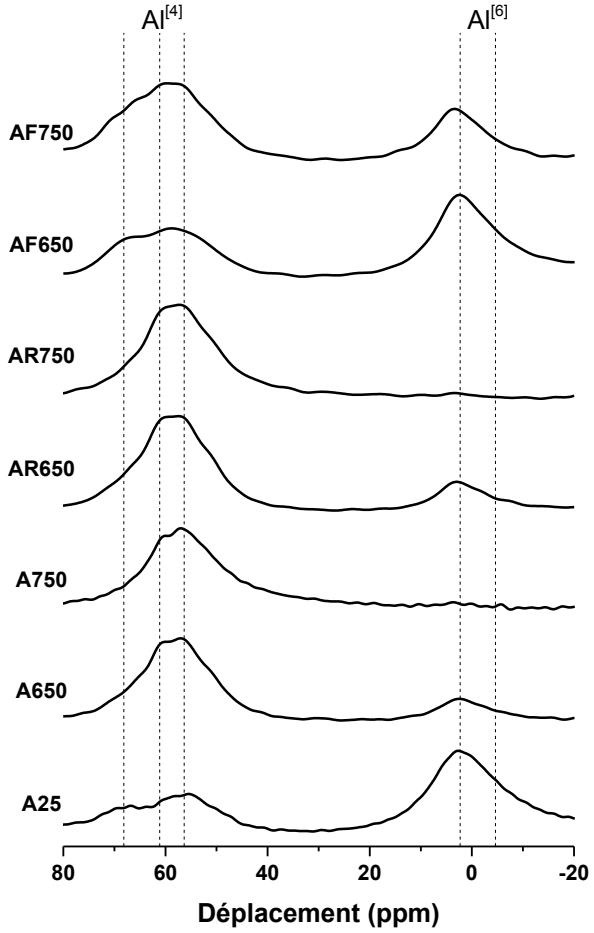


Figure 1. Spectres RMN MAS de l'Al^{27} des différents types d'argilites crue et calcinées.

Tableau 1. Résultats des décompositions des spectres RMN MAS de l'Al^{27} des différents types d'argilites crue et calcinées.

Échantillon	Quantité d'aire associée à chaque contribution par décomposition du spectre (%)	
	$Al^{[4]}$	$Al^{[6]}$
A25	30,3	69,7
A650	81,3	18,7
A750	93,6	6,4
AR650	80,6	19,4
AR750	95,3	4,7
AF650	43,2	56,8
AF750	67,9	32,1

Annexe III – C. Tableau récapitulatif des caractéristiques des différents types d'argilites et du métakaolin M1.

Source minérale	S_{BET} (± 1 m²)	Masse volumique (± 0,01 g / cm³)	Mouillabilité (± 30 µL / g)	d_{50} (± 5 µm)	Couleur
M1	17	2,40	905	10	Blanc
A25	38	2,61	665	17	Gris
A600	30	2,65	505	41	Ocre
A650	32	2,67	485	28	Ocre
A700	25	2,72	495	176	Ocre
A750	5	2,72	535	161	Ocre
A800	6	2,72	700	139	Ocre
AR600	35	2.65	425	19	Ocre
AR650	34	2.64	485	27	Ocre
AR700	25	2.66	510	26	Ocre
AR750	17	2.67	535	26	Ocre
AF600	33	2.66	465	15	Gris
AF650	31	2.65	420	21	Gris
AF700	30	2.64	480	17	Gris
AF750	29	2.62	530	21	Gris

Annexe III – D. Données relatives aux décompositions des spectres RMN MAS du ^{27}Al de l'argilite crue A25, du mélange S1A25AF750 et S1AF750.

Echantillon	Position (ppm)	Largeur (ppm)	Aire (%)	Attribution	Références
S1AF750	72,6	6	3,4	$Al^{[4]}$ – $Ca_3Al_4O_7$	4
S1AF750	66,0	8	13,0	$Al^{[4]}$ – illite/plagioclase	3
S1AF750	58,2	12	62,1	$Al^{[4]}$ – réseau géopolymère	1, 4
S1AF750	50,0	5	2,4	$Al^{[4]}$ – nepheline	2
S1AF750	2,5	10	14,1	$Al^{[6]}$ – smectite illite	1
S1AF750	-6,0	10	4,0	$Al^{[6]}$ – kaolinite	6
S1A25AF750	72,6	6	2,9	$Al^{[4]}$ – $Ca_3Al_4O_7$	4
S1A25AF750	66,0	11	13,1	$Al^{[4]}$ – illite/plagioclase	3
S1A25AF750	58,2	12	39,1	$Al^{[4]}$ – réseau géopolymère	1, 4
S1A25AF750	2,5	12	36,8	$Al^{[6]}$ – smectite illite	1
S1A25AF750	-6,0	10	8,1	$Al^{[6]}$ – kaolinite	6
A25	67,0	12	17,2	$Al^{[4]}$ – illite/ plagioclase	1
A25	56,0	12	13,1	$Al^{[4]}$ – smectite illite	7
A25	2,4	12	54,5	$Al^{[6]}$ – smectite illite	3
A25	-6,0	12	15,2	$Al^{[6]}$ – kaolinite	6

