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Titre :
Contribution to the requalification of Alkali Silica Reaction (ASR) damaged structures: Assessment of the ASR advancement in aggregates

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Abstract

Contribution to the requalification of ASR-damaged structures: Assessment of the ASR advancement in aggregates

In order to answer the questions of the ASR-affected structures owners, this work focused on a part of a global methodology, which is proposed originally by the LMDC and EDF, aiming to reassess the mechanical behavior of ASR-damaged constructions. To achieve this purpose, the chemical advancement of ASR in the aggregates recovered from the structure should be evaluated. Thus, this work focuses on the assessment of the potentially reactive silica content with two main methods: indirectly by expansion test and directly by chemical methods. The presentation of this manuscript is around the following points:

- A relevant and rapid expansion test on mortars to link the reactive silica content to measured expansion. The experimental condition: 1 mol/l NaOH solution conserved at 60°C is chosen to test different aggregate sizes, specimen sizes and natures of aggregate.
- A fast chemical method of selective dissolution to measure directly the silica available for ASR. Acid/basic methods are tested and compared; HF / HF+HCl method is found to be the most effective.
- A chemo-mechanical model to analyze the effect of aggregate size and specimen size, and evaluate the chemical advancement of ASR.

Finally, a methodology is proposed to calculate the kinetics constant in the framework of structural requalification.

Key words: alkali-silica reaction (ASR), chemical advancement, reactive silica, expansion test, chemical test, chemo-mechanical model, kinetic constant, selective dissolution
Contribution à la requalification des structures endommagées par l’alcali-réaction : Evaluation de l’avancement de l’alcali-réaction dans les granulats

Afin de répondre aux questions des propriétaires de structures atteintes de réaction alcali-silice (RAS), ce travail se concentre sur une partie d’une méthodologie globale, proposée initialement par le LMDC et EDF, et dont le but est l’étude du comportement mécanique des constructions endommagées par la RAS. Pour atteindre cet objectif, l’avancement chimique de la RAS des granulats récupérés dans les structures affectées doit être évalué. Ainsi, ce travail est consacré à la quantification de la silice potentiellement réactive des granulats, par l’utilisation de deux approches : une approche indirecte par un test d’expansion et une approche directe par des méthodes chimiques. La présentation du manuscrit s’articule autour des points suivants :

- Un test d’expansion pertinent et rapide sur mortiers pour relier la quantité de silice réactive à l’expansion mesurée. Les conditions expérimentales suivantes ont été choisies pour tester différentes tailles et natures de granulats, ainsi que différentes tailles d’éprouvettes : solution de NaOH à 1 mol/l et température de conservation de 60°C.

- Une méthode chimique rapide de dissolution sélective pour mesurer directement la quantité de silice réactive disponible pour la RAS. La méthode HF / HF+HCl a été trouvée comme étant la plus efficace.

- Un modèle chemo-mécanique pour analyser les effets de la taille des granulats et des éprouvettes, et évaluer l’avancement chimique de la réaction.

Finalement, une méthodologie est proposée pour calculer la constante cinétique de la réaction dans le cadre de la requalification des structures atteintes de RAS.

Mots clés : réaction alcali-silice (RAS), avancement chimique, silice réactive, test d’expansion, test chimique, modèle chemo-mécanique, constante cinétique, dissolution sélective.
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La réaction alcali-silice (RAS) est une réaction chimique délétère entre les alcalins du ciment et la silice réactive des granulats du béton. La RAS produit des gels expansifs et entraîne l'apparition de fissures dans les granulats et la pâte, causant des problèmes structuraux majeurs, qui peuvent mener à la démolition de l'ouvrage. Cette détérioration se produit dans le monde entier et dans tous les types de structures (comme les barrages, les ponts, les routes). Dans les structures endommagées, les conséquences de la RAS apparaissent après plusieurs années. Pendant un certain temps de latence qui peut durer plus de 10 ans, la réaction prend place dans le béton sans causer de problèmes structuraux. Une des principales interrogations des propriétaires de ces structures atteintes par la RAS est de savoir si cette réaction est presque achevée, ou s'il reste encore plusieurs années de gonflement. Une requalification de ces structures affectées peut aider le propriétaire à décider s'il est nécessaire de démolir ou réparer la structure.


Le LMDC (Laboratoire Matériaux et Durabilité des Constructions) et EDF (Electricité de France) ont donc proposé une méthodologie globale basée sur l'évaluation de l'avancement
chimique de la RAS (Figure 1). Cette méthodologie suppose que les alcalins ne sont pas le facteur limitant de la RAS en raison d'une substitution des alcalins par le calcium dans les gels produits par la réaction [Duchesne et Bérubé 1994, Lagerblad et Trägardh 1992, Jensen 1993]. Ainsi, la quantité de silice réactive est supposée être le facteur limitant de la réaction dans le béton des structures. Basée sur cette hypothèse, la méthodologie propose un essai de laboratoire mesurant la cinétique de consommation de silice et une analyse numérique inverse par éléments finis de la structure affectée (Figure 1). Le coefficient cinétique du modèle est déterminé en laboratoire et l'amplitude finale d'expansion est ajustée en utilisant un déplacement observé sur la structure. La capacité de prédiction du modèle a été validée par la comparaison entre le déplacement de points instrumentés prédits par les calculs et le déplacement mesuré sur la digue (non utilisé pour l'ajustement) [Grimal 2007, Sellier et al. 2009, Bourdarot et al. 2010].

![Figure 1 Résumé de la méthodologie globale [Sellier et al. 2009]](image.png)

1. Objectifs

Ce travail se concentre sur les essais de laboratoire effectués pour évaluer l'avancement chimique de la consommation de silice réactive (deuxième partie de la Figure 1). L'avancement de la consommation de la silice peut être évalué par deux méthodes principales : indirectement par des essais d'expansion comme proposé dans [Grimal 2007, Sellier et al. 2009] ou directement par des méthodes chimiques de quantification de la silice. Dans ce travail, les deux méthodes sont
étudiées. L'essai d'expansion étant la méthode la plus couramment utilisée dans les expérimentations de RAS, elle a donc été analysée en premier. Les essais chimiques sur les poudres obtenues des granulats réactifs peuvent être plus rapides que les essais d'expansion, mais les résultats peuvent ne pas être représentatifs de la RAS dans le béton. Cette partie est donc présentée après les essais d'expansion. Un modèle chemo-mécanique est utilisé pour analyser ces deux méthodes et évaluer l'avancement chimique de la réaction pour une utilisation de requalification de la structure. Ainsi, trois objectifs peuvent être atteints :

1. Proposer un essai d'expansion en laboratoire, rapide et pertinent, dans le but d'évaluer la quantité de silice réactive des granulats. La méthode doit garantir des conditions de conservation contrôlées des éprouvettes, et optimiser la taille des éprouvettes et des granulats.

2. Trouver une méthode chimique pour mesurer la silice disponible dans un granulat, silice susceptible de réagir avec les alcalins contenus dans le béton. La méthode doit être rapide et fiable.

3. Développer un modèle chemo-mécanique pour évaluer l'avancement chimique de la réaction. Ce modèle doit inclure la diffusion des alcalins dans les granulats et la pâte de ciment, le processus chimique de fixation des alcalins, la consommation de la silice et la production de gels de RAS.

Ces trois objectifs sont résumés sur la Figure 2.

![Diagram](image)

*Figure 2  Relation entre les trois objectifs de ce travail.*

### 2. Plan de la thèse et résultats

Pour réaliser ces objectifs, quatre parties sont développées :

*Bibliographie (chapitre 1)*
La bibliographie concernant la Réaction Alcali-Silice est étudiée dans ce chapitre. Comme ce travail se concentre sur les données d'entrée nécessaires à la requalification des structures atteintes de RAS, une grande partie de la bibliographie concerne les méthodes existantes de requalification de structures. Les références spécifiques des techniques développées dans ce travail sont données au début de chaque chapitre.

*Optimisation des essais d'expansion (chapitre 2)*

Dans le but d'obtenir des résultats rapides, un essai d'expansion accéléré à 60°C dans une solution de NaOH est choisi. La quantité d'alcalins est supposée suffisante pour garantir la consommation de toute la silice réactive. De plus, en tenant compte du temps nécessaire aux alcalins pour diffuser dans les éprouvettes et dans les granulats, les éprouvettes et les granulats ne doivent pas être trop volumineux. Différentes tailles d'éprouvettes et de granulats sont testées. Plusieurs types de roches sont évalués pour vérifier si le test d'expansion peut différencier la réactivité des différents granulats.

Les conclusions principales tirées de ces essais nous ont permis de proposer des conditions optimisées pour les essais à effectuer sur les granulats réactifs :

- Dans la condition d'un excès d'alcalins, la concentration en alcalins semble avoir un effet négligeable sur la cinétique d'expansion et sur l'expansion finale.

- Concernant le choix de la taille des granulats, il a été constaté que les expansions finales mesurées sur les éprouvettes contenant des granulats fins ont été atteintes dans des délais plus courts que pour les éprouvettes contenant des granulats plus grossiers. Le temps nécessaire pour atteindre l'expansion asymptotique sur les petites éprouvettes est principalement dû au temps de diffusion des espèces ioniques dans les granulats. Cependant, si les particules sont trop petites, le gel produit par le granulat peut migrer dans la porosité connectée et causer peu d'expansion. Dans le cas du calcaire siliceux, la fourchette de taille 315-630 µm s'est avéré un bon compromis.

- Pour ce qui concerne la taille des éprouvettes, les plus petites (20 x 20 x 160 mm) montrent la cinétique de gonflement la plus grande. Cependant, une partie de l'expansion n'est pas mesurée, en raison d'un effet couplé entre la taille des granulats et la taille des éprouvettes sur l'expansion. Au-delà de la méthodologie de requalification exposée, l'observation de cet effet nous semble également être une conclusion importante de ce travail. Il a ainsi été montré que l'effet pessimum de la taille des granulats sur l'expansion de RAS était un phénomène qui n'était pas seulement intrinsèque au granulat, mais qu'il était aussi provoqué par les conditions expérimentales. Cela peut être expliqué par la proportion de gels de RAS qui est absorbé par le volume de vide créé par la fissuration, causant une diminution de la pression de gel et réduisant de ce fait l'expansion induite.

- Enfin, pour le calcaire siliceux étudié, les petits granulats (315-630 µm) et les petites éprouvettes (20 x 20 x 160 mm) se sont avérés convenables pour un essai rapide d'expansion. Cependant, ces conditions peuvent dépendre de la nature du granulat. Afin
d'optimiser les conditions d'essai selon la nature du granulat, il semble être important de mesurer la réactivité potentielle du granulat. Dans ce but, les essais chimiques (chapitre 3) peuvent être un outil utile.

**Dosage chimique de la silice réactive dans les granulats (chapitre 3)**

Le chapitre 3 présente une étude sur « les essais chimiques » prévus pour mesurer la silice réactive des granulats. La silice réactive est un concept relatif qui est employé pour définir la partie de la silice qui peut réagir avec les alcalins pour produire des gels de RAS. Afin de connaître avec précision la quantité de silice réactive disponible pour la RAS, la meilleure manière serait de simuler l'environnement du béton mais c'est pratiquement impossible considérant le temps de réaction. Les études minéralogiques ont montré que la silice réactive inclut les minéraux amorphes, les minéraux cryptocrystallins et les minéraux cristallins contenant des imperfections. En outre, considérant que tous les types de silice (silice réactive et silice bien cristallisée) ont une certaine solubilité dans un environnement acide ou basique, la méthode doit distinguer les capacités de solubilité de la silice réactive et de la silice bien cristallisée. Ainsi, trois méthodes d'attaque, NaOH-HCl, HCl-KOH, et HF/HF+HCl, ont été employées pour tester différents types de granulats. La quantification chimique a été comparée aux expansions obtenues sur des mortiers contenant ces granulats. Les principaux résultats des analyses trouvées sont :

- Pour l'attaque NaOH-HCl, la haute température (100°C) est efficace pour dissoudre la silice. Cependant, l'essai n'a pas pu distinguer la dissolution de la phase réactive et de la phase bien cristallisée. L'attaque NaOH-HCl semble dissoudre les minéraux bien-cristallisés, qui ne réagissent pas avec les alcalins dans les conditions réelles du béton.
- L'attaque HCl-KOH s'est avérée ne pas convenir puisque le quartz non-réactif a été attaqué. En outre, cette attaque permet seulement un essai à la fois et, il n'est pas possible de distinguer les différentes formes de silice.
- L'attaque HF/HF+HCl s'est avérée le meilleur compromis puisqu'elle a séparé les silices réactives et non-réactives. Bien que ce soit une attaque acide, le résultat a montré la meilleure corrélation avec les essais de gonflement sur mortiers. En outre, cette méthode est rapide (24h) et simple.

**Modélisation chemo-mécanique (Chapitre 4)**

Le chapitre 4 propose un modèle chemo-mécanique amélioré pour analyser les résultats des essais d'expansion et pour évaluer l'avancement chimique de la réaction. Ce modèle est basé sur un modèle précédemment développé par Multon et al [2009]. Afin de déterminer l'expansion de la RAS, la diffusion et la fixation des alcalins dans les granulats et l'endommagement du béton ont été considérées. Des modifications étaient nécessaires pour prendre en compte la diminution de l'expansion avec le rapport "taille de éprouvette / taille de granulat" et la non-linéarité de l'expansion avec la teneur en silice réactive des granulats, phénomènes observés pendant les expériences (chapitre 2). Les questions principales au sujet du modèle sont résumées ci-dessous :
Cinq paramètres de la modélisation physico-chimique ont été évalués par l'ajustement des courbes d'expansion obtenues sur les plus grosses éprouvettes.

Les paramètres ajustés ont été employés pour évaluer l'expansion de la RAS des autres éprouvettes de plus petites dimensions et conservées dans différentes concentration de NaOH. Le modèle peut reproduire les différences d'expansion dues à la taille des granulats, la taille des éprouvettes et la nature des granulats. Il valide la fonction proposée pour représenter les effets combinés des tailles de granulats et d'éprouvettes et de la quantité de silice réactive.

*Méthodologie d'étude de la constante cinétique de l'expansion (Chapitre 5)*

Le chapitre 5 récapitule les résultats des chapitres 2, 3 et 4 en présentant une méthode pour calculer la constante cinétique d'expansion, qui est utile pour établir la cinétique d'expansion du béton in situ. Le calcul de ce paramètre à partir du modèle micro chemo-mécanique montre qu'il varie avec les différentes tailles de granulat et est peu affecté par la taille de l’éprouvette. Enfin, une méthodologie est proposée pour calculer la constante cinétique dans le cadre de la requalification structurelle.
Alkali-Silica Reaction (ASR) is a deleterious chemical reaction between the alkali hydroxides from the concrete pore solution and the silica of reactive aggregate in concrete. ASR produces expansive gels and causes cracking of aggregate and paste, sometimes resulting in major structural problems which could lead to extensive maintenance, repair and demolition in extreme cases. This deterioration occurs worldwide and in all types of structures (such as dams, bridges, roads, breakwaters). In damaged structures, the consequences of ASR become noticeable after a period which could be as short as 5 years. During a latent time, the reaction takes place in the concrete without causing structural problems. The latent time can last more than ten years. One of the main concerns for the owners of these ASR-damaged structures is to know whether the reaction is almost finished or if many years of swelling still remain. A requalification of the ASR-affected structures could help the owner to decide whether to demolish or repair the structures.

Several methods have been proposed to reassess ASR-affected structures [Léger et al. 1995, Li et al. 2000, Li et al. 2001, Li and Coussy 2002, Malla and Wieland 1999, Saouma and Perotti 2006, Saouma et al. 2007, Saouma 2009]. Most of them are based on the measurement of residual expansion on core samples drilled in affected structures. The residual expansion tests, which keep the samples in a controlled environment (at 38°C, R.H. > 95%) have some limits. The limits include: 1) the reactive silica in large aggregates cannot be consumed totally considering the duration of the test [Sellier et al. 2009], 2) the ASR-gels do not have the same composition in accelerated tests as in real structures [Urhan 1987], 3) alkali leaching during the tests can have a deleterious effect on the assessment of the asymptotic expansion [Rivard et al. 2003, Rivard et al. 2007], 4) the high moisture conditions (>95%) are difficult to control, which leads to significant variations of ASR expansions for relative humidity (R.H.) ranging between 95% and 100% [Poyet et al. 2006]. These limits lead to differences between calculated results obtained with data coming from this residual expansion test and in-situ observations performed on structures [Sellier et al. 2009].

Therefore, the LMDC (Laboratory of Materials and Durability of Construction) and EDF (Electricité de France) have proposed a global methodology based on the assessment of chemical
advancement (*Figure 1*). This methodology assumes that the alkali content in concrete is not the limiting factor in ASR due to the substitution of alcalis by calcium in the ASR gels [Duchesne and Bérubé 1994, Lagerblad and Trägardh 1992, Jensen 1993], and the limiting factor in concrete structure is the quantity of silica. Based on this assumption, the methodology proposes a laboratory test dealing with the silica consumption kinetics and a numerical finite element inverse analysis of the affected structure (*Figure 1*). The kinetic coefficient of the model is determined in the laboratory and the final swelling amplitude is fitted using one observed structural displacement. The model prediction capability has been validated through the comparison between the displacement of instrumented points predicted by the calculations and the displacement measured on the dam (not used for the fitting) [Bourdarot et al. 2010, Grimal 2007, Sellier et al. 2009].

### Figure 1  Global methodology summary [Sellier et al. 2009]

<table>
<thead>
<tr>
<th>AAR kinetic and swelling amplitude assessment</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Affected structure</strong></td>
</tr>
<tr>
<td>Core samples drilled in various zones:</td>
</tr>
<tr>
<td>- Wet, dry, concrete type…</td>
</tr>
<tr>
<td>Structural monitoring:</td>
</tr>
<tr>
<td>- Displacements</td>
</tr>
<tr>
<td>- Temperatures</td>
</tr>
<tr>
<td>- Moistures</td>
</tr>
<tr>
<td><strong>Laboratory tests:</strong></td>
</tr>
<tr>
<td>Assessment of reactive silica consumption kinetic</td>
</tr>
<tr>
<td>Reactive silica consumption measurement for each drilling zone and for each aggregate size range</td>
</tr>
<tr>
<td><strong>Finite element inverse analysis of the affected structure:</strong></td>
</tr>
<tr>
<td>Swelling amplitude assessment</td>
</tr>
<tr>
<td>Search for swelling amplitude compatible with:</td>
</tr>
<tr>
<td>- environnemtal conditions</td>
</tr>
<tr>
<td>- reactive silica consumption kinetics</td>
</tr>
<tr>
<td><strong>Finite element analysis</strong></td>
</tr>
<tr>
<td>- Displacements and damage patterns prediction</td>
</tr>
<tr>
<td>- Repair efficiency assessment…</td>
</tr>
</tbody>
</table>

### 3. Objectives

This work focuses on the laboratory tests performed to assess the chemical advancement of silica consumption (the second part of *Figure 1*). The advancement of silica consumption can be assessed by two main methods: indirectly by expansion test as proposed in [Grimal 2007, Sellier et al. 2009] or directly by chemical methods of silica quantification. In this work, the two methods are investigated. Expansion test is the most usual method used in ASR experimentation,
so it is analyzed firstly. Chemical test on powders made from aggregate can be faster than expansion test but the results may not be representative of the ASR in concrete. Therefore, it is presented after the expansion tests. A chemo-mechanical model is used to analyze these two methods, and evaluate the chemical advancement for the use of structural requalification. Thus, three objectives should be achieved:

1. Propose a fast and relevant expansion test in the laboratory to evaluate the reactive silica content in aggregates. The method should guarantee reliable conservation conditions of specimens and optimize the size of specimen and aggregate.

2. Find a chemical method to measure the silica available in an aggregate to react with the alkali contained in the concrete. The method should be fast and convenient.

3. Develop a chemo-mechanical model to evaluate the chemical advancement. This model should include the diffusion of alkali in aggregate and in cement paste, the chemical process of the fixation of alkali, the consumption of silica and the production of ASR gels.

These three objectives are summed up in Figure 2.

<table>
<thead>
<tr>
<th>Expansion test</th>
<th>Chemical measurement of reactive silica</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Curve fitting</td>
</tr>
<tr>
<td></td>
<td>Chemo-mechanical modeling</td>
</tr>
<tr>
<td></td>
<td>Assessment of chemical advancement</td>
</tr>
</tbody>
</table>

*Figure 2  Relation between the three objectives of this work*

4. **Plan of the thesis**

In order to achieve these objectives, four parts are developed:

*Bibliography (chapter 1)*

Before the investigations, references concerning Alkali-Silica Reaction are studied. As this work focuses on the input data necessary to reassess ASR-damaged structures, a large part of the bibliography concerns the methodology of requalification of structures. Specific references of the techniques developed in this work are given at the beginning of each chapter.
**Optimization of an expansion test (chapter 2)**

In the purpose of getting rapid results, an accelerated expansion test at 60°C and in NaOH solution is chosen. Considering that the amount of alkali is sufficient to guarantee the consumption of all the reactive silica, conservation in solutions with different alkali concentrations is tested. In addition, taking account of the time needed for alkalis to diffuse in the specimens and in the aggregate, the specimens and the aggregates should not be too large. Different specimen and aggregate sizes are tested. Several types of rocks are tested to verify whether the expansion test can differentiate the reactivity of different aggregates.

**Chemical measurement of reactive silica in aggregate (chapter 3)**

Several methods exist for attacking silica. However, these methods cannot attain the objective of directly measuring the total amount of silica available for ASR. Thus, a literature survey is made to summarize and analyze the existing methods. Inspired by these methods, acid and/or basic attacks are chosen to test different types of aggregates. Combined with the mineralogical studies - XRD and petrographic studies, the chemical results are compared and discussed in order to choose the most relevant method in comparison with the expansion test.

**Chemo mechanical modelling (chapter 4)**

This part includes the improvement of an existing microscopic model to understand the mechanism involved the development of expansion in ASR-damaged specimens. The microscopic model is based on the model built by Multon et al. [2009]. Modifications should be conducted due to the differences in experimental conditions (specimens immersed in alkali solution instead of conservation in air at 95% R.H. as in the previous work), and due to the tested samples (particularly the effect of the sizes of the specimens on the expansions, which was not considered in the previous work).

**Methodology to assess the kinetics constant of expansion (chapter 5)**

This chapter, based on the findings of Chapter 2, 3 and 4, aims to re-build the expansion kinetics in the framework of structural modelling. It includes two parts:

- Introduction of the significance of the kinetics constant in the laboratory test.
- Presentation of a methodology to calculate the kinetics in the framework of structural requalification.

The conclusion recalls the main results of the investigations and proposes some perspectives, which could be used for requalification of structures damaged by ASR.
1. Introduction

Alkali-Silica Reaction (ASR) is a common type of Alkali-Aggregate Reaction (AAR). It is a deleterious chemical reaction occurring in all types of structures: dams, bridges, roads and breakwaters, containing alkali reactive aggregates. Three main factors are considered to be necessary for this reaction: the high alkali content in the pore solution, reactive silica in aggregate and the humidity in the environment. These three factors are indispensable elements stimulating the alkali-silica reaction. Reviewing the history of the ASR in 1935, Holde explored the reactions between cements and certain aggregates [Comby-Peyrot 2006], and in 1940 Stanton described the nature of the reagents of ASR and observed the disorders in the structures. In 1941, the hydraulic structure “Parker Dam” (USA) was first identified as affected by alkali aggregate reaction [Corneille et al. 1991]. Afterwards, many structures were gradually found to be affected by this harmful reaction.

The interest in research in this field has increased because of the risk to structure safety and the high cost of structure repairs. Figure I-1 shows the number of papers recorded in the proceedings of ICAAR (International Conference on Alkali-Aggregate Reaction in Concrete), which demonstrates the increasing trend of research into the reaction in the past three decades. The research is distributed in four main fields: the mechanism of ASR, prevention of ASR, diagnosis and assessment of damage, and management of damaged structures. In this work, particular attention is paid to the requalification of the damaged structures.
Chapter I

Considering the complexity of ASR, which refers to the chemical process, the materials and the mechanical consequences, this chapter introduces the background of ASR from different standpoints. Firstly, the mechanism of the chemical reaction is presented and the factors affecting the reaction are summarized. Then the mechanical consequences are presented from the material point of view. The incidence on structures in the field and in the laboratory is illustrated to give a global concept of the damage. Then the methods of diagnosis are explained that detect ASR damage macroscopically. Later, the models used to requalify the structures are introduced and the method used in LMDC is highlighted. Finally, the plan of this work is described.

