Investigation of the Formation and Evolution of Alkali-silica Reaction Gel in a Chemical Model System Simulating a Cementitious Environment

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Acknowledgement
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**IV CONCLUSIONS**
List of Symbols

**Roman symbols**

- \( m_0 \) [g] Mass of the sample before the thermal treatment
- \( m_T \) [g] Mass of the sample after the thermal treatment
- \( n \) [-] Number of associated bridging oxygen with silicon
- \( n' \) [-] Mean degree of connectivity
- \( n_{CH} \) mol Total molar of Ca(OH)\(_2\)
- \( t \) [s] Time

- \( D_c \) [-] Degree of curvature
- \( G^* \) [Pa] Complex modulus
- \( G' \) [Pa] Storage modulus
- \( G'' \) [Pa] Loss modulus
- \( G'_{\text{max}} \) [Pa] Maximum storage modulus
- \( G'_{\text{min}} \) [Pa] Minimum storage modulus
- \( M_{CH} \) [g/mol] Molar mass of Ca(OH)\(_2\)
- \( M_{CO2} \) [g/mol] Molar mass of CO\(_2\)
- \( M_{H2O} \) [g/mol] Molar mass of H\(_2\)O

- \( \Delta CH \) [g] Mass loss due to dehydration of Ca(OH)\(_2\)
- \( \Delta CC \) [g] Mass loss due to dissociation of CaCO\(_3\)

**Greek symbols**

- \( \alpha \) [%] Fraction of the surface given in Scenario 1
- \( \beta \) [%] Fraction of the surface given in Scenario 2
- \( \lambda \) [%] Fraction of the surface given in Scenario 3
- \( \gamma \) [-] Resultant oscillatory strain
- \( \gamma_0 \) [-] Amplitude of the resultant strain
- \( \sigma \) [Pa] Oscillatory stress
- \( \sigma_0 \) [Pa] Amplitude of the applied stress
- \( \omega \) [1/s] Angular velocity
- \( \delta \) [-] Phase lag between the applied oscillatory stress and the resultant oscillatory strain (0 < \( \delta < \pi/2 \))
### List of Abbreviations

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<td>ASR</td>
<td>Alkali-silica reaction</td>
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<tr>
<td>CH</td>
<td>Ca(OH)$_2$</td>
</tr>
<tr>
<td>SSA$_{BET}$</td>
<td>Specific surface area (m$^2$/g)</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermo-gravimetric analysis</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy-dispersive X-ray spectroscopy</td>
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<td>XRF</td>
<td>X-ray fluorescence</td>
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Summary

Concrete has been the most widely and massively used construction material for its relatively excellent mechanical properties and low cost since Roman times. However, concrete has its own weakness that it is prone to deterioration for many reasons.

Alkali-silica reaction (ASR) is a durability problem causing detrimental expansion and cracking in concrete structure. It is caused by a series of physico-chemical reactions between the reactive silica contained in aggregates and the multiple components in cement paste at the micro scale leading to the formation of ASR gel, which plays a critical role during the generation and evolution of the expansion and the consequent cracking at the macro scale. In this study, ASR gel refers to both the alkali silicate formed from the interaction between the reactive silica and the alkaline solution, and the calcium alkali silicate subsequently formed from the interaction between the alkali silicate and calcium.

In fact, both the basic chemical reactions leading to the formation of ASR gel at the micro scale and the expansion and cracking caused by the deformation in response of expansive force at the macro scale have been relatively well understood. However, the link between the micro scale and the macro scale dealing with the generation and evolution of the interior expansive force from the formation of ASR gel is still unclear.

In this study, the fundamental mechanism of the formation and evolution of ASR gel in the concrete affected by ASR was explored by investigating the formation, evolution and properties of the two types of ASR gel: alkali silicate and calcium alkali silicate at different (nano/micro) scales.

In order to simplify the multiple physico-chemical reactions in ASR, a chemical model system was created to simulate the multiple interactions among the reactive silica contained in aggregates, alkalis, hydroxyls and calcium contained in the cement paste. With this chemical model system, numerous distracting factors in the real cementitious system can be excluded to expose the fundamental mechanism of the formation and evolution of ASR gel for investigation.

As the very first step of ASR, the interaction between the reactive silica present in aggregates and the alkaline solution was simulated and investigated in the chemical model system. The formation and properties of the products (alkali silicates) with different reaction times were emphasized.

The changes of the concentrations of silicon and hydroxyl ions in the solution as a function of time were studied to characterize the dissolution of reactive silica under this condition. It was found that the concentration of silicon in the solution increased as a function of time; the pH level describing the concentration of hydroxyl in the solution decreased with the reaction time. These results suggested the consumption of the hydroxyls in the solution due to its attack on the reactive silica and the consequent release of silicate into the solution during this interaction.
Moreover, the content of the hydroxyl groups contained in the solid phase as well as the specific surface area of the solid phase were investigated. The results showed that the content of the hydroxyl group contained in the solid phase, which was composed of unreacted silica and alkali silicate, increased as a function of time; the specific surface area also increased with the reaction time. This indicated the change of the microstructure of the solid phase during this interaction.

In addition, the evolution of the silicon-oxygen network present in the system during this process were particularly emphasized. It was found that the silicon-oxygen network experienced a depolymerization predominant process and a polymerization predominant process in sequence. As a result, a more complex and cross-linked silicon-oxygen network was formed in the end. Based on the above results, it was deduced that the alkali silicate having a shorter reaction time (1 hour) was less reactive for its further interaction with calcium compared to the one having a longer reaction time (24 hours).

As the subsequent step of the formation of alkali silicate from the interaction between reactive silica and alkaline solution, the interactions between the alkali silicates with different reactivity which were obtained by reacting silica fume with sodium hydroxide solution for 1 hour and 24 hours and the calcium hydroxide with different amounts were investigated. The formation and properties of the products (calcium alkali silicate) from different systems, were particularly emphasized.

It was found that a considerable structure development resulting in the formation of a rigid structure was generated from the interaction between alkali silicate and calcium hydroxide. The results showed that the structure development was favored by the usage of a higher reactive alkali silicate given the same amount of calcium hydroxide.

With the aim of exploring the cause of this structure development, firstly, the calcium hydroxide remaining in the system at different times was quantitatively studied. It was found that the calcium hydroxide was continuously consumed by its interaction with alkali silicate; the consumption of calcium hydroxide was higher in the system containing the alkali silicate with higher reactivity (24 hours).

Afterwards, the evolution of the silicon-oxygen networks present in the system during this interaction was investigated. The results showed that the silicon-oxygen network experienced a depolymerization predominant stage which was largely promoted by the presence of calcium hydroxide, and subsequently a re-polymerization predominant stage when calcium hydroxide was completely consumed in the system. As a result, a more complex and cross-linked silicon-oxygen network with the incorporated calcium was formed.

In addition, the evolution of the microstructure due to the interaction between alkali silicate and calcium hydroxide was studied. The distributions of the elements (calcium, silicon, sodium) at different reaction times were evaluated qualitatively. The evolution of the capillary porosity of the matrix
obtained by image analysis was investigated. The results showed that the porosity decreased as a function of time in all the systems.

Based on these results, a mechanism concerning the formation and evolution of the reaction rim composed of the ASR gel was proposed and used for demonstrating various topics of ASR.

The proposed mechanism was extrapolated to the formation and evolution of the ASR gel at the interface between alkali silicate and calcium. A rigid structure separating the alkali silicate slurry and the calcium hydroxide paste was formed at their interface. It was found that this rigid structure was able to prevent the penetration of both calcium and silicate through itself while allowing the transport of alkalis, similar to the reaction rim proposed by Ichikawa. The results show that the rigid structure was composed of calcium alkali silicate with a calcium to silicon mole (Ca/Si) ratio ranging from 0.22 to 0.53 and an alkali to silicon mole ((Na+K)/Si) ratio ranging from 0.20 to 0.26. According to the results regarding the polymerization degree, the silicon-oxygen network contained in the calcium alkali silicate was mainly composed of chains with interlinkages.

Thereafter, the elastic moduli of the rigid structures formed at the interface of the systems containing different amounts of calcium were investigated with nano-indentation. The elastic modulus of the rigid structure varied from 5 GPa to 20 GPa. The elastic modulus increased with the increase of Ca/Si ratio. Moreover, the more calcium was available for its interaction with alkali silicate, the higher the Ca/Si ratio and consequently the higher the elastic modulus of the formed calcium alkali silicate. These results supported the proposed mechanism concerning the formation and evolution of the rigid structure from the formation of calcium alkali silicate.

In the end, the interaction between the synthetic calcium alkali silicate with different Ca/Si ratios and the sodium hydroxide solutions with different concentrations was investigated.
Samenvatting

Beton is één van de meest gebruikte bouwmaterialen ter wereld al sinds de tijd van de Romeinen vanwege de vrij uitstekende mechanische eigenschappen en lage kostprijs van het materiaal. Desondanks kent beton het nadeel dat het gevoelig is voor diverse vormen van aantasting.

Alkali-silicareactie (ASR) is een duurzaamheidsprobleem dat nefaste expansie en scheurvorming veroorzaakt in betonstructuren. Het is het gevolg van een reeks fysico-chemische reacties tussen de reactieve silica aanwezig in de granulaten en meerdere bestanddelen van de cementpasta. Op microschaal leidt dit tot de vorming van ASR-gel. Deze gel draagt in belangrijke mate bij tot het optreden en verder evolueren van de expansie en de daaruit voortvloeiende scheurvorming op macroschaal. In dit onderzoek heeft de ASR-gel betrekking op zowel de alkali-silicaten die worden gevormd bij de interactie tussen de reactieve silica en de alkalische oplossing, alsook op de calcium alkali-silicaten die daarna worden gevormd door de interactie tussen alkali-silicaten en calcium. De fundamentele chemische reacties die aan de grondslag liggen van de vorming van ASR-gel op microschaal en de mechanismen die leiden tot expansie en scheurvorming op macroschaal zijn eigenlijk vrij goed gekend. Het precieze verband tussen de micro- en macroschaal aangaande het ontstaan en de evolutie van de interne expansieve krachten die voortkomen uit de vorming van de ASR-gel, is evenwel nog steeds niet duidelijk.

In dit onderzoek werd het grond mechanisme betreffende de vorming en evolutie van de ASR-gel in beton aangetast door ASR onderzocht. Daartoe werden de vorming, de evolutie en de eigenschappen van de twee types ASR-gel nader bekeken, m.n. de alkali-silicaten en de calcium alkali-silicaten op verschillende (nano/micro-)schaalen.

Om de meervoudige fysico-chemische reacties bij ASR vereenvoudigd voor te stellen werd een chemisch model ontwikkeld dat de diverse interacties omvat tussen de reactieve silica aanwezig in de granulaten alsook de alkali- en hydroxylgroepen en het calcium aanwezig in de cementpasta. Met behulp van dit chemisch model, kunnen veel randfactoren in cementgebonden systemen worden uitgesloten om zo het grond mechanisme met betrekking tot het ontstaan en de evolutie van de ASR-gel bloot te leggen.

De eerste fase van ASR, m.n. de interactie tussen de reactieve silica aanwezig in de granulaten en de alkalische oplossing werd gesimuleerd en onderzocht door middel van het chemisch model. Daarbij lag de nadruk op de vorming en eigenschappen van de reactieproducten (de alkali-silicaten) uitgaande van verschillende reactietijden.

De wijzigingen in concentratie betreffende de silicium- en hydroxyl-ionen in de oplossing werden bestudeerd in functie van de tijd om de ontbinding van de reactieve silica bij deze condities te karakteriseren. Daarbij werd vastgesteld dat de silicium-concentratie in de oplossing toenam in functie
van de tijd. De pH-waarde die een maat is voor de concentratie aan hydroxyl-ionen in de oplossing nam af met de reactietijd. Deze resultaten suggereren de consumptie van hydroxyl-ionen in oplossing geïnduceerd door aantasting van de reactieve silica en de daaropvolgende vrijstelling van silicaten in de oplossing door deze interactie.

Daarenboven werden het gehalte aan hydroxyl-groepen in de vaste fase alsook het specifieke oppervlak van deze vaste fase onderzocht. De resultaten toonden aan dat dit gehalte aan hydroxyl-groepen in de vaste fase, bestaande uit niet-gereageerde silica en alkali-silicaten toeneemt met de reactietijd. Het specifiek oppervlak neemt ook toe met de reactietijd. Dit wijst op een verandering in de microstructuur van de vaste fase tijdens deze interactie.

Daarnaast werd tijdens dit proces de evolutie van de silicium-zuurstofverbindingen in het systeem nadrukkelijk onder de loep genomen. Er kon worden vastgesteld dat deze verbindingen eerst een uitgesproken depolymerisatieproces ondergaan om vervolgens terug een uitgesproken polymerisatieproces te doorlopen. Als gevolg daarvan werden aan het einde van het proces meer complexe, verknoopte silicium-zuurstofverbindingen gevormd. Uit bovengenoemde resultaten kon worden afgeleid dat de alkali-silicaten met een kortere reactietijd (1 uur) minder reactief zijn voor verdere interactie met calcium dan alkali-silicaten met een langere reactietijd (24 uur).

In een volgende stap, werden de interacties tussen alkali-silicaten met een verschillende reactiviteit onderzocht. Deze werden bekomen door gedurende 1 uur en 24 uur silica fume te laten reageren met natriumhydroxide- en calciumhydroxide-oplossing in verschillende hoeveelheden. De vorming en eigenschappen van de reactieproducten (de calcium alkali-silicaten) van de verschillende systemen werden daarbij nadrukkelijk bekeken.

Er werd vastgesteld dat de interactie tussen alkali-silicaten en de calcium hydroxide resulteert in de vorming van een rigide structuur. Er kon ook worden geconcludeerd dat de structuurontwikkeling in de hand wordt gewerkt wanneer hoog reactief alkali-silicaat kan reageren met een opgegeven gehalte aan calciumhydroxide.

Om de precieze oorzaak van deze structuurontwikkeling te achterhalen werd eerst de hoeveelheid calciumhydroxide die achterbleef in het systeem op verschillende tijdstippen gekwantificeerd. Daaruit bleek dat de calciumhydroxide continue wordt verbruikt tijdens deze interactie met alkali-silicaat. Het verbruik was hoger indien het alkali-silicaat systeem werd bekomen uit de reactie tussen silica fume en natriumhydroxide gedurende 24 uur.

Daarna werd de evolutie van de aanwezige silicium-zuurstofverbindingen tijdens de interactie onderzocht. De resultaten toonden aan dat deze verbindingen dan een dominante fase van depolymerisatie ondergaan. Deze wordt gepromoot door de aanwezigheid van calciumhydroxide. Vervolgens vindt een uitgesproken fase van repolymerisatie plaats waarbij de calciumhydroxide
volledig wordt geconsumeerd. Dit resulteert in meer complexe en verknoopte siliciumzuurstofverbindingen waar calcium deel van uitmaakt.

Bijkomend werd de evolutie van de microstructuur door de interactie tussen alkali-silicaat en calciumhydroxide bestudeerd. De verdeling van de elementen (calcium, silicium, natrium) bij verschillende reactietijden werd op kwantitatieve wijze geëvalueerd. De evolutie van de capillaire porositeit van de matrix werd nagegaan met beeldanalyse. De porositeit bleek af te nemen in functie van de tijd voor alle systemen.

Op basis van al deze resultaten werd een mechanisme aangaande de vorming en evolutie van de laag rond de granulaten bestaande uit ASR-gel gedefinieerd. Deze werd dan gebruikt om diverse ASR gerelateerde fenomenen te verklaren.

Het voorgestelde mechanisme werd geëxtrapoleerd naar de vorming en evolutie van de ASR-gel ter hoogte van de interface tussen alkali-silicaat en calcium. De rigide structuur die de alkali-silicaat slurry scheidt van de calciumhydroxide pasta wordt gevormd nabij deze interface. Deze structuur is in staat om de indringing van zowel calcium als silicium tegen te gaan, terwijl transport van alkaliën, zoals aangegeven door Ichikawa, mogelijk blijft. De rigide structuur bestaat uit calcium alkali-silicaat met een molaire calcium-silicium verhouding (Ca/Si) van 0.22-0.53 en een alkali-silicium verhouding ((Na/K)/Si) van 0.20-0.26. Wat betreft de polymerisatiegraad bestaan de siliciumzuurstofverbindingen die aanwezig zijn in het calcium alkali-silicaat voornamelijk uit verknoopte ketens.

Daarna werden de elasticiteitsmoduli van de rigide structuren, gevormd ter hoogte van de systeeminterface met verschillende hoeveelheden calcium, onderzocht met behulp van nanoindentatie. De elasticiteitsmodulus van de rigide structuur varieerde tussen 5 GPa en 20 GPa. De elasticiteitsmodulus nam toe met de Ca/Si verhouding. Daarenboven was er meer calcium beschikbaar voor interactie met alkali-silicaat naarmate de Ca/Si verhouding hoger was en bijgevolg de elasticiteitsmodulus van het gevormde calcium alkali-silicaat hoger was. Deze resultaten zijn in overeenstemming met het voorgestelde mechanisme betreffende de vorming en de evolutie van de rigide structuur uitgaande van de vorming van calcium alkali-silicaat.