Annexe III – E. Micrographies des échantillons $S1_{1,01}M1^{0,70}$ $KP^{9,3}$, $S1_{1,01}M1^{0,70}$ $P^{2,8}$, $S1_{1,01}M1^{0,70}$ $B^{2,8}$, $S1_{1,01}M1^{0,70}$ $NaB^{10,0}$, $S1_{1,01}M1^{0,70}$ $LiB^{3,7}$ et $S1_{1,01}M1^{0,70}$ $CaB^{6,1}$.

Les microstructures des échantillons $S1_{1,01}M1^{0,70}$ en présence des différents additifs sont présentées dans la **Figure 2**. L'ajout de composés phosphatés entraîne l'apparition de particules traduisant que la géopolymérisation n'est pas totale, vis-à-vis de l'échantillon de référence. Un comportement similaire est observé lors de l'addition d'acide borique. L'ajout de borates alcalins entraîne des modifications microstructurales. Plus particulièrement, les échantillons $S1_{1,01}M1^{0,70}$ $NaB^{10,0}$ et $S1_{1,01}M1^{0,70}$ $CaB^{6,1}$ présentent des particules probablement associées, respectivement à du tétraborate de sodium et à de la colémanite n'ayant pas réagi. L'ajout de tétraborate de lithium, LiB, induit la formation de zones de fracture ponctuelles à la surface de l'échantillon. Cela peut être lié à la nature du cation alcalin utilisé.