2. Alkali silica reaction (ASR)

2.1. Mechanisms of the reaction

Understanding the mechanism of the ASR is a basic step to know the reasons causing the degradation, and also is helpful in evaluating the attacked structures and then finding methods to prevent the damage. However, until now there has not been a consensus on the mechanism. The disagreements have led to two main theories: one of them considers that the ASR occurs on the surface of the aggregate and then forms gel diffusing into the pore solution [Dent Glasser and Kataoka 1981], the other thinks that all the reagents of ASR meet and react in the pore solution and then precipitate in gel [Dron and Brivot 1993]. The main principle of the mechanism proposed by Dent Glasser and Kataoka [1981] includes two processes:

- Ionic species (such as Na⁺, K⁺, OH⁻) diffuse around the aggregates, and then disrupt the silanol and siloxane bonds contained in the reactive silicate (Figure I-2).
Chapter I

Figure I-2 Alkalis attack the Si-O bonds (according to [Poole 1992])

- Alkali silicate reacts with the ionic species (Na\(^+\), K\(^+\), Ca\(^{2+}\)) and form ASR gels. This process has been described in detail in [Ichikawa and Miura 2007; Ichikawa 2009]. The Ca\(^{2+}\) ions penetrate the soft alkali silicate which covers the aggregate to re-polymerize the silicate, and pack a rapid reaction rim around the aggregate which allows the penetration of the ionic species (Na\(^+\), K\(^+\), Ca\(^{2+}\) and OH\(^-\) ions). The penetration of these ionic species converts the fresh silicate into bulky alkali silicate gels.

ASR gels can exert high imbibition pressures during the swelling process. The osmotic pressures force the gel to fill in the open pores which are between aggregate and cement paste. Once the volume of the gel is greater than the porous volume, a swelling pressure caused by gel leads to cracking and degrades the concrete (Figure I-3).

Figure I-3 Cracks caused by ASR gel filling the open pores

The role of Ca ions in the formation of gel has been discussed for a long time. Some authors think that Ca ions are indispensable in the formation of gel. Without Ca ions, the silicate ions stay in the solution and do not form gel [Diamond 1989]. However, too much Ca ion in the gel could decrease the capacity of gel to expand [Dent-Glasser 1979, Wilson et al. 1994]. In addition, another role of Ca ions is to substitute and release Na ions, and this process reproduces “new available” alkalis and makes the ASR continue [Wang and Gillot 1991]. However, this substitution process is frequently ignored in laboratory tests since it is a slow process, often
observed in structures in the field [Duchesne and Bérubé 1994, French 1989, Lagerblad and Trägardh 1992].

2.2. Factors affecting ASR

Three components are necessary to induce ASR damage:

1) Reactive silica from aggregate
2) Alkalis, mainly from cement but also from other materials
3) Water from the concrete mix-design and the environment of the field structures.

2.2.1. Reactive silica

Aggregate is the main source of reactive silica, and the silica reactivity depends on the aggregate. Aggregates used in mass and reinforced concrete mainly come from sand, gravel and crushed rock and so on. Sand and gravels are derived from the weathering of rocks. Thus, knowing the petrographic properties of the rocks is helpful for the owners to prevent ASR. *Table I-1* gives a list of rocks which have been considered as reactive to ASR. The reactivity of aggregates depends on several factors, such as the grain size of the aggregate, the angularity of the aggregate and the content of reactive aggregate or mineral form[Multan et al. 2008, Ramyar et al. 2005]. The rocks shown in *Table I-1* represent those that are most prone to ASR, but it does not suggest that these are always prone to ASR.

*Table I-1  Some of the rocks found to be reactive to alkalis (according to [French 1992])*

<table>
<thead>
<tr>
<th>Sedimentary rocks</th>
<th>Igneous rocks</th>
<th>Metamorphic rocks</th>
</tr>
</thead>
<tbody>
<tr>
<td>orthoquartzite</td>
<td>andesite</td>
<td>quartzite</td>
</tr>
<tr>
<td>shale</td>
<td>rhyolite</td>
<td>phyllite</td>
</tr>
<tr>
<td>greywacke</td>
<td>rhyolitic tuff</td>
<td>granite gneiss</td>
</tr>
<tr>
<td>sub-greywacke</td>
<td>silicified tuff</td>
<td>slate</td>
</tr>
<tr>
<td>chert</td>
<td>devitrified glass</td>
<td>amphibole</td>
</tr>
<tr>
<td>siliceous limestone</td>
<td>granite</td>
<td>metabasalt</td>
</tr>
<tr>
<td>siliceous dolostone</td>
<td>pumice</td>
<td>hornblende schist</td>
</tr>
<tr>
<td>sandstone</td>
<td>tuff</td>
<td>mica schist</td>
</tr>
<tr>
<td>argillite</td>
<td>dacitic tuff</td>
<td></td>
</tr>
<tr>
<td>arkose</td>
<td>diorite</td>
<td></td>
</tr>
<tr>
<td>taconite</td>
<td>dacite</td>
<td></td>
</tr>
<tr>
<td>chalcedony</td>
<td>dacitic tuff</td>
<td></td>
</tr>
<tr>
<td>opal</td>
<td>obsidian</td>
<td></td>
</tr>
<tr>
<td>marl</td>
<td>trachyte</td>
<td></td>
</tr>
<tr>
<td></td>
<td>felsites</td>
<td></td>
</tr>
<tr>
<td></td>
<td>basalt (Depends on the roches)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>granophyres</td>
<td></td>
</tr>
</tbody>
</table>
Chapter I

2.2.2. Alkalis

The source of alkalis can be Portland cement, aggregates, chemical admixtures, external sources (such as seawater, deicing salts). Of the above materials, cement is considered as the main source of alkalis [Corneille et al. 1991].

The alkali content of Portland cement is normally measured as sodium and potassium oxides ($Na_2O$ and $K_2O$) expressed as the “equivalent sodium oxide” content as follows:

$$Na_2O_e \% = Na_2O \% + 0.658 \times (K_2O \%)$$  \[I-1\]

$Na_2O_e =$ total sodium oxide equivalent in percent by mass

$Na_2O =$ sodium oxide content in percent

$K_2O =$ potassium oxide content in percent

Portland cements containing less than 0.60% equivalent sodium oxide are considered to be low-alkali cements. This value has been cited in various international specifications as the specification limit of ASR. However, this specification was found not to be effective since some cases with a quantity of alkalis lower than 0.60% has also given rise to harmful expansion [Corneille et al. 1991]. Some reports thought that the neglect of the other source of alkalis (like aggregate, admixture et al.) could be a reason to explain these phenomena [Corneille et al. 1991]. Thus, another calculation of total alkali content of the concrete was proposed. The calculation is based on the consideration of all the sources of alkalis and the percentage of these materials in the concrete. A range of 3~5 kg/m$^3$ $Na_2O_e$ has been proposed as the threshold of ASR by many papers, below this range the ASR expansion is negligible, above this range the ASR expansion increases with the alkali content. In Canadian standards (CSA A23.2-27A), a limit of 1.2 kg/ m$^3$ $Na_2O_e$ is required to control ASR when the “high risk structures” have to be built.

2.2.3. Water

Available moisture is necessary for ASR to occur since the ASR gel forms through imbibing water, and causes expansion within concrete. Concrete with reactive aggregates and high alkali content has shown little or no expansion in very dry environments. Generally, it is believed that a relative humidity of less than 80% will not cause significant expansion due to ASR [Corneille et al. 1991]. The reaction will proceed when the humidity rises above 80%. Although limiting the availability of moisture to the structures is an effective way to reduce ASR damage for some types of structures it is not feasible since for some structures like dams and bridges where humidity is unavoidable [Poyet 2003].

2.2.4. Other factors

Apart from the three factors referred to above, other elements of concrete also have an effect on ASR. For instance, mineral admixtures (such as silica fume, fly ash, blast furnace slag), which are well known for their properties of modifying concrete behaviour physically and
mechanically, can constitute a valid defence against ASR [Corneille et al. 1991, Fournier et al. 2004]. This defence is mainly caused by the reaction between the active component of mineral admixtures, the alkalis in the pore solution of concrete leading to reduction of the alkalinity, the consumption of Ca(OH)$_2$, and the reduction of permeability and moisture diffusion[Carles-Gibergues et al. 2008]. However, due to the substitution of alkalis by calcium ions, the alkali can regenerate and react with reactive aggregate again, which could lead to the invalidation of this ASR defence effect[Multon et al. 2009]. Thus, some authors emphasize that, in order to limit the effects of ASR, mineral admixtures should be added in an abundant amounts such as in[Hobbs 1988, Turriziani 1986] et al.

2.3. Mechanical consequences

Understanding the mechanical consequences of ASR is also very helpful to comprehend and predict the degradation and damage. In this part, the kinetics of the expansion, anisotropy and compressive stress on expansion will be explained from the material point of view.

2.3.1. The kinetics of expansion

The kinetics of expansion has already been described by many authors [Clayton 1989, Larive 1998]: all expansion curves have a high and increasing initial rate of swelling, followed by a decrease of the rate until a long-term expansion asymptote is reached. Different with this classical model, some authors have put forward other explanations. Larive [1998] thinks that the latent time of the reaction depends on the reaction temperature: at ambient temperature, the kinetic curve shows an “S”-form, indicating a very slow rate of expansion at first, then increasing rapidly, and finally gradually slowing down. Carles-Gibergues and Cyr [2002] summarized the results found in the literature about the expansion kinetics of concrete in accelerated tests and concluded that, instead of reaching an asymptote, the ASR-attacked concretes often continue to expand at a low rate.

2.3.2. Anisotropy

The ASR expansion is anisotropic, and thus the expansion results depend on the exposure conditions (wind, localised exposure to sun and moisture), the conditions of measurement and the process of concrete fabrication. This view has been proved in many studies [Ballivy et al. 2000, Larive et al. 2000, Smaoui 2003].

Larive et al. [2000] thought that the anisotropic characteristic of AAR expansion derived from many local factors (such as concrete porosity, tensile strength variation and aggregate distribution) that may affect cracking formation. Smaoui [2003] pointed out that “the form of the sample (such as cylinder, prism), the direction used for the measurement, the methods used during the casting have an important effect on the ASR expansion”. Multon and Toutlemonde [2006] summarized the literature and considered that the anisotropy was influenced by the directions of the cracks. They also quantified the effect of stresses on ASR expansion anisotropy.
This effect of anisotropy due to the direction studied should be considered in the model, in order to avoid over or under estimating the results.

2.3.3. The effect of compressive stress on expansion

According to the literature [Jones and Clark 1996, Larive 1998, Le Roux et al. 1992, Multon and Toutlemonde 2006], the compressive stress influences the kinetics of ASR expansion in the direction of loading and this effect leads to the reduction of expansion in the direction of loading or stress. However, this view has given rise to disputes. Some authors think that this reduction of expansion “decreases” only superficially in the loading direction but actually the expansion is transferred to the direction without load; the volumetric expansions should then be constant. Some authors do not agree with this view. They think that the volumetric expansions depend on the value of the compressive stress [Larive et al. 1996][Smaoui 2003]. Saouma [2009] thinks that, if the compressive stress is “large”, the volumetric increase is reduced due to the formation of structural micro/macro cracks which will absorb the gel without pressurizing the adjacent concrete.

3. Incidence of ASR on civil engineering structures

3.1. ASR-damaged structures in the field

In 1985, a report from ICOLD (International Commission of Large Dams) summarized the damage to dams caused by alkali-aggregate reaction, which involved 24 structures in USA, 5 dams in France, 3 dams in Spain, 2 in India, 2 in Brazil and so on. [Corneille et al. 1991]. Another report [Charlwood 2009] gives statistical data on the dams damaged by AAR (Figure I-4).
Some other countries have also reported the incidence of AAR on structures. Gilks and Curtis [2003] reported on the Mactaquac Dam in Canada; Jabarooti and Golabtoonchi [2003] on an Iranian dam; Malla and Wieland [1999] a dam in Switzerland. In France, among 130 large concrete dams examined for ASR, 30% show swelling effects, 10 need special attention (strain > 10µm/m/year), 3 have great problems: Le Chambon, Maury and Temple-sur-Lot. And hundreds of bridges are also involved in ASR problems [Larive 1998]. Some authors give summaries of this incidence, Fu et al. [2004] and Li [2004] present the structures affected in China; Durand et al. [2004] summarize ASR history in Québec, Canada; Leemann et al. [2004] present the affected underground structures in Switzerland, Richardson [2004] gives a survey of recent research cases in the Republic of Ireland. In addition to the cases mentioned above, new cases seem to be explored and published every year all over the world. This trend indicates that ASR is not a phenomenon occurring only in certain places or certain countries; it is a universal problem involving many types of structures. Typical ASR damage on structures includes several features, such as:

- Exudation of gels into the surface cracking
- Signs of expansion, relative movement between structural elements;
- Appearance of longitudinal cracks and/or map cracking (random cracking pattern). The cracks of macro and micro level can radiate from the interior of the aggregate out into the surrounding paste.
- Deformation or displacement of the structures

3.2. ASR-damaged concrete in the laboratory

The effect of ASR is investigated on the concrete (reinforced concrete, beam) or mortar in laboratory studies as well as in field studies. The same type of cracks have been observed: 1) map-cracking occurs in elements free of major stress or poorly reinforced [e.g. ICAAR proceedings], 2) for reinforced concrete or in elements subjected to loading stress, cracks reflect the arrangement of the underlying rebars or the direction of major stress [e.g. Fan and Hanson 1998, Rivard and Saint-Pierre 2009]. The deformation is found not only to be due to the three factors inherent in ASR (alkali content, reactive silica and water), but also to depend on the stress states and thus on the presence of reinforcing steel. Discussion of the effect of ASR on the mechanical properties (compressive strength, splitting tensile strength, dynamic modulus) has not reached a consensus yet. In some cases, the degree of reduction depends on the experimental conditions, like the nature of the aggregate, the formulation of the concrete, and the type of concrete (normal strength or high strength concrete) [Larive 1998, Multon 2004].

4. Methods of ASR diagnosis

ASR affected structures usually manifest three signs: 1) concrete expansion, 2) surface cracking, and 3) products which may exude on the surface of the concrete, particularly at joints. However, ASR cannot be identified by 1) and 2) alone since there are many reasons which could cause
concrete cracking and expansion. The presence of gel, which can only be confirmed by the use of SEM, is the major sign of ASR development. The diagnosis can be made by the following process (Figure I-5)

![Diagram](Figure I-5)

**Figure I-5**  Process of diagnosis and requalification of damaged structure  
[Fasseu et al. 2003]

### 4.1. Site inspection

In the process of diagnosis, the site inspection mainly includes measuring the cracking and deformation of the structures.

**Measurement of the cracking** [Fasseu et al. 2003, Godart et al. 1992]

The measurements are made with a crack-meter on several reference patterns with four axes (horizontal, vertical and two bisectors) in an area of 1 m². For reasons of accuracy, only the cracks having opening widths greater than 0.05 mm (threshold of visual detection) are recorded. A “cracking index” (CI) which is used to indicate the extent of cracking, is calculated by the mean of total crack opening per meter (mm/m). This index can be calculated for each axis, or evaluated for the zone:

CI on an axis = the mean of the width of the cracks divided by the length of the axis

CI of the zone = the mean of the four cracking indexes measured on the axes

**Measurement of deformation**

The measurement uses topographical distance measuring equipment. The principle is based on the propagation between transmission and reception by optical reflectors. Generally, the value ($D_m$) is expressed as the deformation per year like: mm/m/year.
Analysis of the results of cracking and deformation

Initial cracking and deformation are the signals that attract attention to the pathology of the structures. The following surveillance is important to evaluate the behaviour of the structures over time. After a long period of close observation, the results can be analyzed on the damage degree of the structures. Usually a structure with deformation greater than 0.5 mm/m/year is considered as seriously affected by an expansive reaction [Fasseau et al. 2003].

4.2. Fluorescence uranyl test

The purpose of this test is to determine whether ASR is the reason for the observed cracking, because the presence of deformation and cracking can be caused by other problems. The examination of the products on the surface of cracking is helpful to determine the pathology. Fasseu et al. [2003] suggests the fluorescence test: the products of ASR are identified by “staining” them with uranyl ions, which have a characteristic greenish yellow fluorescence under short-wave UV light (Figure I-6).

![Figure I-6](image)

*Figure I-6  Test of cores with uranyl acetate under UV light in [Fasseu et al. 2003]*

This method is rapid to test the presence of ASR gel but it cannot exclude the presence of DEF crystal. Thus SEM or other petrographic methods are necessary to identify ASR. Figure I-7 shows the different forms of ASR gel and DEF crystals under the test of SEM.
4.3. Residual expansion

The most usual test to measure the residual expansion of the damaged structures is conducted on cores extracted from the ASR affected structures under conditions of storage at 38°C and 95% R.H. (Relative Humidity). A classic expansion curve is shown in Figure I-8 [LPC 1997].

![Residual expansion curve](Image)

*Figure I-8  Residual expansion curve (at 38°C, R.H. > 95%) [LPC 1997]*

**Phase A:** This period can vary largely, but according to the [LCPC 1997], this period is considered as the first 8 weeks. The expansion of this period is mostly due to hydraulic shrinkage and the absorption of water by the hydrophilic products. Therefore, the expansion in phase A is not taken accounts in the ASR expansion. However, it arises the discussion about whether no ASR expansion occurs during in this period [Multon et al. 2008].
**Phase B:** The expansion during this period (8~52 weeks) is mainly attributed to ASR swelling. The curve increases slowly, and shows no evident asymptotic aspect. The swelling of this phase is generally thought to be representative of the residual expansion.

**Phase C:** This phase lasts about two months. The reduction of the expansion can be attributed to desiccation when the samples are taken out of the humid environment. Requalification of structures affected by ASR

5. Requalification of structures affected by ASR

Considering the consequences of AAR (such as internal cracking, surface cracking, displacement of structures), the owners seek to know whether the reaction is almost finished or whether there still remains many years of swelling. Thus, an evaluation of the potential AAR expansion could help the owner to make a reliable choice between different scenarios, including the demolition of the structure or the implementation of repair solutions. In this part, a few requalification methods are presented.

5.1. **Method of Léger** [Léger et al. 1995]

The advantage of this model is that it takes several factors into account in detail: external factors (compressive stress, temperature, and moisture), material factors (reactivity of the aggregates) and mechanical consequences. The methodology is based on the assumption that the observed concrete expansion is proportional to the applied and induced compressive stress state, temperature, moisture and the reactivity of the concrete constituents. The numerical modelling of the structure swelling process is rationalized with the evaluation of these elements. The methodology is given in Figure I-9.

Moisture model \( F_M \)
Temperature model \( F_T \)
Reactivity model \( F_R \)
Mechanical model \( F_C \)

Spatial distribution of AAR expansion
\[
\text{CTMR} (x, y, z) = [F_C * F_T * F_R * F_C]
\]

Magnitude of AAR expansion
Displacement \((x, y, z) = \beta * \text{CTMR} (x, y, z)\)

(\(\beta\): a calibration factor to adjust the computed displacements against the observed ones)

*Figure I-9  AAR simulation model [Léger et al. 1995]*

22
5.2. Method of LCPC

The methodology proposed by the LCPC (Laboratoire Central des Ponts et Chaussées) is described in [Li et al. 2000, Li et al. 2001, Li and Coussy 2002, Seignol et al. 2009]. This method highlights the effect of the material on ASR (Figure I-10). It builds a model considering the reaction swelling kinetics at a material level. This material model is calibrated with the in situ structural data, and then a comprehensive time-space scaled assessment is conducted by a two-step algorithm for the model parameter calibration. This part emphatically introduces the material model, and roughly presents the necessary data for the in situ investigations.

![Diagram of “consistent assessment method”](image)

### 1) Material modelling of ASR swelling:

The material model involves two aspects: the progressive formation of expansive ASR product and the material response to this internal swelling. The authors use “the system free energy” (as in Equation I-2) which takes account of material elastic deformation energy and chemical energy to characterize the reaction’s progress.

\[
Ψ (ε, ξ) = \frac{1}{2} E_s (ε-κξ)^2 + \frac{1}{2} E_m ε^2 + \frac{1}{2} A_0 (1-ξ)^2
\]

Material elastic deformation energy  ASR chemical energy

- Ψ: the system free energy
- ε: the reversible material deformation
- ξ: the global reaction-expansion extent in a range of [0,1]
- κ: the coefficient of ASR expansion
- E_s: the modulus representing the internal pressure exerted by the swelling gel
- E_m: the modulus withstanding the autogeneous tension in the solid matrix
- A_0: the initial chemical force
Chapter I

This model (chemo-elastic model) is only suitable for laboratory conditions with free expansion and it cannot be used in structures with severe material degradation (like cracking and surface delamination). To apply it to degraded structures, which have an evident structure effect on the degradation, the authors modified this model and built two other models (imposed chemo-plastic model and coupled chemo-plastic model). In these two models, two parameters: the irreversible deformation $\varepsilon_p$ and the internal hardening variable $\chi$ are introduced to characterize the plastic characteristics of the material.

**Imposed chemo-plastic model:**

$$\Psi[(\varepsilon-\varepsilon_p), \chi, \xi] = \frac{1}{2} E[(\varepsilon-\varepsilon_p)-\beta\xi]^2 + \frac{1}{2} E_h \chi^2 + \frac{1}{2} A_0 (1-\xi)^2$$

(I-3)

**Coupled chemo-plastic model:**

$$\Psi[(\varepsilon-\varepsilon_p), \chi, \xi] = \frac{1}{2} E (\varepsilon-\varepsilon_p)^2 + \frac{1}{2} E_h (\beta\xi-\chi)^2 + \frac{1}{2} A_0 (1-\xi)^2$$

(I-4)

### 2) Investigations

The investigations included: a) the laboratory test of residual expansion conducted with the extracted cores, b) in situ investigation which includes the structural evolution involving the detection of the structure dimensional variation and surface cracking evolution of the attacked concrete, and the thermal-hydrometric conditions including analyses of the internal temperature and humidity of the structure.

### 5.3. Method of Saouma

This model is described in [Saouma and Perotti 2006, Saouma et al. 2007, Saouma 2009]. The model is rooted in the chemistry (kinetics of the reaction), physics (crack gel absorption, effect of compression) and mechanics of concrete. Considering all the factors, the expansion can be deduced on the basis of the following equation:

$$\varepsilon_v^{AAR} (t) = \Gamma_t (f_t'|w_c, \sigma_1|COD_{max}) \Gamma_{\xi} (\sigma', f_{\xi'}) g(H) \xi(t, \theta) \varepsilon^\infty |_{\theta=\theta_0}$$

(I-5)

This equation of volumetric ASR strain is composed of five elements:
\( \Gamma_1 (\epsilon \, [0,1]) \) is a function that reduces the expansion in the presence of large tensile stresses (macrocracks absorbing the gel).

\( \Gamma_c (\epsilon \, [0,1]) \) accounts for the reduction in ASR volumetric expansion under relatively high compressive stresses (microcracks under compression and gel expansion reduction due to pluri-axial state of compressive stresses).

g(H) represents a reduction function on account of the relative humidity.

\( \xi(t,0) \) expresses the chemical evolution depending on reaction time and temperature. This kinetic law is taken from the work of Larive [1998]. \( \epsilon^\infty \mid_{\theta = \theta_0} \) is the final volumetric expansion as determined from laboratory tests at temperature \( \theta_0 \).

Based on the above theory, a methodology of structure evaluation is proposed as shown in Figure I-11. Since ASR is a thermodynamically induced reaction, the thermal analysis can provide a temporal map of the internal temperature. Following the thermal analysis, the stress analysis is performed on the difference between actual and stress-free temperature. In this step, the thermal temperature must be transformed to temperature of stress since different finite element meshes are used in these two calculations. The system identification includes the determination of chemical kinetics parameters, the structure analysis with an initial set of assumptions, the comparison of computed results with displacements recorded on the dam, and an update of the input parameters.

1. Thermal analysis
2. Stress analysis
3. System identification
   \[ \Downarrow \]
   Structure evaluation

**Figure I-11  Diagram of analysis procedure of structure evaluation**

5.4. **Method used in LMDC**

5.4.1. **Background of the method**

In the past two decades, the modelling of ASR in evaluating affected structures has developed significantly. The conventional residual expansion method can be used to evaluate the chemical kinetics. The main experimental condition is “storing the specimens at 38°C and in Relative humidity > 95%”. However, there are numerous criticisms that can be made of this method:

1) **Relative humidity**

Bérubé and Frenette [1994] showed that the condition of humidity higher than 95% made the results subject to variations among labs, and thus led to bad repeatability and reproducibility.
This can be explained by the difficulty of precisely controlling such R.H. during the experiments, and RH variations between 95 and 100% can lead to significant variations of ASR expansions [Poyet et al. 2006].

2) Alkali leaching

Alkali leaching is the loss of alkali of concrete into the external environment. This phenomenon was found and attested with a mortar bar in air with relative humidity > 95% [Bérubé et al. 2002, Rivard et al. 2003, Rivard et al. 2007] or in water/solution [Roger and Hooton 1991]. Due to the alkali leaching from the concrete, the ASR expansions can be stopped by the lack of alkali.

3) Composition of ASR gels

The composition of the gel produced by the alkali silica reaction is greatly influenced by the environmental conditions (such as temperature, RH, alkali content). The gel obtained in the laboratory is different from the gel found in situ regarding the nature and chemical composition [Grimal 2007, Grimal et al. 2008, Sellier et al. 2009]. In some cases, gels from concrete cast in the laboratory show a high alkali concentration (Figure I-12a) while gels from in-situ concrete cores show a small alkali content and are often crystallized (Figure I-12b).