Tenslotte werd de interactie tussen synthetisch calcium alkali-silicaat met verschillende Ca/Si verhoudingen en natriumhydroxideoplossing met verschillende concentraties onderzocht.
In this chapter, the background, objective and scope of this research are given. The methodology and outline of the present thesis are provided.
1.1 Background

The word, concrete, comes from the Latin word “concretus” which means compact or condense. This perfectly describes the fundamentals of a modern concrete: aggregates are glued together by cement paste to form a compact, condense and composite material giving strength after its hardening. Due to its excellent performance of manipulation during production as well as its featured mechanical properties after the hardening process, concrete has become the building material used in the largest volume since Roman times.

Generally, concrete is a durable material if it is properly designed, produced and maintained. However, concrete degradation may occur for many reasons. Once it happens, various properties of concrete deteriorate leading to the failure of concrete structure eventually.

On the one hand, if the exterior environment of a concrete is harmful, e.g. overloading, chloride penetration, sulfate attack and so on, the corresponding properties of concrete will deteriorate causing the degradation of concrete. On the other hand, if the aggressive attack on concrete is from the interior, the matrix of concrete can be damaged causing the deterioration as well, e.g. alkali-silica reaction (ASR) shown in Figure 1.1, delayed ettringite formation and so on.

![Figure 1.1: Examples of ASR at different scales: (a) a severely cracked opaline siliceous fine aggregate due to ASR under optical microscope [1]; (b) ASR found on the surface of a concrete beam (photo taken by Prof. Luc Taerwe in Tongji University, Shanghai); (c) deterioration caused by ASR, Sixth Street Viaduct Bridge, Los Angeles.](image)

ASR, as the focus of this research, has been studied for almost one century since it was firstly spotted during the 1920s and 1930s in California, USA. People observed severe cracking within several years after the construction of concrete structures despite of their decent execution of construction standard and quality control [2]. However, it took another ten years until the pioneer Stanton (Figure 1.2) disclosed the existence of alkali-silica reaction and demonstrated it as an intrinsic degradation process happening between the constituents of a concrete [3]. In Stanton’s landmark paper in the 1940s [4], he managed to identify the cause of this unusual cracking and attributed it to the acid soluble...
alkali content of the cement. Furthermore, he proposed to set the largest equivalent sodium oxide content not triggering ASR as 0.60% by mass. This approach was extremely far reaching that even today, limiting the alkali content of cement is still one of the most efficient and convenient ways to prevent ASR. The upper threshold of the alkaline content in cement not triggering ASR given by Stanton, 0.60%, is one of the most essential common knowledge of concrete for a person working in either industry or academy.

Figure 1.2: Thomas Stanton with the California State Division of Highways and a Bridge Parapet Wall that is showing signs of damage due to ASR [5].

During the following decades, research about ASR was carried out at many places in the world. The directions of the research also vary: from evaluating the ASR-reactivity of aggregates to optimizing the limit of alkali content for different cements; from the chemical and physical mechanisms at the micro scale to its consequence on the mechanical properties of concrete at the macro scale; from the standard of construction to the diagnosis and possible repair after ASR occurred. Thanks to the significant contribution from a tremendous number of researchers and engineers, up to now, ASR has never been so clear to this world. Yet, we are still far away from eliminating ASR in concrete. Instead, the situation is getting tougher and tougher according to the increasing number of published scientific articles dedicated to ASR in the last two decades shown in Figure 1.3, bearing in mind that scientific research is always associated with the practical demand.
There are mainly two reasons for the difficulty of handling ASR in practice. First, different aggregates show different ASR-reactivity [7]. The vulnerability of the aggregate to ASR depends not only on the amount of alkalis contained in the cement, but also on the type, quantity and size of the aggregate containing reactive silica used for concrete. Those factors increase the potential risk of triggering ASR in a concrete even under a “safe” condition, i.e. a conventional inert aggregate may show a limited ASR-reactivity when it is crushed into a smaller size. Second, the mechanism about how the expansive pressure is generated and accumulated from the physico-chemical interaction between the reactive silica in aggregates and the cement paste is still unclear. More specifically, the link between the formation of products due to ASR at the micro scale and the mechanical response of concrete at the macro scale is missing. Actually, this aspect is also one of the most controversial issues of ASR. As a consequence, unfortunately, we cannot quantitatively evaluate the risk of expansion and cracking due to ASR with the basic knowledge of the used raw materials alone. For the same reason, a conservative evaluation of the vulnerability of an aggregate to ASR has to be used in the classical accelerated tests [8-10] to avoid any possible ASR even this will inevitably cause some waste and overestimation. Moreover, the ambiguity on this topic blurs our understanding about the possible link between ASR and pozzolanic reaction where they share a series of multiple interactions among calcium, alkalis and silica. Pozzolanic reaction describes a series of chemical reactions between the pozzolanic material which is a silica-rich material added to the cementitious system and the calcium hydroxide formed from the cement hydration resulting in the formation of calcium silicate hydrate with a considerable cementing properties [11].
Therefore, the present work is aiming at exploring the fundamental mechanism connecting the formation of the products due to ASR at the micro scale with the generation and accumulation of the interior expansive force at the macro scale from a chemical, physical and mechanical point of view. A simplified but representative chemical model system was developed to simulate ASR under laboratory conditions. With the help of such a chemical system, the formation and properties of the main product of ASR (ASR gel) under different conditions and its influence on the ASR process can be studied.

1.2 Objectives and Scope of the Research

The research objective of this study is to explore the fundamental mechanism of the formation and evolution of ASR gel in the concrete affected by ASR.

ASR gel is chosen as our research target considering its extremely essential role in the whole process of ASR: from its formation from the interaction between the reactive silica in aggregates and the pore solution of cement paste at the beginning, to the deteriorative consequence in the end when expansion and cracking occur. In this sense, the formation and evolution of the ASR gel are informative for us to look into the fundamental mechanism of ASR.

ASR gel can be either amorphous or crystalline [12]. ASR gel, herein, refers to the reaction products formed from both the initial stage where reactive silica interacts with the alkaline solution of cement paste to form alkali silicate, and the subsequent stage where alkali silicate interacts with the calcium in the cement paste to form calcium alkali silicate.

The objective of this work can be divided into four subtopics according to the sequence of ASR in a concrete:

- The formation and properties of alkali silicate from the interaction between reactive silica in aggregates and alkaline solution of cement paste.
- The formation and properties of calcium alkali silicate from the interaction between alkali silicate with calcium present in cement paste.
- The formation and properties of calcium alkali silica formed at the interface between alkali silicate and cement paste where calcium is abundantly present.
- The influence of the pore solution of cement paste on calcium alkali silica.
1.3 Methodology

With the need of investigating the fundamental mechanism of ASR, a chemical model system has been developed to simplify the complex situation in concrete. In this chemical model system, ASR gel including alkali silicate and calcium alkali silicate can be synthesized under different conditions to simulate various but typical circumstances in the concrete affected by ASR. The chemical, nano/micro structural and mechanical properties of the synthetic ASR gel can be characterized.

The formation and evolution of alkali silicate from the interaction between reactive silica and alkaline solution, as well as the formation and evolution of calcium alkali silicate from the interaction between alkali silicate and calcium is studied separately in the chemical model system. In the first step, the influence of various factors on the properties of alkali silicate is evaluated. Based on this, the behavior of the alkali silicate as the product of the initial stage of ASR can be characterized. Subsequently, the investigation on the formation and evolution of the calcium alkali silicate is conducted. The physical, chemical, nano/micro structural and mechanical properties of the calcium alkali silicate are studied to disclose how the properties of alkali silicate hydrate and the quantity of calcium influence its properties.

Afterwards, the interface between the reactive silica in an aggregate and the cement paste is simulated with the chemical model system. The calcium alkali silicate formed at such an interface can be investigated from chemical, micro structural and mechanical points of view. Finally, the influence of the alkaline solutions with different concentrations on the properties of the synthetic calcium alkali silicate is studied.

1.4 Outline

The outline of this thesis is shown in Figure 1.4. In Chapter 2, an overview is provided to clarify our current knowledge and understanding of ASR. A detailed literature review is given on several specific aspects relating to the research objective to reveal the research scope and significance. In Chapter 3, a brief introduction of the chemical model system using for simulating ASR under laboratory condition is provided. In Chapter 4 and Chapter 5, the formation of alkali silicate from the interaction between reactive silica and an alkaline solution as well as the formation of calcium alkali silicate from the interaction between alkali silicate and calcium is investigated in sequence. A mechanism about the generation of the expansive force from the formation and evolution of ASR gel is proposed in Chapter 6 based on the results of Chapter 4 and Chapter 5. With the aim of extrapolating the proposed
mechanism, the formation and evolution of calcium alkali silicate at an interface between alkali silicate and calcium hydroxide are realized in a calcium-alkali-silicate system in Chapter 7. Afterwards, the elastic modulus of the calcium alkali silicate formed at the interface is investigated in Chapter 8. In addition, the interaction between the synthetic calcium alkali silicate and the sodium hydroxide solution is studied in Chapter 9.

Notably, the chapters containing experimental work are organized in the same way: after giving a brief introduction about the necessary background, the used materials and methods are given. Subsequently, the presentation of the results and the discussion are provided. Eventually, the summary of the chapter is given.
Figure 1.4: Outline of the thesis.
Chapter 2 – State of the art

After introducing the basics of alkali-silica reaction in concrete, a detailed review about the fundamental process of the formation of ASR gel and its connection with the interior expansive pressure build-up process is given to clarify and disclose the research purpose, scope and significance from a theoretical point of view.

Chapter 3 – Introduction of the Chemical Model System

An overview about the chemical model system using for simulating ASR in a laboratory is given.

Chapter 4 – Formation of Alkali Silicate in the Chemical Model System

The interaction between the reactive silica in aggregates and the pore solution of cement paste is studied in this chapter. The reactive silica in aggregates is simulated with silica fume and the pore solution of cement paste is simulated with an alkaline solution. The physical and chemical properties of the product of this interaction, alkali silicate, are studied comprehensively. The influence of reaction time on the nano/micro structure of alkali silicate is particularly emphasized.

Chapter 5 – Formation of Calcium Alkali Silicate in Chemical Model System

The interaction between alkali silicate and calcium is studied in this chapter. The calcium source present in the form of both cation (Ca^{2+}) and free Ca(OH)_2 in a concrete is simulated with a Ca(OH)_2 paste. The structure development generated from this interaction is particularly emphasized. Rheological and chemical approaches are used for disclosing the influence of calcium and the type of alkali silicate on the formation and evolution of calcium alkali silicate. Afterwards, the chemical and nano/micro structural properties of the calcium alkali silicate formed in this stage are investigated.

Chapter 6 – Mechanism Proposal

Based on the results from the previous chapters, a mechanism about the generation of the interior expansive force from the formation and evolution of calcium alkali silicate is proposed in this chapter.

Chapter 7 – Formation of the Reaction Rim in a Calcium-alkali-silicate System

In this chapter, the formation and evolution of the reaction rim in the concrete affected by ASR is idealized in a calcium-alkali-silicate system. The calcium alkali silicate formed at the interface between alkali silicate and calcium hydroxide is believed to be the cause of the formation of the reaction rim. The elemental composition and nano/micro structure of the calcium alkali silicate found at the interface are investigated.
Chapter 8 – Investigation on Elastic Modulus of the Reaction Rim Formed in a Calcium-alkali-silicate System

The elastic modulus of the reaction rim formed at the interface between alkali silicate and calcium hydroxide is studied. The relationship between the elastic modulus and the elemental composition of the calcium alkali silicate is investigated as well.

Chapter 9 – Studies on Interaction Between Synthetic Calcium Alkali Silicate and Sodium Hydroxide

The interaction between the synthetic calcium alkali silicate with different calcium to silica ratios and the sodium hydroxide solutions with different concentrations is investigated in this chapter.

Chapter 10 – Findings, Extensive Discussion and Recommendation

In this chapter, the main research findings are reviewed. Afterwards, extensive discussion about the role of lithium on mitigating ASR in concrete as well as the extrapolation of the proposed mechanism to demonstrate the link between ASR and pozzolanic reaction is given. Contributions of the present work are summarized. Recommendation for future research is listed.
In this chapter, an overall introduction of ASR is given in the first place, the chemical reactions and the corresponding products are reviewed to introduce the multiple interactions among reactive silica, alkaline solution and calcium. Numerous theories and models dealing with the mechanism of the generation and accumulation of the interior expansive force resulting in deterioration of the ASR-affected concrete, are particularly emphasized to reveal our research purpose, scope and significance.
2.1 Fundamentals of ASR

Theoretically, there are three types of alkali-aggregate reactions which can cause degradation of concrete [2, 13]:

a) Alkali-silica reaction;

b) Alkali-silicate reaction (clay minerals);

c) Alkali-carbonate reaction (argillaceous dolomitic limestone).

As the topic of the present study, alkali-silica reaction refers to a series of chemical and physical interactions between the reactive silica contained in aggregates and the multiple constituents of cement paste, including alkalis (Na⁺/K⁺), hydroxyls (OH⁻) and calcium present in different forms. The process of ASR consists three stages occurring in sequence:

(i) The formation of the reaction products (ASR gel) including alkali silicate and calcium alkali silicate from the multiple interactions between reactive silica and cement paste;

(ii) The generation and accumulation of the interior expansive force due to the formation of ASR gel;

(iii) The occurrence of expansion and cracking.

The first stage is primarily a series of chemical reactions between the reactive silica present in aggregates and the multiple constituents (alkalis and hydroxyls) present in the cement paste of concrete. In the first place, once the reactive silica in an aggregate comes into contact with the alkalis and hydroxyls present in the pore solution of cement paste, alkali silicate will form from the process of silica dissolution and alkali incorporation. Subsequently, once alkali silicate comes into contact with Ca²⁺ present in the pore solution of cement paste, calcium is able to interlink alkali silicates to form calcium alkali silicate. As long as both alkali silicate and calcium alkali silicate stay in such a system, further evolution due to their interaction with other constituents present in the cement paste can be expected.

The second stage is considered critical for the deterioration due to ASR, since it connects the formation and evolution of ASR gel at the micro scale with their mechanical consequences at the macro scale. Unfortunately, the mechanism of this process is not clear due to its complexity of transferring microscale interactions to macroscale mechanical behavior. Despite of this, ASR gel has been widely identified as the key component of this process.

The third stage refers to the deterioration of the concrete matrix, such as swelling at the micro scale, expansion and cracking at the macro scale. Comparing to the former stages, this stage is much
easier to be noticed from the outside of a concrete. Actually, this stage is purely a dynamic process of stress and deformation. The stress is the interior expansive forces generated in the second stage. In response of that, deformation occurs in the concrete matrix according to its mechanical properties.

Obviously, the deterioration of concrete due to ASR is a mechanical consequence of the interior expansive force resulting from the formation of the ASR gel which is generated by a series of physico-chemical interactions among the multiple constituents of concrete matrix. Therefore, as the key component in the whole process, ASR gel has been chosen as our research emphasis to explore the mechanism of the generation and accumulation of the interior expansive forces due to ASR.

2.2 Formation of Alkali Silicate

2.2.1 Pore Solution

Due to the hydration of Portland cement, the pore solution of the cement paste mainly contains hydroxides including calcium hydroxide (Ca(OH)$_2$), sodium hydroxide (NaOH) and potassium hydroxide (KOH). Most of Ca(OH)$_2$ is present in a solid form because of its extremely low solubility in an alkaline solution. NaOH and KOH are present as cations (Na$^+$, K$^+$) and anions (OH$^-$) in the pore solution. Therefore, the pore solution of a concrete generally contains cations including Ca$^{2+}$, Na$^+$ and K$^+$; anions including OH$^-$ and other constituents (aluminum, iron, etc.) as shown in Table 2.1.

| Table 2.1: Measured concentrations in the pore solution of a concrete [mg/L]. |
|---------------------------------|---------------|--------------|---------------|---------------|---------------|---------------|---------------|
| Age $^a$ (months)               | 10             | 4             | 9             | 10            | 10            | 10            | 10            |
| w/c $^b$                        | 0.50           | 0.36          | 0.50          | 0.50          | 0.50          | 0.50          | 0.35          |
| Na                              | 1500           | 1800          | 600           | 3200          | 4200          | 1600          | 300           |
| K                               | 6300           | 5700          | 600           | 6000          | 100           | 7500          | 700           |
| Ca                              | 90             | 20            | 470           | 50            | 1             | 15            | 130           |
| Mg                              | 0.20           | 0.10          | 0.20          | 0.10          | 0.06          | 0.15          | 0.10          |
| Al                              | 5              | 30            | 5             | 5             | 2800          | 15            | 5             |
| Si                              | 6              | 6             | 6             | 6             | 6             | 6             | 6             |
| Fe                              | 0.50           | 0.50          | 0.50          | 0.50          | 0.90          | 0.70          | 0.50          |
| pH                              | 13.4           | 13.2          | 13.1          | 13.5          | 13.3          | 13.4          | 12.4          |

Reproduced from [14]

$^a$ Age of cement paste sample before the pore solution pressing and analysis [months]

$^b$ Water to cement ratio
The amount of sodium and potassium in the pore solution depends on their original quantity in the Portland cement, which is considered as the most important parameter for the mitigation of ASR. The pH of the pore solution, denoting the concentration of OH\(^-\) in the pore solution, usually varies from 12.7 to 13.7 [15] which is higher than that of a saturated Ca(OH)\(_2\) solution. It means that, the concentration of Ca\(^{2+}\) in the pore solution is lower than its saturation concentration of 0.011 mol/L in water (K\(_{sp}\)=5.5 x 10\(^{-6}\)) due to the common-ion effect which depresses the release of Ca\(^{2+}\) from Ca(OH)\(_2\).