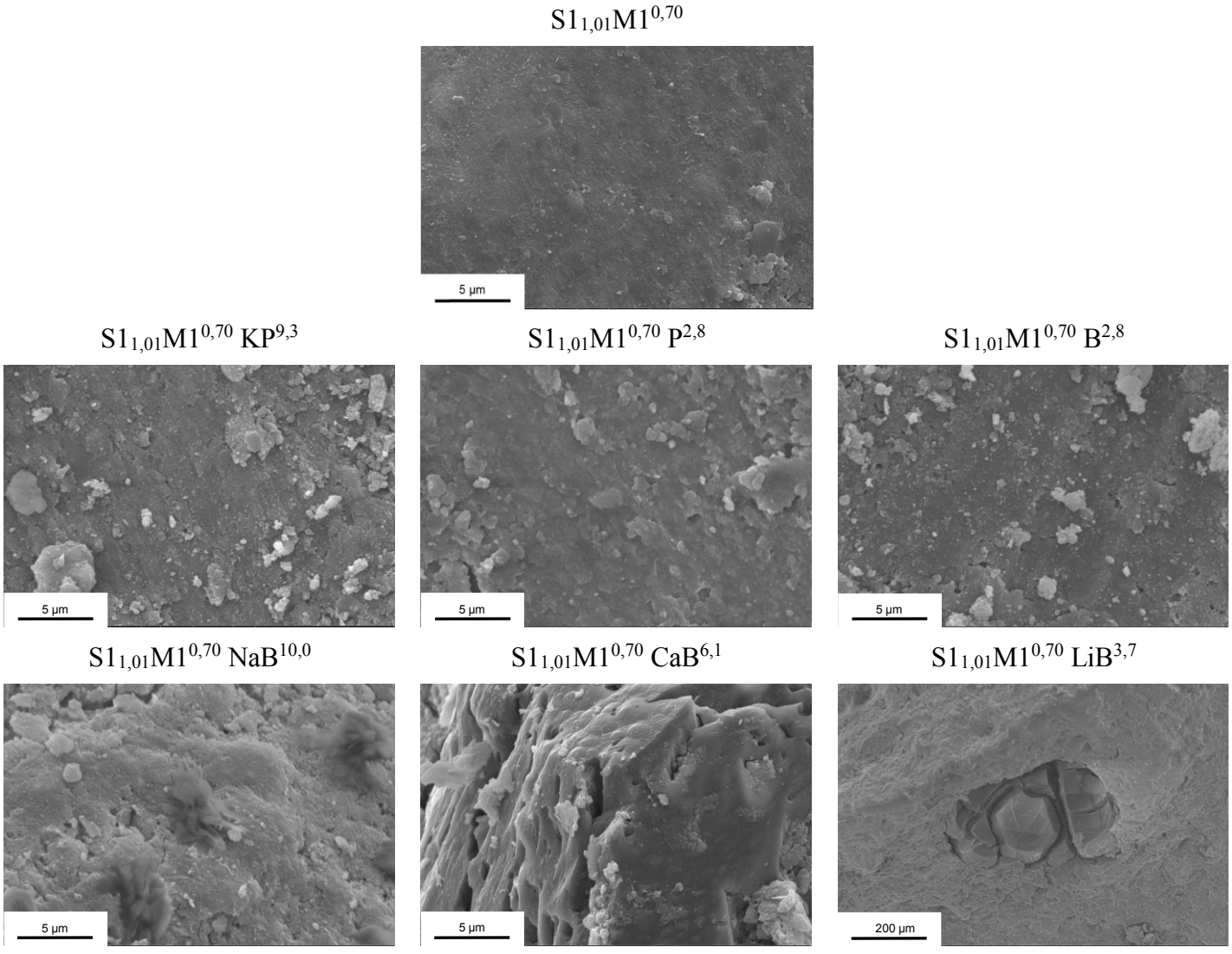


Figure 2. Micrographies MEB de l'échantillon $S1_{1,01}M1^{0,70}$ avec et sans additifs.

Annexe III – F. Détail du calcul de la quantité relative de réseau géopolymères pour les échantillons à base d'additifs.

La quantité relative de réseau géopolymère est obtenue par la différence de deux quantités de réseau. Le premier correspond au réseau géopolymère (**Eq. 1**) auquel est soustrait la quantité de réseau secondaire formé à base des cations formateurs de verres introduits par l'intermédiaire des additifs (**Eq. 2**).

$$n_{géo} = \frac{nSi\left(Si\ Q^4\ 4Al + Si\ Q^4\ 3Al + Si\ Q^4\ 2Al\right) + nAl\ (Al^4)}{ntot} \qquad \textbf{Eq. 1}$$

$$n_{sec} = \frac{nP\left(P\ Q^1\ 1Al + P\ Q^1\ 1Si + P\ Q^1\ 1P\right) + nB\ (B^4)}{ntot} \qquad \textbf{Eq. 2}$$

Avec : $n_{géo}$ la quantité de réseau géopolymère (%$_{mol}$), n_{sec} la quantité de réseau secondaire (%$_{mol}$), nSi, nAl, nP et nB les nombres de mol respectifs de Si, Al, P et B (mol), ntot le nombre de moles contenu dans l'échantillon (mol) et Si Q^4 xAl, Al^4, P Q^1 1y et B^4 les intensités des différentes contributions RMN issues de la décomposition des spectres RMN (%).

Annexe III – G. Etude des différences entre le tétraborate de lithium amorphe et cristallisé.

Deux références de tétraborates ont été utilisées au cours de la thèse : LiB et LiB_{cr}. Une étude par diffraction des rayons X (**Figure 3.A**) a mis en évidence la nature cristallisée ($Li_2B_4O_7$) du LiB_{cr} et le caractère très majoritairement amorphe du LiB.

Afin d'expliquer les différences observées lors de la synthèse de géopolymères à base de ces deux tétraborates de lithium, des analyses en spectroscopie Raman ont été menées. Les solutions $S1_K^{0,70}$ utilisées pour la synthèse des échantillons S1M1 (avec et sans additifs) ont ainsi été étudiées (**Figure 3.B**). Le spectre de la solution $S1_K^{0,70}$ présente deux dômes intenses associés respectivement aux espèces siliceuses réactives (Q^0, Q^1 et Q^2) et peu réactives (Q^{2c}, Q^3, Q^{3c} et Q^4) [8, 9, 10, 11]. L'ajout de LiB_{cr} dans la solution conduit à un liquide trouble, dû à l'absence de dissolution du tétraborate cristallisé, qui ne permet pas l'obtention d'un spectre Raman correct. Le tétraborate amorphe se dissout et conduit à une faible diminution de la contribution des espèces réactives (Q^0, Q^1 et Q^2), contrairement au tétraborate de sodium qui conduit à une très forte diminution de la quantité d'espèces siliceuses réactives.