Figure I-12 SEM and EDS of gels in laboratory and gels in field [Grimal 2007, Sellier et al. 2009]
Urhan [1987] attributes this difference of gel between laboratory and in situ structures to the impact of temperature on the chemical equilibrium of gel production. The “residual expansion test” is conducted at a higher temperature (38°C) than the average in situ temperature of the attacked structures (23°C), in the aim of obtaining the potential expansion in a short time [Fasseu et al. 2003, Rivard 2002]. This difference of temperatures leads to a variation of chemical products.

Some other authors think that the reason for gel variation should be the substitution process between alkalis and calcium as it is known that alkalis can be substituted by calcium. However, this process occurs only over a long period [Lagerblad and Trägardh 1992] [Jensen 1993] [Duchesne and Bérubé 1994]. In other words, this substitution takes place mostly in the field cases, and rarely occurs in laboratory tests since the duration of laboratory tests is always one or two years.

4) **Effect of aggregate size**

In cores drilled from large structures like dams, the time necessary to reach the centre of the large aggregate is considerably longer than 52 weeks even in accelerated conditions. This could explain why the curve of the residual expansion test does not reach a final asymptote. It is suggested that the duration of 52 weeks given by the method is not sufficient to show the total expansion that can be expected for the tested concrete.

5) **Direction of coring**

The casting direction has an important effect on the expansion since the behaviour of concrete is often anisotropic [Larive, 2000, Multon et al. 2008, Smaoui et al. 2004]. Thus, cores obtained along different directions can lead to different residual expansions. This difference between the axial and transversal cores leads to large scatter in the results, and leads to difficulties in obtaining a reliable assessment.

Considering the imprecision of the “conventional residual expansion test”, especially the notable failure of this test to predict the expansion of Temple-sur-Lot dam (in France) [Grimal 2007] [Sellier et al. 2009], a new method has been developed.

5.4.2. **Methodology of LMDC method**

The aim of LMDC method was to assess the safety level of degraded structures with a finite element code [Bourdarot et al. 2010, Grimal 2007, Sellier et al. 2009]. This method takes account of the long-term behaviour of ASR gels with the substitution between alkali and calcium. The substitution guarantees a continuous regeneration of alkali, which can thus react with the totality of the reactive silica. Therefore, the method pays attention to the consumption of silica with a sufficient supply of alkali. The method involves a laboratory test dealing with the silica consumption kinetics and a numerical finite element inverse analysis of the dam, which includes the consumption kinetics measured in the laboratory. The kinetic coefficient of the model is determined in the laboratory and the final swelling amplitude is fitted using only one observed structural displacement rate. The model prediction capability has been validated through the
comparison between the displacement of instrumented points predicted by the calculations (not used for the fitting) and the variations measured on the dam.

The method consists of three steps (*Figure I-13*):

1) **In-situ measurement of the affected structure.** The purpose of this step is to collect the information necessary for the modelling step. The information should include the surveillance of displacements, temperatures, and moisture of the affected structures. It should also contain the information from the different core samples: the saturation degree, the aggregates and cement used in the concrete.

2) **Tests in laboratory.** The tests in laboratory are conducted with the aggregates recovered from the damaged structures. The purpose is to assess the consumption kinetics of reactive aggregate under the consideration of the aggregate size effect.

3) **Finite element inverse analysis of the affected structure.** This step combines the results of step 1) environmental conditions and step 2) reactive silica consumption kinetics to obtain swelling amplitude.

Finally, calculations are performed to predict the future displacements and damage fields of the dam. The damage degree can be given as in *Figure I-14* to show the progress of degradation.
5.4.3. Principle and application of the method

5.4.3.1. Principle

The principle of the method involves mainly the silica consumption kinetics, which is based on the following assumptions:

The chemical advancement of the reaction can be presented by the degree of silica consumption, which varies with different reaction time (Equation 1-6). For a certain aggregate size, the value of A is in the range of 0~1 (0: the beginning of the reaction, 1: the completion of the reactive silica reaction).

\[
A(t) = \frac{Si_{\text{reacted}}(t)}{Si_{\text{reactive}}(t = 0)}
\]  

(Equation I-6)

\(Si_{\text{reacted}}\) represents the silica consumed at time t,
\(Si_{\text{reactive}}\) represents the total reactive silica content of the aggregate

The kinetic law shows that the chemical advancement is a function of the degree of saturation Sr and the temperature T [Grimal, 2007, Grimal et al. 2008, Poyet 2003, Poyet et al. 2004], thus the derivative of chemical advancement with respect to the reaction time t can be presented in Equation I-7:
\[ \frac{\partial A}{\partial t} = \alpha_{ref} \exp\left( -\frac{Ea}{R} \left( 1 - \frac{1}{T_{ref}} \right) \right) \times \left( \frac{\left( S_r - S_r^{threshold} \right)}{\left( 1 - S_r^{threshold} \right)} \right) (S_r - A) \] (I-7)

\( \alpha_{ref} \): the constant of the kinetics,
\( Ea \): the activation energy of the AAR (~47 kJ/M),
\( R \): the gas constant (8.31 J/M/K)
\( T_{ref} \): the absolute temperature of the test,
\( T \): the current absolute temperature
\( S_r \): the degree of the saturation of concrete porosity
\( S_r^{threshold} \) is the minimal saturation degree necessary to allow the evolution of the chemical reaction, equal to 0.2 according to the value of [Grimal 2007].

\( S_r \) can be obtained from the non-linear equation of mass transfer and solved numerically with the finite element method and boundary conditions imposed from the measurement of in-situ degree of the saturation [Grimal 2007, Sellier et al. 2009].

The mechanical advancement of the reaction can be expressed by the increase of the volume of aggregate (\( \Phi^{ASR} \)), which is caused by the production of gel. Supposing that all the gel effect is isotropic in a free swelling specimen, then:

\[ \varepsilon^{ASR}(t) \approx \left( A(t) \Phi^{ASR} - \Phi^{ASR,threshold} \right) \geq 0 \] (I-8)

If the aggregate is sufficiently large, which means \( \Phi^{ASR} >> \Phi^{ASR,threshold} \), the total expansion can be expressed as \textit{Equation I-9} and shown in \textit{Figure I-15}:

\[ \varepsilon^{ASR} \approx A(t) \Phi^{ASR} \] (I-9)

\textit{Figure I-15 Variation } \varepsilon^{ASR}, A, \Phi \textit{with time}
5.4.3.2. Application

The application of the method is based on the testing of aggregates extracted from two types of cores drilled from the affected structures, which have been called sound aggregates and affected aggregates.

Silica consumption kinetics with sound aggregate

The sound aggregates come from sound zones of large aggregates or can be taken in dry zones of the structure. The purpose of using this type of aggregate is for knowing the reactive silica in the aggregate ($S_{reactive}^{\text{Si}}$).

Evaluate the structure with affected aggregate

The affected aggregates can be extracted from wet zones or zones affected by ASR. From the laboratory tests of this type of aggregate, the residual reactive silica ($S_{\text{residual}}^{\text{Si}} = S_{\text{reactive}}^{\text{Si}} - S_{\text{reacted}}^{\text{Si}}$) can be obtained. If the time of drilling cores is $t_1$, which is relative to the time from the construction of the structure to the time of drilling core, then the chemical advancement $A(t_1)$ can be calculated from Equation I-10:

$$A(t_1) = \frac{S_{\text{reacted}}^{\text{Si}}}{S_{\text{reactive}}^{\text{Si}}} = 1 - \frac{S_{\text{residual}}^{\text{Si}}}{S_{\text{reactive}}^{\text{Si}}}$$ (I-10)

Since the chemical advancement is independent of the absolute expansion of the structures, this $A(t_1)$ value, deduced from the laboratory condition, can also represent the chemical advancement of silica consumption in the field. Thus, the kinetics constant of the expansion can be deduced from Equation I-11:

$$\frac{1}{\alpha_{\text{ref}}} = \frac{\int_{t_0}^{t_1} \exp \left( - \frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right) \times \left( \frac{S_r - S_{\text{threshold}}^{\text{Sr}}}{1 - S_{\text{threshold}}^{\text{Sr}}} \right) (S_r - A) \, dt}{A(t_1)}$$ (I-11)

Once the kinetic constant is known, the assessment of the swelling amplitude can be conducted with the displacements in the field (Equation I-9). And then, the finite element method (including the mechanical aspect – creep and damage effects) can be used. To summarize the fitting process, the swelling is assumed to be proportional to the advancement rate and proportional to the amplitude $\phi_{\text{ASR}}$, and thus the advancement rate is proportional to the advancement and proportional to the amplitude $\phi_{\text{ASR}}$ as shown in Equation I-12:

$$\dot{\phi}_{\text{ASR}}(t) = \frac{\partial A(t)}{\partial t} \phi_{\text{ASR}} = \left( \alpha_{\text{ref}} \exp \left( - \frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right) \right) \times \left( \frac{S_r - S_{\text{threshold}}^{\text{Sr}}}{1 - S_{\text{threshold}}^{\text{Sr}}} \right) (S_r - A) \phi_{\text{ASR}}$$ (I-12)
The only unknown parameter is $\Phi^{ASR}$. This value can be obtained through curve fitting with the measurements of in-situ displacement (Figure I-16).

In summary, the LMDC method can determine the chemical kinetics of aggregate consumption of the structure in the field (with the parameters of saturation degree and temperature) through the laboratory experimental analysis of the sound aggregate extracted from the sound zone of the affected structure. It can also evaluate the damage degree of the concrete and predict the future deterioration by analyzing the chemical kinetics of the aggregates extracted from the damaged zone of the affected structure.

6. Plan of the thesis

According to the knowledge referred above, the requalification of ASR affected structures involves: 1) knowing the chemical advancement of silica consumption in aggregate recovered from the structure, 2) combining the chemical advancement analysis with environmental conditions in the field to evaluate the structure. This work focuses on improving laboratory tests to assess the chemical advancement of silica consumption. In the previous work [Grimal 2007], only expansion tests were performed to assess the ASR advancement in the aggregates. This work focuses on a direct method of "chemical test" to measure the silica content and an indirect method of "expansion test" to know the expansion caused by reactive aggregate are proposed, and then a chemo-mechanical method is used to analyze these two methods and assess the chemical advancement. The work is separated into four chapters:

Chapter 2 (optimization of an expansion test) aims to find a fast and relevant method to assess the expansion in a laboratory test. In this method, the conservation conditions of specimens and the size of specimen and aggregate are taken into account. Several aggregates are tested with the method to verify whether the expansion test can differentiate between the reactivity of different aggregates.

Chapter 3 (chemical measurement of reactive silica in aggregate) has the purpose of finding a fast and convenient chemical method to measure the reactive silica of aggregate. Inspired by the
analysis of existing methods, acid and/or basic attacks are chosen to test different types of aggregates. Combined with the mineralogical studies - XRD and petrography - and the expansion results, the chemical results are compared and discussed.

Chapter 4 (chemo-mechanical modelling) develops a chemo-mechanical model to analyze the expansion of a given mortar. This chapter includes two parts: 1) development of a microscopic model based on previous work [Multon et al. 2009] to understand the mechanism involved in the reaction; 2) relation between the microscopic model and the structural requalification.

Chapter 5 (Methodology to assess the kinetics constant of expansion) aims to introduce the kinetics constant of expansion which is helpful to re-build the expansion kinetics in the framework of structural modelling. The significance of this parameter in the laboratory test is introduced firstly, and then a methodology to calculate the kinetics in the framework of structural requalification is proposed.

At the end, a general conclusion is made on summering the main results of this work and proposing some perspectives for the future works.
Chapter II

Chapter 2

Optimization of an Expansion Test

1. Introduction

This chapter aims to improve a laboratory method for expansion measurement since the usual tests appear to be difficult to use in structural assessment. The development involves optimizing the conservation conditions and the size of the specimen and aggregate. A combined effect of the aggregate and specimen sizes on ASR expansion is thus pointed out: for a given mortar, the expansion is lower in small specimens than in large specimens. Therefore, the ratio ‘specimen size / aggregate size’ has to be sufficiently high to decrease this scale effect and obtain relevant measurements. The discussion finally suggests how this test can be optimized to provide fast and relevant results for use in structure reassessment.

The most usual test is the residual expansion test at 38°C in air at 95% RH, which is performed on cores drilled from damaged structures [Bérubé et al. 2002, Fasseu et al. 2003, Multon et al. 2008]. However, several criticisms can be made of this usual laboratory test: (1) the reactive silica in the core of the aggregates is never reached in a short time because of the large size of the aggregates used in structures (the asymptotic expansion is not achieved after one year of measurement) [Sellier et al. 2009] (2) the ASR-gels do not have the same composition in accelerated tests as in real structures because of the impact of temperature on chemical equilibrium [Urhan 1987] and the substitution process between alkalis and calcium [Duchesne and Bérubé 1994, Lagerblad and Trägardh 1992, Jensen 1993] (3) alkali leaching during the tests can have a deleterious effect on the assessment of the asymptotic expansion [Bérubé et al. 2002, Rivard et al. 2003, Rivard et al. 2007, Rogers and Hooton 1991], (4) the high moisture conditions (higher than 95% RH) are difficult to control, which leads to significant variations of ASR expansions for RH ranging between 95 and 100% [Poyet et al. 2006]. It therefore seems unrealistic to use the ASR-expansions obtained on cores in accelerated conditions to assess the future expansion of concrete in the damaged structures. This view has been proved correct in the structural analysis of a French dam (small residual expansion in accelerated laboratory test and significant expansion measured on the dam) [Grimal 2007, Sellier et al. 2009]. Therefore, a method has been proposed to use reliable experimental information and avoid the uncertainty due to imperfect conditions of control in laboratory tests [Sellier et al. 2009]. In this method, the
future ASR expansions are determined through a finite elements analysis of the structures using two experimental data:

1) measurements performed directly on the structures to determine the amplitude of ASR expansion,

2) laboratory expansion tests on aggregate extracted from the structures to assess the expansion kinetics.

The laboratory tests are necessary to determine how the reaction advances according to the size of the aggregate [Sellier et al. 2009].

The aim of this chapter is to optimize the expansion test in terms of conditions of conservation, size of specimens and size of aggregates. Several experimental conditions were tested in order to rapidly evaluate the totality of the residual reactive silica. The conservation of the specimens should guarantee that all the residual reactive silica is consumed in a short period of time. Tests were carried out in NaOH solutions so that there was enough alkali to consume all the reactive silica, and at 60°C to accelerate the reaction. Alkalis had to reach all the reactive silica quickly. Therefore, the specimens and the aggregates could not be too large in order to decrease the time for alkalis to diffuse in the specimens and in the whole aggregate. Finally, the tests were performed on several types of rocks to verify whether they could differentiate between the reactivity of different aggregates.

2. Basic knowledge


1. Hydroxyl ions present in the cement paste reach and diffuse in the aggregates (Figure II-1a).
2. Hydroxyl ions attack reactive silica, followed by the reaction with alkalis in the cements, and create ASR gel in and around the aggregate. The external periphery of aggregate will be attacked firstly since the hydroxyl ions contained in cement paste arrive to attack reactive component of aggregate primarily. The gel can fill the connected porous volume surrounding the aggregate in a thickness $t_c$ without leading to damage [Furusawa et al. 1994, Multon et al. 2009, Poyet et al. 2007] (Figure II-1b).
3. Once the connected porosity is filled, the pressure in the gels increases and causes cracking of the aggregate and the cement paste surrounding the aggregate [Multon et al. 2009]. The propagation of cracks in specimens with large ‘size of the aggregate’ to ‘size of the specimen’ ratios is rapid and can occur for low pressures whereas it is more difficult for larger specimens and needs higher pressure (Figure II-1c). This scale effect can be justified by fracture mechanics.
concepts [François et al. 1993, Lemaître and Chaboche 1988]. The maximal normal stress in the vicinity of an inclusion is given by:

\[ \sigma(r) = \frac{K_I}{\sqrt{2\pi r}} \]  

where \( \sigma \) is the maximal normal stress at the point M located at \( r \), the distance from the edge of the inclusion (Figure II-1c) and \( K_I \) is the stress intensity factor obtained from the relation:

\[ K_I = p_g \cdot f \left( \frac{R_a}{L} \right) \]  

where \( f \) is a function increasing with the ratio \( R_a/L \), with \( R_a \), the radius of the aggregate and with \( L \), the dimension of the specimen. Assuming that the aggregates have spherical shapes, and \( p_g \), the gel pressure can be assessed from [Multon et al. 2009, Multon et al. 2010]:

\[ p_g = M_g \left\{ \frac{4}{3}\pi R_a^3 s V_{gel}^{mol} - \varphi \frac{4}{3}\pi \left( R_a + t_c \right)^3 - R_a^3 \right\} \]  

with \( M_g \) the gel elastic modulus, \( s \) the reactive silica content, \( V_{gel}^{mol} \) the molar volume of the gel, \( \varphi \) the concrete porosity, and \( t_c \) the thickness along which the gel can migrate from the aggregate to the cement paste.

Fracture mechanics concepts show that the greater the ratio ‘size of the aggregate’ to ‘size of the specimen’, the larger the normal stress at a given distance from the aggregate. Thus, the greater this ratio is, the smaller the pressure can be in the gel to reach the tensile stress at the boundary of the specimen (Figure II-1c).

4. Once cracks have reached the boundary of the specimens, ASR gels can be absorbed by the cracks [Saouma and Perotti 2006] and then leach off through the porosity induced by cracking, thus the pressure in the gels falls, which stops the expansion (Figure II-1d). If the cracks occur at lower pressure, i.e. for experiments with high ‘size of the aggregate’ to ‘size of the specimen’ ratio, lower expansions can be measured, as observed in previous experimental works [Bakker 1983, Zhang et al. 1999].
The analysis of the background shows the importance of the concept of stress intensity factor in the understanding of the development of ASR expansion in concrete. The larger the stress intensity factor $K_I$ is, the faster cracks appear and the cracking always leads to perturbation of the expansion through gel permeation and exudation. Therefore, for several expansion tests, the stress intensity factor $K_I$ has to be constant to maintain comparable mechanical conditions. The aim of this work is first to optimize the expansion test but also to understand the effect of specimen size and aggregate size on expansion. Thus the study was performed on three sizes of specimens (20x20x160 mm, 40x40x160 mm and 70x70x280 mm) and four sizes of aggregates (0-315 µm, 315-630 µm, 630-1250 µm and 1250-2500 µm).

### 3. Experimental conditions

#### 3.1. Materials

The cement used was a standard CEM I 52.5R (specific gravity: 3.1, surface area (Blaine): 400 m²/kg). Its chemical composition is given in Table II-1. Five aggregates were used as crushed sands in the experiments: siliceous limestone (SL), quartzite (Q), opal (O), quartz aggregate (QA) and marble (NR). Their chemical compositions are given in Table II-1. The first three aggregates are known to be alkali-reactive and thus to develop ASR gels in a concrete environment. They were chosen in three different categories of rocks: sedimentary (SL), metamorphic (Q) and igneous (O). The reactive limestone (SL) contained mostly calcite and quartz, with traces of dolomite, feldspars and phyllosilicates. Quartzite contained mainly quartz with traces of muscovite and tridymite; opal contained principally quartz and tridymite. The last two aggregates were considered as non-reactive. The non-reactive marble was almost exclusively composed of calcite. The aggregate in the tests included four classes of reactive aggregates: C1 (0-315 µm), C2 (315-630 µm), C3 (630-1250 µm) and C4 (1250-2500 µm), and one class of non-reactive aggregate (0-2500 µm).

| Table II-1 Chemical composition of cement and aggregates (% by mass) |
|-------------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
|                         | SiO₂     | Al₂O₃    | Fe₂O₃    | CaO      | MgO      | Na₂O     | K₂O      | Na₂O_eq  | SO₃      | LOI      |
| Cement                  | 20.1     | 5.6      | 2.0      | 62.5     | 3.1      | 0.2      | 0.9      | 0.8      | 3.2      | 1.7      |
| Non-reactive marble     | -        | -        | -        | 54.4     | 0.5      | 0.001    | -        | -        | 0.01     | 43.0     |
| Siliceous limestone     | 15.4     | 1.5      | 0.7      | 40.4     | 1.4      | 0.4      | 0.4      | 0.7      | 4.2      | 35.6     |
| Quartzite               | 87.7     | 4.0      | 1.0      | 0.4      | 0.2      | 0.1      | 0.9      | 0.7      | 0.1      | 1.1      |
| Opal                    | 92.7     | --       | 0.3      | 0.2      | 0.2      | 0.1      | 0.1      | 0.2      | 1.1      | 6.0      |
| Quartz                  | 92.2     | 3.7      | 1.1      | 0.1      | 0.1      | -        | 0.01     | 0.01     | 0.2      | 0.6      |
3.2. Sample preparation

Mortars had a water-cement ratio of 0.5 and a sand (1512 kg/m$^3$) - cement (504 kg/m$^3$) ratio of 3. For the reference specimens, the sand was only composed of the non-reactive marble. For all the other specimens, the sand contained 30% of the aggregate under study and 70% of non-reactive marble. (Since the objective of this test is to research the effect of aggregate size and specimen size in the condition of enough alkalis, the pessimum of the reactive aggregate content was not considered. The percentage of 30% was used for all the types of aggregate in order to have a reliable expansion without changing the granularit. Also, the previous studies in [Multy et al. 2010] under 60°C, R.H. > 95% were conducted with 30% reactive aggregate. To comparing with the previous works, in this study, the same percentage was used.) Mixtures were adjusted to fixed alkali contents (Na$_2$O$_{eq}$) by adding NaOH in the mixing water in order to have an alkali concentration in the mortar pore solution close to the concentration in the conservation solution (0.77, 1.0 and 1.25 mol/l).

3.3. Expansion measurements

Deformation was measured on mortar prisms (20x20x160 mm, 40x40x160 mm and 70x70x280 mm) using the scale micrometer method (specimens had shrinkage bolts in the two extremities). Each length change value was the mean of three values from three replicate specimens. Expansion measurements were performed after the prisms had cooled from the conversation temperature to 20°C (~12h) in the NaOH solution.

3.4. Specimen conservation

3.4.1. Procedure

After demoulding, the specimens were first kept in sealed bags at 20°C for 14 days. Then, they were immersed in NaOH solutions for the 14 following days. The aim of this step was to obtain the same concentration of alkali in the pore solution as in the conservation solution. It was also intended to decrease the non-ASR expansion due to water absorption. The expansions were measured during this period, and the same amplitudes were obtained for both reactive and reference specimens. Thus, it was deduced that the expansions of the reactive specimens in this period were due to water absorption, and they were therefore neglected in the following analyses. After this period, the temperature of the solutions was increased to 60°C.

3.4.2. Choice of the solution concentration

In order to test the effect of alkali concentration on ASR expansion, mortars containing siliceous limestone were kept in NaOH solutions of three different concentrations: 0.77, 1.0 and 1.25 mol/l. The mortars contained 15% of the size class C2 (315-630 µm), 15% of the size class C3 (630-1250 µm) and 70% of the non-reactive aggregate. The solutions were changed at about 250 days in order to verify if the alkali concentrations were still sufficient to react with aggregate.
The curves of the reactive mortars showed high initial rates of swelling (Figure II-2), followed by a low rate of expansion up to a final asymptote. The final expansions for the three concentrations 0.77, 1.0 and 1.25 mol/l were 0.70%, 0.65% and 0.60% respectively. The difference between two consecutive concentrations appeared to be negligible considering that the standard deviation for the specimens was in the range of 0~0.02%. Finally, no changes were observed in the expansion rates at 250 days when the solutions had been changed (Figure II-2). Thus, the alkali concentrations could be considered to have little influence on ASR expansions in our tests, and an NaOH concentration of 1 mol/l was chosen for the following tests.

![Figure II-2 Expansions on specimens with siliceous limestone (SL) and with non-reactive limestone (reference R) kept in NaOH solutions (0.77, 1.0 and 1.25 mol/l)](image)

4. Combined effect of aggregate and specimen sizes

4.1. Mortar mixtures

In order to study the effect of the size of the specimens, three kinds of prisms were used: 20x20x160 mm, 40x40x160 mm and 70x70x280 mm. The particle size distributions were obtained by adding 30% of reactive aggregate of the four different size classes (C1, C2, C3, C4) to 70% of a continuous size distribution (0–2500 µm) of non-reactive aggregate, the particle size distributions were different for the five mortars. A previous study on these kinds of mixtures [Multon et al. 2010] had shown that the effect of the difference of particle size distributions on the porosity of mortars did not appear to be significant. During the casting process, super plasticizer was added for the fines aggregate under the consideration of the workability of the mortars. During the experiments, all mortar prisms were conserved at 60°C in the 1 mol/l NaOH solution.
4.2. Experimental results

For the non-reactive aggregate, the final expansion is 0.015%, the final mass variation is 1.03%. In order to assess mass variations and expansions only due to ASR, net values were calculated and used in the following parts of the study. They were obtained by subtracting the measurements of reference mortars (without reactive aggregate) from those obtained on the reactive specimens. Figures II-3, II-4 and II-5 present the mass variations and the ASR expansions obtained on 20x20x160 mm, 40x40x160 mm and 70x70x280 mm specimens, respectively. All the curves show a high and increasing initial rate of mass and swelling, followed by a decrease of the rate until a long-term asymptote is reached.
Figure II-3  Kinetics curves of prismatic specimens 20x20x160 mm containing the reactive aggregate siliceous limestone kept in NaOH solution (1.0 mol/l)
Figure II-4  Kinetics curves of prismatic specimens 40x40x160 mm containing the reactive aggregate siliceous limestone kept in NaOH solution (1.0 mol/l)
Chapter II

(a) Mass variation

(b) expansions

Figure II-5  Kinetics curves of prismatic specimens 70x70x280 mm containing the reactive aggregate siliceous limestone kept in NaOH solution (1.0 mol/l)
In addition to the expansion measurement, the cracking patterns were observed and the crack widths were measured at 290 days with a video-microscope (Figure II-6). Crack widths were assessed on 15 points taken in at least 15 regions of the specimens in order to obtain relevant average values. No cracking was observed for the reference prisms and for the prisms containing the particles of size C1 (0~315µm), which is in accordance with the small expansion. For the other specimens, the crack widths are given in Table II-2. The largest specimens (70x70x280 mm) presented the widest cracks (Figure II-6 and Table II-2). The smallest prisms (20x20x160 mm) had the smallest cracks (Figure II-6 and Table II-2), which were below the measurement limit of the video-microscope (<10 µm). These differences between the large specimens and the small ones can be explained by Equation II-2: the large specimens have a smaller value of \( f(R_a/L) \), thus for the same stress intensity the gel pressure \( p_g \) is greater, which leads to a larger widths of cracks. The differences between crack widths of mortars containing different aggregate sizes were not significant (Table II-2).