2.2.2 Silica in Aggregates

As the major constituent of concrete, aggregates are inert granular materials such as sand, gravel or crushed stones. Due to its huge influence on the properties of the fresh and hardened concrete, the selection of aggregates is of great importance for the production of concrete. Besides the size and shape of the aggregate, the chemical stability of the aggregate is one of the most important aspects to be evaluated during the selection process, especially its reactivity to ASR.

The most common reason causing ASR is the use of reactive siliceous minerals contained in the aggregates in concrete. Silica, as the major constituent of most aggregate around the world, is commonly found as quartz which is stable under normal conditions due to its well-organized silicon-oxygen tetrahedral structure [16]. Chert, as one of the disordered and reactive form of silica, has a random network [17] making it vulnerable to alkalis and hydroxyls contained in the pore solution of cement paste.

Based on the forms of silica contained in the aggregate, the reacting aggregate can be classified as fast reacting aggregate (e.g. volcanic rocks and chert) and slow reacting aggregate (e.g. sandstone, gneiss, granite) [18]. For the first type of reacting aggregate, amorphous silica is the reacting mineral; for the second type of reacting aggregate, crystalline silica like quartz is the reacting mineral. The products of the reactions with those two types of reacting minerals in concrete are quite different.

2.2.3 Interaction between the reactive silica in aggregates and pore solution

In the context of ASR, the alkali denotes sodium and potassium. However, the reaction between alkalis and reactive silica is never a primary step of ASR. More importantly, the attack of hydroxyls in the pore solution of cement paste on the reactive silica contained in aggregates is the initial step of ASR. As soon as the reactive silica comes into contact with the pore solution of cement paste, Si-O-Si linkages of silica, also known as siloxane, are attacked by OH\(^-\) to generate Si-OH linkages (silanol)
leading to the hydrolysis of silica (Equation 2.1). As OH⁻ continually attacks siloxane, the silica tetrahedral networks will break down. Subsequently, the alkalis in the pore solution of cement paste penetrate into the silicates to counter balance the negative charges of the silicates which are generated during the reaction given in Equation 2.2. The counterbalance process is illustrated in Equation 2.3 where R denotes alkalis [19]. This process is schematically shown in Figure 2.1.

\begin{align*}
OH^- + Si - O - Si &\rightarrow (Si - O^-) + (Si - OH) \quad \text{Equation 2.1} \\
Si - OH + OH^- &\rightarrow Si - O^- + H_2O \quad \text{Equation 2.2} \\
Si - O^- + R^+ &\rightarrow Si - O \ldots R \quad \text{Equation 2.3}
\end{align*}

![Schematic diagram](image)

Figure 2.1: Schematic diagram of the interaction between reactive silica and alkaline solution.

### 2.2.4 Further evolution

Due to the minimal energy variations between different alkali silicate, the alkali silicate present in the system is in a metastable state [20]. Different alkali silicate may interlink with each other to form a more polymerized alkali silicate [21], see Equation 2.4 where R denotes alkalis. The polymerization
process of alkali silicate is believed to be a dynamic distribution of different species between larger colloidal silica and intermediately sized anionic fractions, rather than a continuous stepwise growth seen with organic polymerization [22, 23]. It should be noted that, the formation of Si-O-Si in Equation 2.4 does not mean the dissolution of silica is a reversible process that the original silica is formed again. Actually, the formation of Si-O-Si given in Equation 2.4 only denotes the construction of siloxane bonds. The overall silicon-oxygen network contained in the product is completely different from that contained in the original silica. An example concerning this difference is schematically shown in Figure 2.2.

\[
\text{H}_2\text{O} + 2(\text{Si} - \text{O} \ldots \text{R}) \rightarrow \text{Si} - \text{O} - \text{Si} + 2\text{ROH}
\]

Equation 2.4

Figure 2.2: Schematic representation of an example of the difference between (a) original silica and (b) its product after the condensation. The siloxane bond and the corresponding oxygen contained in the original silica under attack are indicated with red; the siloxane bond formed from condensation and the corresponding oxygen are indicated with blue.

2.2.5 Influencing factors

There are many factors affecting the process and products of the interaction between the reactive silica and the alkaline solution in the first step.

First of all, the concentration of OH\(^-\) in the pore solution is the most essential one. The higher the OH\(^-\) concentration, the more OH\(^-\) is available to attack siloxane bonds and destroy the silica tetrahedral network to form alkali silicate [24] at a higher reaction rate. Actually, even the network of a crystalline silica (quartz) can be affected by OH\(^-\) given sufficient time and exposure to alkaline solution [17].
Furthermore, from a nano structural point of view, the more OH⁻ present in the pore solution, the lower polymerization degree of the formed alkali silicate and vice versa [25].

Second, the reactivity of the silica contained in aggregates depends on both the forms of silica and the particle size of the aggregate. On the one hand, the form of silica is associated with the vulnerability of the silica network to the attack of alkaline solution in the sense that the less ordered the network, the more reactive the silica is and vice versa. This is why opal and chert are more reactive than quartz. On the other hand, the particle size of the aggregate which contains the reactive silica matters as well. The smaller the size of the aggregate, the larger the surface area is exposed to the alkaline solution and vice versa. Already back in the 1940s, Stanton [4] found that the expansion due to ASR would decline from its maximum as the proportion of the reactive aggregate in that concrete decreased and increased. A similar phenomenon was also found with respect to the particle size of the aggregate. This phenomenon is called the pessimum effect. However, the mechanism of this effect is still controversial [26-29]. Therefore, the possible application of the pessimum effect in preventing ASR is not practical. It should be noted that the surface area referred in the specific surface area also includes the interior surface of the open pores in the aggregates.

Third, the reaction time of the interaction between the reactive silica and the alkaline solution matters as well. As the reaction time increases, more and more silica is attacked and converted into alkali silicate. Regarding the polymerization of alkali silicate, a longer reaction time promotes the polymerization of alkali silicate [30]. This phenomenon has been verified by many researches. As shown in Figure 2.3, the fraction of the less polymerized specie which gives the signal as Peak 1 (Q₁) which represents the end of the chain of silicon-oxygen network is getting smaller and smaller as a function of time. While the fraction of the more polymerized species which give the signal as Peak 2 (Q₂) representing the chain of silicon-oxygen network and Peak 3 (Q₃) representing the sheet of silicon-oxygen network are getting larger and larger as a function of time. It means the alkali silicate present in this system tends to polymerize to form a more cross-linked silicon-oxygen network.
Figure 2.3: Dissolution of amorphous silica gel in lithium hydroxide after (a) 100, (b) 200, (c) 300, (d) 400, (e) 800, and (f) 1000 minutes of reaction measured by $^{29}$Si Nuclear Magnetic Resonance, modified from [30].

Fourth, different alkalis have different interactions with the reactive silica. It was reported that the silica’s interaction with potassium hydroxide (KOH) had the largest dissolution rate; while the one with lithium hydroxide (LiOH) had the least; the one with sodium hydroxide (NaOH) had a moderate rate of dissolution [30, 31]. However, lithium was found to be the easiest one to get incorporated in the silicon-oxygen network of alkali silicate compared to sodium and potassium [32, 33]. Moreover, the micro structure of the silicon-oxygen network of the alkali silicate containing different alkalis also varies. The alkali silicate formed from the interaction between reactive silica and KOH is more polymerized than the one formed from the interaction between reactive silica and LiOH; the one formed from the interaction between reactive silica and NaOH has a moderate polymerization degree [30].
2.3 Formation of Calcium Alkali Silicate

2.3.1 Calcium Source

In cement paste, calcium is mainly present in three forms: free Ca(OH)$_2$ in the matrix of cement paste, Ca$^{2+}$ in the pore solution and the calcium incorporated in calcium alkali silicate. Notably, the calcium incorporated in calcium alkali silicate can be released into the solution under certain conditions [34]. These three types of calcium are in a dynamic equilibrium.

The free Ca(OH)$_2$ (CH) is the main source of calcium in the matrix of the cement paste. Most of it is present as crystals [34], but other types are also reported [35]. The preferable presence of CH in the vicinity of the aggregate surface has been reported as shown in Figure 2.4 [35]. This benefits its further interaction with alkali silicate near the aggregate surface.

In a word, as one of the by-products of Portland cement hydration, CH is largely present in the matrix of the cement paste and co-exists with its dissolution products, Ca$^{2+}$, CaOH$^+$ and OH$^-$ at the saturated or supersaturated state.

Figure 2.4: A deposit of CH in the vicinity of an aggregate surface, modified from [35].
The pH level of the pore solution of cement paste varies from 12.7 to 13.7, higher than that of a saturated Ca(OH)$_2$ solution (pH=12.4). Therefore, the dissolution of Ca(OH)$_2$ is depressed by the high alkaline environment and the concentration of Ca$^{2+}$ in the pore solution is lower than its saturated concentration. The concentration of Ca$^{2+}$ in such a pore solution of cement paste can be calculated with the solubility and dissociation constant of Ca(OH)$_2$ in water under room temperature. Notably, due to the high concentration of OH$^-$ in the pore solution, the presence of CaOH$^+$ as the intermediate product of the dissolution of Ca(OH)$_2$ cannot be ignored. Hence, the dissolution of CH can be considered as a two-step process shown in Equation 2.5 and Equation 2.6:

$$\text{Ca(OH)}_2(s) \rightarrow \text{CaOH}^+(aq) + \text{OH}^-(aq) \quad K_{\text{Equation 2.5}} = 9.3 \times 10^{-5} \quad \text{Equation 2.5}$$

$$\text{CaOH}^+(aq) \rightarrow \text{Ca}^{2+}(aq) + \text{OH}^-(aq) \quad K_{\text{Equation 2.6}} = 4 \times 10^{-2} \quad \text{Equation 2.6}$$

where s denotes solid, aq denotes aqueous meaning the marked reactant or product exists in a solution.

The variation of the concentrations of both Ca$^{2+}$ and CaOH$^+$ in the pore solution of cement paste under different pH levels is given in Figure 2.5. As can be seen in the figure, the concentration of Ca$^{2+}$ is extremely low in the pore solution of cement paste, Ca$^{2+}$ with such a low concentration is hardly enough to ensure a continuous supply to its interaction with alkali silicate. In other words, once the small amount of Ca$^{2+}$ in the pore solution is consumed by its interaction with alkali silicate at an early age, the interaction between alkali silicate and Ca$^{2+}$ will come to an end, unless additional Ca$^{2+}$ is released into the solution by the dissolution of CH. Moreover, CaOH$^+$ present in the pore solution may interact with alkali silicate as well.

![Figure 2.5: The variation of the concentration of Ca$^{2+}$ and CaOH$^+$ with pH.](image)

Furthermore, Ca$^{2+}$ as well as the free CH and CaOH$^+$ present in the pore solution, is experiencing a dynamic equilibrium in the concrete matrix. On the one hand, because of the high alkaline environment in the cement paste, the dissolution of CH is significantly depressed, Ca$^{2+}$ and CaOH$^+$ tend
to combine with OH\(^-\) to form CH. Therefore, calcium is mainly present as CH, both Ca\(^{2+}\) and CaOH\(^+\) are rare. On the other hand, both Ca\(^{2+}\) and CaOH\(^+\) can be consumed by their interaction with alkali silicate to form calcium alkali silicate leading to the lowering of their concentrations in the pore solution. As a consequence, the dissolution of CH is activated, i.e. additional Ca\(^{2+}\), CaOH\(^+\) and OH\(^-\), are released into the pore solution to compensate for their consumption. This process indicates that, the free CH in the cement paste is acting as a “buffer” to maintain the consistent concentrations of Ca\(^{2+}\) and CaOH\(^+\) [36]. In the meantime, additional OH\(^-\) is also provided for its further attack on reactive silica [37].

The release of calcium from calcium alkali silicate often comes with an ion-exchange effect between the alkalis present in the solution and the calcium incorporated in the silicon-oxygen network of calcium alkali silicate. For example, with the increase of the concentration of alkali hydroxide in the solution, more and more calcium incorporated in calcium alkali silicate is replaced by alkali and released into the solution [38, 39]. Nevertheless, the amount of calcium released by calcium alkali silicate is believed to be limited since the incorporation of calcium in calcium alkali silicate is thermodynamically favorable compared to that of alkalis.

### 2.3.2 Interaction Between Alkali Silicate and Calcium

Once alkali silicate, formed from the interaction between the reactive silica and the pore solution of cement paste, comes into contact with the Ca\(^{2+}\) in the pore solution of cement paste, calcium alkali silicate will form from the interlinkage of different alkali silicate by Ca\(^{2+}\) as shown in Equation 2.7, where R denotes alkalis.

\[
\text{Ca}^{2+} + 2 (\text{Si} - \text{O} \ldots \text{R}) \rightarrow (\text{Si} - \text{O} \ldots \text{Ca} \ldots \text{O} - \text{Si}) + 2\text{R}^+ \quad \text{Equation 2.7}
\]

During this process, calcium acts as a bridge to link different alkali silicate to form the product containing a more complex and cross-linked silicon-oxygen network as shown schematically in Figure 2.6. During this process, Ca\(^{2+}\) replaces alkali cation [38] or H\(^+\) [40] in alkali silicate to get incorporated into the silicon-oxygen network resulting in an overcharging phenomenon that, the negative surface charge of alkali silicate or calcium alkali silicate is over neutralized to positive by the divalent cation Ca\(^{2+}\) [41, 42], as shown in Figure 2.7. In other words, calcium determines the surface charge of calcium alkali silicate during this process [43, 44]. This phenomenon of overcharging could lead to the aggregation or coagulation of calcium alkali silicate [45, 46] due to the lack of repulsive forces between calcium alkali silicate particles during their evolution later on. In addition, the consumption of alkali silicate by its interaction with calcium could promote further dissolution of the reactive silica by lowering the concentration of the dissolved alkali silicate in the pore solution.
2.3.3 Further Evolution

As long as an increasing number of calcium alkali silicate forms and stays in this system, further evolution of calcium alkali silicate will occur. Generally speaking, this evolution can be illustrated from two levels. From a scale concerning individual calcium alkali silicate, other constituents including alkalis, alkali silicate and calcium present in the system can affect the elemental composition of calcium alkali silicate and consequently alter its micro structure. From a scale concerning groups of calcium alkali silicate, they tend to interact with each other to form a product showing some chemical and mechanical features.

For individual calcium alkali silicate, it can interact with other constituents such as alkalis, alkali silicate and calcium present in the cement paste. First, during the interaction between calcium alkali silicate and alkalis, an ion-exchange process between the incorporated calcium and the free alkalis in solution occurs. The alkalis, mainly sodium and potassium, exchange with the calcium to get themselves incorporated in the silicon-oxygen network of calcium alkali silicate [38, 39, 47, 48]. This process brings about not only the change of the elemental composition of calcium alkali silicate but also the modification of the micro structure of the affected calcium alkali silicate even in a short term [49]. Second, the interaction between calcium alkali silicate and the calcium present in cement paste has a greater and more direct impact on the composition and nano structure of calcium alkali silicate.
compared to alkalis. As additional calcium gets incorporated into the networks of calcium alkali silicate by exchanging with alkali [41], the calcium to silica mole (Ca/Si) ratio of the calcium alkali silicate increases. This process increases the risk of the rupture of silicon-oxygen network of calcium alkali silicate resulting in the decrease of the polymerization degree [50], especially under the continuous attack of OH\(^{-}\). In other words, the presence of calcium in the pore solution of cement paste not only changes the elemental composition of calcium alkali silicate but also promotes the breakage of the tetrahedral network with the help of OH\(^{-}\). Third, the interaction between calcium alkali silicate and alkali silicate only occurs when all the available CH is fully consumed. This interaction leads to the formation of another type of calcium alkali silicate with lower calcium content, higher alkali content and higher polymerization degree [51, 52]. These results have been extended recently by Baingam et al. [53] by stating that, both an increasing number of dissolved silicate and sodium in the pore solution could result in the formation of calcium alkali silicate with an extremely low Ca/Si ratio.

With respect to the particle growth of calcium alkali silicate, the evolution is often associated with the processes of coagulation, nucleation and growth. The coagulation of silica or calcium alkali silicate describes a process in which, well-dispersed particles in a solution lose their mutual repulsive force and get interconnected to form a network of a gel as the function of time schematically shown in Figure 2.8. The interlinkages between particles resulting in the coagulation are so weak that they can be easily destroyed by a disturbance, for example, ultrasonic wave. Once the disturbance stops, those interlinkages can be rebuilt. Therefore, coagulation is a mechanically reversible process.

As the trigger of the coagulation of calcium alkali silicate, Ca\(^{2+}\) determines and controls the whole process of coagulation [54, 55]. As long as Ca\(^{2+}\) is present in the pore solution, it will neutralize the negative charge on the surface of calcium alkali silicate lowering the repulsive forces between calcium alkali silicate particles. Once those repulsive forces are no longer big enough to expel calcium alkali silicate particles, coagulation happens and calcium alkali silicate particles tend to interlink physically with each other [56]. Different scenarios of coagulation under different concentrations of Ca\(^{2+}\) are shown in Figure 2.8 as well.
Another type of evolution concerning the calcium alkali silicate groups is the nucleation and growth process [57-59]. As calcium alkali silicate accumulates due to its continuous formation, the clustering and condensation of calcium alkali silicate particles activate the nucleation and growth process. Although the nucleation and growth processes are often believed to be involved in the dissolution-precipitation process during the cement hydration [54], these processes also apply to the interaction between particles of calcium alkali silicate.