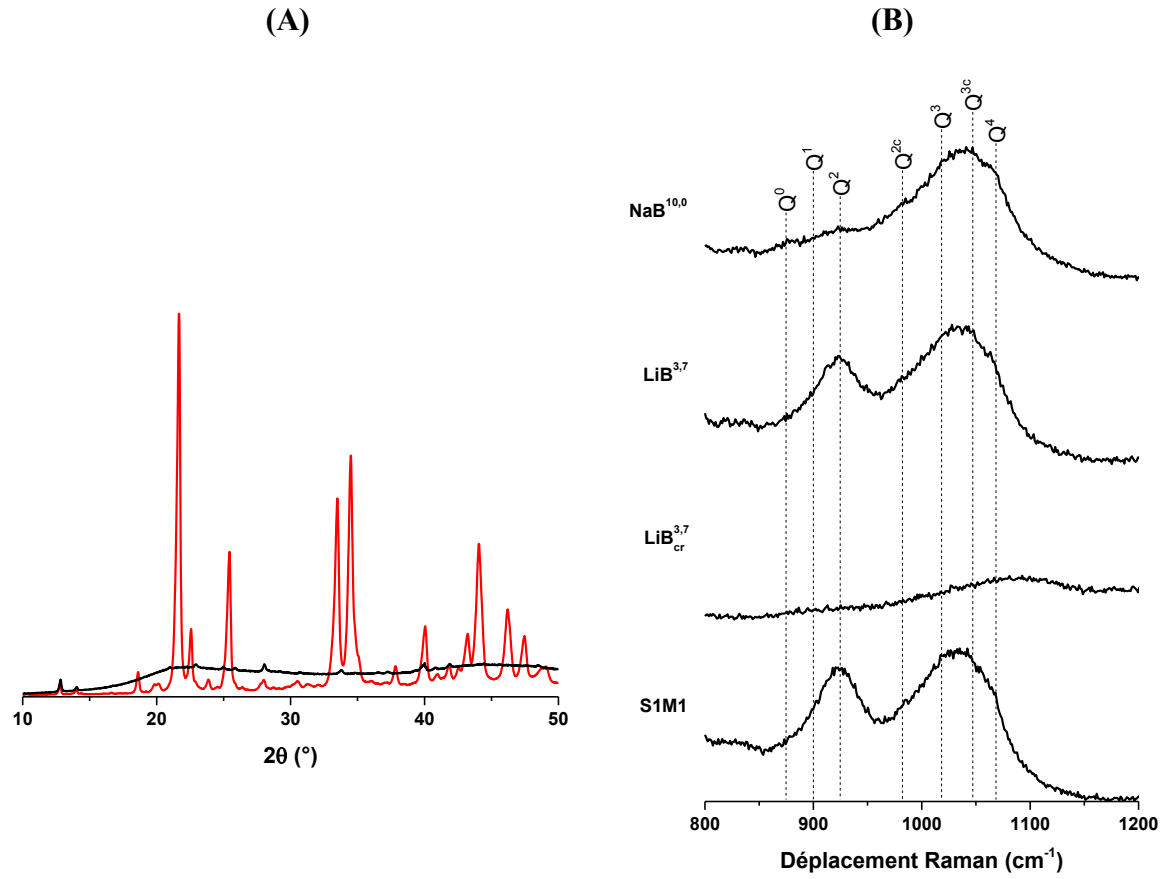


Figure 3. (A) diffractogrammes de (—) LiB et (—) LiB_{cr} et **(B)** spectres Raman des solutions alcalines silicatées associées aux échantillons S1M1, $LiB_{cr}^{3,7}$, $LiB^{3,7}$ et $NaB^{10,0}$.

Annexe III – H. Présentation des mesures de module d'Young par échographie ultrasonore.

La technique d'échographie ultrasonore est une méthode non-destructive qui permet de mesurer les vitesses des ondes longitudinale et transversale se propageant dans un matériau, afin d'en déduire la valeur du module d'Young. C'est un dispositif opérant en mode milieu infini en transmission, doté de deux paires de transducteurs basse fréquence (600 KHz) à contact, qui a été employé en raison de la forte atténuation des ondes dans les matériaux étudiés. Le principe de la mesure est illustré sur la **Figure 4**. Préalablement rectifié pour présenter deux faces parfaitement parallèles, l'échantillon possède une épaisseur de l'ordre de 5-8 mm. Un générateur de signaux relié au transducteur émetteur génère le signal qui traverse l'épaisseur de l'échantillon jusqu'au transducteur récepteur. Le couplage entre les transducteurs et le matériau est assuré par un agent de couplage commercial visqueux. Pour déterminer le temps de propagation (relevé à partir d'un oscilloscope), il faut soustraire le temps correspondant au pic maximal de l'écho obtenu en présence de l'échantillon, à celui pour lequel les deux transducteurs sont directement couplés sans matériau. En divisant l'épaisseur par cette valeur de temps pour les deux modes de propagation, il est possible de déduire les valeurs de vitesses de propagation des ondes longitudinale (V_L) et transversale (V_T). Les valeurs du module d'Young sont enfin calculées d'après l'**Eq. 3**.