Figure II-6  Cracking patterns of specimens cast with siliceous limestone (a) 70x70x280 mm (b) 40x40x160 mm and (c) 20x20x160 mm
### Table II-2  Crack widths in µm

<table>
<thead>
<tr>
<th></th>
<th>20x20x160 mm</th>
<th>40x40x160 mm</th>
<th>70x70x280 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2 / 315-630 µm</td>
<td>&lt;10</td>
<td>50</td>
<td>360</td>
</tr>
<tr>
<td>C3 / 630-1250 µm</td>
<td>&lt;10</td>
<td>60</td>
<td>335</td>
</tr>
<tr>
<td>C4 / 1250-2500 µm</td>
<td>&lt;10</td>
<td>55</td>
<td>300</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td>&lt;10 µm</td>
<td>~ 55 µm</td>
<td>~ 335 µm</td>
</tr>
</tbody>
</table>

### 4.3. Effect of specimen size

Analysis of the ASR expansions demonstrated the significant effect of the size of specimens. First, the largest specimens showed the slowest rate of ASR-expansion whatever the aggregate size (Figure II-7). This can be likely explained by the diffusion of the alkalis in the specimens. The initial alkali concentration in the pore solution was sufficient to initiate the reaction. Alkalis were quickly fixed by the ASR gel and supplementary alkalis were necessary to maintain gel production. These alkalis came from the solution and diffused in the mortar. Thus, they needed longer to reach the core of the largest specimens than the small ones.

The second effect was on the amplitude of the asymptotic ASR expansion, where the largest specimens showed the highest asymptotic ASR expansion (Figure II-7). This was particularly significant on the large aggregate class 1250-2500 µm (ASR expansions were twice as large for the 70 mm size specimens as for the others). This observation shows the significant coupling effect between specimen size and aggregate size and confirms the assumptions made in the ‘background’ section.

For the same size of aggregate, the proportion of aggregate particles close to the surface of the prism compared to the total aggregate increases with decreasing cross section of the prism. The gel created by the aggregate particles close to the surface of the prism is lost more easily than for the inner particles. In consequence, for the same size of aggregate, the smaller the specimen, the more significant the amount of gel lost by the cracks. This can possibly explain the lower expansion measured (Figure II-7).
Figure II-7 ASR expansions on prismatic specimens containing siliceous limestone (a) 20x20x160 mm (b) 40x40x160 mm and (c) 70x70x280 mm kept in NaOH solution (1.0 mol/l)
In order to quantify the combined effect of the aggregate and the specimen size, the ASR-expansion versus the ratio of the specimen size (the minimal dimension of the specimen which means the length of the section. For example, 20 x20 x160mm, the specimen size was taken as 20 mm) to reactive aggregate size (the average value of the aggregate size) is plotted in Figure II-8.

![Figure II-8 The final ASR expansions according to the 'Prism size / Particle Size' ratio](image)

For small aggregates (circled in Figure II-8), the ASR-expansions were small due to the effect of the connected porous volume as explained in the ‘background’ section. For larger aggregates, the ‘prism size / particle size’ ratio had an important effect on measured expansions even for ratios greater than 100. For example, the 315-630 µm aggregates presented expansion about 20% larger for the 70x70x280 mm specimens (ratio equal to 200) than for the 40x40x160 mm ones (ratio equal to 100 – Figures II-7a and II-8). Such ratios are largely higher than usual values, which lie between 5 to 10, taken to choose a specimen size according to aggregate size for compressive strength for example. Therefore, it appears to be impossible to break free of this scale effect when performing expansion tests, which leads to part of the expansion being neglected compared to structural conditions. It is thus necessary to take this fact into account when analysing the expansion tests that can be carried out with the theoretical development presented in the background.

4.4. Effect of aggregate size

The effect of the reactive aggregate size on the ASR expansion has already been largely studied. Research has shown that the ASR expansion increases as the reactive particle size is reduced. This is the case in the works of [Hobbs and Gutteridge 1979, Kuroda et al. 2004 and Zhang et
al. 1999], who obtained maximum expansions for size classes of 150-300 μm (opal), 80-150 μm (quartz glass) and 150-300 μm (andesite), respectively. However, when the experiments are performed with particles smaller than a few tens of a μm, it has frequently been shown that the expansion does not increase continuously with the reduction of particle size. Some authors obtained insignificant expansion when the sizes of the reactive particles were under 50 to 150 μm [Kawamura et al. 1983, Kodama and Nishino 1986, Zhang and Groves 1990]. Only a few exceptions of very small particles led to significant ASR expansions, all involving opal aggregates [Diamond and Thaulow 1974, Kelly et al. 1948, McConnell et al. 1947]. Other research works clearly show a pessimum effect for particle size, but for particles much larger than 100 μm [Baronio et al. 1987, Diamond and Thaulow 1974, Feng et al. 2002, Lenzner and Ludwig 1980, Xie et al. 2003, Zhang and Groves 1990]. These investigations were usually performed on specimens of the same size. The originality of the study presented here is to have used three sizes of specimens with the same aggregate classes.

For all the specimens, it can be observed that the prisms containing small reactive particles (0-315 μm) have the lowest expansion (lower than 0.15% - Figures II-3 to II-5). For the three other aggregate sizes, the ASR expansions are significant and higher than 0.5%. The difference of ASR expansions for the small aggregate can likely be explained by the effect of the connected porosity. For the smallest aggregates, more of the gel can migrate in this connected porosity than for larger aggregates and thus little ASR gel is available to cause expansion [Multon et al. 2009, Multon et al. 2010]. At 150 days, the ASR expansion presents a pessimum effect whatever the specimen size (Figure II-9a), as already observed during previous investigations. But, after 400 days, when asymptotic expansions had been reached, the pessimum had totally disappeared for the largest specimens (Figure II-9b). For the largest aggregates, part of the difference of expansion can be explained by a delay in the ASR expansion due to the diffusion of the alkali in the aggregate [Multon et al. 2010].
The results of measurement confirm that the expansion rate was slower in the largest particles whatever the size of the specimens (Figures II-3 to II-5). However, even when the asymptotic value was reached, ASR expansion remained lower for the largest aggregates in the smallest specimens (Figure II-9b). This result shows that the pessimum effect is not only due to the diffusion of alkalis in the aggregate, meaning that it is not an intrinsic phenomenon but could be due to a scale effect that depends on the ‘specimen size / aggregate size’ ratio.

In addition, the pessimum effect of aggregate size appears to be related to the expansion capacity of the mortars. Compared with a previous study [Multon et al. 2009] which was performed on mortars kept in saturated atmosphere (R.H. > 95%), the present study showed a pessimum effect moving towards smaller aggregate. The mortars conserved in the alkali solution were more expansive than the specimens in saturated atmosphere due to the presence of sufficient alkali and probably due to large effect of alkali leaching from the test prisms at R. H. > 95%. Thus, it can be concluded that the more expansive the mortar is, the more significant is the scale effect. This can be explained by equations II-1 to II-3. The mortar is very expansive, which means that more gel is produced (i.e. the gel molar volume is higher), and then the gel pressure is larger than for less expansive mortar (Equation II-3). The cracks appear for a constant value of the stress factor \( K_I \). In consequence, if the pressure increases, the function \( f \) referred to \( R_a/L \) must become smaller to keep \( K_I \) constant. This means that the ratio \( R_a/L \) decreases and explains why the pessimum moves towards smaller aggregate (Equation II-1 and II-2). In the contrary, the pessimum effect...
can disappear for a sufficient large specimen dimension which could lead to a high L/R₃ (as in Fig.II-8).

5. Test on aggregates of different natures

The aim of this part was to study the expansion test on several natures of aggregate to verify how it could differentiate between the reactivity of different aggregates.

5.1. Mortar mixtures

In previous investigations [Multon et al. 2009], the reactive aggregate of sizes 315-630 µm and 630-1250 µm showed the same expansion in the condition of 60°C, R.H. > 95%. Therefore, it was decided to use aggregate of size 315-1250 µm for these experimentations. Thus, the mortars had the following particle size distribution: 30% of 315-1250 µm and 70% of the marble of size 0-2500 µm. The aggregates included four types of rocks: siliceous limestone, quartzite, opal and quartz. The mortars were casted in the size of 20 x 20 x160 mm. All the mortars were conserved in a 1 mol/l NaOH solution at 60°C.

5.2. Results

The ASR expansions obtained for these four aggregates are plotted in Figure II-10.

![Figure II-10  ASR expansions according to the nature of the aggregate](image)

After a slight delay, the mortar containing opal appeared to be the most reactive, with rather fast expansion and an asymptotic value of about 1.35%. The expansion of the mortar containing siliceous limestone was quite fast too, but the final expansion was less (about 0.6%). The mortar with quartzite aggregate presented a slow expansion rate at the beginning but reached a final
value about 0.5%, which was quite close to that of the siliceous limestone. ASR expansion of the mortar with quartz aggregate was small compared to the other three, but not totally innocuous in the testing conditions. These results are consistent with experimental feedback on these aggregates. Opal is known to be very reactive and to present large expansion if the amount of available alkali is sufficient, while the other two reactive aggregates are usually less reactive and present similar ASR expansions. In fact, due to the large pressure developed by ASR gels, the specimens containing opal were greatly damaged and cracked (crack width of about 425 µm – Figure II-11). The analysis performed in the ‘background’ section suggests that a great proportion of the ASR gel should have permeated through these large cracks and thus not contributed to the expansion. This was due to the large amount of reactive silica contained in opal, which induced high gel pressure (Equation II-3) and thus a greater stress intensity factor (Equation II-2) for opal than for the siliceous limestone.

![Figure II-11: Cracking patterns of specimens cast with opal (20x20x160 mm)](image)

6. Discussion
The previous observations show the difficulty of obtaining a fast but relevant expansion test on specimens. In expert assessments, the owners of structures often expect fast results. To this end, it is interesting to note that the time necessary to reach the expansion asymptote (assumed here to be reached when the difference between two consecutive measured expansions is lower than 0.015% ) increases with the specimen and the aggregates sizes (Table II-3). This influence can be explained by the diffusion of ionic species into the specimen and the aggregates. Thus, the shortest time necessary to achieve expansion is about 56 days (Table II-3), obtained for the smallest specimens (20x20x160 mm) and for aggregate class C2 (315-630µm). For larger aggregates and specimens, the time is always longer than 100 days (Table II-3). Moreover, it is always difficult to obtain much material from existing structures that are still in use. From this point of view, too, working on small specimens is interesting. The most relevant, fast and convenient tests should use small expansive particles (315-630µm) and small specimens (20x20x160 mm). But, in this condition, a part of the expansion is neglected because of the combined effect of aggregate and specimen size (expansions measured on 20x20x160 mm specimens are 30% lower than expansions obtained on 70x70x280 mm specimens). Moreover, section 5.2 shows the effect of the aggregate nature on cracking due to differences in reactive silica content. It could disturb the analysis of the measured expansions. To decrease this disturbance, the same stress intensity factor $K_I$ should be taken. This means that for different
nature of aggregate the aggregate size and specimen size should be chosen carefully to have the same $K_i$ value (Equations II-2 and II-3). This method will be introduced in detail in Chapter 5.

### Table II-3  Time necessary to achieve asymptotic expansion (in days)

<table>
<thead>
<tr>
<th></th>
<th>315-630µm</th>
<th>630-1250µm</th>
<th>1250-2500µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>20x20x160 mm</td>
<td>56</td>
<td>120</td>
<td>148</td>
</tr>
<tr>
<td>40x40x160 mm</td>
<td>134</td>
<td>148</td>
<td>302</td>
</tr>
<tr>
<td>70x70x280 mm</td>
<td>301</td>
<td>342</td>
<td>393</td>
</tr>
</tbody>
</table>

*the asymptotic expansion is assumed to be reached when the difference between two consecutive measured expansions is lower than 0.015%.

7. Conclusion

The main aim of this chapter was to analyse the expansion test in terms of conservation conditions, size of specimens (20x20x160 mm, 40x40x160 mm and 70x70x280 mm), and size of aggregate (0-315 µm, 315-630 µm, 630-1250 µm and 1250-2500 µm) in order to obtain fast and relevant expansions. This test is only a part of a global methodology using measurements performed directly on structures, finite element calculations and laboratory expansion tests on aggregate extracted from structures to assess the expansion kinetics. The tests are used to assess the residual reactive silica content in the aggregates of various sizes used in the structure to determine the advancement of the reaction according to the size of the aggregate and thus to assess the kinetics of future expansions [Sellier et al. 2009].

The following conclusions can be drawn:

1. For the siliceous limestone aggregate, the expansion tests in three concentrations of NaOH solution (0.77 mol/l, 1 mol/l, 1.25 mol/l) showed that, in the condition of abundant alkalis, the expansion is not significantly influenced by the alkali concentration in the range of NaOH concentration studied here.
2. For the same size of aggregate, small prisms needed the shortest time to achieve final expansions. For the same size of specimen, small aggregate took the shortest time to reach the final expansions. These results can likely be explained by the faster diffusion of ionic species into the porosity of small prisms and into the aggregate.
3. A combined effect of the aggregate and specimen sizes on ASR expansions has been highlighted. It appears that, even with a ‘specimen size / aggregate size’ ratio higher than 100, the scale effect still exists. It could be explained by the effect of the cracking on the gel pressure. After the cracking, a part of the increasing volume due to ASR gel formation can be accommodated by the cracks volume and a part of the gels can permeate out the specimens, causing a decrease of the gel pressure and thus reducing the induced expansion.
4. A fast and convenient tests should use small reactive particles (315-630 µm) and small specimens (20x20x160 mm). But in this condition, a part of the expansion is neglected because of the coupled effect of aggregate and specimen size. So the results should be analyzed through the concept of stress intensity factor in order to take all the parameters into account in the measured ASR expansions.

5. Even if the expansion measurements are used through a finite element analysis, the expansion tests should be performed in comparable conditions. Therefore, nonlinear effects due to connected porosity or cracking should be avoided or well enough understood to be taken into consideration.
Chapter 3

Chemical measurement of reactive silica in aggregate

1. Introduction

The method of requalification of ASR-damaged structures proposed by [Grimal 2007, Sellier et al. 2009] is based on a numerical finite element inverse analysis of the structure, which uses the silica content of the aggregates measured in laboratory tests. One of the basic assumptions of the method is that the potential expansion of the concrete is proportional to the remaining reactive silica within the aggregates. This assumption is based on the consideration that the alkali content is not the limiting parameter of the reaction, since alkalis can be regenerated by calcium ions [Duchesne and Bérubé 1994, Lagerblad and Tragardh 1992] and thus continue to attack the silica [Sellier et al. 2009].

In the previous work [Grimal 2007, Sellier et al. 2009], the chemical analysis were not performed. In this work, the chemical test was highlighted since the results could be obtained faster than expansion test. The chemical method of requalification highlights the interest of measuring the quantity of reactive silica in aggregates. However, this apparently simple question involves complex notions related to the interpretation and the measurement of the so-called "reactive silica".

The term "reactive silica"

The subjective term "reactive silica" has no absolute meaning since it depends on the conditions of attack (temperature, pressure, type and concentration of solution in contact with silica). Some types of silica known as reactive in a given environment (e.g. in concrete) can be considered as inert or not reactive for other conditions. Obviously, in our context, the term must be taken as the silica that dissolves in contact with concrete pore solution, producing gels leading to the expansion of the concrete. The most commonly incriminated minerals subject to ASR are considered to be [Corneille et al. 1991]: 1) amorphous minerals such as glass and opal, 2) cryptocrystalline minerals such as chalcedony, and 3) crystalline minerals such as quartz,
feldspar and phyllosilicates when they contain imperfections (deformations and/or alterations of the crystalline lattice).

**Measurement of reactive silica**

The most representative test to evaluate the reactive silica content available for ASR in concrete would simulate real concrete conditions in terms of pH, pressure and humidity temperature. However, under these conditions, ASR usually lasts several decades, even hundreds of years in the case of concrete containing very large aggregates, so the measurement of total silica consumption seems impractical.

A few accelerated methods exist for attacking silica in aggregates. Standard chemical methods are used to evaluate the potential reactivity of aggregates, by comparing the dissolved silica with criteria chosen to correspond to ASR-damaged concretes. For instance, ASTM C289 allows the measurement of dissolved silica after crushed aggregates (150-300 µm) are attacked in 1N sodium hydroxide solution for 24h at 80°C. The result obtained is used to classify the aggregate as deleterious or not, but not intend to quantify the reactive silica.

Other tests are available in the literature to quantify reactive silica but they are initially intended for supplementary cementing materials (SCM) such as fly ash [Forest 1962, Hulett and Weinberger. 1980, Richartz 1984, Sivapullaiah et al. 1998], metakaolin [Murat and Arnaud 1988] or rice husk ash (RHA) [Mehta 1978]. All these methods, which involve the attack of silica, can be divided into two groups: basic attack and acid attack.

One example of basic attack (other than ASTM C289) is given by Mehta [1978], who created the “Silica reactivity index” for RHA, defined as the percentage of available silica which dissolves in an excess of boiling 0.5N NaOH in 3 minutes (sample <45µm). According to its author, this method gives "an indication of the reactivity of silica present in a material". However, there is no guarantee that the value obtained concerns the total reactive silica content.

Acid attacks are more commonly found in the literature and different types of acid are used, typically: HCl, HF and organic acids. Sivapullaiah et al. [1998] compared the effectiveness of different HCl concentrations (1 to 5 mol/l) to dissolve silica in fly ash. They found that concentrations between 2 and 3 mol/l correlated well with the compressive strength of lime/cement fly ashes. Fly ash European standard NF EN 450-1 [2005] defines reactive silicon dioxide as the fraction of SiO₂ which is soluble after treatment of the ash with HCl and boiling KOH solution for washing. This method, also used for other SCM such as metakaolin [Badogiannis et al. 2004], sewage sludge ash [Cyr et al. 2007], slag and other pozzolans [Papadakis et al. 2002], is sometimes criticized for the uncertainty concerning whether crystalline silica is dissolved [Paya et al. 2003].

The HF method is usually less criticized, since it allows the amorphous silica to be distinguished from the crystalline form. At the beginning of the HF attack application, researchers focused on finding an appropriate HF concentration and reaction time to attack only the amorphous phase, leaving the crystalline phase [Diamond 1986, Hulett and Weinberger 1980]. However, the results
obtained were uncertain, depending mostly on the materials used in the experiments. For example, Hulett and Weinberger [1980] tested fly ashes and concluded that, with 1% HF attack for 16-20 h, the glass phases could be mostly dissolved. Diamond [1986] tested different types of fly ashes and found that 1% HF and 4 hours were the optimized reaction conditions to etch the glass phases. This uncertainty led to unreliability of the results, and a new method was therefore proposed, based on the different dissolution rates of amorphous and crystalline silica. For example, the rate at which quartz dissolved at 25°C with 0.10 mol/l HF was roughly 2.8-3.0 (mg·m⁻²·hr⁻¹), while, for vitreous material under the same attack conditions, the rate was 136-150 (mg·m⁻²·hr⁻¹). This method was successfully used by Murat and Arnaud [1988] to measure the amorphous phase of activated kaolinite and montmorillonites, and used by Pichon et al. [1996] to quantify the amorphous phase of pozzolanic materials.

Organic methods have been applied to determine the amorphous silica in RHA as a rapid analytical method. One of these methods is based on the mechanism of amorphous silica reacting with glycerol reagent to produce glycerosilicate solution which can be titrated with an aqueous glycerol solution of barium hydroxide. This method has been used only on fine materials up to now. For example, Kreshkov et al. [1965] tested it on clay, and Payá et al. [2001] used it for testing rice husk ash (size: 10~17 µm).

The aim of this chapter is to test and compare three methods, chosen as being simple and rapid, to quantify the amount of reactive silica in five aggregates (including three materials known be affected by ASR). These methods, which are based on selective dissolution in bases and/or acids, have not been used so far to study alkali-reactive aggregates (or when they have, it was only to evaluate the reactivity to alkalis and not to precisely quantify the proportion of reactive silica). The reliability of the methods is evaluated by correlating the reactive silica contents with expansion measurements of mortars containing the aggregates presented in the previous chapter.

2. Methods and materials

2.1. Analytical methods and mortar test

Aggregates

The chemical composition of the aggregates was determined using a Perkin Elmer 2100 atomic absorption spectrophotometer with flame atomization. Loss on ignition was measured by calcination at 1000°C. Mineralogical properties were obtained by X-ray powder diffraction using a Siemens D5000 diffractometer equipped with a monochromator and using a Kα (λ = 1.789 Å) cobalt anticathode. Measurements were made with a 20 step interval of 0.04° (5°-70°) and an acquisition time of 2s per step. The particle size distribution of the crushed materials used for the dissolution tests was measured by laser granulometry in water, using a Cilas 1090. The petrographic observations by optical microscopy were carried out with thin sections in transmitted light with crossed polars.
Chapter III

2.2. Materials

Five materials were selected for the tests: three aggregates known to be alkali-reactive (siliceous limestone - SL, quartzite - Q, and opal - O), and one material considered as non-reactive (quartz aggregate - QA). The three reactive aggregates were chosen to cover a wide range of types and geological origins, from low to high kinetics of silica dissolution: an igneous rock (opal: high kinetics), sedimentary rock (siliceous limestone: low kinetics), a metamorphic rock (quartzite: low kinetics). For the chemical tests; the aggregates were crushed to particle sizes of less than 80 µm (mean diameter of 20 µm). Special attention was paid to avoiding overgrinding of aggregates, in order to limit the appearance of the “soluble surface layer on ground quartz” already observed by other authors [e.g. Iler 1979]. This thin amorphous phase around the aggregates could lead to an overestimation of the reactive silica content.

2.2.1. Chemical and mineralogical properties

The chemical compositions of the aggregates are given in Table III-1. Quartzite, opal, and quartz aggregate were mainly composed of silica, while the siliceous limestone had only a limited SiO₂ content. In order to identify the forms of reactive silica, petrographic analyses were carried out on each aggregate type.

<table>
<thead>
<tr>
<th>Aggregates</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>SO₃</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>92.7</td>
<td>--</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>1.1</td>
<td>6.0</td>
</tr>
<tr>
<td>SL</td>
<td>15.4</td>
<td>1.5</td>
<td>0.7</td>
<td>40.4</td>
<td>1.4</td>
<td>0.4</td>
<td>0.4</td>
<td>4.2</td>
<td>35.6</td>
</tr>
<tr>
<td>Q</td>
<td>87.7</td>
<td>4.0</td>
<td>1.0</td>
<td>0.4</td>
<td>0.2</td>
<td>0.1</td>
<td>0.9</td>
<td>0.1</td>
<td>1.1</td>
</tr>
<tr>
<td>QA</td>
<td>92.2</td>
<td>3.7</td>
<td>1.1</td>
<td>0.1</td>
<td>0.1</td>
<td>--</td>
<td>0.01</td>
<td>0.2</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Opal

The XRD pattern of opal (Figure III-1) shows relatively broad diffraction lines at d-spacing between 5.60 and 3.42 Å (2θ = 18.37° ~ 30.3°). According to the classification proposed by Jones and Segnit [1971], the sample can be considered to be opal-CT, characterised by a structure consisting of randomly interstratified layers of α-tridymite and α-cristobalite [Jones and Segnit 1971], with a high degree of disorder [Wilson et al. 1974]. Depending on the relative amounts of cristobalite and tridymite, the position of the main opal peak shifts from 4.04 Å (2θ = 25.60°), which is typical of α-cristobalite, to 4.11 Å (2θ = 25.13°), characteristic of α-tridymite. In the sample studied here, the position of the main peak was centred at about 4.11 Å (2θ = 25.13°), closer to the tridymitic one. The well-pronounced secondary peak at 4.3 Å (2θ = 23.98°)
confirms a high relative amount of tridymite. The XRD pattern also indicates the presence of quartz, confirmed by the diffraction lines at 3.34 and 4.26 Å ($2\theta = 31.08^\circ$ and $24.25^\circ$).