There are two nucleation modes: the heterogeneous nucleation occurring at high CH concentration and homogeneous nucleation happening at low CH concentration as shown in Figure 2.9. The homogeneous nucleation, whose rate is mainly determined by the super-saturation of calcium alkali silicate in the system, usually leads to a preferable growth of calcium alkali silicate parallel to the surface of the anhydrous cement particles or existing calcium alkali silicate nuclei, see Figure 2.9 (a). While the heterogeneous nucleation, whose rate is largely determined by the concentration of calcium present in the solution, often leads to a preferable growth of calcium alkali silicate perpendicular to the surface of the anhydrous cement particles or existing calcium alkali silicate nuclei [54, 55, 60, 61] see Figure 2.9 (b). As the consequence of nucleation and growth, the network of calcium alkali silicate gets densified by the condensation of calcium alkali silicate particles. The foreign particles acting as nuclei [61, 62] are connected with calcium alkali silicate, favoring the rigidification of the network of calcium alkali silicate eventually.
2.3.4 Influencing Factors

There are two critical factors influencing the formation of calcium alkali silicate. As stated in the previous subsections, the concentration of Ca$^{2+}$ governs the formation of calcium alkali silicate. During the interaction between alkali silicate and calcium in the first place, calcium acts as a bridge to link different alkali silicate. Hence, the more calcium is present in the system, the more calcium is available to generate the interlinkage and consequently to form more calcium alkali silicate with a higher Ca/Si ratio. After the formation of calcium alkali silicate, the concentration of calcium in solution continually affects the composition and nano structure of calcium alkali silicate as mentioned in the previous subsection. Most importantly, the presence or absence of CH determines at which stage the system is: the stage of the formation of calcium alkali silicate when CH is present or the stage of the evolution of calcium alkali silicate which interacts with additional alkali silicate when CH is absent.

The other factor is alkali silicate. Obviously, alkali silicate with different polymerization degrees has different behaviors during its interaction with calcium. For example, alkali silicate with high polymerization has limited available places for the interlinkage or incorporation of calcium at the beginning. Consequently, the reaction rate is low and the polymerization degree of the formed calcium alkali silicate is high. Alternatively, the alkali silicate with low polymerization degree provides a large
number of places for the interlinkage or incorporation of calcium, consequently the reaction rate is high and the polymerization degree of the formed calcium alkali silicate is low. This favors the further interaction between calcium alkali silicate and alkali silicate. However, hardly any studies have been conducted on this topic to the best of the author’s knowledge.

Moreover, alkali silicate incorporated by different alkalis is supposed to behave differently during its interaction with calcium. For example, an increasing number of lithium incorporated in alkali silicate depresses the alkali-calcium exchange process leading to the formation of calcium alkali silicate with a lower Ca/Si ratio [63, 64]. Also, it was reported that the calcium alkali silicate formed in a system with the presence of large number of lithium salt which was added to prevent ASR was able to form a thick layer to cover the reactive silica and prevent further OH⁻ attack [64, 65]. This phenomenon is closely associated with the mechanism of using lithium salt on the mitigation of ASR.

2.4 Occurrence of Deterioration in ASR

2.4.1 Deterioration Mode

The deterioration of ASR in concrete often appears as an expansion and cracking. Visible cracking caused by ASR can be found either in the hardened cement paste or at the interior of an aggregate as shown in Figure 2.10. Obviously, both the expansion and cracking are caused by the internal expansive force generated by the formation of ASR gel. Once this force exceeds the strength limit of cement paste or aggregate, deterioration would occur at the corresponding position. However, the mechanism of the generation and accumulation of the expansive force is not clear.

Figure 2.10. Cracking caused by ASR gel (arrow) found both in the cement paste and in the interior of the aggregates, reproduced from [66].
2.4.2 Interior Expansive Force

Bearing in mind that it is the key mechanism to link the ASR gel formation at the micro scale with the deterioration at the macro scale, the internal expansive force generated and accumulated from the formation of ASR gel has attracted the most research attention for decades. Compared to our relatively comprehensive understanding about the chemical reactions in the first stage as well as the mechanical performance of concrete in response to the internal expansive force at the later stage of ASR, unfortunately, the mechanism of the generation and accumulation of the expansive force is still controversial. In this subsection, a literature review about several classical theories and models concerning this topic is given.

Our understanding about the generation of the interior expansive force started from the theory proposed by Powers in 1955 stating that it was the formation of the expansive products causing the expansion of concrete [67]. Later, Glasser [68] in 1979 proposed that the expansive pressure in ASR was coming from the osmotic pressure. This theory verified the assumption raised by Hanson [69] and was supported by Struble et al. [70] in 1981 by stating that the synthetic ASR gel was able to swell due to imbibed water. During the 1980s, Chatterji [71] attributed the generation of the interior expansive force to the mass difference of the materials located inside and outside of the reaction site. Moreover, Prezzi et al. [72, 73] proposed that the expansive force in ASR was from the electrical repulsive force in the electrical double layer in the 1990s. However, none of those studies could satisfactorily answer all the questions concerning the occurrence of ASR and the consequent deterioration.

![Image](image_url)

Figure 2.11: The appearance of the reaction rim (indicated with arrows) in concrete, reproduced from [5, 37].

When the dispute and ambiguity on explaining the mechanism of the generation and accumulation of the interior expansive force mentioned above are fully realized, the existence of an object called “the reaction rim” associated with ASR has attracted our attention. The appearance of
the reaction rim in concrete is shown in Figure 2.11. The first observation of a reaction rim dates back to 1982, when Glasser et al. [41] found out that a “shell” was formed which covered the surface of a silica gel exposed to a solution of alkalis and calcium. However, at the early age, the reaction rim and its properties only existed in the prediction of Wang and Gillott [36] stating that, the reaction rim was associated with the concentration gradients of Ca\(^{2+}\) and alkalis across itself at some distance away from the aggregate surface, as schematically shown in Figure 2.12. In their model, the concentration of calcium experienced a decrease from the outside of the rim to the inside of the rim; while the concentration of alkalis underwent firstly an increase from the outside of the rim to the core of the rim and secondly a decrease from the core of the rim to the inside of the rim. It means that, the reaction rim was an intermediate zone between the cement paste where calcium is abundantly present and the aggregate surface where silica dissolution occurred. This assumption was fully supported by the results of Brouxel [74] and extended by Bleszynski and Thomas [75] stating that, the reaction rim was consisted of calcium alkali silicate with a high calcium content. Of course, controversies regarding the elemental composition of the calcium alkali silicate constituting the reaction rim do exist, i.e. it was reported that the calcium alkali silicate constituting the reaction rim had a low calcium content or even no calcium at all [76]. However, this cannot be considered as a principle problem, since the composition of the reaction rim is believed to be sensitive to the location as shown in Figure 2.12. Another possible reason for this controversy is the contamination from other constituents located at the neighboring areas [77].

Figure 2.13: Preliminary schematic representation of the reaction rim, reproduced from [36].

Until late in 2000s, the reaction rim was only considered as one of the by-products of the chemical interaction between the reactive silica contained in aggregates and the constituents from cement paste, until Ichikawa [37, 78] in 2007 and 2009 linked it closely to the generation and accumulation of the interior expansive force which leads to ASR deterioration. In his theory which is shown in Figure
2.13 (a)-(c), he proposed that the reaction rim was composed of calcium alkali silicate formed from the interaction between alkali silicate and Ca$^{2+}$ in the cement paste. After its formation, the reaction rim was able to behave as a semi-permeable membrane to prevent the escape of alkali silicate from the reaction site between the rim and the aggregate surface, while allowing the penetration of Ca$^{2+}$ and alkalis (Na$^+$/$K^+$) through it. Therefore, alkali silicate would continuously form and accumulate in the region between the reaction rim and the aggregate surface, Figure 2.13 (d). This continuous accumulation of alkali silicate would unavoidably apply an expansive force on the reaction rim. In return, the reaction rim provides a constraint around the reaction site with its rigid structure. Once this expansive force exceeds the strength of the reaction rim, cracking would occur as shown in Figure 2.13 (e). Remarkably, this theory successfully illustrates that different types of ASR gel play different roles during the generation and accumulation of the expansive force with the observation of the reaction rim surrounding the aggregate at the macro scale.

Unfortunately, up to now, the information about how the reaction rim is generated, why it is able to act as a semi-permeable membrane to prevent the transport of alkali silicate while allowing the penetration of other constituents including alkalis and calcium, how rigid it is to provide a considerable constraint on the reaction site and to what extent the reaction rim could resist the expansive force due to the accumulation of alkali silicate, is still missing. Moreover, the occurrence of those multiple interactions among reactive silica, alkalis, hydroxyls and calcium at the interface of the reactive aggregate with the cement paste brings more uncertainties and consequently more difficulties for answering those questions.
2.4.3 Occurrence of Expansion and Cracking

After the interior expansive force exceeds the strength of either the hardened cement paste or the aggregate, deterioration due to ASR occurs. Obviously, this process is purely a mechanical process. Numerous theories and models were proposed. However, this aspect is beyond the research scope of the present thesis.

2.5 Troubleshooting

The above subsections given a comprehensive review about the whole process of ASR and the related physico-chemical reactions, as shown in Figure 2.14. It is clear that the critical part for having a better understanding about the mechanism of ASR is investigating the formation and evolution of ASR gel formed from a series of physico-chemical reactions in ASR. This is the emphasis of the present study.
2.6 Summary

The occurrence of ASR can be divided into two stages happening in sequence: the formation and evolution of ASR gel and the generation of the interior expansive force leading to deterioration.

As the decisive and prior stage of the generation of the interior expansive force, the formation and evolution of ASR gel consists of two steps: the formation of alkali silicate from the interaction between the reactive silica in aggregate with the alkalis and hydroxyls in the pore solution of cement paste; the formation of calcium alkali silicate from the interaction between alkali silicate with the calcium from the cement paste. Therefore, the investigation on ASR gel can be conducted on the above two steps separately.

The following concluding remarks can be made:

- In order to improve the understanding about the mechanism of ASR, the formation and evolution of ASR gel should be focused.
• The formation and evolution of alkali silicate from the interaction between reactive silica and alkaline solution needs to be studied in the first place.

• As the subsequent step of the formation and evolution of alkali silicate, the formation and evolution of calcium alkali silicate from the interaction between alkali silicate and calcium should be investigated.
INTRODUCTION OF THE CHEMICAL MODEL SYSTEM

In the first section of this chapter, the necessity of creating a chemical model system to simulate ASR under laboratory conditions from a chemical point of view is given. A number of model systems from the previous studies are reviewed. Critical factors which need to be considered during the creation of the model system are discussed. The model used in the present work is introduced. More particularly, various properties of raw materials are given.
3.1 Origin

Due to the complexity of the interaction between the reactive silica present in aggregates and the cement paste, too much factors can affect the interaction and the corresponding products. For example, different minerals contained in the aggregates apparently have different behaviors with respect to their interaction with the pore solution of cement paste. As the media delivering alkalis, hydroxyls and calcium to the aggregate surface to trigger ASR, the pore solution of cement paste is the very place where the ASR gel forms and evolves. The concentrations of the components present in the pore solution depend on various factors, e.g. water to cement ratio, type of cement and so on. Obviously, this has a huge influence on the process of ASR. Moreover, the interface of the aggregate surface with the cement paste, where ASR occurs, is in the region of the interfacial transition zone (ITZ) of a concrete and is one of the most heterogeneous systems in the concrete matrix [79] making the situation in a real case even more ambiguous. In the light of this consideration, it is extremely difficult to study the fundamental mechanism of ASR in a cementitious system.

From a practical point of view, in addition, the investigation of ASR needs to be accessible in laboratory conditions. On the one hand, ASR gel can be found either at the interface between the aggregate and cement paste or in the interior of some micro cracks in the aggregates. As a result, great variations between samples collected at different places can be expected [77]. However, it is hard to attribute these variations to the intrinsic differences between samples or some unavoidable contaminations from neighboring areas, not mentioning the difficulties of sample collection. On the other hand, ASR is a long-term issue of a concrete: it takes years until visible deterioration occurs. In other words, the formation of ASR gel and its multiple impacts on the ASR-affected concrete take a long time to be noticed at the macro scale, making it nearly impossible to observe the process in the field by monitoring or other techniques from the very beginning. Actually, during the long duration of ASR, contaminations from external environment could affect the interior situation as well.

Based on the above considerations, a simplified chemical model simulating ASR in laboratory conditions meets our demands from both a scientific and a practical point of view.

3.2 Chemical Model System for Idealization of ASR

Going back to the 1980s, Struble and Diamond [70, 80] created a simplified system using an ion-exchange resin to synthesize ASR gel artificially from calcium, silica gel and alkaline solutions under different conditions. In the 1990s, Cong and Kirkpatrick [81] used two types of opal and cristobalite to simulate the reactive silica present in aggregates in their model system. Based on these two classical
chemical models, successors [51, 53, 82-85] made use of different types of silica to obtain various types of ASR gel by simulating ASR happening under different conditions.

Based on the above discussion, obviously, the key point of creating a chemical model system to simulate ASR in a laboratory is looking for appropriate materials to substitute the reactive silica present in aggregates, multiple constituents (Na⁺, K⁺ and Ca²⁺) present in the pore solution of cement paste and the free Ca(OH)₂ present in the matrix of cement paste.

3.2.1 Alkaline Solution

The pore solution of cement paste in concrete contains numerous cations mainly including Na⁺, K⁺ and Ca²⁺, anions mainly including OH⁻. Notably, due to the extremely low concentration of Ca²⁺, the pore solution herein is addressed as the alkaline solution for convenience. Ca²⁺ will be considered separately further in this section with respect to the calcium source.

The concentrations of the alkalis vary based on their original quantity in the Portland cement used for mixing. Typical examples of concrete using different types of cement are given in Table 2.1 (Section 2.2.2). According to the pH level of a concrete, the concentration of hydroxyl present in the pore solution of cement paste varies from 0.05 mol/L to 0.50 mol/L, high enough to generate a considerable attack on the siloxanes of a reactive silica leading to the hydrolysis of silica.

In the present work, therefore, an alkaline solution of NaOH or KOH with a concentration of 1 mol/L was chosen to simulate the presence of alkalis and hydroxyls in the pore solution of cement paste. This concentration gives a pH of 14.0 which is high enough to trigger ASR at beginning, and ensures the pH of the system being always above 12.5, simulating the alkaline environment in concrete. A NaOH or KOH solution with a concentration of 1 mol/L was made by dissolving pellets of NaOH or KOH respectively in the deionized and CO₂-free water.

3.2.2 Silica Source

The reactive silica present in aggregates, as probably the only silica source in the concrete matrix, is one of the most essential participants of ASR. However, the reactive silica present in aggregates behaves differently for many uncertainties, e.g. whether and how much reactive silica is present in aggregates.
Based on these considerations, a type of silica fume (Elekem Microsilica Grade 940U) was chosen as the silica source in the model system. This silica fume is a grey and fine powder as shown in Figure 3.1. The particle size distribution is given in Figure 3.1. It is clear that, majority part of silica fume has a particle size less than 1 µm indicating it has a high specific surface area (m²/g). This makes the silica fume highly reactive to its interaction with an alkaline solution. Notably, the peak located at about 200 µm is due to the agglomeration of the silica fume. The chemical composition of the silica fume in the form of oxides is given in Table 3.1, where potassium, sodium and aluminum are present with limited amount aside from the majority presence of silica. According to the X-ray diffraction (XRD) pattern of the silica fume as shown in Figure 3.2, the silica fume is amorphous. It gives a broadened peak centered at about 20° (2Θ) due to the presence of regions with local atomic order or crystals with extremely small size. Therefore, the silica fume used in this study is an amorphous silica with fine particle size. The expected high reactivity of the silica fume to the alkaline solution favors its role of simulating the reactive silica present in aggregates and accelerating the process.

However, it should be noted that, the silica fume used in the present study to simulate the reactive silica in aggregates has a much higher reactivity with respect to its interaction with the pore solution of cement paste compared to the one in aggregates. This unavoidably accelerates the reactions and has some influences on the products.

Table 3.1: Elemental composition of silica fume (provided by Romy Suryaningrat Edwin) [%].

<table>
<thead>
<tr>
<th>Compositions</th>
<th>SiO₂</th>
<th>CaO</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>SO₃</th>
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</thead>
<tbody>
<tr>
<td>Content</td>
<td>94.2</td>
<td>0.6</td>
<td>1.0</td>
<td>0.5</td>
<td>0.7</td>
<td>1.0</td>
<td>1.1</td>
<td>0.3</td>
</tr>
</tbody>
</table>
3.2.3 Calcium Source

Based on the discussion in 2.3.1, most of the calcium is present as free CH and Ca\(^{2+}\) in cement paste though the concentration of Ca\(^{2+}\) is extremely low. Therefore, a CH paste was made to simulate the calcium source in the chemical model system. The CH paste was prepared by adding CH powder into 1mol/L NaOH solution at a liquid to solid mass ratio of 3 to keep its uniformness as a paste. Notably, the undissolved CH in the CH paste is completely different with the one present in concrete. In the cementitious system, CH is formed from cement hydration where it grows continuously by crystallization. Therefore, the phase of portlandite in concrete is composed of larger crystals of CH while the undissolved CH in the CH paste using in the present study is completely in the form of dispersed particles with small size. However, this must have limited influence on the reactions since the very form of calcium participating the reactions is Ca\(^{2+}\). Both forms of CH need to give Ca\(^{2+}\) to get themselves involved in the process of ASR.