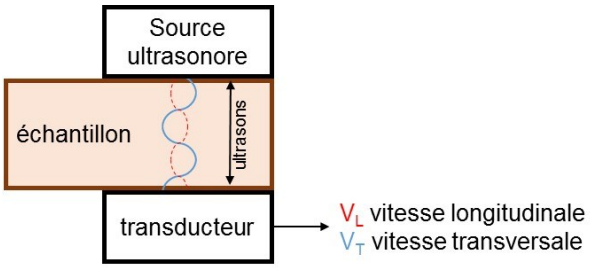


Figure 4. Schéma de principe de la mesure ultrasonore.

$$E = \rho \frac{3*V_L^2 - 4*V_T^2}{\left(\frac{V_L}{V_T}\right)^2 - 1} \qquad \textbf{Eq. 3}$$

Avec E : le module d'Young (GPa), ρ : la masse volumique apparente (g/cm³), V_L : la vitesse longitudinale (m/s) et V_T : la vitesse transversale (m/s).

Annexe III – I. Données issues d'analyses par porosité mercure sur les échantillons S1M1 et $S1M1_{0,7}A650_{0,3}$ $NaB^{8,5}$ avant et après traitement à 90 °C.

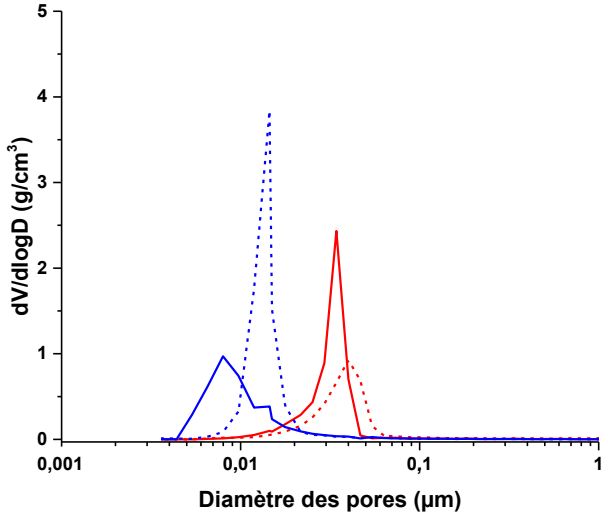


Figure 5. Distribution porosimétrique des échantillons (—) S1M1 20 °C, (- - -) S1M1 90 °C, (—) $S1M1_{0,7}A650_{0,3}$ $NaB^{8,5}$ 20 °C et (- - -) $S1M1_{0,7}A650_{0,3}$ $NaB^{8,5}$ 90 °C.

Tableau 2. Données relatives aux analyses de porosité mercure.

Echantillon	**S1M1**		**$S1M1_{0,7}A650_{0,3}$ $NaB^{8,5}$**	
Température (°C)	*20*	*90*	*20*	*90*
Porosité (%)	42,2	48,1	46,5	40,5
Taille moyenne (nm)	10	15	36	42

Annexe III – J. Exemple de fissures et de fractures apparaissant dans les blocs d'argilites suite à leur préparation.

(a)



(b)



Figure 6. Photographies de bloc d'argilites **(a)** fissuré en surface et **(b)** fracturé sur une zone de carottage (les lignes rouges sont des guides de lecture pour visualiser les zones de rupture).

Annexe III – K. Cartographies X des échantillons S1M1, S1M1A650 B et S1M1A650 NaB.