![Figure III-1 XRD pattern of opal](image)

The petrographic analysis of thin sections (*Figure III-2*) showed the presence of cryptomicrocrystalline quartz (chalcedony) spherulites (A) reaching sizes around 100 µm, surrounded by a glassy phase (B, black in polarised light). Small crystals of xenomorphic quartz (C), presenting a certain degree of undulatory extinction, were also observed. SEM observations (*Figure III-3*) confirmed the presence of different textures of silica in this aggregate.
Chapter III

Figure III-2 Petrographic analysis of opal in polarised and natural lights. A: chalcedony spherulites – B: amorphous phase – C: quartz
Figure III-3  SEM observations and EDX of opal aggregate. 
(A,B: amorphous silica, C: quartz)

Siliceous limestone
The XRD pattern of raw SL and the pattern of SL after leaching in 0.25 mol/l HCl (Figure III-4) showed that this aggregate was composed of calcite and dolomite, with significant amounts of impurities including quartz, plagioclase feldspars, micas, kaolinite and pyrite. A small amount of amorphous silica was also found in some spectrum patterns, especially visible after HCl pretreatment. In addition to calcite, present in the form of micritic crystals containing many debris of fossils, thin-section observations (Figure III-5) showed the presence of small spherulites probably made of chalcedony (A) and microquartz (A) enclosed in calcite grains. Larges veins of xenomorphic quartz (B) presenting high undulatory extinction were also observed. Amorphous silica was difficult to identify by optical microscopy, but has already been seen in this type of aggregate [Guédon et al. 2000]. Figures III-6 and III-7 illustrate the morphologies and compositions of different minerals found in this aggregate.
Chapter III

Q : Quartz
C : Calcite
D : Dolomite
F: Felspar
K : Kaolinite
M: Mica
Py: Pyrite

Figure III-4  XRD pattern of siliceous limestone
Figure III-5  Petrographic analysis of siliceous limestone (SL) in polarised and natural lights. A: microquartz and spherulites, B: quartz with undulatory extinction
Figure III-6  SEM observations and EDX of siliceous limestone aggregate

Figure III-7  Mapping (SEM+EDX) of siliceous limestone aggregate

1. Calcite
2. Dolomite
3. Quartz
4. Feldspars or micas
Quartzite

As shown in the XRD pattern (Figure III-8), quartzite mainly contained quartz, and also a certain amount of phyllosilicate minerals (mica-type such as muscovite). Examination of thin-sections (Figure III-9) showed that this rock was mainly composed of heterometric quartz grains of sizes varying from less than 1 µm (A) up to a few hundreds of µm (B, C). The presence of primary (C) and recrystallised (B) quartz grains was noted. The former (C) were irregular, showed undulatory extinction and were separated by an intergranular cement (D) composed of microquartz and micas. The latter (B) were usually much better defined and no undulatory extinction was observed. Muscovite minerals were often found, sometimes concentrated in areas containing microquartz (E), as large particles (F) or as a cementing agent (D). According to Sims and Nixon [2003], the intergranular phase is responsible for the alkali-reactivity of this kind of aggregates. SEM observations (Figure III-10) confirmed the presence of cracked quartz grains (A) surrounded by zones containing quartz and micas (B). Some small automorphic quartz grains (C) and zircon particles (D) were also found.

Figure III-8  XRD pattern of quartzite
Figure III-9 Petrographic analysis of quartzite (Q) in polarised and natural lights.
1) Various sizes of quartz grains (A,B), presence of micas (E).
2) Primary quartz particles (C), micas (F) and intergranular cement (D).
3) Quartz grains (A,B) and micas (E).
4) Primary quartz particles (C) and intergranular cement (D).
Figure III-10  SEM observations and EDX of quartzite aggregate
Quartz aggregate

The XRD pattern of quartz aggregate (Figure III-11) shows only quartz, with visible traces of other minerals.

![XRD pattern of quartz aggregate](image)

**Figure III-11  XRD pattern of quartz aggregate**

Thin sections (Figure III-12) reveal: (a) Particles composed of quartz grains of a few hundreds of µm, some of them presenting undulatory extinction. Contrary to quartzite, the boundaries of each grain are free of micas or microquartz. (b) Large homogeneous quartz grains having a well defined extinction without rolling.
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Figure III-12  Petrographic analysis of quartz aggregate (QA) in polarised and natural lights. 1) small quartz grains and 2) large homogeneous quartz grains. A: quartz

Types of silica in aggregates and potential of reactivity

The mineralogical and petrographic studies allowed us to determine the types of silica found in the aggregates. Table III-2 summarizes the results in terms of qualitative evaluation, with the potential reactivity of each silica type as classified in the literature [Sims and Nixon 2003, Broekmans 2004]

Table III-2  Potential reactivity and occurrence of silica types (related to silica content) in aggregates

<table>
<thead>
<tr>
<th>Types of silica</th>
<th>Potential of reactivity</th>
<th>Opal</th>
<th>Siliceous limestone</th>
<th>Quartzite</th>
<th>Quartz aggregate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total content of silica (%)</td>
<td></td>
<td>92.7</td>
<td>15.4</td>
<td>87.7</td>
<td>92.2</td>
</tr>
<tr>
<td>Quartz without undulatory extinction</td>
<td>Weak</td>
<td>Scarce</td>
<td>Scarce</td>
<td>Majority</td>
<td>Majority</td>
</tr>
<tr>
<td>Quartz with undulatory extinction</td>
<td>Strong</td>
<td>Frequent</td>
<td>Majority</td>
<td>Scarce</td>
<td>Not observed</td>
</tr>
<tr>
<td>Microquartz (intergranular)</td>
<td>Strong</td>
<td>Not observed</td>
<td>Scarce</td>
<td>Frequent</td>
<td>Not observed</td>
</tr>
<tr>
<td>Chalcedony-like spherulites</td>
<td>Very strong</td>
<td>Frequent</td>
<td>Scarce</td>
<td>Not observed</td>
<td>Not observed</td>
</tr>
<tr>
<td>Amorphous phase</td>
<td>Very strong</td>
<td>Frequent</td>
<td>Scarce</td>
<td>Not observed</td>
<td>Not observed</td>
</tr>
</tbody>
</table>
2.2.2. Expansion potential

The expansion tests presented in the previous chapter give a good estimation of the difference of reactivity potential of these aggregates (Figure III-13). These results confirm that opal (O), siliceous limestone (SL) and quartzite (Q) are alkali-reactive, and that quartz aggregates (QA) can be considered as a poorly reactive material. The results of the chemical measurements presented below will be compared to these measurements in the final discussion.

![Figure III-13 ASR expansion of mortars containing different types of aggregates](image)

30% aggregates (315-1250 µm) + 70% non-reactive aggregate (0-2500 µm), mortar size: 20x20x160mm

3. Methods for the chemical extraction of reactive silica: results and discussion

Three methods, using principles mainly based on the literature review, were used to quantify the amount of potentially reactive silica in aggregates (Figure III-14).

The selective dissolution processes are described in the following sections. They can be divided in two categories: basic attack (NaOH) and acid attack (HCl and HF). Two of the three methods included two steps: a main attack to dissolve the silica contained in the aggregate, followed by a washing phase to dissolve the silica which had precipitated in the first step.
3.1. **NaOH attack (100°C and 60°C) – cold HCl washing**

This method is based on US standard ASTM C289 and French standard XP P18-594 [2004], since it consists of attacking silica with 1M sodium hydroxide solution. The use of a basic solution is a reasonable choice to get close to a cement-based environment. These standards were modified for our purposes, since the goal was not to evaluate the reactivity potential of an aggregate but to determine the silica content available for ASR.

Considering the long duration of NaOH attack at ambient temperature, the tests were carried out at a high temperature (100°C) to accelerate the reaction. The dissolution of silica as a function of reaction time (up to 96 hours) was measured on all the materials tested. A few tests were also performed at 60°C, a temperature usually used in ASR tests [Cyr et al. 2007, NF P18-454, Sellier et al. 2009].

The aggregate was crushed to particle sizes smaller than 80 µm in order to quickly attack all the silica inside the grains. With coarse particles, the reagent would need a long time to reach the centre of the particles. The analyses of dissolved silica were made at different reaction times (up to 96 h at 100°C or 150 days at 60°C) to estimate the kinetics of dissolution. It was assumed that only reactive silica was attacked (this hypothesis is discussed later). The residue of the NaOH attack was then washed with HCl in order to dissolve the gel which was likely to precipitate during the basic attack [Bulteel et al. 2002]. If the washing was not performed, some of the dissolved silica which had precipitated could not be measured in solution and this could lead to an underestimation of the reactive silica.

In aggregates containing only small amounts of silica and for which some minerals (e.g. calcite) could interfere with the extraction method (for instance by consuming the reagents), a pretreatment was conducted to eliminate the matrix and so refine the active fraction. The process,
used here with aggregates made of limestone, consisted in dissolving the calcareous part of the aggregate in 0.25 mol/l HCl at 0 °C for almost 30 min (until there is no CO₂ released). The low concentration and low temperature aimed to avoid attacking silica [Goto 1955]. This kind of pretreatment is recommended in standards such as French XP P18-594 [2004], for limestone contents higher than 15%.

3.1.1. Procedure

The procedure of the test is divided in two steps. In the first part, 1.5 g of sample is weighed and put into a 75 ml sealed steel container. After addition 50 ml of 1 mol/l NaOH solution (L/S=33.3 ml/g), the container is put in a constant-temperature oven at 100°C or at 60°C for different test times. At a given age, the solution is filtered and analysed using atomic absorption. The second step of the test consists in transferring the filtered residue into a beaker, adding 300 ml of cold HCl (1 mol/l), putting the beaker in an ice-water bath (~0°C, to avoid silica gel precipitation during the acid attack) for 30 minutes and then filtrating the solution for SiO₂ measurement by atomic absorption. The total dissolved silica is taken as the sum of the values obtained for the two steps.

3.1.2. Mechanisms of attack

When silica is exposed to a strong alkaline solution such as NaOH, there is an acid-base reaction between the hydroxyl ions in solution and the acidic silanol (Si-OH) groups [Dent Glasser and Kataoka 1981] as follows:

\[ \equiv \text{Si-OH} + \text{OH}^- \rightarrow \equiv \text{Si-O}^- + \text{H}_2\text{O} \]

As further hydroxyl ions penetrate the structure, some of the siloxane linkages (Si-O-Si) are also attacked:

\[ \equiv \text{Si-O-Si} \equiv + \text{OH}^- \rightarrow 2 \equiv \text{Si-O}^- + \text{H}_2\text{O} \]

The negative charges on the terminal oxygen atoms are balanced by alkali cations (Na⁺) that simultaneously diffuse into the structure. The disruption of siloxane bridges weakens the structure, and if there are sufficient reserves of alkali hydroxide, the process continues to produce an alkaline silicate solution.

This mechanism is suitable for both amorphous silica and crystalline silica but, in this last case, the solubility is much lower. For example, in 25°C aqueous solution at pH=14, the solubility of vitreous silica is approximately 21 times the solubility of quartz (~125 mol/l for vitreous silica compared to ~6 mol/l for quartz) [Paul 1982].

The reaction mechanism can be simplified as follows [Bulteel et al. 2002, Garcia-Diaz et al. 2006]:

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### 3.1.3. Results and discussion

**Tests at 100°C**

The curves of silica dissolution for the materials after the two steps of the method (NaOH at 100°C followed by cold HCl washing) are shown in Figure III-15a. The results are presented as the percentage of dissolved silica with respect to all the material. The curves of O, SL and QA reached an asymptote in the measuring times, while the curve of Q was still increasing at the end of the test. To obtain the asymptotic values, all the five curves were fitted by using a typical equation for dissolution:

\[
Si_{\text{dissolved}} = Si^{\infty} (1 - e^{-at})
\]  

(III-1)

where \(Si_{\text{dissolved}}\) is the amount of silica dissolved at time \(t\), \(Si^{\infty}\) is the asymptotic value for \(t=\infty\), and \(a\) is a parameter depending on the nature of aggregate. The \(Si^{\infty}\) value was obtained through curve fitting, and this value was considered to be representative of reactive silica. The kinetics of the silica dissolution can give qualitative information about reactive components since the different forms of silica show dissimilar kinetics [Dron and Brivot 1993]. Thus, the initial reaction rate and the evolution of reaction rate over time were deduced (Figure III-15b) according to the derivative of Equation III-1. The rate of silica dissolution can be interpreted as the consumption rate of reactive sites in the chemical environment, so high rates can be associated with very reactive components.

Among the reactive aggregates, opal gave the highest dissolved silica value (Figure III-15). The initial rate of dissolution was very high, but it decreased rapidly, meaning that the dissolution process was quick. These results are in accordance with the degree of reactivity of this aggregate (Figure III-13) and with the nature of silica determined by petrographic observations.

Siliceous limestone (SL) led to 9.5% of dissolved silica, representing almost 2/3 of the silica in this aggregate (9.5% / 15.4%).

Quartzite (Q) gave quite a high value of SiO\(_2\), considering that it was almost exclusively composed of quartz, which was expected to be weakly reactive (Table III-2). The value was around 5 times higher than that of SL, which was inconsistent with the expansion results (Figure III-13) showing that Q had a similar reactivity to that of SL. The kinetics of dissolution of Q was slow and the dissolution curves increased continually with the reaction time. This result raised some doubts about whether this method falsely counted part of the crystalline silica as reactive.

Finally, QA gave the lowest value of all, in accordance with the expansion results.
$Si_{\text{dissolved}} = Si^\infty (1 - e^{-kt})$

Figure III-15  Dissolved silica (a) and reaction rate (b), as a function of reaction time, after NaOH (100°C)-HCl attack
Test at a different temperature (60°C)

Considering the doubts concerning the possible attack of well crystallised silica when NaOH was used at 100°C (high temperature might increase the solubility of silica), some supplementary tests on aggregate SL were carried out at 60°C. This temperature corresponded to the one used in accelerated expansion tests.

The results are given in Figure III-16, with reaction times in hours and days when the attacks were carried out at 100°C and 60°C, respectively. The comparison of these two curves shows that almost the same asymptotic values were found for the two temperatures, meaning that the solubility of the silica was similar. Only the kinetics was different since the initial dissolution rate decreased from 1.1 to 0.014 %/h when the temperature passed from 100 to 60°C.

The Arrhenius law (Equation III-2) was used to calculate the activation energy, using equation 3. The rate constants $k_1$ ($T_1 = 373$ K, 100°C) and $k_2$ ($T_2 = 333$ K, 60°C) were deduced from the results presented in Figure III-16, by using the initial rate of dissolution ($t=0$).

\[
k = Ae^{-E_a/RT}
\]

where $k$ is the rate constant, $T$ the temperature (in Kelvin), $E_a$ the activation energy, $A$ the prefactor and $R$ the gas constant (8.314 J/mol·K).

\[
E_a = \frac{R \ln \frac{k_1}{k_2}}{\left( \frac{1}{T_2} - \frac{1}{T_1} \right)}
\]

The apparent activation energy $E_a$ calculated was 113 kJ/mol, a value higher than those usually found in the literature (for example 96 kJ/mol [Dron and Brivot 1993]). The difference could have been caused by the materials tested and test method. The value here was based on the results of siliceous limestone after NaOH attack and subsequent HCl attack, whereas the value of [Dron and Brivot 1993] was deduced from the results of opal only after NaOH attack. The precipitation was not taken into account by [Dron and Brivot 1993]. However, in the work of [Dron and Brivot 1993], the precipitation of the silica after the NaOH attack was high as shown in Figure III-17. At 60°C, only 20% of the silica dissolved by the NaOH attack was in the solution; the rest was in a gel that precipitated in the solution (i.e. 80%, dissolved by the HCl washing). At 100°C, 70% of silica was found in the solution, so only 30% was contained in the gel. The large presence of gel at 60°C could cover the surface of the particle and prevent the dissolution of silica, which could lead to a decrease of $k_2$ and thus to a higher value of $Ea$. 
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Figure III-16 Dissolved silica of siliceous limestone (SL) as a function of time after NaOH-HCl attack at 60°C and 100°C. Note the scale for reaction time: hours at 100°C and days at 60°C

Figure III-17 Comparison of dissolved silica after NaOH and HCl attack at 60°C and 100°C

3.2. HCl (heated) - KOH (boiled)
This method is found in standards such as NF EN 450-1 to evaluate the reactive silicon dioxide in fly ash to be used in concrete. Many papers have already reported results using this procedure for other supplementary cementing materials [Badogiannis et al. 2004, Cyr et al. 2007, Papadakis et al. 2002, Paya et al. 2003]. In this method, the aggregate is firstly attacked by concentrated HCl (12 mol/l) in order to destroy the silica network and produce silica gel. KOH (4.5 mol/l) is then used mainly to dissolve the gel and also to attack the remaining reactive silica.
3.2.1. Procedure

The procedure of the test is divided into two steps. In the first part, 5 g of sample is weighed and dispersed in a porcelain dish with 125 ml of water. After addition of 200 ml of concentrated HCl (12 mol/l), the solution is evaporated to dryness on a sand bath. The operation is repeated two more times with 100 ml concentrated HCl. Then, the residue is treated with 100 ml diluted HCl (3 mol/l), heated, filtered and washed with boiling water until free from chloride ions. The solution is then analysed using atomic absorption. The second step of the test consists of transferring the residue into a steel container, adding 500 ml KOH (4.5 mol/l) and leaving to stand for 16 h at room temperature. Then the solution is boiled under reflux for 4 hours, filtrated, and washed with water and diluted HCl (1.2 mol/l). The solution is analysed for SiO₂ using atomic absorption. The total dissolved silica is taken as the sum of the values obtained for the two steps.

3.2.2. Mechanisms of attack

Generally, silicate glasses and silicate minerals can be attacked by acid, leaving a residue of hydrated silica which forms a gel. This process can be explained as the acid removing the iron atoms, which are incorporated in the continuous silicon-oxygen frameworks, leaving the siloxane structures to yield gelatinous silica. Paul [1982] described the acid attack of silicate glass. Although at lower pH values the exchange of cation with hydrogen ion seems favoured, the silicic acid does not ionize and thus offers a high activation barrier for the diffusion of positive ions. This can explain why only a little soluble silica (< 0.1% at 35°C) is detected in glass in an acid environment.

\[
\text{ASiO}_3(\text{glass}) + H^+ \rightarrow H_2\text{SiO}_3 + A \quad (A: \text{cations like Na}^+, \text{Ca}^{2+}, \text{Al}^{3+} \ldots)
\]

However, under the conditions of high acid concentration and high temperature, this exchange between cation and hydrogen ion occurs frequently, and finally produces gel. This method was summarized by Iler [1979] to synthesize gel by acidifying silicate minerals.

3.2.3. Results and discussion

Table III-3 presents the results of the HCl attack, followed by the KOH washing. The tests were carried out using particles of less than 80 µm and a liquid-solid ratio of 80. It should be noted that no soluble silica was measured after the concentrated HCl attack (first stage of the method), since the attacked silica formed a gel that was dissolved only after the KOH washing.

It can be seen from the results that opal (O) again released much more silica (77%) than the other materials. The dissolved silica of the other reactive aggregates (SL and Q) reached lower values (2.4 and 5.4%, respectively). The non-reactive aggregate QA released 5.4% of its silica, which is the same value as for quartzite. Let us recall that this method, although it is now used for the quantification of active silica and alumina in fly ash (European standard EN 450-1), was initially intended to measure insoluble residue in cement, as specified in European standard NF EN 196-2 [2006]. So it might be accurate for fly ash, but some doubts remain here about its effectiveness in
distinguishing between reactive (e.g. quartzite) and non-reactive (e.g. quartz aggregate) aggregates, since it seems that the extremely severe acid environment favours the attack of well crystallized quartz.

Table III-3  Results of dissolved silica with HCl-KOH method

<table>
<thead>
<tr>
<th></th>
<th>O</th>
<th>SL</th>
<th>Q</th>
<th>QA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved SiO$_2$*</td>
<td>77.1</td>
<td>2.4</td>
<td>5.4</td>
<td>5.4</td>
</tr>
</tbody>
</table>

*in % of the total aggregate mass

3.3. HF attack
This method is found in the literature [Diamond 1986, Hulett and Weinberger 1980, Murat et al. 1988, Pichon et al. 1996] for the quantification of the amorphous silica in fly ash or pozzolanic materials. It is based on the fact that the amorphous silica dissolves rapidly in diluted HF solution, and the rate of dissolution can be distinguished from the dissolution of crystalline phases. Different reaction times are obtained, and the kinetics of amorphous phase dissolution can be deduced using a graphic method.

Considering that some aggregates such as siliceous limestone contain calcite, which can consume HF and interfere with the silica dissolution, a second acid, HCl, was added into HF solution in that case. In this paper, 1 mol/l HCl was chosen to add into 1.5% HF to test siliceous limestone. This second acid is known not to affect the dissolution of silica since Liang and Readey [1987] tested the effect of 1 mol/l HCl on fused silica and quartz and found that, with and without HCl, the final values of dissolved silica showed no marked differences.

3.3.1. Procedure
1.5 g of sample were put into a plastic container, mixed with 1.5% HF (or HF + 1 mol/l HCl) in the proportions of 200 ml liquid /g solid, and left for reaction at 4°C in the aim of obtaining a clear difference between the dissolution of amorphous phase and crystalline phase [Liang and Readey 1987]. At reaction times ranging between 1 and 24 h, the solution was filtered and washed with distilled water. The solution was then analysed for SiO$_2$ by atomic absorption.

3.3.2. Mechanisms of attack
Fluorine ion is a strong nucleophilic reagent; it has the same mechanism of attack of silicon-oxygen frameworks as OH$. However, HF is a stronger reagent than alkalis, for two reasons: 1) the electronegativity of F is 3.98, greater than oxygen (3.44), 2) the hydrogen ion (H+) as an electrophilic reagent helps fluorine ion to disrupt the Si-O bond [Budd 1962]. The reaction mechanism is as follows:
The mechanism can be simplified to:

\[ 6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O \]

This equation applies at low temperature (< 86°C). At high temperature, \( H_2SiF_6 \) can decompose to \( SiF_4 \), and \( SiF_4 \) is easy to volatilize (boiling point: ~86°C).

3.3.3. Results and discussion

A typical curve of dissolution kinetics of aggregates in HF is given in *Figure III-18*. The curve increases with the reaction time and two different phases are observed: a rapid dissolution (phase I) followed by a constant rate of dissolution characterized by a linear evolution (phase II). In phase I, the high reaction rate lasts about 2 hours (between 1 and 4 hours) and is mainly due to the quick dissolution of the reactive phase. In phase II, the reaction rate slows down, but the reaction still keeps an upward trend even after 24 hours. This phase is usually considered to be representative of the attack of crystallised minerals such as quartz. The reactive phase is estimated by extrapolating the linear trend to \( t=0 \), since it can be assumed that the crystallised phases are also dissolved from the beginning.
The kinetics of dissolution of the aggregates in HF (O, Q and QA) or in HF+HCl (SL) are given in Figure III-19. The two-phase evolution obtained for the aggregates is consistent with the works of [Murat and Arnaud 1988 and Pichon et al. 1996], who worked on pozzolans. The results deduced from these curves (reactive silica content, end of phase I and dissolution rate of crystalline phase) are shown in Table III-4.

\[
\begin{align*}
\text{SiO}_2 &= 0.37t + 50.5 \\
\text{SiO}_2 &= 0.41t + 7.6 \\
\text{SiO}_2 &= 0.28t + 2.9 \\
\text{SiO}_2 &= 0.14t + 6.9
\end{align*}
\]

Figure III-19 - Evolution of dissolved silica in HF as a function of time at 4°C, L/S=200ml/g
(a) Opal (b) Siliceous limestone (c) Quartzite (d) Quartz aggregate

<table>
<thead>
<tr>
<th></th>
<th>O</th>
<th>SL</th>
<th>Q</th>
<th>QA</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Amorphous SiO(_2)</strong> (%)</td>
<td>50.4</td>
<td>6.9*</td>
<td>7.6</td>
<td>2.7</td>
</tr>
<tr>
<td><strong>End of phase I (~ h)</strong></td>
<td>1</td>
<td>3</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td><strong>Dissolution rate of crystalline phase (%/h)</strong></td>
<td>0.38</td>
<td>0.14</td>
<td>0.41</td>
<td>0.28</td>
</tr>
</tbody>
</table>

* HF+HCl
As for the other methods, O gave the highest value, much higher than the other aggregates. SL and Q were in the same range, and also showed a similar reactivity in expansion tests (*Figure III-13*). QA gave the lowest value, in accordance with the fact that this aggregate is considered as poorly reactive.

A supplementary test with HF only was made for the siliceous limestone. A value of 5.3% was found, compared to 6.9 when HF-HCl was used. This 20% difference cannot be caused by the attack by the added HCl, because Liang and Readey [1987] found that the addition of 1 mol/l HCl in HF solution did not change the dissolution of silica in fused silica and quartz. The difference may be attributed to the fact that, under the effect of HCl acid, more silica was released from the enclosure of calcite (no pre-treatment was made for acid attacks) and participated in the reaction with HF. HF also dissolved calcite, but the production of CaF$_2$ which has low solubility, was likely to precipitate around the silica and prevent it from being attacked. Thus, it was considered that the result of HF+HCl was more reliable.