In the CH paste, obviously, the dissolution of CH is significantly depressed by the large amount of hydroxyls given by NaOH in the solution. As a result, the concentration of Ca\(^{2+}\) is extremely low (about 3.2 mmol/L). In the meantime, abundant CH is present in the paste and ready for donating Ca\(^{2+}\) and OH\(^{-}\) once they are consumed. In other words, free CH here is acting as a buffer to maintain the concentration of Ca\(^{2+}\) and OH\(^{-}\) as we expected.
3.3 Summary

Based on the above discussion, the following conclusions can be made:

- In this study, the process of ASR will be simulated in a chemical model system.
- In the chemical model system used in this study, the alkaline solution containing alkalis and hydroxyls is simulated by a NaOH/KOH solution; the reactive silica contained in aggregates is simulated by silica fume; the calcium source present in the cement paste is simulated by a CH paste.
PART II

MECHANISM OF FORMATION AND EVOLUTION OF THE REACTION RIM
In this chapter, the interaction between the reactive silica present in aggregates and the alkalis and hydroxyls present in the pore solution of cement paste is simulated in the chemical model system and investigated experimentally. Various properties of the solid and liquid phases are investigated. Depolymerization and polymerization processes occurring during this interaction and their influence on the silicon-oxygen network present in the system are emphasized.
4.1 Background

Silicon dioxide (SiO$_2$), also known as silica, is one of the most abundant materials on earth. Amorphous silica, closely related with the material involved in our research, has a more open and dis-organized arrangement of its silicon-oxygen network. This makes it vulnerable to the attack of hydroxyls during its interaction with alkaline solutions compared to crystalline silica [86]. The silicon-oxygen network present in crystalline silica and amorphous silica are schematically shown in Figure 4.1, where the silicon-oxygen network in the crystalline silica is much more uniform and organized compared to that in the amorphous silica.

![Figure 4.1: 2D schematic representation of the silicon-oxygen network present in (a) crystalline silica (quartz); (b) amorphous silica.](image)

The interaction between the silica and the alkaline solution has been studied over a century due to its extreme importance in both academic and industrial fields. As the first step of ASR, an introduction of this process is given in the following.
FORMATION OF ALKALI SILICATE IN THE CHEMICAL MODEL SYSTEM

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Figure 4.2: Schematic representation of the attack of OH⁻ on the network of silica in a solution. (a) Accommodation of OH⁻; (b) alternation of the network by OH⁻; (c) breakage of the network and silicate release. The dotted line represents the interface between the silica on the left and the solution on the right. Reproduced from [86] with modification.

Once silica comes into contact with the alkaline solution, the hydroxyls get adsorbed and accommodated between two –OH groups on the surface of the tetrahedral network of silica, as shown in Figure 4.2 (a) and (b) [86]. Subsequently, Si-O-Si linkages (siloxanes) on the surface of silica are destroyed by these hydroxyls to generate Si-OH bonds (silanols) leading to a local hydrolysis as stated by Brinker [87]. During this process, the accommodated OH⁻ is consumed and the siloxanes on the surface of silica are destroyed. As a consequence, the influenced silicon-oxygen network on the surface of silica is modified from a relatively closed structure to a more open and dis-organized one. If OH⁻ is sufficiently provided by the alkaline solution, more siloxanes can be attacked by OH⁻ resulting in further hydrolysis. This will eventually lead to the break-down of the affected silicon-oxygen network releasing monomers of silicate into the solution as shown in Figure 4.2 (c). This process is also known as de-polymerization concerning the decrease of polymerization degree which stands for the connectivity of silicon in the network. This process is governed by the following Equation.

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

Equation 4.1

The formed silicate is negatively charged, therefore it can be neutralized by the cations like alkalis present in the solution. As a result, alkali silicate is formed. This process is shown in Equation 4.2 where R denotes alkalis including Na⁺ and K⁺.

\[ ≡ \text{Si} - \text{O}^- + \text{R}^+ \rightarrow ≡ \text{Si} - \text{O} ... \text{R} \]  

Equation 4.2

Certainly, alkali silicate cannot dissolve in the solution infinitely. After the saturation concentration of the alkali silicate is reached, the newly-formed alkali silicate is present as undissolved
alkali silicate in the system. Consequently, unreacted silica (if it is still present), dissolved alkali silicate and undissolved alkali silicate co-exist in such a system.

The destruction of the siloxane bonds in the silicon-oxygen network of silica loosens the network enabling this structure imbibing water [88]. As a result, the total volume of the solid products is larger than that of the solid reactants resulting in an increase of the volume of the solid system. This increase has been closely associated with the generation of the interior expansive force in ASR [89-91].

Considering the minimum energy variation between different alkali silicates [20], the alkali silicates remaining in the system can interlink with each other to form a more complex type of alkali silicate with larger size and polymerization degree [92]. This process is known as condensation or polymerization as shown in Equation 4.3 [21].

\[-\text{SiOH} + \text{HOSi} \rightarrow -\text{SiOSi}^- + \text{H}_2\text{O}\]  
Equation 4.3

During this process, the connectivity of the silicon-oxygen network increases [22, 23]. It should be noted that de-polymerization, describing the decrease of the connectivity, can happen at the same time as polymerization. On the one hand, de-polymerization destroys the tetrahedral network of silica. On the other hand, polymerization builds a more complex and dis-organized silicon-oxygen network as schematically shown in Figure 4.3.

Once silica comes into contact with alkaline solution, a large number of alkali silicate can be continuously released from the affected tetrahedral network of silica by de-polymerization. This provides the reactants such as monomers, dimers and so on for condensation and polymerization [87]. Eventually, the system will reach a meta stable state once the rate of de-polymerization equals that of polymerization [20]. Various properties of the species contained in the system change accordingly during this process.
Many factors affect de-polymerization and polymerization processes. Among them, the quantity of silica available for reaction is one of the most essential ones. The more silica is available for the reaction, the more de-polymerization can occur given an unlimited amount of alkalis and hydroxyls [93]. As a result, more siloxanes in the silicon-oxygen network are destroyed to generate more alkali silicate. This results in an increasing amount of alkali silicate in the system promoting the polymerization process [21, 94, 95]. As a consequence of polymerization, the silicon-oxygen network gets more cross-linked [25, 95].

Moreover, de-polymerization and polymerization processes are also influenced by the contact time between the silica and the alkaline solution. The longer the contact time is, the more time for the interaction between silica and alkaline solution. Consequently, the more alkali silicate can be generated. For the silicon-oxygen networks in the system, de-polymerization predominates the system.
FORMATION OF ALKALI SILICATE IN THE CHEMICAL MODEL SYSTEM

at an early age; polymerization takes over and as the predominant effect at a later age. Eventually, depolymerization and polymerization reach an equilibrium.

Therefore, the reaction time as well as the quantity of silica strongly influences the interaction between reactive silica and alkaline solution. During this process, the properties of the alkali silicate present in the system change significantly. In the sequel of this chapter, the interaction between reactive silica and alkaline solution will be investigated to disclose the formation and further evolution of alkali silicate by evaluating various properties of the products.

4.2 Materials and Method

4.2.1 Preparation of Alkali Silicate Slurry

As stated in Chapter 3, the interaction between silica fume and 1 mol/L NaOH solution is used for simulating the first step of ASR where the reactive silica in aggregates interacts with the pore solution of cement paste. The silica fume simulates the reactive silica; the 1 mol/L NaOH solution simulates the alkaline solution. The preparation process is as follows:

a) 1 mol/L NaOH solution was added to the silica fume at a liquid to solid mass ratio of 3 to ensure sufficient silica for the partial silica dissolution [83]. This is similar to the situation in ASR [6];

b) The mixture of 1mol/L NaOH solution and silica fume was sealed in a polypropylene bottle, and filled with N₂ to prevent contamination;

c) The mixture was mixed with a rotary mixer (Figure 4.4 (a)) at a speed of 60 rpm at room temperature. This ensures the mixture was satisfactorily mixed without introducing impurities;

d) The mixing was stopped after the desired mixing time;

e) Sample collection.

Figure 4.4: (a) The rotary mixer; (b) the centrifuge; (c) the glove box.
4.2.2 Sample Collection and Treatment

4.2.2.1 Solid Sample

After the desired mixing time (0 hour, 1 hour, 6 hours, 12 hours, 18 hours, 24 hours and 48 hours), the bottle with mixture was taken off the rotary mixer for sample collection and other necessary treatment afterwards. Immediately after the mixture was taken off the rotary mixer, it was poured into a container filled with isopropanol to cease any further reactions in the chemical model system by removing the water. After 1 hour of immersion, the mixture of alkali silicate slurry and isopropanol was filtered with a funnel under vacuum to obtain the residue. Afterwards, the residue was immersed in isopropanol again for 24 hours for further stopping the reactions. In order to completely remove the water from the samples, the volume ratio of isopropanol to the collected alkali silicate slurry was about 100. After the desired storage time, the mixture was filtered again to remove isopropanol. In the end, the residue was vacuum dried for 4 days until it was ready for analysis.

The solvent-exchange drying method used in this study was thought to have the least influence on the microstructure of samples without introducing impurities [96, 97]. Notably, all the solid samples waiting for analysis after drying were stored in a plastic glove box (Figure 4.4 (c)) filled with N₂ to prevent any contamination.

4.2.2.2 Liquid Sample

The concentrations of silicon and hydroxyl in the system at different reaction times were measured with an Inductively Coupled Plasma coupled with Optical Emission Spectrometry (ICP-OES) and a pH meter, respectively. The alkali silicate slurries mixed for 0 hour, 1 hour, 6 hours, 12 hours, 18 hours, 24 hours and 48 hours were collected for analysis.

Notably, the conventional method of acquiring solution from slurry by filtering several times is time-consuming and prone to contamination. Accordingly, a method combining centrifuge and filtering was designed. The process is as follows:

a) After the desired reaction period, the mixture was poured into the container for centrifuge;

b) The container with the mixture was centrifuged at 3000 rpm for 3 minutes, the centrifuge machine is shown in Figure 4.4 (b);

c) After the centrifuge, the liquid layer located at the top was filtered twice through filter papers with particle retention of 12-15 µm first and 2 µm in sequence to get a clear solution for further analysis. This procedure was carried out in the glove box filled with N₂, as shown in Figure 4.4 (c);
d) The acquired solution was distributed evenly into two parts to analyze the concentrations of silicon and hydroxyl, respectively. This procedure was carried out in the glove box filled with $N_2$;

e) The samples were stored in a fridge at a temperature of 5 °C for 3 hours at most, until their analysis.

### 4.2.2.3 Acid-thermal Treatment

In order to evaluate the quantity of hydroxyl groups (-OH) in alkali silicate, an acid-thermal treatment proposed originally by Bulteel et al. [98] was followed with minor modification.

![Figure 4.5: Schematic representation of the acid-thermal treatment.](image)

According to Bulteel et al. [98] as schematically shown in Figure 4.5, a series reactions would occur once HCl solution is added to the alkali silicate slurry. After the neutralization of access OH$^-$ in the slurry with H$^+$ from HCl, additional H$^+$ will exchange with the incorporated alkalis in alkali silicate leading to the protonation of alkali silicate to form silanols and/or silicic acid. The newly formed -OH groups could be removed as water vapor by evaporation during the thermal treatment. Obviously, the accuracy of this method to evaluate the quantity of hydroxyl group in alkali silicate was highly influenced by the efficiency of protonation. Therefore, the volume ratio of the HCl solution to the alkali silicate slurry was set as about 100 to ensure the abundance of H$^+$ for a full protonation of alkali silicate.

The process of this treatment in detail is as follows:
a) After the desired mixing time, 40 g of alkali silicate slurry was poured into a container with a 0.5 mol/L HCl solution;
b) The mixture of alkali silicate slurry and HCl solution was mixed with a magnetic stirrer for 1 hour at room temperature;
c) When the mixing time was finished, the mixture was filtered with vacuum;
d) The residue was dried under vacuum for 4 days under room temperature;
e) After drying, the sample was heated up to 1000 °C in an oven at a rate of 10 K/min.

The mass difference before and after the thermal treatment is the mass of the water evaporated during the dehydration process. The quantity of hydroxyl group in alkali silicate can be calculated based on the mass difference. The calculation is shown in Equation 4.4, where $m_0$ denotes the mass of the sample before the thermal treatment (g); $m_T$ denotes the mass of the sample after thermal treatment (g); $M_{H_2O}$ denotes the molar mass of water (g/mol).

$$\text{Molarity of hydroxyl group per gram} = \frac{(m_0 - m_T)}{M_{H_2O} \times m_0}$$

Equation 4.4

4.2.3 Characterization Method

4.2.3.1 Solution Analysis

In order to study the dissolution of silica fume under alkaline environment, the concentration of silicon in the solution acquired from alkali silicate slurry was measured with an ICP-OES (Thermo ICAP 6500 Duo) device as shown in Figure 4.6 (a) at CENTEXBEL, Ghent, Belgium. The plasma settings were the following. RF power 1150W, pump rate 50 rpm, auxiliary gas flow 0.5 L/min, nebulizer gas flow 0.5 L/min, coolant gas flow 12 L/min, purge gas flow normal mode.

Aiming at investigating the consumption of OH\(^-\) due to its interaction with silica fume, the concentration of OH\(^-\) remaining in solution was calculated from the pH level measured with a pH meter (Metrohm 913, Figure 4.6 (b)) in a glove box filled with N\(_2\). The calibration of the pH meter was carried out by following the instructions given in the pH meter with three types of standard solutions having their pH level at 4, 7 and 10 respectively. The slope of the calibration curve is fitted as 94.83%. The waiting time for the stabilization of the display was not more than 2 minutes for each measurement.
4.2.3.2 Specific Surface Area Analysis

The specific surface area (SSA) of the solid product was measured with the nitrogen absorption method following the Brunauer-Emmett-Teller (BET) model with VacPrep 061 for the pre-vacuum treatment and TriStar 3000 for the measurement at Department of Inorganic and Physical Chemistry of Ghent University, Faculty of Sciences, Ghent University, as shown in Figure 4.6 (c).

Figure 4.6: (a) ICP-OES; (b) pH meter; (c) TriStar 3000.

4.2.3.3 Silicon-oxygen Network Analysis

In order to obtain information on the silicon-oxygen networks present in the system, $^{29}$Si solid-state cross-polarization (CP) / Magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra were acquired at ambient temperature on a Varian Inova 400 spectrometer (9.4 T wide bore magnet) [99], as shown in Figure 4.7, in 7 mm ceramic zirkonia rotors tightly closed with a double o-ringed Torlon end cap. Magic angle spinning was performed at 4 kHz. Both probe (12 l/min) and upper-barrel (12 l/min) cooling were used to avoid sample heating during the experiments. The signal of talc was used to determine the Hartmann-Hahn condition ($\omega_{1H} = \gamma_H B_{1H} = \gamma_{Si} B_{1Si} = \omega_{1Si}$) for cross-polarization and to calibrate the silicon chemical shift scale (-98.0 ppm). Acquisition parameters used were: a spectral width of 28.3 kHz, a 90° pulse of 7.9 $\mu$s, a spin-lock field for CP of 40 kHz, a contact time for cross-polarization of 1.5 ms, an acquisition time of 15 ms, a recycle delay time of 5 s and 20000-40000 accumulations. High power proton dipolar decoupling during the acquisition time was set to 65 kHz. The NMR tests were carried out in the group of Organic and Bio-Polymer Chemistry, Institute for Materials Research, University of Hasselt.
4.3 Results and Discussion

4.3.1 System Description

The appearance of the mixture mixed for 24 hours is shown in Figure 4.8 (a). The mixture is a black slurry composed of a liquid and a solid phase. After 24 hours of standing still, the appearance of the slurry is shown in Figure 4.8 (b), where the liquid phase at the top was slightly yellow while the solid precipitated at the bottom.

Figure 4.8: (a) Appearance of slurry; (b) appearance of mixture after being left at rest.
4.3.2 Concentration of Silicon and pH Level

The changes of the concentrations of silicon and hydroxyl during the interaction between silica fume and NaOH solution were measured with ICP-OES and pH meter, respectively. The results are shown in Figure 4.9.

As shown in Figure 4.9, the pH level of the solution drops significantly in the first 24 hours. This is caused by the consumption of OH\(^-\) during its interaction with silica fume. From 24h to 48h, the decrease of pH slows down. In particular, the pH level is about 12.2 at 24 h; the pH level is 11.8 at 48h. Accordingly, the concentration of OH\(^-\) is 0.006 mol/L when the pH is 11.8; the concentration of OH\(^-\) is 0.016 mol/L when the pH is 12.2. The concentration of OH\(^-\) provided by the NaOH solution at the very beginning was 1 mol/L. This indicates that most OH\(^-\) (98%) present in the solution has been consumed in the first 24 hours during which OH\(^-\) attacks the siloxanes and destroys the tetrahedral network of silica. Moreover, the pH level is lower than that of a saturation solution of Ca(OH)\(_2\) (pH=12.4) at about 19h, which is marked with a dotted line in Figure 4.9. It means that if Ca(OH)\(_2\) is present in this solution and the interaction between alkali silicate and calcium is ignored, the concentration of OH\(^-\) in this solution is low enough to trigger the dissolution of Ca(OH)\(_2\) to release Ca\(^{2+}\) and OH\(^-\) reaching saturation under these conditions.