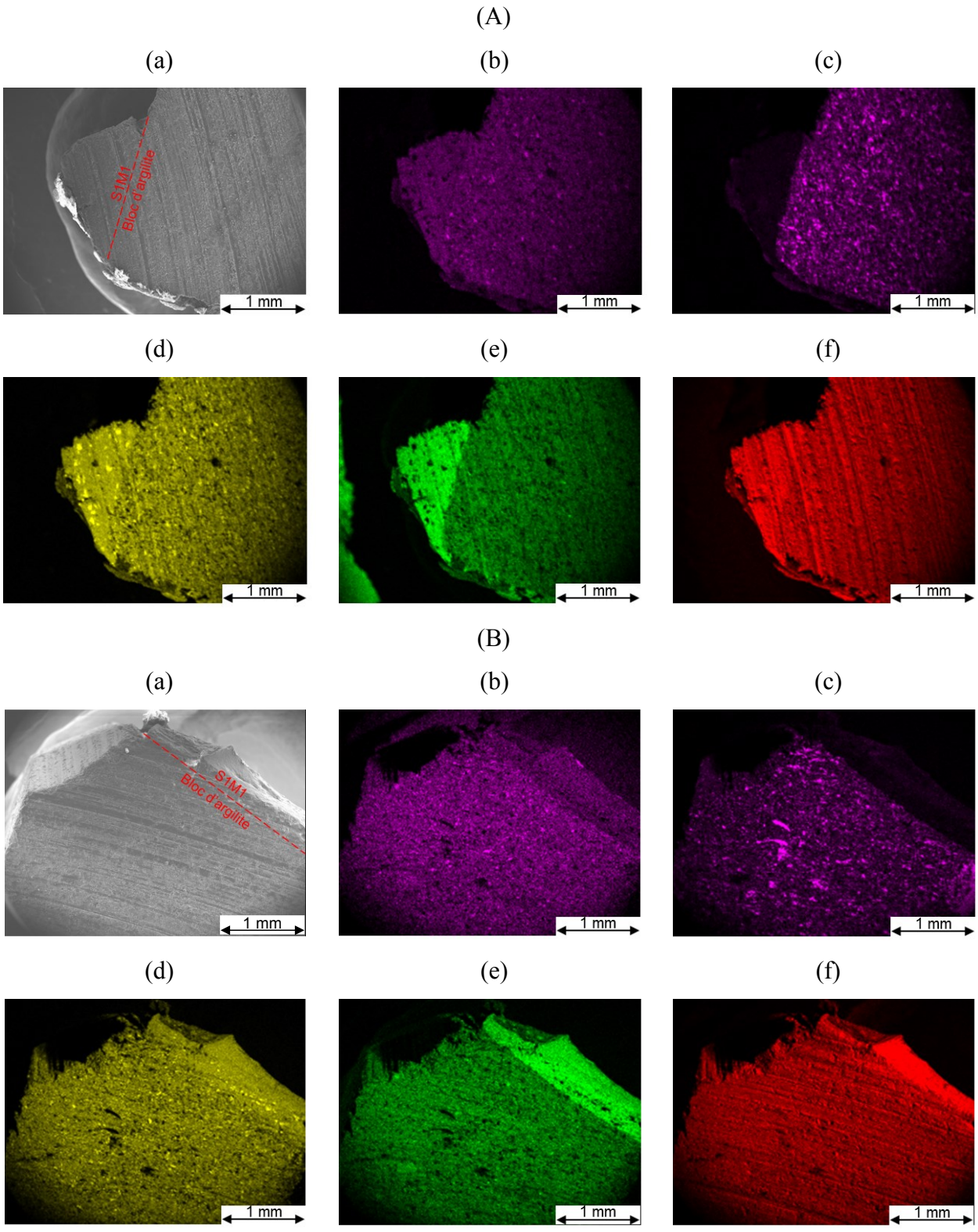


Figure 7. Cartographies X de l'échantillon S1M1 mis en contact avec un bloc d'argilites à **(A)** 20 et **(B)** 90 °C, avec **(a)** la photographie MEB, et l'intensité en pixel des raies **(b)** K (K_α = 3,312 keV), **(c)** Ca (K_α = 3,690 keV), **(d)** Si (K_α = 1,739 keV), **(e)** Al (K_α = 1,486 keV) et **(f)** O (K_α = 0,525 keV).