The dissolution rates of crystalline phase for the materials containing mostly silica (O, Q, and QA) were of the same order of magnitude (between 0.28 and 0.41 %/h) and were controlled by the dissolution of quartz. The differences probably depended on the properties of the attacked crystallized phases, such as the surface area and the porosity, which controlled the diffusion process of the solution in the aggregate. In the case of siliceous limestone, the slower rate of dissolution (0.15 %/h) was probably due to the presence of calcite, which made the silica more difficult to reach than in the other aggregates.

### 3.4. Comparison of the methods and discussion

The three methods presented in the previous section were effective in attacking silica in aggregates (*Figure III-20*) but, as discussed, some doubts remained about the nature of the dissolved silica. It is important to know if the silica quantified by these methods is only the part of the silica that is reactive, i.e. the one responsible of the degradation of concrete due to ASR, or if a part of the crystallised silica, which should remain stable in the long term in a cement-based material, is also dissolved.

The reliability of the methods is now discussed by comparing, in *Figure III-21*, the results of the three methods (*Figure III-20*) with the asymptotic expansions measured using the mortar-bar test (*Figure III-13*).
Figure III-20  Dissolved silica of each material for the three tests used.

Figure III-21  Final expansion of mortar bars as a function of dissolved silica for aggregates O, Q, QA and SL, for the three methods used.
NaOH-HCl

Basic attack is thought to be representative of the real structure environment. However, this method did not seem reliable, for many reasons:

- As seen in Figure III-22, the dissolution of silica at high pH is difficult to control and high variations of SiO₂ can be obtained for small differences of pH
- For a given aggregate, no different rates of dissolution can be distinguished (as for HF attack), which would allow the separation of the different forms of silica. Thus the dissolved silica is calculated from an asymptotic value obtained by curve fitting. Knowing that, at high temperature, the kinetics of quartz dissolution increases rapidly [Liang and Readey 1987], some concerns arose about whether this method attacked part of the well-crystallized silica. It led to an overestimation of the reactive silica available for ASR in concrete. The decrease of the temperature (from 100 to 60°C) did not improve the results, and the duration of tests became problematic (tens of days). Since high temperatures are usually used in accelerated ASR tests, some concerns could arise about the effectiveness of evaluating reactive aggregates in mortars and concrete at these temperatures.
- No correlation can be highlighted with expansion measurements (Figure III-21).

An improvement of the method would be to more accurately reproduce the pore solution of concrete that attacks the aggregates, as in the method proposed by Bulteel et al. [2002]. However, this kind of method leads to the production of hydrates (which include silica), and thus makes the measurement of silica complicated and time-consuming.

![Figure III-22 The solubility of quartz and amorphous silica at 25°C (from Tucker [2001])](image-url)
**HCl-KOH**

This method is derived from the analysis of cements and standardized for fly ash (EN 450-1). It has been successively used for the measurement of the reactive part of fly ash. However, the results obtained on aggregates seem to deviate from the practical expansion results (Figure III-21). The main disadvantage seen in the present study is that the severe acid environment combined with hot conditions led to the dissolution of well-crystallised quartz (e.g. QA). With only one test at a given time, it seems impossible to distinguish between the different forms of silica. So in order to guarantee correct separation of reactive and stable silica, it seems to be preferable to use a method which gives the kinetics of dissolution.

**HF**

When compared to the former methods, the advantage of HF attack is that it allows the calculation of the reactive silica by dissociating the dissolution curves into two phases. These two phases are distinguished by their dissolution abilities. Thus, for the HF method, there is less problem of counting parts of quartz as reactive as mentioned in the other methods. A good correlation is found with the expansion results, as confirmed by the value of the coefficient of determination ($R^2=0.96$).

Although this method is based on an acid attack, it seems to be the best compromise to quantify the active fraction of silica in alkali-silica reactive aggregates. The method is rapid (in 24 hours) and simple and allows the different forms of silica to be separated.

**4. Conclusion**

The quantification of the reactive silica is necessary to assess the residual expansion of structures damaged by ASR. The originality of this work is to investigate three methods used to measure the reactive silica in various aggregates in the sole aim of quantifying the part of silica potentially available for ASR in concrete. Knowing the sensitivity of quartz dissolution to the liquid/solid ratio and temperature conditions, the most representative tests would use real structure conditions for these two parameters. The use of the real conditions of liquid / solid ratio and temperature of ASR-damaged structures would lead to long measurements; this would hardly be effective for the assessment. That is why fast methods are necessary.

Three methods were tested: one basic attack - NaOH (100°C and 60°C)-HCl - and two acid attacks - HCl-KOH and HF. The reactive silica was quantified in five materials, including three reactive aggregates and two non-reactive materials. The results show that NaOH attack at 100°C is more effective than attack at 60°C but the high reaction temperature seems to cause the attack of a part of the well-crystallized minerals and thus leads to confusion between the silica which can be soluble in chemical tests and the silica which would really react with alkali in concrete (with lower liquid/solid ratio and lower temperature). HCl-KOH attack is found unsuitable since the results of reactive aggregate – Quartzite, and the non-reactive aggregate – Quartz aggregate, are the same. Comparing the chemical quantification with the expansion results, the HF method presents the best accordance with the mortar tests. It cannot be concluded that these values of the HF method are the exact amounts of “reactive silica” because the acid attack cannot represent the
real environment of alkali-silica reaction. However, this method appears to provide a reliable approach for roughly evaluating the amount of reactive silica in the material.

Finally, among the different tests, HF/HF+HCl attack is the best compromise since it satisfies the objectives fixed initially: a rapid (24 h) and simple test which allows the separation of reactive and non-reactive silica. Moreover, the dissolution results obtained by this method show a high correlation with expansion tests.
1. Introduction

The development of a microscopic ASR model is a major concern of researchers trying to understand the mechanisms involved in the reaction and to predict future expansion of concrete. Previous modelling investigated the different aspects of the reaction: the mechanical consequences of an expansive aggregate in cement paste [Bazant and Steffens 2000, Comby-Peyrot et al. 2009, Goltermann 1994], the chemical mechanisms driving attacks of the aggregate by hydroxyl ions [Furusawa et al. 1994], and their coupling [Bazant and Steffens 2000, Multon et al. 2009, Poyet et al. 2007, Nielsen et al. 1993, Sellier et al. 1996, Suwito et al. 2002]. The work presented here is based on the microscopic model developed by Multon et al. [2009]. This microscopic model is based on some of the previous models [Furusawa et al. 1994, Nielsen et al. 1993, Poyet et al. 2007, Suwito et al. 2002] and attempts to predict the damage and the expansion of a Representative Elementary Volume (REV) of concrete containing a mix of reactive aggregates of different sizes. The attack of the reactive silica by alkali was determined through the mass balance equation, which controls the diffusion mechanism in the aggregate and the fixation of the alkali in the ASR gels. The mechanical part of the model is based on the damage theory in order to assess the decrease of stiffness of the mortar due to cracking caused by ASR and to calculate the expansion of a Representative Elementary Volume (REV) of concrete [Multon et al., 2009]. However, the experimental results which were presented in the Chapter 2 revealed a serious imperfection of this model: it does not take the effect of the specimen size into account. The main aim of this chapter is to take this parameter into consideration. Another modification appears in the experimental conditions. In the experimentation analysed by Multon et al. [2009], the specimens were kept in air at 95% RH without an external supply of alkali. In this study, the model considers the presence of alkali at the external boundaries of the specimens. In this chapter, the previous model is first presented with the new developments of the effect of the specimen size. Then, the experimental results obtained from the former chapters are used to calibrate and discuss the validity of the model. At the end, the results of this microscopic model
are used to assess the chemical advancement used in the model of structure qualification [Sellier et al. 2009].

2. Principles

2.1. Mechanics of ASR

The model was first based on the mechanisms proposed by Dent Glasser and Kataoka [1981] and on considerations made by Jones [1988]:

- The hydroxyl ions diffused around the reactive aggregate, attack and destroy the Si-O bonds, and then form ASR gel in presence of water and calcium ions.
- Gel permeates through the connected pores which exist between aggregate and cement paste and fills a part of the connected porosity [Jones 1988]. When the volume of gel is greater than the porous volume, it exerts a pressure on the cement paste, which causes cracking and expansion of the concrete.

2.2. Assumptions

Based on the mechanisms above, several assumptions were made to simplify the physical and chemical process of this reaction. Simplifications have to be assumed in order to model ASR expansion in accordance with most phenomena.

2.2.1. Geometry

The reactive aggregate is taken to be spherical. The Relative Elementary Volume (REV), which represents the surroundings of the aggregate in the concrete paste, is assumed to be spherical too (Figure IV-1), and it can be deduced as in Equation IV-1, depending on the size and content of the aggregate.

![Figure IV-1](image)

*Figure IV-1  Definition of the Relative Elementary Volume for several reactive aggregate sizes [Poyet et al. 2007]*
\[ R_{REV}^a = \frac{R_a}{\sqrt[3]{\Phi_a C_{agg}}} \]  

(IV-1)

\( a \): a superscript relative to the size fraction of the reactive aggregate with mean radius \( R_a \)

\( R_{REV}^a \): the REV radius corresponding to aggregate size fraction \( a \)

\( \Phi_a \): the volume fraction of reactive aggregates with mean radius \( R_a \)

\( C_{agg} \): the volume fraction of all the aggregate per m\(^3\) of concrete.

The number of reactive aggregates per m\(^3\) of concrete \( N_a \) is equal to:

\[ N_a = \frac{\Phi_a C_{agg}}{\frac{4}{3} \pi R_a^3} \]  

(IV-2)

All the aggregates of a given size are assumed to expand in the same way (same kinetics and same amplitude).

### 2.2.2. Transport of alkali

As explained in the introduction to this chapter, the model was modified to take the specific experimental conditions into account. In the expansions analysed in this part, the specimens were immersed in NaOH solution (1 mol/l).

#### 2.2.2.1. Diffusion of alkali in cement paste

The diffusion of the ionic species into the cement paste is considered as roughly homogeneous. In Poyet’s work [Poyet 2003], the coefficient of diffusion of alkali in cement paste was estimated approximately \( 10^{-11} \) m\(^2\)/s while the coefficient of diffusion in aggregate was \( 10^{-15} \) m\(^2\)/s [Suwito et al. 2002]. Therefore, Multon et al. [2009] considered that the diffusion in the paste was much more rapid than the diffusion in the aggregate and thus the diffusion in the cement paste was considered not to affect the kinetics of ASR-expansion. This assumption was made for the analysis of small specimens (20 mm) not exposed to an external supply of alkali. However, the observations made on the experimental measurements presented in Chapter 2 show that this cannot be assumed for large specimens (like 40x40x160 mm and 70x70x280 mm). Therefore, the model was modified in order to consider the effect of the alkali diffusion in the cement paste and to predict the different dissolution rates observed according to specimen size.

Because there is an external supply of alkali, the alkali diffuses first towards the aggregates close to the external boundary of the specimens, which react before the aggregates in the core of the specimens (Figure IV-2). This means that all the aggregates of a given size cannot have the same expansion at the same time (difference of kinetics), which is in opposition to the assumption made above. Only complete discretization of the whole specimen would allow this difference of expansion to be considered. This type of approach has been proposed by [Comby-Peyrot et al. 2009]. In our work, the phenomenon of diffusion in the specimen was simplified. The quantity coming into the specimen was approximated by a mean flow of alkali proportional to the
difference of concentration between the external alkali concentration and that a quarter of the way into the specimen (Figure IV-2). This $\frac{1}{4} l$ is an empiric value. The greater this value is chosen, the higher the difference of alkalis concentrations is, and then the faster the rate of alkalis diffusion will be. In the contrary, the smaller this value is, the slower the rate of alkalis diffusion will be. It is difficult to have a value representative of reality. In our calculations, $\frac{1}{4} l$ was found to be more representative.

![Figure IV-2  Diffusion of Na\(_2\)O\(_{eq}\) in paste](image)

2.2.2.2. Diffusion of alkali in aggregate

The aggregate was taken as spherical in this model. The concentrations of the ionic species diffusing into the aggregate depend only on the time and on the radius $r$ from the centre of the reactive aggregate (Figure IV-3).
2.2.3. Threshold of alkali concentration

In the model of Multon et al. [2009], a threshold of alkali concentration of 0.625 mol/l of Na⁺, was considered, under which ASR did not occur. It was based on the strong non-linearity between the pH and the solubility of the silica, since “the solubility of silica is quite constant in a solution having a pH of less than 9 or 10 but increases rapidly for higher pH” [Urhan 1987]. In concrete, this threshold of alkali concentration has been pointed out by numerous experiments and evaluated at between 3 and 5 kg/m³ [Hobbs 1993, Rogers and Hooton 1991, Shehata and Thomas 2000, Thomas et al. 1996]. Thus, in mortar tests (in air, R.H.>95%), the concentration of alkali played an important role in attacking silica.

In this work, all the mortars were kept immersed in alkali solution and, thus, the alkali was supplied in abundant quantities. The experiments performed on specimens immersed in three alkali concentrations (0.77, 1 and 1.25 mol/l) showed few differences. Considering a threshold of 0.625 mol/l, the expansion of the mortars kept in 0.77 mol/l solution should be significantly slower than the expansion of the mortars kept in 1.25 mol/l solution. With this threshold, the alkali concentration in the aggregate has to be higher than 0.625 mol/l before the reactive silica is attacked. The speed is then proportional to the difference between the alkali concentration in the paste and the threshold. Then, the concentration gradient between the paste and the aggregate remains too small to induce the same reaction speed as for the other concentration. But it has been observed that the swelling kinetics is quite similar (Chapter 2). Therefore, the gradient must be the same and consequently the alkali consumption by the silica must begin as soon as alkalis are present in the aggregate, without a threshold. The results of this assumption will be studied in the following investigations. The threshold observed in concrete specimens exposed to air or water without alkali could be explained by the retention of alkali in CSH rather than by a
threshold effect on the silica dissolution. This fixation consumes alkali, which can no longer react with silica, and causes an apparent threshold effect.

2.2.4. Effective ASR gel

The composition of ASR gel varies and depends on many parameters of the reaction. The range of Na$_2$O / SiO$_2$ ratio was found to be 0.1~0.4 [Kawamura and Fuwa 2003, Taylor 1990, Thaulow et al. 1996]. In the model used here, the Na$_2$O / SiO$_2$ ratio is assumed to be equal to a mean value 0.2 obtained in laboratory experiments in [Kawamura and Fuwa 2003] and used in [Multon et al. 2009]. It means that 1 mole of Na$_2$O$_{eq}$ reacts with 5 moles of SiO$_2$ to give 1 mole of ASR gel. Then the total volume of gel can be calculated by Equation IV-3:

$$V_{gel} = \sum n_i \times V_{gel}^{mol}$$

(IV-3)

$n_i$ (mol): the number of moles of ASR gel produced by the aggregate size $i$

$V_{gel}^{mol}$ (m$^3$/mol): the molar volume of the gel

After gel has formed, it can permeate through the connected porous volume and partly fill it. It can also leach off the specimens into the solution through the cracks. The previous model [Multon et al. 2009] only considered the first phenomenon. However, the gel lost in these two ways does not produce significant pressure. The proportion of gels staying in the connected porosity was calculated as the total volume of porosity filled by the gel with an equivalent thickness $t_c$, which was assumed to be constant with the size of the aggregate [Poyet et al. 2007, Sellier 1995]. Thus, the volume of this part of the gel filling the porosity can be expressed as in Equation IV-4.

$$V_{por} = \frac{4}{3} \pi (R_a^3 + t_c^3) - R_a^3 \cdot p$$

(IV-4)

$R_a$: the radius of the particles

$t_c$: the thickness of gels (around aggregates) filling the porosity

$p$: the connected porosity

A part of the rest of the gel $<V_g - V_{por}>$ is assumed to leach off the specimens into the solution, which does not produce significant pressure either. This part depends on the scale effect “specimen size/aggregate size”: the smaller the “specimen size/aggregate size” ratio, the more the gel leaches off. This phenomenon is also affected by the nature of the aggregate. As explained in the analysis of the experiments, the greater the reactive silica content is, the stronger is the non-linearity due to leached gel. Fracture mechanics concepts show that the aggregates closer to the external boundary lead first to cracks connected with the external solution. In order to quantify this effect, it can be assumed that these aggregates lose more gel than the aggregates located in the core of the specimens. As for the diffusion in cement paste, this will lead to a gradient of deformation between the external boundary and the core and thus to internal stresses, which it is impossible to consider with this model. Due to the complexity of quantifying this
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phenomenon by theoretical concepts, only a numerical model including a mesh of aggregate
[Comby-Poyrot et al. 2009] and an empirical relationship can be proposed here to assess the
consequences on ASR expansions. A mean leaching is assumed that applies equally to all the
aggregates of a given size. The decrease of the gel volume effective in the expansion measured
on the specimen is given by Equation IV-5.

\[ V = \left( V_g - V_{por} \right) + \exp \left( -c \frac{\phi}{l} s^\chi \right) \]  

(IV-5)

**V**: the volume of the gel available to produce pressure  
**V<sub>g</sub>**: the total volume of gels  
**V<sub>por</sub>**: the volume of gel filling the connected porosity  
**c**: the scale effect coefficient, fitted to take account of the stress concentration induced by the gel, 
considering the effect of the ratio of ‘aggregate size / specimen size’ and the nature of the 
aggregate  
**\phi**: the aggregate size  
**l**: the specimen size  
**s**: the amount of reactive silica (mol/m<sup>3</sup> of aggregate)  
**\chi**: silica content exponent, fitted to take into account the stress concentration induced by the gel 
considering the reactive silica content due to the nature of the aggregate

2.2.5. Mechanical consideration

No modifications were made to the mechanical part of the model. The model assumes a stress-
free state of the specimens. The mechanical behaviour of the aggregate and of the cement paste 
in the REV (Relative Elementary Volume) are considered as isotropic [Poyet et al. 2007]. The 
expansion due to ASR occurs over a long period. During this period, the materials are subjected 
to progressive stresses which cause creep strains in the concrete. To calculate the effect of creep 
strain on the ASR expansion, a long-term Young’s modulus is used. For the same stress, using 
the long-term modulus rather than the instantaneous modulus leads to larger strains. The strains 
are then equal to the sum of the instantaneous strains due to the ASR gel pressure and the creep 
strains of the cement paste under the ASR gel pressure. If the stresses become higher than the 
tensile strengths of the materials, cracking and damage occur in the concrete. In the following 
calculations, the crack density is consistent with the damage to the concrete calculated by the 
model (the damage is defined as the decrease of the long-term Young’s modulus due to 
cracking). After cracking, the gel is assumed to permeate into the cracks.

3. Physicochemical modelling

This part presents the equations of the diffusion of the alkali ions into the cement paste and into 
the aggregate and ends with the assessment of the volume of ASR gel created. As presented in 
[Multon et al. 2009], the alkali diffusion into the aggregate is controlled by the mass balance 
equation. A depletion term is used to represent the consumption of alkali during the formation of
the ASR gel. Finally, the volume of gel produced by the reaction is proportional to the amount of alkali consumed in the mass balance equation. Two points are different in the modelling presented here: the specimens are immersed in NaOH solution (1 mol/l) and the alkali diffusion in the cement paste is taken into account.

3.1. Mass balance equations

3.1.1. Alkali diffusion in cement paste

The variation of alkali content in the cement paste is due to the diffusion of alkali from the external solution to the aggregate through the cement paste. Without an external supply of alkali, the variation between the cement paste and the aggregate is equal to the sum of the flux of alkali at the boundary \( r=R_a \) between all the aggregate and the paste. Due to the immersion in NaOH solution, alkali comes into the cement paste from the solution. It is assessed by a sink term \( S_{cp} \).

Therefore, the mass balance equation for the alkali diffusion in the cement paste is:

\[
(1 - C_{agg}) \frac{\partial}{\partial t} \left( p_{cp} C_{Na}^{cp} \right) = \sum_a N_a D_a A\pi R_a^2 \frac{\partial C_{Na}^a}{\partial r} (R_a) + S_{cp}
\]  

(IV-6)

with:

- \( C_{agg} \): the aggregate concentration per m\(^3\) of concrete,
- \( p_{cp} \): the porosity of the cement paste,
- \( S_r \): the saturation degree,
- \( C_{Na}^{cp} \): the mean alkali concentration in the cement paste,
- \( N_a \): the number of reactive aggregate of size \( a \) per m\(^3\) (Equation IV-2),
- \( C_{Na}^a \): the concentration of alkali in the aggregate per m\(^3\) of mortar,
- \( D_a \): the coefficient of diffusion of alkalis into the aggregate.

As explained above, the quantity coming into the specimen is determined by a mean flux of alkali calculated between the external boundary and the inner quarter of the specimen. This flux supplies alkali through the external surface of the specimens \( S_{sp}^{df} \). The total amount of alkali coming into the specimen is the product of the mean flux by this external surface area. For 1 m\(^3\) of mortar, the sink term is this total amount of alkali divided by the volume of the specimen \( V_{sp} \). Thus, the sink term in Equation IV-7 is:

\[
S_{cp} = D_{cp} \left( \frac{C_{Na}^0 - C_{Na}^{cp}}{1/4} \right) S_{sp}^{df} V_{sp} = D_{cp} \left( \frac{C_{Na}^0 - C_{Na}^{cp}}{1/4} \right) \frac{4hl}{l^2h} = D_{cp} \frac{C_{Na}^0 - C_{Na}^{cp}}{1/4}^2
\]  

(IV-7)

with:

- \( C_{Na}^0 \): the alkali concentration in the solution (equal to 1 mol/l),
- \( D_{cp} \): the coefficient of diffusion of alkalis into the cement paste,
Chapter IV

$S_{\text{sp}}$: the external surface area of the specimens (for the sake of simplicity, area is estimated at 4$hl$, with $l$ the specimen size in the transverse direction and $h$ the height of the specimen)
and $V_{\text{sp}}$: the volume of the specimen (equal to $l^2 h$).

3.1.2. Alkali diffusion in aggregate

As explained in [Multon et al., 2009], the flux of alkali ($\text{Na}^+$ and $\text{K}^+$) between the cement paste and the aggregate is assessed by the mass balance equation with the assumed spherical symmetry:

$$
\frac{\partial}{\partial t} \left( p_a S r C_{Na}^a \right) + \frac{\partial}{\partial r} \left( D_a r^2 \frac{\partial C_{Na}^a}{\partial r} \right) + S(C_{Na}^a) = 0
$$

(IV-8)

with:

- $t$: the time
- $p_a$: the porosity of the aggregate,
- $S_r$: the saturation degree,
- $r$: the distance from the centre of the aggregate,
and $S(C_{Na}^a)$: the depletion term that represents alkali consumption.

The boundary conditions are:

- at the centre of the aggregate ($r=0$), the flux is equal to zero;
- at the external boundary ($r=R_a$), the alkali concentration is equal to $C_{Na}^{cp}$, the alkali concentration in the cement paste.

3.1.3. Consumption of alkalis

The consumption kinetics of alkalis is assumed to be proportional to the concentration of alkali present in the aggregate. Thus, the depletion term of the mass balance equation is:

$$
S(C_{Na}^a) = f \cdot C_{Na}^a
$$

(IV-9)

$S(C_{Na}^a)$: the amount of alkali fixed per m$^3$ of aggregate
$f$: the alkali fixation coefficient with a unit of (mol/m$^3$ of aggregate) per (mol/m$^3$ of solution) per second
$C_{Na}^a$: the concentration of alkali in the aggregate

The alkali fixation ends when all the reactive silica contained in the aggregate has been consumed by alkali. As the $\text{Na}_2\text{O}/\text{SiO}_2$ ratio of the gel is assumed to be equal to 0.2, the alkali fixation stops when the alkali concentration is equal to 0.2 times the reactive silica content of the aggregate.
3.2. Formation of ASR gels

Finally, the number of moles of ASR gel produced in the aggregate \( a \) is equal to the number of moles of Na\(_2\)O consumed by the reaction, thus half the number of moles of Na\(^+\):

\[
n^a_s = \frac{4}{3} \pi R^3 \times \int_0^t \frac{S(C_{Na}^a)}{2} dt
\]

(IV-10)

4. Mechanical modelling

From the main results of the chemical modelling, \( V_g \) (the volume of available ASR gel), the strain induced on the REV and the expansion of the damaged concrete can be determined. In the REV (Relative Elementary Volume), the mechanical equations are used for two media: \( a \), the aggregate under study, and \( SC \), the concrete surrounding the studied aggregate (medium including cement paste and other aggregate – Figures IV-4 and IV-5). The ASR gel is taken to be incompressible. The cracking due to ASR is considered as isotropic and the mechanical problem is assumed to be non-linear due to the introduction of the damage variable. The main equation used in the model is obtained as follows.

The cement paste and aggregate are first considered as elastic. Therefore, the ASR expansion can be taken into account as an imposed strain in the aggregate elastic constitutive law:

\[
\sigma_a = \lambda_a tr e_a I + 2\mu_a e_a - (3\lambda_a + 2\mu_a) e_{imp1}(t)
\]

(IV-11)

where

\( e_{imp1} \) is the imposed strain applied to the aggregate due to the increasing volume which can be caused by ASR gels and aggregate cracking.