The concentration of silicon measured by ICP-OES is the concentration of the dissolved alkali silicate in the solution. As shown in Figure 4.9, the concentration of silicon increases dramatically in the beginning and reaches a value of about 0.94 mol/L at 18h. From then on, the concentration of silicon experiences a slower increase to 1.03 mol/L at 24h and eventually 1.25 mol/L at 48h. This
indicates that most dissolved alkali silicate was formed and released into the solution in the first 18 hours. This is consistent with the results of the pH level, showing that a large amount of dissolved alkali silicate is released by the interaction between the silica fume and the NaOH solution resulting in a significant increase of silicon concentration and a dramatic decrease of pH level in the first 18 hours (Zone I). From 18h to 24h (Zone II), the increase of the concentration of silicon slows down indicating that the dissolved alkali silicate might approach its saturation. The pH level continues to decrease in the meantime suggesting a continuous consumption of OH\(^-\) during this period. This consumption is likely caused by both the limited interaction between OH\(^-\) and silica fume to form alkali silicate and the interaction between OH\(^-\) and the existing alkali silicate. Considering the minor increase of the concentration of silicon resulting from the formation of alkali silicate which newly enters the solution, the considerable decrease of the pH level during this period can be mainly attributed to the interaction between OH\(^-\) and the existing dissolved alkali silicate. From 24h to 48h (Zone III), the concentration of silicon and pH level experience little change suggesting the system is at an equilibrium at this moment.

Based on the above results, it is clear that as long as the interaction between the silica fume and the NaOH solution continues, OH\(^-\) in the solution is continuously consumed. As a result, the concentration of silicon in the solution which is representing the concentration of the dissolved alkali silicate, increases significantly until it approaches its saturation. Eventually, the system reaches an equilibrium when the concentrations of silicon and OH\(^-\) hardly change.

4.3.3 Silicon-oxygen Network

The evolution of the silicon-oxygen network, which is contained in both the silica fume as the reactant and the alkali silicate as the product, characterizes de-polymerization and polymerization processes during the interaction between the silica fume and the sodium hydroxide solution.

For the sake of convenience, it is necessary to introduce the standard notation of Q\(^n\) nomenclature to interpret the NMR spectra [81], as schematically shown in Figure 4.10. Q represents a given tetrahedron; the exponent n represents the number of associated bridges of oxygen with silicon. In this way, a Q\(^4\) tetrahedron has four oxygen bridges with silicon suggesting the existence of a complete interlinked silicon-oxygen organization, e.g. a 3D structure. A Q\(^3\) tetrahedron has three bridging oxygens and one non-bridging oxygen suggesting this tetrahedron has one bond available for bridging. Notably, the non-bridging oxygen can be bonded to another cation other than silicon, e.g. bonded to a proton to form an –OH group as indicated in Figure 4.10. A Q\(^2\) tetrahedron has two bridging oxygens and two non-bridging oxygens indicating the existence of a less cross-linked silicon-
oxygen network compared to $Q^3$. $Q^2$ is usually found to be present as part of a chain. A $Q^1$ tetrahedron has only one bridging oxygen with silicon and three non-bridging oxygens, which is usually found to be present at the end of a structure. $Q^0$ tetrahedron has four non-bridging oxygens and is usually present as monomer Si(OH)$_4$.

Figure 4.10: Schematic illustration of a $Q^n$ system.

Solid samples collected from the alkali silicate slurry at certain times (0 hour, 1 hour and 24 hours) were performed for $^{29}$Si NMR analysis. The NMR results are shown in Figure 4.11.

Figure 4.11: $^{29}$Si NMR results of the silicon-oxygen networks in alkali silicate slurry with different reaction times.
As shown in Figure 4.11, the silica fume contains $Q_2$, $Q_3$ and $Q_4$. In particular, the fraction of $Q_4$ is more than 60%, the fraction of $Q_2$ is about 21% and that of $Q_3$ is about 17%. This suggests the silica fume is mainly composed of the fully cross-interlinked silicon-oxygen network ($Q_4$) with some other species of $Q_3$ and $Q_2$. The possible appearance of the silicon-oxygen network of the silica fume is given in Figure 4.12, where the non-bridging oxygen in $Q_3$ and $Q_2$ are expected to be bonded with a proton as $–OH$.

Figure 4.12: Possible appearance of silicon-oxygen networks of silica fume with the proportion of $Q_2:Q_3:Q_4 = 1:1:3$ based on NMR results.

For the sample collected from the alkali silicate slurry after 1 hour of reaction, its NMR spectrum shifts downfield (the left) compared to that of silica fume indicating an ongoing de-polymerization featured by an increasing amount of $Q_2$ and $Q_3$ at the expense of $Q_4$. In particular, the fraction of $Q_4$ decreases from more than 60% in the silica fume to about 40% at 1h; the fraction of $Q_3$ increases from about 17% in the silica fume to about 23%; the fraction of $Q_2$ increases from about 21% in the silica fume to about 36%. Obviously, during this process, a large number of $Q_4$ (or even part of $Q_3$) are attacked by $OH$ to generate $Q_2$ leading to the formation of a less cross-linked silicon-oxygen network. As a result, the silicon-oxygen network is destroyed. Notably, $Q_4$ here could represent the unreacted silica fume present in the system.

For the sample collected from the alkali silicate slurry after 24 hours of reaction, the fraction of $Q_4$ decreases from about 40% to about 29%; the fraction of $Q_3$ increases significantly from about 23% to about 57%; the fraction of $Q_2$ decreases from 36% to about 13%. The decrease of the fraction of $Q_4$ confirms the ongoing de-polymerization process during which $Q_4$ is decomposed. The increase of the fraction of $Q_3$ can be caused by two effects: the de-polymerization of $Q_4$ and the polymerization of $Q_2$ [21]. Similarly, the decrease of the fraction of $Q_2$ can also be attributed to two processes: the de-polymerization of $Q_2$ to form $Q_1$ or $Q_0$, the polymerization of $Q_2$ to form $Q_3$. The processes of de-
polymerization and polymerization are schematically illustrated in Figure 4.13. However, the featured peaks assigned to Q\(^4\) and Q\(^6\) cannot be found in Figure 4.11. Therefore, the decrease of the fraction of Q\(^2\) is caused by its polymerization to form Q\(^3\). This conclusion is consistent with the results given in Figure 4.9, indicating that a low value of pH benefits the occurrence of polymerization [100]. In this sense, it is clear that the silicon-oxygen network present in the system at 24h is experiencing both depolymerization and polymerization making it more complex and cross-linked compared to that from the system at 1h [25, 95, 101].

![Figure 4.13: Schematic representation of de-polymerization and polymerization.](image)

Based on the above results and discussion, the evolution of the silicon-oxygen network during the interaction between silica fume and NaOH solution can be described as follows:

a) The silica fume is mainly composed of Q\(^4\), Q\(^3\) and Q\(^2\).

b) Once the silica fume is in contact with NaOH solution, siloxanes of the tetrahedral network of silica fume are decomposed by the attack of OH\(^-\) leading to the de-polymerization of the silicon-oxygen network. The de-polymerization predominates the system at 1h.

c) At 24h, the alkali silicate present in the system tends to interlink with each other to form a more polymerized alkali silicate resulting in the polymerization. Accordingly, a more complex and cross-linked silicon-oxygen network is formed.

### 4.3.4 Specific Surface Area (SSA\(_\text{BET}\)) and –OH Groups

During the interaction between the silica fume and the NaOH solution, the specific surface area (SSA\(_\text{BET}\)) and the quantity of the hydroxyl group contained in silicon-oxygen network will change accordingly. The results are shown in Figure 4.14.
As shown in Figure 4.1, SSA_{BET} increases with time. In the first 12 hours (Zone I), it slightly increases from about 19 m$^2$/g to about 23 m$^2$/g. In the next 6 hours from 12h to 18h (Zone II), SSA_{BET} increases significantly to about 37 m$^2$/g. From 18h to 48h (Zone III), SSA_{BET} slightly increases to about 44 m$^2$/g. Apparently, more surface areas accessible for N$_2$ are generated during the interaction between the silica fume and the NaOH solution. It is possible that the attack of OH$^-$ decomposes the silicon-oxygen network generating a more open microstructure which is more accessible for N$_2$. In the first 12 hours, the slight increase of SSA_{BET} is probably due to the limited contact of the siloxanes with the hydroxyls. Because the original silicon-oxygen network is probably able to protect the siloxane bonds located in the interior of the network from the attack of OH$^-$ limiting the increase of the SSA_{BET}. As the reactions proceed progressively, more and more siloxane bonds are destroyed. As a result, the network gets more and more open resulting in the exposure of more siloxane bonds which are originally located at the interior, to the attack of OH$^-$. This leads to a significant increase of SSA_{BET}. In the end, due to the decreased concentration of OH$^-$, the attack of OH$^-$ on the silicon-oxygen network slows down leading to the slight increase of SSA_{BET}.

The quantity of hydroxyl group contained in the silicon-oxygen network undergoes a similar but less significant increase during this process, compared to the SSA_{BET}. As indicated in Figure 4.1, in the first 12 hours (Zone 1), the quantity of hydroxyl group increases notably from 1.17 mmol/g to 2.98 mmol/g. From 12h to 48h (Zone 2), it increases slightly from 2.98 mmol/g to 3.20 mmol/g. This is generally consistent with the results of SSA_{BET}.

It should be noted that, the hydroxyl group is mainly generated by the breakage of siloxane bonds during de-polymerization; while be eliminated by the re-construction of siloxane bonds during
polymerization. It means that the quantity of hydroxyl group contained in the silicon-oxygen network is largely influenced by the factors affecting de-polymerization and polymerization processes.

4.3.5 Further Discussion on De-polymerization and Polymerization

De-polymerization and polymerization occur during the interaction between the silica fume and the NaOH solution. The de-polymerization predominates the silicon-oxygen network at the earlier age while the polymerization prevails at the later age. During de-polymerization, OH⁻ as well as alkalis from solution attacks the siloxane bonds of the silicon-oxygen network of silica fume leading to the reduction of the polymerization degree. As a result, the silicon-oxygen network present in the system is less cross-linked.

At the later age, the increase of content of alkali silicate contained in the system as well as the decreased pH level stimulates polymerization. During polymerization, the silanols present in alkali silicate tends to interlink with each other to generate siloxanes forming a more complex and disordered alkali silicate with a higher polymerization degree. It should be clarified that, the original silicon-oxygen network is destroyed during de-polymerization to form smaller species. During polymerization, those smaller species interlink with each other to construct a new silicon-oxygen network. Therefore, the de-polymerization and polymerization here are never a pair of reversible processes. The silicon-oxygen network formed from polymerization has a more complex and disorganized structure compared to the original one.

To summarize, during de-polymerization, hydroxyls and alkalis destroy the original silicon-oxygen network of silica fume leading to the formation of alkali silicate with a decreased polymerization degree at the early age. As polymerization starts to take over and eventually predominates the silicon-oxygen network present in the system, a more complex and dis-ordered silicon-oxygen network is generated by the re-construction of siloxane bonds at the later age.

4.4 Summary

In this chapter, the interaction between the silica fume and the NaOH solution is simulated in the proposed chemical model system and studied experimentally. The evolution of pH and silicon concentration in solution is measured with a pH meter and ICP-OES, respectively. The change of the silicon-oxygen network during this process were investigated with ²⁹Si NMR. The changes of the specific surface area and the content of hydroxyl groups of the samples were analyzed as well.
Based on the above results and discussion, the following concluding remarks can be made:

- During the interaction between the silica fume and the sodium hydroxide solution, the specific surface area and the quantity of the hydroxyl group contained in the solid phase increase accordingly; the concentration of silicon in the solution increases, while the concentration of $OH^-$ decreases.

- During the de-polymerization process at the early age of the interaction between the silica fume and the sodium hydroxide solution, the alkalis and hydroxyls decompose the siloxane bonds in the silicon-oxygen network leading to the destruction of the tetrahedral network of the silica fume. As a result, a less cross-linked silicon-oxygen network of alkali silicate is formed.

- Polymerization occurs at the later age. During this process, the alkali silicate formed from de-polymerization tends to interlink with each other to form a more cross-linked alkali silicate which has a more complex and dis-ordered silicon-oxygen network.
In this chapter, formation of calcium alkali silicate from the interaction between alkali silicate and calcium hydroxide is characterized through rheological, chemical and nano/micro structural approaches. The cause of the formation of a rigid structure from this interaction is particularly emphasized.
5.1 Background

5.1.1 Interaction Between Alkali Silicate and Calcium

Alkali silicate, as the product of the reaction between reactive silica and alkaline solution, can interact with calcium to form calcium alkali silicate. The corresponding equations are given by the sequence:

\[
\text{Equation 5.1} \quad \text{Ca}^{2+} + (\text{Si} - \text{O} \ldots \text{R}) \rightarrow (\text{Si} - \text{O} \ldots \text{Ca})^+ + \text{R}^+
\]

\[
\text{Equation 5.2} \quad (\text{Si} - \text{O} \ldots \text{Ca})^+ + (\text{Si} - \text{O} \ldots \text{R}) \rightarrow (\text{Si} - \text{O} \ldots \text{Ca} \ldots \text{O} - \text{Si}) + \text{R}^+
\]

where R denotes alkalis, e.g. sodium and potassium; both O...R and O...Ca mean the bonds are like a strong Van der Waals force [102]. Firstly, calcium exchanges with the alkali in the alkali silicate to get incorporated in the silicon-oxygen network releasing alkali to the solution simultaneously. Secondly, as a divalent cation, the calcium incorporated in an alkali silicate has one more place available for another incorporation as shown in Equation 5.2. It is clear that the alkalis released into solution are able to participate further reaction with the reactive silica. In this sense, this process has been related with the calcium-alkali recycling effect causing a continued expansion which is often found in an old concrete [103].

It is clear that calcium acts as a bridge to link two tetrahedrons [104]. Besides the calcium-alkali exchange process, the negatively charged surface charge (zeta potential) of the alkali silicate as the reactant and the calcium alkali silicate as the product can be partly neutralized due to the overcharging effect which is mentioned in Chapter 2 and elsewhere [42, 43]. This neutralization process can be visualized by the evolution of the zeta potential as a function of Ca\(^{2+}\) concentration in the system containing calcium alkali silicate, as shown in Figure 5.1. As a result, the repulsive forces between the particles of alkali silicate and calcium alkali silicate decrease and inevitably lead to the coagulation of the system [45, 46].
5.1.2 Coagulation and Rigidification

5.1.2.1 Coagulation

Coagulation is a process during which particles dispersed in a solution or sol get interconnect with each other to form a complex network due to the decrease of the repulsive forces between particles. This process can be evaluated by monitoring the change of the particle size. Clearly, the factors influencing the repulsive forces between particles can affect the process of coagulation. In the present study, it is the calcium supplied by the added calcium hydroxide that triggers and determines coagulation [54, 55]. From a mechanical point of view, the bonds formed during coagulation are too weak to endure a considerable mechanical stress. In addition, those bonds are easy to be rebuilt. This makes the coagulation process mechanically reversible [57, 58]. However, it does not mean there is no further evolution following coagulation. Rigidification usually occurs as the subsequent process of coagulation.

5.1.2.2 Rigidification

Rigidification describes a process during which the structures become stiff and rigid for a variety of reasons. In the present study, rigidification is caused by the formation of additional bonds, which increase the connectivity of network. Once it happens, additional bonds or particles form or precipitate to strengthen the existing network leading to an irreversible structure development [57, 58].
Compared to the bonds associated with coagulation, this type of bonds are much stronger and usually associated with the chemical reactions.

5.1.3 Structure Development

Based on the above introduction, the formation of calcium alkali silicate from the interaction between alkali silicate and calcium at the nano scale is linked with the structure development at the macro scale by the processes of coagulation and rigidification. Their relationship is described in Figure 5.2.

![Figure 5.2](image.png)

Figure 5.2: Schematic representation of the relationship between the reactions at nano scale and the structure development at macro scale.

At the nano scale, the physico-chemical reactions happening during the formation and evolution of calcium alkali silicate trigger and determine the generation and strengthening of the bonds between particles during coagulation and rigidification processes at the micro and meso scale. At the macro scale, the structure development of the system is largely influenced by the generation and evolution of the bonds in the network. Therefore, the reactions are directly connected with the structure development by the processes of coagulation and rigidification which are at the micro/meso scale. This is the key point to understand the methodology of the investigations in this chapter.
5.2 Materials and Methods

5.2.1 Materials and Sample Preparation

5.2.1.1 Alkali Silicate Slurry

The alkali silicate slurry was obtained by mixing the silica fume (Elkem 940U) with 1 mol/L of NaOH at a liquid to solid mass ratio of 3 on a rotary mixer. Detailed information about the materials and procedures to prepare the two types of alkali silicate slurries with different reaction times is given in Chapter 4. The first type of alkali silicate slurry has 1 hour of reaction time; the second one has 24 hours of reaction time. The detailed information about the properties of those two types of alkali silicate is also given in Chapter 4.

In the study of this chapter, those two types of alkali silicate slurries are chosen as the reactants of their interaction with calcium hydroxide paste at different proportions.