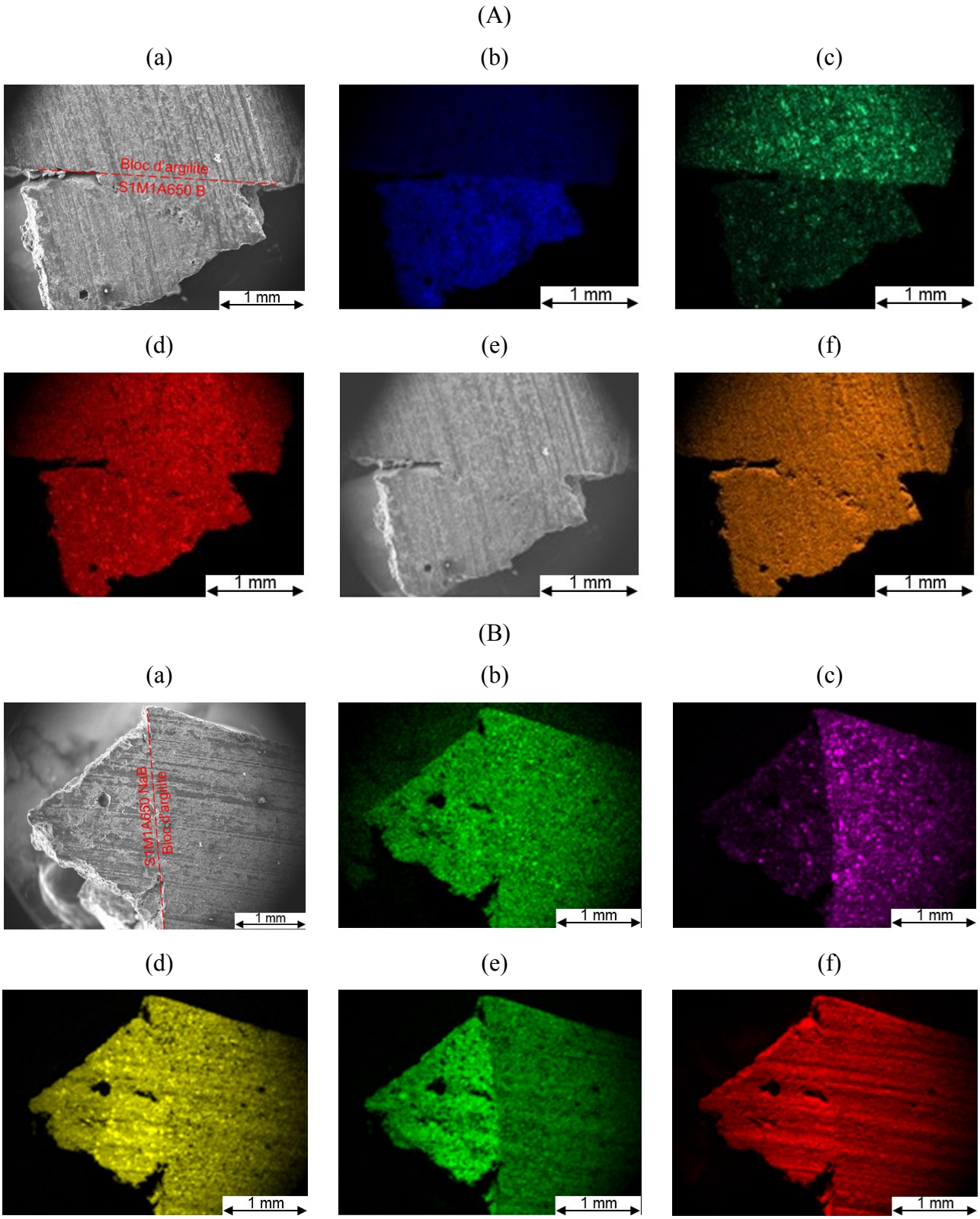


Figure 8. Cartographies X de l'échantillon S1M1A650 B mis en contact avec un bloc d'argilites à **(A)** 20 et **(B)** 90 °C, avec **(a)** la photographie MEB, et l'intensité en pixel des raies **(b)** K (K_α = 3,312 keV), **(c)** Ca (K_α = 3,690 keV), **(d)** Si (K_α = 1,739 keV), **(e)** Al (K_α = 1,486 keV) et **(f)** O (K_α = 0,525 keV).