The constitutive law of the medium \( SC \) only considers the elastic effect of the material:

\[
\sigma_{sc} = \lambda_{sc} tr e_{sc} I + 2\mu_{sc} e_{sc}
\]

(IV-12)

with

\(\sigma\) the stress matrix for each material,
\(\varepsilon\) the strain matrix for each material,
\(I\) the unit matrix,
\(\lambda\) and \(\mu\) are, for each material:

\[\lambda = \frac{E\nu}{(1+\nu)(1-2\nu)}\]

(IV-13)
and

\[ \mu = \frac{E}{2(1+v)} \]  

(IV-14)

\( E \): the Young's modulus  
\( v \): the Poisson's coefficient of the medium.  
\( \varepsilon_{\text{imp}1} \): the imposed strain applied to the aggregate.

When the chemically imposed strains become too large, the tensile stresses in the cement paste can be higher than the tensile strength and cracks appear in the material. Cracking causes a decrease in the Young’s modulus. It is taken into account by a damage evaluation model. The damage evaluation method is based on the strain equivalence principle [Lemaître and Chaboche 1988]: the cracked medium (initial Young’s modulus \( E_0 \)) is replaced by an equivalent medium without cracks but with a lower modulus \( E_d \) leading to the same displacement as the cracked one with the initial Young's modulus [Multon et al. 2009]:

\[ d = 1 - \frac{E_d}{E_0} \]  

(IV-15)

Cracks close to the aggregate are assumed to be filled by the ASR gels and, in the mechanical problem, three parts are distinguished (Figure IV-5): the central aggregate (between radii 0 and \( R_a \)), the cracked zone filled by the gel (between radii \( R_a \) and \( R_{cz} \)) and the part of the REV not yet cracked. As the gel reaches the cracks connected to the reactive aggregate, the radius \( R_{cz} \) corresponds to the radius \( R_d \) used to determine the damage (Figure IV-5). The gel pressure is constant in both the aggregate and the cracked zone. It is then applied to the internal boundary of the surrounding uncracked concrete. The modulus of the whole medium surrounding the aggregate is equal to \( E_d \) according to the damaged Young’s modulus evaluated above. The following behaviour equation, concerning the part of the REV surrounding the aggregate and filled by the ASR gel, has to be added. The constitutive law of this part is:

\[
\sigma_{zz} = \lambda_{fs} \text{tr} \varepsilon_{zz} I + 2\mu_{zz} \varepsilon_{zz} - (3\lambda_{zz} + 2\mu_{zz})\varepsilon_{\text{imp}2}(t)
\]  

(IV-16)

where

\( \varepsilon_{\text{imp}2} \) is the imposed strain applied to the cracked zone of the surrounding concrete due to the presence of ASR gel in the cracks.
The chemically imposed strains are assessed from the relative increase of volume due to the production of gel by ASR. The part of the gel which fills the porous volume surrounding the aggregate and the part of the gel leached off the specimen do not participate in the pressure and thus in the expansion. The last equation is given by chemical modelling:

\[
\frac{4}{3} \pi R_g^3 \varepsilon_{\text{imph}} + \frac{4}{3} \pi \left( R_{cz}^3 - R_a^3 \right) \varepsilon_{\text{imp}2} = \left< V_g - V_{\text{por}} \right>^+ \times \exp \left( -c \frac{\phi}{l} \right)
\]

where \( \left< X \right>^+ \) is equal to \( X \) if \( X > 0 \) or equal to 0 if \( X \leq 0 \).
The mechanical modelling uses only five parameters: the Young’s modulus and the Poisson’s coefficient of the aggregate and mortar \((E_a, \nu_a\) and \(E_m, \nu_m\)) and the tensile strength of the mortar \(f_t\). No fitting is necessary for the mechanical part.

5. Application and comparison with experiments

Calculations were performed to analyse the experiments presented in Chapter 2 (expansion tests) with the chemo-mechanical model presented above. Some of the necessary parameters were firstly determined with tests carried out on 70x70x280 mm specimens. The parameters obtained were applied to predict the expansion curves of the two other specimen sizes (40x40x160 mm, 20x20x160 mm) in the same environmental conditions and immersed in different alkali concentrations (0.77, 1 and 1.25 mol/l). In order to assess the capability of the model to represent and predict real ASR expansions, the analysis is divided into three parts. First, different experimental points necessary for modelling are briefly recalled. Then, the assessment of all the parameters is explained. Finally, a discussion analyses the model.

5.1. Experimental conditions

The experimental results used in the calculation have already been presented and analysed in the previous chapters. Therefore, in this part, only the features used by the model are introduced briefly.

Expansion was measured on mortar prisms with a sand (1512 kg/m\(^3\)) to cement (CEM I 52.5R, 504 kg/m\(^3\)) ratio of 3, and a water-cement ratio of 0.5. The sand contained 30% of reactive aggregate and 70% of non-reactive marble.

**Effects of aggregate size and specimen size on expansion**

Siliceous limestone was used as reactive aggregate. Four aggregate size classes: C1 (0~315 µm), C2 (315-630 µm), C3 (630-1250 µm) and C4 (1250-2500 µm) and three specimen sizes 70x70x280 mm, 40x40x160 mm, 20x20x160 mm were used to research the effect of aggregate size and specimen size on expansion. Alkali content (Na\(^+\)) of mortar was added into the mixtures of cement paste in order to obtain an alkali concentration in the pore solution of 1 mol/l. The specimens were conserved in 1 mol/l NaOH solution at 60°C.

**Effects of alkali concentrations on expansion**

The specimen size of 20 x 20 x 160 mm and aggregate size range of 315-1250 µm were chosen to investigate the effect of alkali concentrations and aggregate nature on the expansion. Three NaOH contents were added into the mixture of cement paste for the siliceous limestone to obtain different alkali concentrations in the pore solution (0.77, 1 and 1.25 mol/l). Correspondingly the specimens were stored respectively in 0.77, 1 and 1.25 mol/l NaOH solutions.
Effects of aggregate nature on expansions

For the study of the aggregate nature, two supplementary mixtures were cast with Opal, Quartzite and Quartz Aggregate (aggregate size range of 315-1250 µm) and conserved in 1 mol/l solution.

5.2. Assessment of the parameters

Table IV-1 sums up the various parameters of the two models, stating the symbols, the method used for identification, the values and the units. The following parts explain how the values were obtained.

<table>
<thead>
<tr>
<th>Parameter identification</th>
<th>Parameter</th>
<th>Symbol</th>
<th>Identification</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Physicochemical modeling</strong></td>
<td>Aggregate</td>
<td>Reactive silica content</td>
<td>$s$</td>
<td>measurement</td>
<td>$3.0 \times 10^4$</td>
</tr>
<tr>
<td></td>
<td>Coefficient of diffusion</td>
<td>$D_a$</td>
<td>curve fitting</td>
<td>$5.0 \times 10^{-15}$</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td></td>
<td>Porosity</td>
<td>$p$</td>
<td>usual value**</td>
<td>0.01</td>
<td>%</td>
</tr>
<tr>
<td></td>
<td>Paste</td>
<td>Coefficient of diffusion</td>
<td>$D_{cp}$</td>
<td>curve fitting</td>
<td>$5.0 \times 10^{-13}$</td>
</tr>
<tr>
<td></td>
<td>Porosity of mortar</td>
<td>$p_{mort}$</td>
<td>measurement</td>
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<td>%</td>
</tr>
<tr>
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<td>Thickness of the connected porous interface zone</td>
<td>$t_c$</td>
<td>curve fitting</td>
<td>$14.0 \times 10^{-6}$</td>
<td>m</td>
</tr>
<tr>
<td></td>
<td>Gel</td>
<td>Molar volume of ASR gel</td>
<td>$V_{gel}^{mol}$</td>
<td>curve fitting</td>
<td>$4.2 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>Alkali fixation coefficient</td>
<td>$f$</td>
<td>previously determined*</td>
<td>$-6.5 \times 10^7$</td>
<td>m$^3$/m$^3$/s</td>
</tr>
<tr>
<td></td>
<td>Scale effect coefficient</td>
<td>$c$</td>
<td>curve fitting</td>
<td>0.037</td>
<td>(mol/m$^3$)$^\chi$</td>
</tr>
<tr>
<td></td>
<td>Silica content exponent</td>
<td>$\chi$</td>
<td>curve fitting</td>
<td>0.75</td>
<td>-</td>
</tr>
<tr>
<td><strong>Mechanical modelling</strong></td>
<td>Aggregate</td>
<td>Young’s modulus</td>
<td>$E_a$</td>
<td>usual value**</td>
<td>70000</td>
</tr>
<tr>
<td></td>
<td>Poisson’s coefficient</td>
<td>$\nu_{ai}$</td>
<td>usual value**</td>
<td>0.2</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Mortar</td>
<td>Young’s modulus</td>
<td>$E_{REV}$</td>
<td>usual value**</td>
<td>9000</td>
</tr>
<tr>
<td></td>
<td>Poisson’s coefficient</td>
<td>$\nu_{REV}$</td>
<td>usual value**</td>
<td>0.2</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Tensile strength</td>
<td>$f_t$</td>
<td>usual value**</td>
<td>3</td>
<td>MPa</td>
</tr>
</tbody>
</table>

*results determined in [Multon et al. 2009]
5.2.1. Parameters of the physicochemical and mechanical modelling

**Parameters of the physicochemical modelling:**

The reactive silica contents per m$^3$ aggregate are shown in Table IV-2. The porosity of the aggregate was taken as equal to 0.01% [Poyet 2003]. The porosity of the mortar determined for the same kind of materials in a previous experimental study was around 18% [Multon et al. 2010]. The alkali fixation coefficient was calculated and determined in a previous work [Multon et al. 2009].

<table>
<thead>
<tr>
<th>Reactive silica</th>
<th>SL</th>
<th>O</th>
<th>Q</th>
<th>QA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage (%)*</td>
<td>6.9</td>
<td>50.4</td>
<td>7.6</td>
<td>2.7</td>
</tr>
<tr>
<td>Content in m$^3$ aggregate (mol/m$^3$)</td>
<td>3000</td>
<td>21900</td>
<td>3300</td>
<td>1170</td>
</tr>
</tbody>
</table>

* Results obtained from HF/HF+HCl method (Chapter 3)

The last five parameters of the physicochemical modelling (coefficient of diffusion in aggregate $D_a$ and in paste $D_{cp}$, thickness of the connected porous interface zone $t_c$, molar volume of ASR gel $V_{gel}^{mol}$, scale effect coefficient $c$) were obtained by curve fitting on the expansions measured on the specimen of size 70x70x280 mm with four different size classes (C1~C4) of aggregate SL, as shown in 5.2.2.

**Mechanical modelling:**

All the parameters of the mechanical modelling (Table IV-1) were obtained from the literature. The Young’s modulus of an equivalent siliceous limestone was determined in experiments reported by [Larive 1998]. The other values were obtained from [Multon et al. 2009]. The instantaneous Young’s modulus of the mortar was taken as equal to 27000 MPa. The creep effect was taken into account by the use of a long-term Young’s modulus equal to one third of the instantaneous Young’s modulus. The Poisson’s coefficients of aggregate and mortar were taken as 0.2. The tensile strength of the mortar was evaluated at 3 MPa.

5.2.2. Identification by curve fitting

As seen in Figures IV-6 and IV-7, the six parameters to be fitted - coefficient of diffusion in aggregate ($D_a$) and in paste ($D_{cp}$), thickness of the connected porous interface zone ($t_c$), molar volume of ASR gel ($V_{gel}^{mol}$) and the coefficients of non-linearity ($c$ and $\chi$) - have different effects on the expansion curves. Considering their influences on the form of the expansion curves, these effects can be classified in two categories:
1) **Parameters affecting the final expansion**

The molar volume of ASR gel ($V_{gel}^{mol}$), the thickness of the connected porous interface zone ($t_c$) and the coefficients of non-linearity ($c$ and $\chi$) are parameters affecting the final expansion. As shown in Figure IV-6, the influence of individual parameters on the expansion curve is presented under the condition of fixing the other parameters. The parameter $V_{gel}^{mol}$ has an increasing effect on final expansion (Figure IV-6a), which means that the higher the molar volume of ASR gel, the larger the final expansion. $t_c$ represents the thickness of the connected porous zone (Figure IV-1) and has a decreasing effect on final expansion (Figure IV-6b). If the thickness is large, a lot of ASR-gel is necessary to fill the connected porous zone and the final expansion is small. In contrast, if the thickness is too small, the ASR-gel is present in excessive amounts after filling the connected porous zone, and this leads to a large final expansion. This picture is clear for small particles (Figure IV-7). The parameters $c$ and $\chi$ have a negative effect on final expansion since they represent the loss of gel into the external solution, which does not produce expansion (Figures IV-6c and IV-6d).

![Figure IV-6](image1)

(a) Effect of the molar volume of ASR gel  
(b) Effect of the thickness of the connected porous interface zone

![Figure IV-6](image2)

(c) Effect of scale effect coefficient  
(d) Effect of silica content exponent

*Figure IV-6  Effect of four parameters on the final expansion*
The values of these parameters were obtained by curve fitting. It was performed on the expansion curves measured using the largest specimens (70x70x280 mm) since they were less affected by the scale effect. The parameters $V_{gel}^{mol}$ and $t_c$ were firstly determined through fitting the final expansions measured on mortars containing the smallest (0-315 µm) and the largest (1250-2500 µm) particles. Then the value of $c$ was fitted in order to obtain final expansions of the aggregate size classes: 315-630, 630-1250, 1250-2500 µm close to the experimental results. All the three parameters above were determined without considering the effect of the silica content exponent ($\chi = 0$) since the mortar involving the curve fitting contains the same aggregate: siliceous limestone. Once these three parameters were fixed, the value of $\chi$ was determined by fitting the final expansion of mortars containing opal as aggregate. The fitting results of final expansion are shown in Figure IV-8.

Figure IV-7  Effect of $t_c$ on the final expansion with the small particle size (0-315µm)

Figure IV-8: Experimental and calculated final expansions measured on 70 x 70 x 280 mm specimens
2) **Parameters affecting the expansion kinetics**

The coefficient of diffusion in aggregate \( (D_a) \) and in paste \( (D_{cp}) \), and also the thickness of the connected porous interface zone \( (t_c) \) are the parameters affecting the expansion kinetics. These three parameters show different influences on the shape of the curves (Figure IV-9).

\( D_a \) changes the latent time (the time necessary to measure expansion) and the initial expansion rate (Figure IV-9a). A high \( D_a \) leads to a high rate of alkali diffusion in the aggregate, and thus alkalis need a short time to initiate the reaction and cause expansion. It also explains why the initial expansion rate increases with \( D_a \). It should be noted that \( D_a \) can differ with the nature of the aggregate.

\( D_{cp} \) does not have an effect at the beginning of expansion, because the alkalis present in the pore solution are sufficient to diffuse into the aggregates and cause the initial expansion. However, when alkalis are consumed by the reaction with the reactive silica, aggregates need an external supply of alkalis to keep expanding, and thus the effect of \( D_{cp} \) becomes important. The expansion rate increases with \( D_{cp} \), but the increasing trend is more obvious from \( 5.0 \times 10^{-14} \) to \( 5.0 \times 10^{-13} \) \( m^2/s \) than from \( 5.0 \times 10^{-13} \) to \( 5.0 \times 10^{-12} \) \( m^2/s \) (Figure IV-9b). The increase of \( D_{cp} \) has only a slight effect on the expansion rate. Due to this fact, ASR expansion rate is driven by “diffusion into the aggregate”. \( t_c \), the thickness of the connected porous interface zone, has an impact on the final expansion and also on the expansion kinetics through its effect on the latent time (Figure IV-9c). The higher \( t_c \) is, the longer the latent time is. High values of \( t_c \) signify large volumes of porous zone, which can accommodate a lot of ASR gel without producing expansion, and thus a long time to fill the porous zone and then produce gels available for expansion.

( a) Effect of \( D_a \) on the form of expansion curves  
(b) Effect of \( D_{cp} \) on the form of expansion curves
(c) Effect of \(t_c\) on the form of expansion curves

**Figure IV-9** The effect of parameters \(D_a\), \(D_{cp}\), \(t_c\) on the shape of expansion curves under the conditions of fixing other parameters

The fitting of the three parameters is quite difficult and has to be performed simultaneously. Here, the fitting was carried out using the expansion obtained on the largest particles (1250-2500 \(\mu\)m). \(D_a\) was chosen to give a good initial rate of expansion for these specimens. Then \(D_{cp}\) was determined so that the calculated curve was quite close to the experimental points. The values of the parameters obtained by fitting are shown in *Table IV-1*.

**Figure IV-10** ASR expansions of specimens 70x70x280 mm for different sizes of aggregates
5.3. Discussion

5.3.1. Curve fitting

The aim of this part is to discuss the ability of the model to represent the expansion measured on large specimens by the curve fitting presented above.

Benefits

The description of the expansion kinetics by the model is globally quite good: presence of a latent time before the initiation of the expansion, followed by a high rate of expansion and ending by a low rate to reach the final expansion.

The model distinguishes the differences of expansion curves due to the differences of size of the aggregate particles and of the aggregate nature. The experimental programme points out two main conclusions for 70x70x280 mm specimens: the small particles (smaller than 315 µm) present very small expansions while particles larger than 315 µm present almost the same ultimate expansion whatever their size. The small expansion can likely be explained by the ability of the porous zone connected to the aggregate to accommodate the gel without causing pressure and thus expansion. In this model, this is obtained for a porous zone about 14 µm thick, which appears to be realistic. With this assumption alone, the larger the particles are, the larger the expansion is. This is in contradiction with the measured expansions, which are quite constant for the three largest particles. This point can be explained by the permeation of gel in cracks towards the external solution. This leaching could cause lower gel pressure in specimens containing the largest particles. This phenomenon is quite difficult to quantify by a theoretical approach. The model proposes an empirical relation to assess the volume of gel leached according to the specimen size and the aggregate nature, and its consequences on the expansion (Equation IV-5).

Limits

The curves obtained by the model do not fit perfectly with the experimental results. An absolute difference of 0.05% is observed between the calculated and the measured expansions for the particles of 315-630 µm and 1250-2500 µm. This difference is mainly due to the scale effect coefficient \(c\). Equation IV-5 implies a maximum for the expansion curve according to the size of the particle. Thus the model cannot predict the same final expansion value for three different aggregate sizes. The value of \(c\) determined for the calculations (equal to 0.037) appears to be the best to take this limit into account.

The most important limitation of this model is the difficulty of representing the kinetics of the expansion measured on the large specimens for all particle sizes and particularly for particles of 315-630 µm and 630-1250 µm. The calculations give a higher rate of expansion than is found experimentally. A better fit is possible for these particles with smaller coefficients of diffusion in the aggregate but, in this case, the expansion kinetics which was obtained from the large particles is too slow for small particles. Only different values of \(D_a\) could lead to good curve fitting of expansion. But since these aggregates have the same nature, these differences of \(D_a\) values seem incomprehensible.
Chapter IV

This difference between modelling and experimental results can also be attributed to the diffusion in the cement paste (coefficient of diffusion $D_{cp}$). As explained above, if $D_{cp}$ is too high, the diffusion in the cement paste becomes instantaneous, but if the value is too low, expansions are too slow and it is impossible to fit the measured expansion. Therefore, the diffusion in the cement paste appears to be poorly represented by the sink term added into the model; and the global calculated kinetics remains quite different from the measured expansions. This problem can be due to the way of taking the diffusion of alkalis into consideration. In the model, the alkali concentration in the mortar pores is assumed to be the same in the whole specimen. In reality, the alkali concentration is not uniform in the specimen since the migration of ionic species in the pores depends on the distance of the pores to the external boundary of the specimen. However, this limit is clear for large specimens, for which the diffusion in the specimen has a large effect, but it is much less critical for smaller specimens, as shown in the next part.

5.3.2. Prediction of expansions with different specimen sizes

Once the curve fitting had been performed on the expansions measured on the 70x70x280 mm specimens, all the other expansions were calculated without any additional fitting. The calculations were carried out and compared with the expansions obtained with the four aggregate classes and two specimen sizes (20x20x160 mm, 40x40x160 mm – Figures IV-11 and IV-12). The final ASR expansions of most of the specimens were quite well predicted. Table IV-3 shows the percentage of the difference between calculated and measured final expansions compared with the maximal value among the measured final expansions of the same specimen size. The global kinetics appeared well estimated. The worst calculation was obtained for the largest aggregate size in the smallest specimens (difference of 28%) likely due to the lowest ‘specimen size/aggregate size’ ratio (equal to 10 for the aggregate of 1250-2500 µm in 20x20x160 mm specimens).

Figure IV-11  Calculated and measured ASR expansion for specimen of size 20x20x160 mm
Chapter IV

Table IV-3* Evaluation of the differences between the calculated and measured final expansions

<table>
<thead>
<tr>
<th></th>
<th>2x2x16</th>
<th>4x4x16</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1 (0-315 μm)</td>
<td>+7%</td>
<td>-1%</td>
</tr>
<tr>
<td>C2 (315-630 μm)</td>
<td>-3%</td>
<td>+9%</td>
</tr>
<tr>
<td>C3 (630-1250 μm)</td>
<td>-6%</td>
<td>+16%</td>
</tr>
<tr>
<td>C4 (1250-2500 μm)</td>
<td>+28%</td>
<td>+10%</td>
</tr>
</tbody>
</table>

*Value obtained from \( \frac{\varepsilon_{\text{cal}} - \varepsilon_{\text{mes}}}{\text{max}(\varepsilon_{\text{mes}})} \), with max (\( \varepsilon_{\text{mes}} \)): the maximal value among the measured final expansions of the same specimen size.

5.3.3. Prediction of specimens immersed in different alkali concentrations

In this part, the ASR expansions of 20x20x160 mm specimens containing reactive aggregates of two sizes (15% of 315-630 μm and 15% of 630-1250 μm) immersed in three different alkali concentrations (0.77, 1.0 and 1.25 mol/l) were calculated without any additional fitting. The calculated curves and experimental curves are shown in Figure IV-13.
The difference between the final expansion predicted by the model (0.70%) and the mean measured expansion (0.65%) is lower than 10%. The calculation does not show any difference in final expansions between the three alkali concentrations. The model assumes that all the reactive silica is consumed in the three conditions and, thus, the volume of ASR gel created is the same, leading to the same ASR-expansion. The aim of this part was to verify the ability of the model to evaluate the effect of the alkali concentration surrounding the specimens. It was obtained by the assumption exposed above (see 2.2.3): in the case of specimens immersed in alkali solutions, no alkali threshold has to be considered since there is enough OH\(^-\) to satisfy the consumption of reactive silica, and the reaction can be not stopped due to the lack of OH\(^-\) ions (unlike for specimens exposed to a saturated environment [Multon et al, 2009]). This assumption was well supported by the experimental results. If the alkali threshold was considered, the differences between the specimens kept in the three concentrations would be very large and the kinetics would not fit the experimental measurements well.

5.3.4. Prediction of specimens cast with different types of aggregate

In this part, the ASR expansions of 20x20x160 mm specimens cast with opal, Quartzite and Quartz Aggregate, and containing two reactive aggregate sizes (15% of 315-630 µm and 15% of 630-1250 µm), were calculated. Because of the difference of nature, additional fitting was used to determine \(D_a\) of each aggregate (equal to 5.0 x 10\(^{-14}\) m\(^2\)/s for opal, 4.0 x 10\(^{-16}\) m\(^2\)/s for quartzite and 2.0 x 10\(^{-16}\) m\(^2\)/s for quartz aggregate). The calculated curves showed good agreement with the experimental results in terms of kinetics and final expansions (Figure VI-14).
However, the curve of opal obtained by the model did not fit with experimental results perfectly. At the beginning of the experiment, the slopes of the two curves were the same but, after about 50 days, the measurements showed a speeding-up of the expansions which was not predicted by the calculation. It could be likely attributed to crack opening for opal specimens. As explained in Chapter 2, the specimens containing opal aggregate present much larger cracks than specimens of the same size cast with the other aggregates. These cracks could cause a great increase in the diffusion phenomenon, which could accelerate the reaction. The model considers the diffusion as constant in spite of cracks opening.

![Figure VI-14 ASR expansion curves of 20x20x160 mm specimens containing different nature of aggregates](image)

5.3.5. **Interest and limitations of the model**

5.3.5.1. **Comparison with the previous work [Multon et al. 2009]**

In order to discuss the interest and the limitations of the model, the improvements made relative to the previous model [Multon et al. 2009] will first be summed up:

- Considering that the diffusion of alkalis in the large specimen size is not instantaneous, the concentrations of alkalis in the cement paste do not remain constant with reaction time. A coefficient of alkali diffusion in the cement paste was added to take these conditions into account.
Experiments showed the impact of the sizes of the aggregate and specimen on the expansion. It can be explained by the effect on the final expansion of gel leaching through the cracks. This phenomenon appears to be amplified when the reactive aggregate contains a lot of reactive silica. It appears difficult to use the theoretical considerations of fracture mechanics presented above to quantify this phenomenon. Therefore, it was quantified by an empirical function to assess the volume of gel lost according to the ‘aggregate size / specimen size’ ratio and to reactive silica content.