5.2.1.2 Ca(OH)$_2$ Paste

The Ca(OH)$_2$ (CH) paste was made to simulate the calcium source in real concrete where it is present both as Ca$^{2+}$ in the pore solution of the cement paste and as free CH in the matrix of cement paste especially near the aggregate surface [35]. The Ca$^{2+}$ present in the pore solution of cement paste is believed to be the form of calcium reacting with alkali silicate; the free CH is considered as the buffer of both Ca$^{2+}$ and OH$^{-}$. Once the concentrations of Ca$^{2+}$ and OH$^{-}$ are reduced due to their reactions, the free CH can compensate for this consumption by its dissolution as shown in Equation 5.3.

$$\text{Ca(OH)}_2 \rightarrow \text{Ca}^{2+} + 2\text{OH}^- \quad \text{Equation 5.3}$$

The Ca(OH)$_2$ paste was made by adding CH powder to 1 mol/L of NaOH solution at a liquid to solid mass ratio of 3, and mixing on a rotary mixer until its use. The 1mol/L of NaOH solution used here is to maintain a high pH level in the CH paste as well as a constant liquid to solid mass ratio. The CH paste made in this way contains both Ca$^{2+}$ with a small concentration and free CH dispersed in the paste. The mixing time for the CH paste to reach its uniformity before its use was set to 1 hour to limit the adverse influence of the structure development generated in the CH paste [105] on the measurement.

5.2.1.3 Addition of Ca(OH)$_2$ Paste to Alkali Silicate Slurry

After the desired mixing period for the two types of alkali silicate slurries (1 hour and 24 hours), different amounts of CH paste were added to the alkali silicate slurries. Immediately, the mixture was intensively mixed with a kitchen blender for 30 seconds to reach its uniformity in a short time. Afterwards, the mixture was mixed in the rotary mixer again at a rate of 60 rpm for 150 seconds to
remove the air bubbles introduced by the intensive mixing. Thereafter, the mixture was poured into the container of the rheometer for oscillatory measurement.

Table 5.1: Labels of the samples

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<thead>
<tr>
<th>Sample No.</th>
<th>Mixing time of alkali silicate slurry</th>
<th>Ca/Si ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1H-0.1</td>
<td>1 hour</td>
<td>0.1</td>
</tr>
<tr>
<td>S1H-0.3</td>
<td>1 hour</td>
<td>0.3</td>
</tr>
<tr>
<td>S24H-0.1</td>
<td>24 hours</td>
<td>0.1</td>
</tr>
<tr>
<td>S24H-0.3</td>
<td>24 hours</td>
<td>0.3</td>
</tr>
</tbody>
</table>

The labels of the different samples are given in Table 5.1. In particular, the quantity of the Ca(OH)$_2$ paste added to the two types of alkali silicate slurries was set to make the calcium to silicon mole (Ca/Si) ratio of the system as 0.1 and 0.3 respectively.

5.2.1.4 Sample Collection and Treatment

After the desired period of reaction, the samples from different systems were collected and used for further analysis. The time of the sample collection is shown in Figure 5.3. The collected samples were immediately immersed in isopropanol for 7 days to remove water, and therefore to stop the reactions. Afterwards, different treatments and preparations are conducted according to the requirements of the different measurements.

For the tests including X-ray Diffraction (XRD), Thermo Gravimetric Analysis (TGA) and $^{29}$Si Nuclear Magnetic Resonance (NMR), the samples were taken out of isopropanol and dried under vacuum for 7 days and grinded into powder until they were ready.

For the test of the Scanning Electron Microscope (SEM) equipped with Energy-dispersive X-ray Spectroscopy (EDS), the samples were dried for 2 weeks in a desiccator where Ca(OH)$_2$ and silica gel were present to prevent contamination. This is to avoid damage caused by vacuum drying to the microstructure. Thereafter, the samples were prepared by following the method proposed by Stutzman [106]. The appearance of the sample ready for SEM-EDS is shown in Figure 5.4 (a), the sample for XRD, TGA and NMR before and after grinding is shown in Figure 5.4 (b).
5.2.2 Characterization Methods

5.2.2.1 Oscillatory Rheology

During the structure development process induced by a series of physico-chemical reactions between alkali silicate and calcium, the generation and evolution of the bonds between particles have an extremely huge influence on the establishment and growth of the network which affects the response of a material to an applied stress. Therefore, the generation and evolution of the bonds between particles constituting the network during the physico-chemical interaction at the micro scale can be characterized with the mechanical response of the system to an externally applied stress. It
means Link 2 as indicated in Figure 5.2 can be clarified. This research is completely within the scope of rheology, especially the oscillatory rheology [107].

In the light of this consideration, oscillatory rheology measurements were carried out to characterize the formation and evolution of the bonds with the structure development at the macro scale. In this subsection (5.2.2.1), the theoretical background of oscillatory rheology and its application to the present study are introduced. The experimental setup, parameters and program for the measurement are given afterwards.

(1) Rheology and Oscillation

Theoretically, the buildup of a structure can be measured using two techniques of rheology:

(a) Static Yield Stress Measurement

Static yield stress measurement aims at studying the buildup of a structure during a certain period before the rigidification occurs. In its application to a cementitious material, the timespan of the process is estimated from about 15 minutes to 60 minutes after the mixing of cement with water. Therefore, only the coagulation process is taken into account for static yield stress measurement [108]. The subsequent rigidification process resulting in the growth and strengthening of the network is out of consideration. Accordingly, the static yield stress measurement does not meet the demand of the present research.

(b) Oscillation Measurement

In this technique, a minor amplitude oscillatory stress is applied to the material. By measuring the mechanical response of the material to the stress, the mechanical properties of the material are obtained. In order to describe this process, the complex shear modulus $G^*$ which is composed of two conceptual factors: storage modulus $G'$ and loss modulus $G''$, are introduced. The storage modulus $G'$ is responsible for the elastic part of the response of a material; the loss modulus $G''$ is responsible for the viscous part of the response of a material.

By setting the value of the applied stress at an appropriate level, the “weak” bonds of the network can be completely destroyed without disturbing the “strong” ones. In this way, the coagulation associated with the “weak” bonds can be differentiated from the rigidification associated with the “strong” bonds. Simultaneously, the structure development can be characterized by evaluating the evolution of storage modulus and loss modulus.
Therefore, oscillatory rheology measurement is capable of evaluating the generation and evolution of the bonds induced by the physico-chemical reactions between alkali silicate and calcium, as well as its influence on the structure development in the present study.

(2) Experimental Parameters

The parameters involved in this process and their relationships are given as follows:

\[ \sigma = \sigma_0 \cdot \cos(\omega \cdot t) \]  
\[ \gamma = \gamma_0 \cdot \cos(\omega \cdot t - \delta) \]  
\[ \sigma(t) = G^\star(\omega) \cdot \gamma(t) \]  
\[ G^\star = \frac{\sigma_0}{\gamma_0} \cdot (\cos \delta + i \cdot \sin \delta) \]  
\[ G^\star = G' + i \cdot G'' \]

- \( \sigma \): Oscillatory stress [Pa]
- \( \sigma_0 \): Amplitude of the applied stress [Pa]
- \( \omega \): Angular velocity [1/s]
- \( t \): Time [s]
- \( \gamma \): Resultant oscillatory strain [null]
- \( \gamma_0 \): Amplitude of the resultant strain [null]
- \( \delta \): Phase lag between the applied oscillatory stress and the resultant oscillatory strain [null] 
  \((0 < \delta < \pi/2)\)
- \( G^\star \): Complex shear modulus [Pa]
- \( G' \): Storage modulus [Pa]
- \( G'' \): Loss modulus [Pa]

(3) Measuring Setup

In this measurement, an Anton Paar MCR 201 rheometer with a vane was used. The setup is shown in Figure 5.5.
(4) Measuring Program

The measurement consists of 6 cycles, each of them contains two stages: the strain sweep for the breakage of “weak” bonds; the time sweep for the buildup of both “weak” and “strong” bonds. The strain sweep lasts for 1 minute, the time sweep lasts for 9 minutes. So 1 cycle of the measurement lasts for 10 minutes; the whole measurement consisting 6 cycles lasts for 1 hour in total. The duration of the measurement is strictly limited with the consideration of avoiding the damage caused by too much rigidification of the sample to the rheometer. This program is shown in Figure 5.6.
During the breakage stage, an amplitude strain up to 100% is applied to the material to destroy only the “weak” bonds between particles. Notably, the maximum amplitude strain is set to be larger than the critical amplitude strain of this material to ensure the complete removal of the “weak” bonds which are associated with coagulation while not destroying the “strong” bonds which are associated with rigidification. Afterwards, during the measurement in the buildup stage, a minor strain of 0.1%, which is much below the critical amplitude strain was applied to the measured material to obtain the mechanical response of the material without disturbing any bond contained in the material.

By measuring the storage modulus $G'$ and loss modulus $G''$ throughout all the cycles, the formation and evolution of the bonds between particles resulting in the structure development, as well as the viscosity of the material, can be characterized from a mechanical point of view.

Notably, $G'_{\text{max}}$ of each buildup stage is the last measuring point of the corresponding buildup stage as indicated in Figure 5.6. $G'_{\text{min}}$ of each buildup stage is the 10th measuring point of the next buildup stage after the breakage stage as indicated in Figure 5.6. Because the minimum storage modulus of a buildup stage can only be obtained in a relatively stable system after removing all the weak bonds during the breakage stage.
5.2.2.2 XRD Analysis

XRD measurements were carried out to identify crystalline phases by using a Thermo Scientific ARL X’tra Diffractometer equipped with a Peltier cooled detector at a scanning rate of 0.8 °/min from 5 ° to 70 ° at the Department of Inorganic and Physical Chemistry, Ghent University. The setup is shown in Figure 5.7.

![Figure 5.7: Thermo Scientific ARL X’tra Diffractometer equipped with a Peltier cooled detector.](image)

5.2.2.3 TGA Analysis

TGA/DTA tests were carried out to identify specific phases by quantifying the mass loss at different temperatures with a NETZSCH STA 449 F3 Jupiter thermal analyzer at the Department of Inorganic and Physical Chemistry, Ghent University, as shown in Figure 5.8. During the measurements of TGA/DTA, the samples were heated from room temperature to 1000°C at a rate of 10 K/min under N₂ atmosphere to avoid any contamination.
With the curves of TGA results, the amounts of CH and calcite present in the samples collected at different reaction time can be calculated based on their mass loss ranging from about 400 °C to 500 °C and about 600 °C to 800 °C, respectively. The corresponding equations are given as follow:

\[ \text{Ca(OH)}_2 \rightarrow \text{CaO} + \text{H}_2\text{O} \]
\[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \]

For the calculation of the mass loss from the TGA curves, a tangent method [110] was used for the determination of the mass loss due to the decompositions of specific phases. An example of using this method to analyze the TGA results is given in Figure 5.9.
Although most steps in the present study were carried out in a glove box filled with N₂, the presence of calcite caused by carbonation (see Equation 5.11) can still be found according to its typical mass loss ranging from 600 °C to 750 °C in Figure 5.9. This inevitably influences the evaluation of the quantity of CH remaining in the system. In the light of this consideration, a correction to the CH content was carried out in the present study by taking into account the quantity of CH consumed by carbonation. The calculation method of this correction is given by Equation 5.12. However, it should be noted that the correction was only used for evaluating the total consumption of CH rather than obtaining the quantity of CH remaining in the system. Because calcium carbonate cannot easily provide Ca²⁺ for its interaction with any other components. It means the calcium carbonate can be considered as an inert phase in the system.

\[
\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}
\]  
Equation. 5.11

\[
n_{\text{CH}} = \Delta \text{CH} \times \frac{\text{M}_{\text{CH}}}{\text{M}_{\text{H}_2\text{O}}} + \Delta \text{CC} \times \frac{\text{M}_{\text{CH}}}{\text{M}_{\text{CO}_2}}
\]  
Equation. 5.12

where:

- \(n_{\text{CH}}\): total molar of \(\text{Ca(OH)}_2\);
- \(\Delta \text{CH}\): mass loss (in mol) due to dehydration of \(\text{Ca(OH)}_2\);
- \(\Delta \text{CC}\): mass loss (in mol) due to de-carbonation of calcite;
- \(\text{M}_{\text{CH}}\): molar mass of \(\text{Ca(OH)}_2\), equals 74 g/mol;
- \(\text{M}_{\text{H}_2\text{O}}\): molar mass of \(\text{H}_2\text{O}\), equals 18 g/mol;
$M_{\text{CO}_2}$: molar mass of CO$_2$, equals 44 g/mol.

5.2.2.4 $^{29}$Si NMR Analysis

$^{29}$Si NMR analysis was used for investigating the evolution of the silicon-oxygen network present in the system throughout the physico-chemical reactions between alkali silicate and calcium. The setup and parameters of the measurement have already been given in Chapter 4.

5.2.2.5 SEM-EDS Analysis

After the preparation of the sample for electron scanning microscopy by following the procedures proposed by Stutzman [106], back-scattered electron (BSE) images of the selected regions of the samples from different systems were obtained by using JEOL JSM-5600 instrument equipped with a BSE detector at the Department of Materials Science and Engineering of Ghent University, operating at an acceleration voltage of 20 kV, as shown in Figure 5.10 (d) and Figure 5.10 (e) where the mould for impregnation, instruments for carbon coating and polishing are given in Figure 5.10 (a)-(c), respectively. The BSE images were used for morphology inspection and porosity analysis. Elemental mapping analysis, including calcium, silicon and sodium, were also conducted on those selected regions to reveal the elemental distribution by using the SEM equipped with EDS.
5.3 Results and Discussion

5.3.1 Oscillatory Rheology

In this section, the evolution of the properties related to oscillatory rheology of the systems were investigated through different aspects, which are given as follows.

The porosity analysis based on BSE images has been carried out in the present study to investigate the evolution of microstructure. A method called overflow [111] was used for determining the upper threshold of the grey level of porosity. In order to ensure the representativity of the images, 20 BSE images were taken for each sample for the porosity analysis.
5.3.1.1 Evolution of Storage Modulus and Loss Modulus

The evolutions of storage modulus and loss modulus of each sample throughout the measuring period were obtained. For each sample, in the first place, the evolutions of both storage modulus and loss modulus during the buildup stages are given; afterwards, the evolution of both storage modulus and loss modulus during the breakage stages are given. In this way, a general impression about this process from an oscillatory rheological point of view can be obtained.

In Figure 5.11, the evolution of the storage modulus of S1H-0.1 is given. The time sweep of the buildup stage and the strain sweep of the breakage stage are indicated as well as the maximum storage modulus of the buildup stage from 1800 s to 2400 s and the minimum storage modulus of the buildup stage from 3000 s to 3600 s.

![Figure 5.11: Evolution of the storage modulus of S1H-0.1 (interaction between alkali silicate (1 hour) and CH at Ca/Si = 0.1) during the buildup stages.](image)

As shown in Figure 5.11, after each breakage step, the storage modulus increases dramatically indicating that the structure is generated rapidly during this period. In addition, the maximum values of the storage modulus of all the buildup stages are similar. This suggests that the quantities of the structure newly formed during each buildup stage are comparable with each other.

The evolution of the loss modulus of S1H-0.1 during the buildup stages is presented in Figure 5.12. The time sweep of the buildup stages and the strain sweep of the breakage stages are indicated as well.
As shown in Figure 5.12, the loss modulus increases within each buildup stage after the strain sweep. This indicates that the viscosity of the system increases during the buildup stages after the breakage stages. The similar increasing trend of the loss modulus within the buildup stages suggests that the evolution of the viscosity is similar to that of the structure development.

The evolutions of the storage modulus and loss modulus during the strain sweep of the breakage stages are shown in Figure 5.13. This approach ensures the complete destruction of the reversible (weak) bonds between the particles of the structure.
According to the evolutions of $G'$ and $G''$ during the breakage stages shown in Figure 5.13, a general trend and feature can be found. Both $G'$ and $G''$ decrease throughout a breakage stage at
different rates. Eventually, they intersect with each other at a certain value of strain amplitude. Before the intersection, $G'$ is larger than $G''$ indicating the system is solid-like; after the intersection, $G''$ is larger than $G'$ indicating the system is liquid-like. This transition confirms that, the purpose of destroying the weak bonds associated with the reversible mechanical process of coagulation has been reached. The intersecting point is the critical strain amplitude for the system. The information provided by these results helps us to separate the strong bonds between particles resulting in the irreversible mechanical process of rigidification from the weak bonds leading the reversible mechanical process of coagulation.

The evolutions of the storage modulus and loss modulus in the buildup and breakage stages of S1H-0.3, S24H-0.1 and S24H-0.3 are given in Appendix A.

In this subsection, the evolution of the storage modulus and the loss modulus during the buildup stages and the breakage stages has been investigated. Both the storage modulus and loss modulus increase significantly in the buildup stages while decrease during the breakage stages. A critical strain amplitude has been reached in every breakage stage, ensuring the complete destruction of the weak bonds which is associated with the reversible mechanical process of coagulation. In this way, the coagulation can be differentiated from the rigidification.

In the following subsections, further investigations will be carried out on the key factors characterizing and determining the structure development due to the interaction between alkali silicate and calcium.

### 5.3.1.2 Total Structure Development

The structure development induced by the interaction between alkali silicate and calcium can be characterized by the evolution of the maximum and minimum storage modulus during the buildup stages. The maximum storage modulus ($G'_{\text{max}}$) is related with the generation of the bonds during the process of structure development. The minimum storage modulus ($G'_{\text{min}}$) is related to the generation of the strong bonds which are associated with the rigidification process. It means, $G'_{\text{max}}$ represents the total structure development; $G'_{\text{min}}$ represents the irreversible structure development; $(G'_{\text{max}} - G'_{\text{min}})$ represents the reversible structure development. The total structure development will be studied firstly.