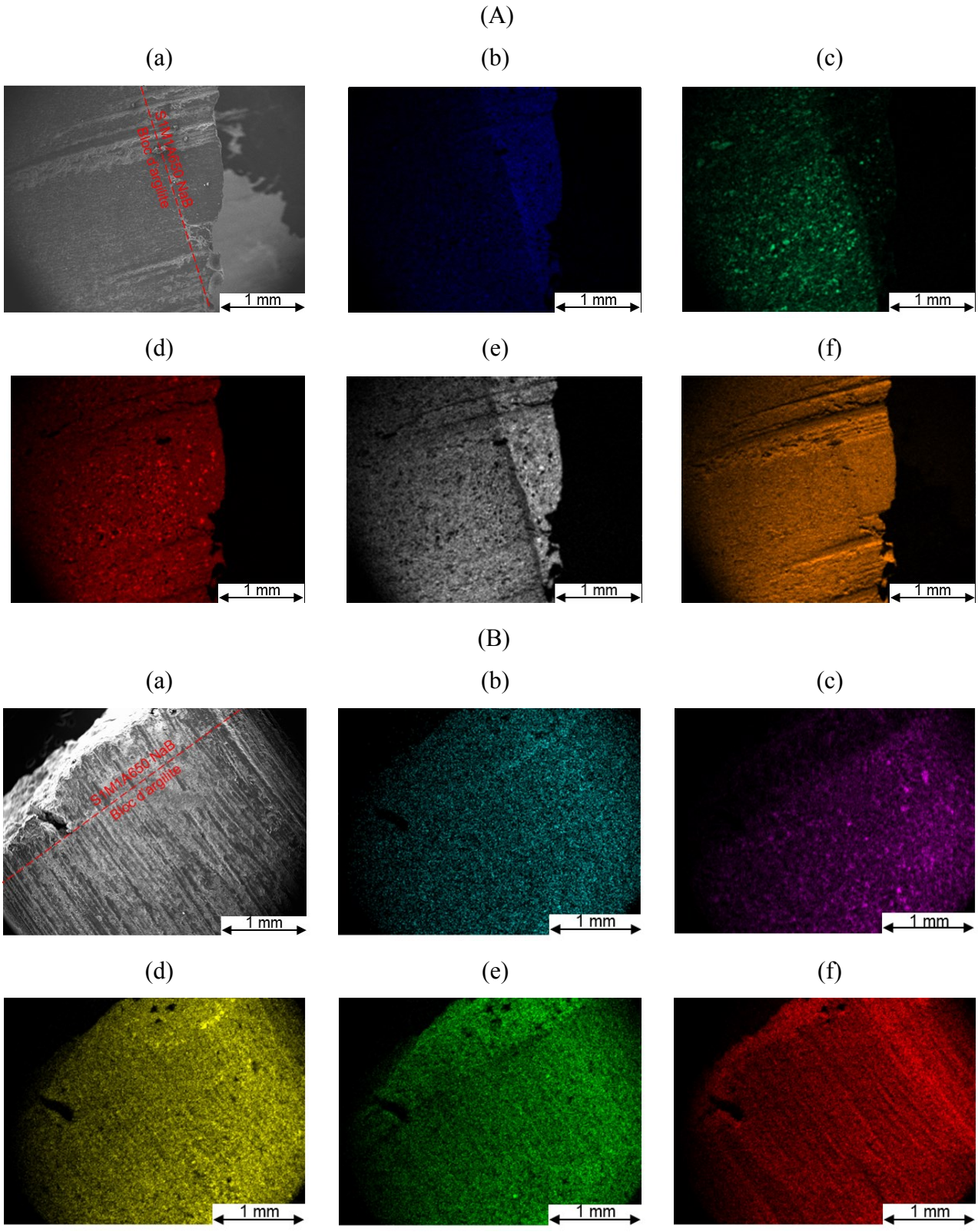


Figure 9. Cartographies X de l'échantillon S1M1A650 NaB mis en contact avec un bloc d'argilite à **(A)** 20 et **(B)** 90 °C, avec **(a)** la photographie MEB, et l'intensité en pixel des raies **(b)** K (K_α = 3,312 keV), **(c)** Ca (K_α = 3,690 keV), **(d)** Si (K_α = 1,739 keV), **(e)** Al (K_α = 1,486 keV) et **(f)** O (K_α = 0,525 keV).

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Résumé

Ce travail s'inscrit dans le cadre du projet Cigéo (Centre industriel de stockage géologique de déchets radioactifs) et a porté sur la valorisation des argilites du Callovo-Oxfordien sous forme de coulis d'injection activé alcalinement. Cette utilisation requiert un liant présentant une importante durée pratique d'utilisation (~24 heures) et une valeur de pH modérée (10-11). Ainsi l'activation thermique de l'argilite a dû être maitrisée afin d'accroitre la réactivité des espèces argileuses tout en limitant la décarbonatation, pour éviter la présence de calcium réactif. Une solution alcaline silicatée potassique, de réactivité modérée (Si/K = 0,70), a été utilisée pour l'activation alcaline des argilites calcinées. Afin de développer le coulis, il a été nécessaire de favoriser la réactivité de l'argilite par addition de métakaolin et d'incorporer des additifs à base de bore. Un coulis dont les caractéristiques correspondent à celles visées a ainsi été obtenu. Enfin, une étude du liant dans des conditions proches de celles de l'utilisation finale (injection entre la couche géologique d'argilites et le chemisage de déchets radioactifs) a été menée. Pour cela, le liant a été mis en contact avec un bloc d'argilites du Callovo-Oxfordien, à une température de 90 °C (température maximale en condition d'usage). Il a ainsi été mis en évidence qu'à 90 °C le réseau géopolymère se réorganise (intégration du bore dans le réseau et formation éventuelle de zéolite). La mise en contact du liant avec l'argilite géologique a aussi permis d'identifier une diffusion du potassium dans les argilites du Callovo-Oxfordien.

Mots-clés : Cigéo, argilites du Callovo-Oxfordien, géopolymère, coulis, durée pratique d'utilisation, valeur de pH, viscosité, bore, phosphore, spectroscopie IRTF et Raman, structure.

Abstract

In the context of Cigéo project (geological industrial disposal for radioactive wastes), this work focuses on the valorization of Callovo-Oxfordian argillite by the formulation of an alkali-activated grout. This application required a high setting time (close to 24 hours) and a moderate pH value (10-11). Thus, the argillite thermal treatment has been adapted to alter clays minerals without decomposing carbonate species (to avoid the presence of reactive calcium). A potassium-based silicate solution, with moderated reactivity (Si/K = 0.70), has been used for the alkali-activation step. Concerning the grout formulation, it has been necessary to enhance the argillite reactivity by the insertion of metakaolin and to add boron-based compounds. The resulting grout was in accordance with the specification. Finally, a study of the binder in an environment close to the using conditions (injection between geological layer and a radioactive waste lining) has been investigated. In this aim, the binder has been casted in contact with the geological argillite at 90 °C. It was evidenced a network reorganization at 90 °C (boron integration in the network and possible formation of zeolite). Potassium diffusion from the binder to the argillite has also been observed.

Keywords: Cigéo, Callovo-Oxfordian argillite, geopolymer, grout, setting time, pH value, viscosity, boron, phosphor, FTIR and Raman spectroscopy, structure.