The parameters fitted in this work have been compared to the parameters issued from [Multon et al. 2009] (Table IV-1). Considering the coefficient of alkali diffusion in the aggregate, it can be noted that the coefficient calculated here is significantly higher. This can be explained by the assumption on the alkali threshold. The first work [Multon et al. 2009] considered the effect of an alkali threshold on the silica dissolution. However, in the present work, the threshold is not considered (see 2.2.3 and 5.3.3). Since the reaction speed is proportional to the difference between the alkalis concentration in the aggregate and the threshold, not considering the threshold leads to a higher value of reaction speed. Therefore, the gradient of alkali concentration is higher in the model studied here. In order to counteract this increase of speed, the coefficient of alkali diffusion has to be decreased.

The molar volume of the gel obtained in this work is higher than in [Multon et al. 2009] (Table IV-3), which is pointed out by the large final expansion measured during the experiments. The difference can be explained by the conditions of conservation (in saturated air in [Multon et al. 2009] and immersed in solution in this work). The ASR gels were created in pore solution with different water contents and alkalis concentrations. The compositions of the gel were therefore different and thus the molar volume was different. Concerning the water, ASR gels formed in specimens kept in solution can absorb much more water than those in saturated air (R.H. >95%). Moreover, the previous work did not pay attention to gel leaching. With the consideration of this phenomenon, the volume of gel has to be greater to reach the same level of expansion. What’s more, comparing with the molar volume of C-S-H gel: 96 x 10^{-6} m^3/mol [Taylor 1990], the value of A-S-H gel in this work is also higher. Except for the reasons mentioned above, it could also be explained by the reason that A-S-H gel is more expansive than C-S-H gel.

The thickness of the connected porous interface zone ($t_c$) is also higher than in the previous work [Multon et al. 2009] (Table IV-4). This value is obtained to fit four aggregate sizes while in the previous work, only two aggregate sizes were studied. Moreover, the molar volume of the gel is higher and therefore more connected porous volume is necessary to accommodate the gel. This value guarantees that the expansion of the small particles was negligible in spite of the high molar volume.
### Table IV-4  Comparison of the parameters with a previous work [Multon et al. 2009]

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Coefficient of diffusion in aggregate $D_a$ (m$^2$/s)</th>
<th>Molar volume of ASR gel $V_{gel}^{mol}$ (m$^3$/mol)</th>
<th>Thickness of the connected porous interface zone $t_c$ (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>from [Multon et al. 2009]</td>
<td>$3.5 \times 10^{-13}$</td>
<td>$54.6 \times 10^{-6}$</td>
<td>$1.8 \times 10^{-6}$</td>
</tr>
<tr>
<td>in this work</td>
<td>$5.0 \times 10^{-15}$*</td>
<td>$420 \times 10^{-6}$</td>
<td>$14.0 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

* Results obtained from siliceous limestone aggregate

5.3.5.2. Limitations of the model

This model allows the prediction of ASR expansions of different specimen sizes containing different particle size classes. However, the present model still has some limitations:

1) For the largest specimens, the kinetic curves have some dissimilarity with the experimental results. This can be explained by the difficulty of taking the diffusion of alkali in the cement paste into account for large specimens.

2) The final expansion of the experimentation with the lowest ‘specimen size / aggregate size’ ratio is not well estimated. Due to the complexity of the phenomenon, the effect of this ratio is taken into account through an empirical function. This test shows the limit in the application range.

6. Conclusion

The experiments on expansion measurements were analysed by a microscopic model using the chemical quantification of reactive silica. The effect of numerous parameters was investigated: aggregate size (four classes) and mixes of aggregate of two sizes, specimen size (three dimensions) and alkali concentration of the external solution. The model proposes some improvements to take the decrease of expansion into account with the ratio of ‘specimen size/aggregate size’ which can be explained by the process of gel leaching and the non-linearity of expansion with the reactive silica content of the aggregate. As in previous work, the diffusion and the fixation of the alkali are assessed with the mass balance equation, the speed of alkali fixation is assumed to be proportional to the alkali concentration in the aggregate and the mechanical modelling uses a damage variable in order to determine the ASR expansion. Five parameters of the physicochemical modelling were determined by curve fitting the expansion curves obtained on the largest specimens. The fitted parameters were used to assess the ASR expansion of the other specimens with smaller dimensions and different conditions of conservation. The model can reproduce the differences of expansion due to the size of the aggregates and specimens and to the aggregate nature. However, the empirical function proposed to take account of the effect of the ratio ‘specimen size/aggregate size’ appears to be limited to...
experiments with high enough ratios (higher than 20). Finally, the model using this empirical function points out the complexity of predicting ASR expansion with micro modelling and states the numerous parameters which have to be taken into account. *The next chapter will show how the model could make a contribution to the methodology for predicting the slow expansion of concrete structures from the fast expansion of mortars in controlled conditions in the laboratory.*
Chapter 5

Methodology to assess the kinetics constant of expansion

1. Introduction

The kinetic constant of expansion is a parameter used in structural modeling to describe the chemical advancement with time. With this value, the kinetics of expansion in situ can be rebuilt. Thus, in order to assess the advancement ($A$) of ASR in affected concretes (and so requalify the structure), the kinetic constant, $\alpha$, of the structural modeling must be determined [Grimal 2007, Grimal et al. 2008, Sellier et al. 2009]. This chapter, based on the findings of Chapters 2, 3 and 4, firstly connects the structural model and micro chemo-mechanical model and explains the meaning of $\alpha$ in the micro chemo-mechanical model, and then proposes a method to assess this parameter in structural requalification.

2. Determination of the kinetic constant according to the aggregate size

The aim of this first part is to show that the kinetic constant $\alpha$ (Equation 1-7 in Chapter 1) depends on the size of the aggregate. The advancement in the specimens is as that in the structures, and can be calculated by:

$$\frac{\partial A}{\partial t} = \alpha_{ref} \exp \left( - \frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) \right) \times \left( \frac{S_r - S_r^{\text{threshold}}}{1 - S_r^{\text{threshold}}} \right) (S_r - A)$$

(Eq.V-1)

$\alpha_{ref}$: kinetic constant,
$E_a$: activation energy of the AAR (~47KJ/M),
$R$: gas constant (8.31 J/M/K),
$T_{ref}$: absolute temperature of the test,
$T$: current absolute temperature
$S_r$: degree of saturation of concrete porosity,
$S_r^{\text{threshold}}$: minimal saturation degree necessary to allow the chemical reaction to take place.
Chapter V

The application of Equation V-1, combining with the gel volume determined by the micro model presented in Chapter 4, allows finding $\alpha$ for the laboratory test. In this case, the temperature of the expansion test was 60°C, thus $T = T_{\text{ref}} = 60°C$. The specimens were saturated with a solution of alkalis, thus $Sr=1$. Therefore, Equation V-1 can be deduced to be:

$$\frac{\partial A}{\partial t} = \alpha_{60}(1 - A)$$

($V$-2)

$\alpha_{60}$: kinetic constant at 60°C

The analytical solution of this equation is:

$$A(t) = 1 - e^{-\alpha_{60}t}$$

($V$-3)

The chemical advancement can be expressed by:

$$A(t) = \frac{V_g(t)}{V_{g_{\text{max}}}} \quad \text{or} \quad A(t) = \frac{Si_{\text{reacted}}(t)}{Si_{\text{reactive}}(t = 0)}$$

($V$-4)

($V$-5)

with:

$V_g$: volume of gel created as a function of time (according to the diffusion phenomenon)

$V_{g_{\text{max}}}$: maximum value of the volume of gel. It stands for the consumption of all the reactive silica.

$Si_{\text{reacted}}$ represents the silica consumed at time $t$.

$Si_{\text{reactive}}$ represents the total reactive silica content of the aggregate

The kinetic constant ($\alpha_{60}$), under the conditions of expansion tests in the laboratory, can be obtained by curve fitting the advancement (Equation V-4) using Equation V-3. In Equation V-4, the volume of gel is calculated by micro modeling (Chapter 4). It can be seen from Figure V-1 that the curves given by the model used in the structural calculations correspond well with the results of the micro chemo-mechanical model.

![Figure V-1](image_url)

(a) (b)

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Figure V-1  Comparison of chemical advancements obtained by the micro chemo-mechanical model and by Equation V-3

The $\alpha$ values calculated (Equation V-3) for the different aggregate sizes and specimen sizes are plotted in Figure V-2. As shown in this figure, the constant of the kinetics ($\alpha$) varies with the sizes of the aggregate and specimen.

In the structural modeling, the value of $\alpha$ is a property of the aggregate and should not be influenced by different specimen sizes. However, differences do appear among specimen sizes (Figure V-2). This can be attributed to the diffusion in the specimen, which has an effect on the kinetics of the gel creation. The values of $\alpha$ are different for each class of aggregate size: $\alpha$ lies between 8 and $70 \times 10^{-3}$ day$^{-1}$. The values of $\alpha$ showed the greatest values for the smallest aggregate. This may be because the diffusion of alkalis is fastest in the smallest aggregates. These calculations confirm that different values of $\alpha$ have to be taken into account according to the aggregate size so that relevant structural calculations can be made, as already proposed in [Grimal 2007, Sellier et al. 2009]. It must be noted that the values of $\alpha$ obtained with the analysis of mortar expansion test cannot be used for the structural assessment because of the different aggregate size and the different environmental conditions.
3. Method to assess the kinetic constant of damaged structures

This part presents the calculation of the kinetic constant $\alpha$ in the framework of the methodology (Figure V-3) of structural requalification. The chemical advancement differs according to the size of the aggregate in the structure concrete: the smaller the aggregate is, the deeper the alkali attacks the aggregate and thus the higher is the chemical advancement. Therefore, the method of requalification proposes to determine the difference of chemical advancement according to the size of the recovered aggregate. Once the aggregates have been recovered, several types of mortars are cast. These mortars should represent the ASR damaged structures, and thus the different sizes of aggregates should be taken into account. It means that the mortars containing each class of recovered aggregate should be evaluated. In the process of casting mortars, all of these classes of recovered aggregates are crushed to the same grain size in order to obtain the same aggregate size distribution in each mortar and thus the same conditions of expansion. Therefore, the differences of total expansion observed during the expansion test depend only on the residual reactive silica contained in the recovered aggregate.

The method can be summarized as follows:

1. Recover the aggregate from damaged concrete in a given structure.
2. Perform the chemical test in order to quantify the potential of reactive silica contained by the aggregate.
3. According to the reactive silica content, choose the best size of aggregate and specimen to carry out a fast, relevant expansion test,
4. Use the chemo-mechanical model to obtain the residual reactive silica of aggregate and deduce the kinetic parameter according to the environmental conditions of the drilling zone.
The kinetic parameters thus obtained for the different sizes of aggregates recovered from damaged concrete could then be used as input data to perform structural reassessment and evaluate the safety level of the damaged structure with a finite element code as proposed in [Sellier et al. 2009].

3.1. Recovery of the aggregate from damaged concrete

For requalification, two types of aggregates are necessary:

- Sound aggregates to evaluate the reactivity of the aggregate, either by expansion tests (Chapter 2) or by the measurement of reactive silica (Chapter 3). These aggregates can be taken from sound zones of large aggregates (not attacked yet) or from dry zones of the structure.

- Attacked aggregates to evaluate the advancement of ASR (using the same test as for sound aggregates). They can be extracted from wet zones or zones affected by ASR.

Obtaining these two kinds of aggregate properly and entirely determines the accuracy of the following steps of the method, so the recovery method should be chosen carefully. It should satisfy the following conditions:

1) paste completely separated from the aggregate. This requirement makes provision for an expansion test (in the future) as sound as with the new aggregate, and also ensures a relevant result of chemical measurement since the remains of paste (C-S-H) would disturb the measurement.
2) aggregate not broken up. Aggregates of different sizes have different chemical advancements
in the affected structures, so to research this effect of aggregate size on degradation, the
recovered aggregates should be kept as whole as possible.

3) reactive silica not dissolved. The reactive silica content in recovered aggregates will be
measured with the HF/HF+HCl method, so for a relevant chemical result the recovery
process should take care not to dissolve the silica in aggregates.

Mechanical, thermal and chemical methods exist to recover aggregates from concretes. Works
are still in progress to propose a suitable method that can be applied to structures such as dams.

3.2. Chemical test for reactive silica content

Chapter 3 shows that the dissolution results obtained by the HF/HF+HCl attack present the
highest correlation with expansion tests. Therefore, the second step of the method is to perform
the HF/HF+HCl attack in order to quantify the potential of reactive silica contained by the
aggregate. However, some doubt arises about the sensitivity of the method to the small
differences of residual silica between the attacked aggregates. At present, a complementary
expansion test has to be conducted when evaluating the chemical advancement. Nevertheless, it
would be interesting to improve the chemical method since it can give the residual silica directly
and is faster than an expansion test.

3.3. Choice of the best size of aggregate and specimen for fast, relevant expansion test

In order to use expansion tests in predictive calculations, it is necessary to clarify all the complex
and coupled phenomena and quantify all the parameters involved during expansion. In particular,
the scale effect, shown in Chapter 2, which could make the measurements vary wildly according
to expansion conditions (conservation, reactive silica content), should be carefully considered.
These effects are partly taken into account in the micro modeling through an empirical function
(Equation IV-5 in Chapter 4) but this function is not perfect (for the largest particles in the
smallest specimens for example) and it could be interesting to decrease the impact of this
function in the analysis of the expansion. The parameters of the scale effect on ASR expansions
measured on specimens are pointed out in Equations II-2 and II-3 of Chapter 2. In order to
decrease the influence of this scale effect on ASR expansion, the stress intensity factor \( K_I \)
(Equation II-2 in Chapter 2) should be the same for the different expansion tests, which means
that the constants \( D_1 \) and \( D_2 \) in Equations V-6 and V-7 should be fixed.

\[
\frac{4}{3} \pi R_a^3 V_{gel}^{mol} - \phi \frac{4}{3} \pi \left[ R_a + t_r \right]^3 - R_a^3 = D_1
\]  

(V-6)
\[ \frac{R_a}{L} = D_2 \]  \hspace{1cm} (V-7)

Once \( D_1 \) and \( D_2 \) are fixed, the aggregate size can be calculated with \textit{Equation V-6}. The values of \( V_{mol}^{gel} \) and \( t_c \) have been determined by curve fitting above. Then the specimen size can be obtained with \textit{Equation V-7}.

For example, in the case of the expansion tests on siliceous limestone and opal aggregates, the reactive silica content was 3000 mol/m\(^3\) for the siliceous limestone and 21900 mol/m\(^3\) for opal. For mortars of siliceous limestone, aggregate class C2 (315-630 \( \mu \)m) and specimen size 20x20x160 mm were chosen, thus \( D_1 \) and \( D_2 \) were equal to 6.8E-11 m\(^3\) and 0.012. In order to have the same stress intensity factor for opal as for siliceous limestone, the aggregate size (the mean diameter) obtained by \textit{Equation V-7} should be about 240 \( \mu \)m and the specimen size should be about 10 mm. With such experimental conditions, the ASR-expansions for these two aggregates could be compared with more accuracy.

### 3.4. Calculation of the kinetic constant in the framework of structural requalification

Finally, under the condition \( T_{ref} = T \) of the structure, the kinetic constant needed for the requalification calculation can then be evaluated by the two following equations [Grimal 2007, Grimal et al. 2008, Sellier et al. 2009]:

\[ \alpha_i^j = \frac{1}{\tau_i} \frac{S_{r_i} - S_{r_0}}{1 - S_{r_0}} \]  \hspace{1cm} (V-8)

with \( \tau_i^j = \frac{A_i^j}{\ln(1 - A_i^j)} \)  \hspace{1cm} (V-9)

\( \Delta t \): \textit{time between the building of the structure and the drilling of the core samples}

\( S_r \): \textit{mean degree of saturation of the concrete in the structure}

\( S_{r_0} \): \textit{degree of saturation above which ASR occurs}, 0.2 according to [Grimal 2007]

The principle of the determination of \( A_i \) is to compare the residual reactive silica obtained on recovered aggregate with the reactive silica obtained on sound aggregate [Grimal 2007, Sellier et al. 2009]. The value of \( A_i \) (in \textit{Equation V-9}) is calculated using \textit{Equation V-10}.

\[ A_i^j(t) = \frac{RRS_i(t)}{RS} \]  \hspace{1cm} (V-10)

with:

\( RRS_i(t) \): \textit{residual reactive silica of aggregate size i}
RS: reactive silica of sound aggregate

In Equation V-10, the residual reactive silica (RRSi) and the reactive silica of sound aggregate (RS) can be obtained in two complementary ways: 1) directly by chemical measurements (but with an HF test, which implies different conditions compared to the concrete environment and is open to discussion), 2) indirectly by the expansion test (which is a better representation of the concrete conditions) and the use of the micro modeling. In the second way, the micro chemo-mechanical model is used to determine RRSi or RS (represented by the reactive silica content s in Table IV-1 in Chapter 4) by fitting the curve of measured expansion.

It is important to note that the advancement \( A_i \) differs according to the aggregate size, thus, the kinetic constants obtained here are for each aggregate size. To obtain an average value of kinetic constant for all the aggregate sizes, a method is proposed in [Grimal 2007].

4. Conclusion

This last chapter proposes a method to assess the kinetic parameter necessary for structural requalification for concrete containing aggregates already attacked and recovered from damaged structures. It is now necessary to test this method in real cases of damaged structures. In the future, the experimental feedback will show whether the qualification of the reactive silica content by two methods (chemical dissolution and expansion) is redundant and if chemical dissolution alone (the fastest method) is relevant to quantify the reactive silica available for ASR with sufficient accuracy.
In order to help the owners of ASR-affected structures to take decisions on the maintenance, repair or replacement of structures, methods of requalification of damaged structures are required. However, the evaluation of structures involves many inter-related factors (such as the environmental conditions – temperature and R.H., chemical components of the reaction, mechanical conditions). Numerous investigations already performed on ASR allow these phenomena to be explained. Several methodologies of requalification have been proposed [Grimal 2007, Grimal et al. 2008, Léger et al. 1995, Li et al. 2000, Li et al. 2001, Li and Coussy 2002, Malla and Wieland 1999, Multon et al. 2009, Saouma and Perotti 2006, Saouma et al. 2007, Saouma 2009, Sellier et al. 2009]. One of the problems of requalification is the reliability of the input data of the model and particularly the residual expansion test performed on specimens kept at 38°C and RH higher than 95%. The analysis of the structural behaviour of a French dam showed the difficulty of using the residual expansion test as input data for structural modeling [Grimal 2007, Sellier et al. 2009]. Therefore, the LMDC and EDF propose a method (Figure 1) to characterize the expansion kinetics through the assessment of the chemical advancement of the reaction in the aggregates contained by the structure concrete [Grimal 2007, Sellier et al. 2009]. This method proposes to assess the chemical advancement by the quantity of residual silica still present in the aggregate. This quantity of residual silica can be measured indirectly by expansion tests or directly by chemical tests.
The objectives of this work concern the laboratory tests as a part of the LMDC program. The research included expansion tests, chemical quantification of reactive silica in aggregates and, finally, the presentation of a micro-mechanical model.

The first chapter presented a literature survey of some existing requalification methods, including the details of the LMDC methodology.

Chapter 2 was devoted to expansion tests. It reported the optimization of an accelerated test by taking three parameters into consideration:

- The conservation conditions of the specimens in solutions, by using different alkali concentrations. They were chosen to consume all the silica in reactive aggregates.
- The aggregate size, which should be small enough for all the reactive silica to be attacked in a minimum of time (the aggregates in large structures such as dams must be broken). However, a minimum value must be fixed otherwise no expansion can be measured.
- The specimen sizes, which can have an effect on the results of expansion test kinetics and final asymptote.

The main conclusions drawn allowed us to propose optimized conditions for tests to be conducted on reactive aggregates:
In choosing the aggregate size, it was found that the expansions measured on specimens containing fine aggregates reached the final expansions in shorter times than specimens with coarser aggregates. The time necessary to reach asymptotic expansion on small specimens (smaller than 40 mm) is mainly due to the time of diffusion of the ion species through the aggregates. However, if the aggregate particles are too small, the gel produced by the aggregate can migrate into the connected porosity and cause little expansion. In the case of siliceous limestone, the size range 315-630 µm was found to be a good compromise.

Concerning the specimen size, the small specimens (e.g. 20 x 20 x 160 mm) were found to reach the final expansion in a short time because the diffusion of the ion species into the specimen was faster than in larger specimens. However, a part of the expansion was not measured because of the coupled effect of aggregate and specimen size on ASR-expansion. Beyond the methodology of requalification, the observation of this effect is also an important conclusion of this work. It was shown that the pessimum effect of aggregate size on ASR-expansion was a phenomenon that was not only intrinsic to the aggregate but was also caused by the experimental conditions. The effect of the cracking on the gel pressure could explain this phenomenon. Indeed, after the cracking, a part of the increasing volume due to ASR gel formation can be accommodated by the cracks volume. Moreover, a part of the gels can permeate out of the specimens. Accommodation by cracks and gels permeation can cause a decrease of the gel pressure and thus reducing the induced expansion.

Finally, for the siliceous limestone studied, small aggregate particles (315-630 µm) and small specimens (20 x 20 x 160 mm) were found to be convenient for a fast expansion test. However, these conditions could depend on the nature of the aggregate. In order to optimize the test conditions according to the nature of the aggregate, it appears to be important to quantify the ‘potential reactivity’ of the aggregate. In this aim, chemical tests (chapter 3) could be a useful tool.

Chapter 3 presented a study on “chemical tests” intended to measure the reactive silica in aggregate. Reactive silica is a relative concept which is used to define the part of silica which can react with alkali to produce gel. In order to know precisely the amount of reactive silica available for ASR, the best way would be to simulate the concrete environment but this is practically impossible considering the long reaction time. Mineralogical studies showed that the reactive silica includes amorphous minerals, cryptocrystalline minerals and crystalline minerals containing imperfections. In addition, considering that all types of silica (reactive silica and well crystallized silica) have certain solubility in an acid or basic environment, the method should distinguish the soluble capabilities of reactive silica and well crystallized silica. With these notions, three methods, NaOH-HCl, HCl-KOH, and HF/HF+HCl attack were used to test different types of aggregates. The chemical quantification was analyzed with respect to the expansion obtained on mortars containing these aggregates. The principal results of the analyses found were:

For NaOH-HCl attack, the high temperature (at 100°C) was effective to dissolve silica. However, the test could not distinguish the dissolution of reactive phase and well-crystallized phase. The NaOH-HCl seems to attack the well-crystallized minerals which would not really react with alkali in concrete.
HCl-KOH attack was found not to be suitable since it attacked the non-reactive quartz. In addition, this attack allows only one test at a time and, with only one result, it is not possible to distinguish the different forms of silica.

HF/HF+HCl attack was found to be the best compromise since it separated the reactive and non-reactive silica. Although it is an acid attack, the result showed the best correlation with the mortar tests. In addition, this method is rapid (24h) and simple.

Chapter 4 proposed an improved “chemo-mechanical model” to analyze the results of expansion tests and assess the chemical advancement of the reaction. This model was based on a model previously developed by Multon et al. [2009]. In order to determine the ASR expansion, the diffusion and the fixation of the alkali in the aggregates and the material damage were considered. Improvement was necessary to take into account the decrease in expansion with the “specimen size / aggregate size” ratio and the non-linearity of expansion with the reactive silica content of the aggregate observed during the experiments (chapter 2). The main points concerning the model are summed up below:

- Five parameters of the physicochemical modeling were evaluated by curve fitting the expansion curves obtained on the largest specimens.
- The fitted parameters were used to assess the ASR expansion of the other specimens with smaller dimensions and different conditions of conservation. The model can reproduce the differences of expansion due to the size of the aggregates and specimens and to the aggregate nature. It validates the function proposed to represent the combined effects of aggregate and specimen sizes and reactive silica content.

Chapter 5 summarized the findings of Chapters 2, 3 and 4 by presenting a method to calculate the kinetics constant of expansion, which is helpful in building the expansion kinetics in the field. The calculation of this parameter from micro chemo mechanical model showed that it varies along with the different sizes of aggregate and is little affected by the specimen size. Then, a methodology was proposed to calculate the kinetics constant in the framework of structural requalification.

Perspectives

The methodology proposed in chapter 5 still needs some improvements, which should be made in the near future. Among them:

- Some methods exist for recovering the aggregate from damaged concrete but their reliability is questionable. A literature survey has been made to compare the existing methods for recovering process, a two-steps strategy is chosen for the following experiments: physical method to delete roughly the cement paste and then a chemical method to dissolve the cement paste as much as possible. Work is still in progress to test the concrete in laboratory and finally applied to structures such as dams.
It could be interesting to test other chemical attacks (e.g. organic acid or other bases) to evaluate the reactive silica in aggregates. This subject matters not only for aggregates, but also for mineral admixtures such as natural or artificial pozzolans.

After these improvements, a complete assessment of an affected concrete using this methodology would need to be performed.
A


B


References


D


References


[F]  


References


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H


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L


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M


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X


Z