As shown in Figure 5.14, the evolutions of the maximum storage modulus of S1H-0.1, S1H-0.3, S24H-0.1 and S24H-0.3 are given. Clearly, the evolutions of the maximum storage moduli of different samples have different trends.
Figure 5.14: Evolutions of total structure development ($G'_\text{max}$).

(1) $S24H\text{-}0.3$

As shown in Figure 5.14, the $G'_\text{max}$ of $S24H\text{-}0.3$ (24 hours, Ca/Si = 0.3) increases from about 50 KPa to about 90 KPa in the second buildup stage. Subsequently, it decreases continuously to about 70 KPa at the end of the last buildup stage of the measurement.

Compared to other samples, $S24H\text{-}0.3$ has the largest $G'_\text{max}$ throughout the measurement. This indicates that $S24H\text{-}0.3$ had the most structure development during all the buildup stages. Bearing in mind that the structure development is induced by the interaction between alkali silicate and calcium, therefore, the physico-chemical reactions in $S24H\text{-}0.3$ produced the most structure development among all the samples. Notably, the structure development described by $G'_\text{max}$ is the structure generated by the formation of both the weak bonds which are associated with coagulation and the strong bonds which are associated with rigidification.

The trend of the evolution of $G'_\text{max}$, as shown in Figure 5.14, increases in the second buildup stage and decreases in the rest stages. This suggests the generation of structure resulted from the physico-chemical reactions reached its maximum in the second buildup stage and slowed down in the later stages.
(2) S24H-0.1

The $G'_{\text{max}}$ of S24H-0.1 (24 hours, Ca/Si = 0.1) increases at a constant rate from about 15 KPa at the end of the first buildup stage to about 50 KPa at the end of the last buildup stage of the measurement. It means a continuous structure development with a constant rate is happening during this period.

Compared to other samples, S24H-0.1 has the second largest $G'_{\text{max}}$. This suggests the structure development in S24H-0.1 is less than that in S24H-0.3 while more than the structure development in other samples. Considering less CH was added to the system of S24H-0.1 compared to S24H-0.3, it is clear that the more calcium is added, the more structure development can be expected given the alkali silicate having 24 hours of reaction. Therefore, on the one hand, the dramatic increase of $G'_{\text{max}}$ during the second buildup stage in S24H-0.3 is probably caused by the abundant presence of CH available for its interaction with alkali silicate eventually leading to more structure development compared to S24H-0.1. On the other hand, the decrease of $G'_{\text{max}}$ during the later buildup stages in S24H-0.3 is perhaps caused by the deceleration of the physico-chemical reactions between alkali silicate and calcium due to the consumption of reactants.

(3) S1H-0.1

The $G'_{\text{max}}$ of S1H-0.1 (1 hour, Ca/Si = 0.1) slightly increases from about 14 KPa to about 15 KPa throughout the measurement. This indicates little structure development is generated in this sample during this period.

Compared to S24H-0.1 which had the same amount of CH added to the system, S1H-0.1 has a much smaller value of $G'_{\text{max}}$ throughout the process. This means that not only the quantity of CH but also the type of alkali silicate, influences the structure development in the system. According to the information given in Table 5.1, two types of alkali silicate are used for reactions: the one obtained by reacting silica fume with 1 mol/L of NaOH solution for 24 hours and the one for only 1 hour, respectively. Based on the above comparison between S24H-0.1 and S1H-0.1, the structure development is favored by the alkali silicate which is made by reacting silica fume with 1 mol/L of NaOH solution for 24 hours, given a certain amount of CH. Additional information needs to be disclosed for further investigation.

(4) S1H-0.3

As shown in Figure 5.14, the $G'_{\text{max}}$ of S1H-0.3 (1 hour, Ca/Si = 0.3) slightly increases from about 7 KPa to about 8 KPa during the measurement. Clearly, S1H-0.3 has the smallest $G'_{\text{max}}$ throughout the
measurement. This indicates that the least amount of structure development is created during this period.

Compared to S1H-0.1 having the same type of alkali silicate, more CH is added to the system of S1H-0.3. However, more addition of CH in S1H-0.3 does not lead to a higher $G'_\text{max}$ than that of S1H-0.1 as we proposed after the comparison between S24H-0.1 and S24H-0.3. On the contrary, $G'_\text{max}$ of S1H-0.3 is much smaller than that of S1H-0.1. This suggests that different reaction mechanisms are responsible for the different processes of structure development in the systems with two types of alkali silicate. This is confirmed by the comparison between S1H-0.3 and S24H-0.3 having the same amount of CH added to two types of alkali silicate slurry.

A hypothesis can be proposed to explain these findings as follows. For S24H-0.1 and S24H-0.3, the alkali silicate formed after 24 hours is reactive enough to interact with calcium as much as possible once it is added. It means the reactive alkali silicate is relatively abundant with respect to the quantity of the added CH. As a result, the more calcium is added to the system, the more physico-chemical reactions occur and consequently the more structure development is generated. For S1H-0.1 and S1H-0.3, the alkali silicate formed after 1 hour is much less reactive than the one in S24H-0.1 and S24H-0.3 according to the results in Chapter 4. Hence, there is not enough reactive alkali silicate to react with the added calcium. Consequently, the physico-chemical reactions between alkali silicate and calcium in the system of S1H-0.1 and S1H-0.3 are not enough to produce structure development.

In addition, considering the method of adding CH paste, another factor probably influences the structure development as well: the more CH is added, the more NaOH solution is introduced to the system to keep the liquid to solid mass ratio constant. This extra solution inevitably has a diluting effect on the process of structure development, once it cannot be offset by the extra structure development generated by the physico-chemical reactions between alkali silicate and the extra calcium added to the system. Notably, additional results will be provided in the rest of the present chapter to verify this hypothesis.

(5) Remarks About Total Structure Development

The structure development resulting from the generation of both weak bonds and strong bonds during the physico-chemical reactions between alkali silicate and calcium is characterized by the evolution of $G'_\text{max}$. Generally speaking, $G'_\text{max}$ increases as a function of time for each sample. S24H-0.3 has the largest $G'_\text{max}$ which significantly increases at the early age and slightly decreases at the later age. S1H-0.3 has the smallest $G'_\text{max}$ which hardly increases throughout the measurement.
The influence of the type of alkali silicate and the quantity of calcium on $G'_\text{max}$ is explained with the proposed hypothesis concerning the mechanism of the interaction between alkali silicate and calcium contributing to the consequent structure development.

Bearing in mind that the structure development defined by $G'_\text{max}$ is contributed by both the weak bonds which are associated with coagulation and the strong bonds which are associated with rigidification. It means that the irreversible structure development associated with the generation of the strong bonds including chemical ones is overshadowed by the reversible structure development. This consideration will be addressed in the following subsection.

5.3.1.3 Irreversible Structure Development

The evolution of the minimum storage modulus ($G'_\text{min}$) which is the 10$\text{th}$ point of each buildup stage is given in Figure 5.15. After each strain sweep of the breakage stage, the reversible structure development associated with the weak bonds present in the system is completely removed. Therefore, the measured $G'_\text{min}$ at this moment represents the irreversible structure development associated with the strong bonds remaining in the system. In the light of this consideration, the evolution of the irreversible structure development during the buildup stages can be characterized by $G'_\text{min}$ as follows.

![Figure 5.15: Evolution of irreversible structure development ($G'_\text{min}$).](image-url)
(1) $S24H-0.3$

$G'_{\text{min}}$ represents the irreversible structure development remaining in the system after the strain sweep of breakage stage. In this sense, the $G'_{\text{min}}$ measured at the beginning of the 2nd buildup stage actually represents the irreversible structure development in the 1st buildup stage; the $G'_{\text{min}}$ measured at the beginning of the 3rd buildup stage represents the irreversible structure development in 1st and 2nd buildup stage and so on.

As shown in Figure 5.15, $G'_{\text{min}}$ of S24H-0.3 increases dramatically from about 40 KPa at the beginning of the 1st buildup stage to 45 KPa at the beginning of the 2nd buildup stage. Subsequently, it slightly increases to about 47 KPa at the beginning of the 3rd buildup stage. Eventually, it decreases a little to about 43 KPa. This indicates that the physico-chemical reactions between alkali silicate and calcium occurring in the 1st buildup stage contributes the most to the irreversible structure development. In the later stages, there is hardly any additional irreversible structure development generated.

Compared to the other samples, S24H-0.3 has the largest $G'_{\text{min}}$ throughout the measurement except the first point. This indicates that the most irreversible structure development is generated in S24H-0.3 among all the samples. Regarding the first point, it is still too soon for the irreversible structure development to be generated.

(2) $S24H-0.1$

$G'_{\text{min}}$ of S24H-0.1 increases at a relatively constant rate from about 5 KPa at the beginning of the 1st buildup stage to about 20 KPa at the beginning of the last buildup stage. This indicates the irreversible structure is continuously generated from the physico-chemical reactions between alkali silicate and calcium throughout the measurement.

Compared to the other samples, S24H-0.1 has the second largest value of $G'_{\text{min}}$ except the first point. This suggests the irreversible structure development in S24H-0.1 is less than that in S24H-0.3 but more than that in the other samples.

Compared with S24H-0.3 having the same type of alkali silicate, less CH is added to S24H-0.1. This results in less irreversible structure development in S24H-0.1 than that in S24H-0.3. This is consistent with the finding from the comparison between $G'_{\text{max}}$ of S24H-0.1 and S24H-0.3. It is clear that both $G'_{\text{max}}$ and $G'_{\text{min}}$ are favored by the increase of calcium addition, given the same type of alkali silicate used in S24H-0.1 and S24H-0.3.
(3) S1H-0.1

According to the results shown in Figure 5.15, the $G'_\text{min}$ of S1H-0.1 (1 hour, Ca/Si = 0.1) increases very little from about 6 KPa at the beginning of the 1st buildup stage to about 7 KPa at the beginning of the last buildup stage. This suggests limited irreversible structure is generated throughout the measurement.

Compared to S24H-0.1 having the same amount of CH addition, $G'_\text{min}$ of S1H-0.1 is much lower than that of S24H-0.1. This means the alkali silicate with higher reactivity in S24H-0.1 also benefits the development of irreversible structure. Notably, this is consistent with the findings from the comparison between the $G'_\text{max}$ of S24H-0.1 and S1H-0.1.

(4) S1H-0.3

As the smallest $G'_\text{min}$ among all the samples, the $G'_\text{min}$ of S1H-0.3 increases very little from about 4 KPa at the beginning of the 1st buildup stage to about 5 KPa at the beginning of the last buildup stage. This means that little irreversible structure is generated from the physico-chemical reactions between alkali silicate and calcium in S1H-0.3.

Compared to S1H-0.1 having the same type of alkali silicate, more CH was added to S1H-0.3. Compared to S1H-0.1, the more CH is added, the smaller the $G'_\text{min}$ is and consequently the less the irreversible structure is generated in S1H-0.3. This trend is opposite with that found from the comparison between S24H-0.1 and S24H-0.3. However, this is consistent with the trend found from the comparison between the $G'_\text{max}$ between S1H-0.1 and S1H-0.3. Therefore, the proposed hypothesis explaining the influence of alkali silicate and calcium on the structure development which is represented by $G'_\text{max}$, also works on explaining the findings about the irreversible structure development.

(5) Remarks Regarding Irreversible Structure Development

The irreversible structure development is characterized by $G'_\text{min}$. The proposed hypothesis for the influence of alkali silicate and calcium on the structure development which is defined by $G'_\text{max}$ is also valid for explaining the findings of $G'_\text{min}$. The more reactive alkali silicate is present in the system; the more irreversible structure is generated given the same amount of the added CH. The more CH is added to the system; the more irreversible structure is generated given the alkali silicate with high reactivity. The system containing the alkali silicate with low reactivity generates limited irreversible structure development regardless the quantity of the added CH.
5.3.1.4 Reversible Structure Development

After investigating the total structure development and irreversible structure development during buildup stages, the reversible structure development which is associated with the generation of the weak bonds can be characterized with $G'_{\text{max}}$ and $G'_{\text{min}}$. The reversible structure development can be calculated with Equation 5.13:

$$\text{Reversible structure development} = \text{total structure development (} G'_{\text{max}} \text{)} - \text{irreversible structure development (} G'_{\text{min}} \text{)}$$  

Equation 5.13

In this way, the reversible structure development during buildup stages is plotted in Figure 5.16. It is important to note that, each point marked in the figure represents the reversible structure development in each buildup stage.

![Figure 5.16: Evolution of reversible structure development ($G'_{\text{max}} - G'_{\text{min}}$).](image)

For S24H-0.3, its reversible structure development continuously decreases from about 50 KPa to about 25 KPa at the end of measurement. This indicates that less and less reversible structure development is generated due to the deceleration of the physico-chemical reactions between alkali silicate and calcium. This trend confirms the results of total structure development and irreversible structure development given in the previous subsections, showing that the generation of structure development slows down at the later age of the measurement. In particular, the irreversible structure
development is rarely generated while less and less reversible structure development is created in the meantime.

For S24H-0.1, its reversible structure development increases from about 10 KPa to about 30 KPa at the end of the measurement. It means more and more reversible structure development is generated during the measuring period due to the physico-chemical reactions between alkali silicate and calcium. This is consistent with the trend of the evolution of its total structure development and irreversible structure development, both of which experience a constant increase throughout the measurement. Compared to S24H-0.3 having the same type of alkali silicate, less calcium is added to S24H-0.1. It means less calcium is provided for its interaction with alkali silicate. Unlike the results of irreversible structure development, the reversible structure development of S24H-0.1 is comparable with that of S24H-0.3 at the end of the measurement. This indicates the reversible structure development is less influenced by the quantity of the added calcium compared to the irreversible structure development.

For S1H-0.1, its reversible structure development slightly decreases from about 9 KPa to about 7 KPa at the end of the measurement. This indicates the reversible structure development in S1H-0.1 is limited. Compared to S24H-0.1 having the same amount of added CH, the reversible structure development of S1H-0.1 is much less than that of S24H-0.1. This suggests that the type of alkali silicate (the reactivity of alkali silicate) influences not only the total structure development and irreversible structure development, but also the reversible structure development.

For S1H-0.3, its reversible structure development hardly changes from its value of about 3 KPa at the beginning of the measurement. It means there is nearly no additional reversible structure development generated in the later buildup stages. This is consistent with the results of the total structure development and the irreversible structure development given in the previous subsections.

5.3.1.5 Remarks of Oscillatory Rheology

In the previous subsections, the oscillatory rheology results have been presented. The influence of alkali silicate and CH on the structure development due to the interaction between alkali silicate and calcium has been investigated. The relationship between the physico-chemical reactions and the structure development has been discussed.
5.3.2 Consumption of Ca(OH)₂

As can be seen in the previous section (5.3.1) regarding the structure development measured by oscillatory rheology, calcium plays an extremely essential role of triggering and governing the coagulation and rigidification processes of the system. In the light of this, the presence and content of calcium remaining in the system is one of the most critical factors to be studied.

Considering the calcium present in the system is introduced externally by adding CH paste to the alkali silicate slurry, the content of CH remaining in the system reflects its consumption during its interaction with alkali silicate. Therefore, the physico-chemical reactions between alkali silicate and calcium can be evaluated. XRD and TGA were combined to provide qualitative and quantitative investigation on the content of CH remaining in the system.

5.3.2.1 Qualitative Analysis

For the sake of accuracy and efficiency of analysis, qualitative analysis was used for checking the presence of CH and calcite with XRD. Only the samples containing CH and calcite were sent for TGA measurement for quantitative analysis. The results of the qualitative analysis to check the presence of CH and calcite of all samples by XRD patterns are given in Table 5.2.

Table 5.2: Presence of Ca(OH)₂ and calcite checked by XRD.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Time [hour]</th>
<th>Presence of Ca(OH)₂ / calcite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.05</td>
<td>1</td>
</tr>
<tr>
<td>S1H-0.1</td>
<td>V/V</td>
<td>V/V</td>
</tr>
<tr>
<td>S1H-0.3</td>
<td>V/V</td>
<td>V/V</td>
</tr>
<tr>
<td>S24H-0.1</td>
<td>V/V</td>
<td>V/x</td>
</tr>
<tr>
<td>S24H-0.3</td>
<td>V/V</td>
<td>V/V</td>
</tr>
</tbody>
</table>

* “V/x” means the presence of Ca(OH)₂ and the absence of calcite according to the XRD results.
According to the results given in Table 5.2, the presence of CH and calcite in the samples can be obtained. It should be noted that the samples (S1H-0.3 at 72h) are found to contain only calcite. It means no additional calcium can be provided by CH once it is consumed by its interaction with alkali silicate at an early age, since the calcium contained in the calcite is “locked” and cannot be released in an alkaline environment.

Figure 5.17: Overview of TGA results.

As shown in Figure 5.17 where the TGA curves are given, the typical mass loss assigned to the decomposition of CH and calcite can be found. Generally speaking, the content of CH present in the system decreases as a function of time indicating the continuous consumption of CH by giving Ca$^{2+}$ to interact with alkali silicate. The visual inspection about the typical mass loss assigned to the decomposition of CH and calcite is consistent with the XRD results given in Table 5.2.

5.3.2.2 Quantitative Analysis

With the quantitative analysis of the TGA results, the content of CH can be obtained, as shown in Figure 5.18.
Figure 5.18: Content of CH remaining in the samples.

For S1H-0.3, it contains the most CH remaining in the system compared to other samples throughout the measurement. The CH present in S1H-0.3 has not been completely consumed until 72h. It means that CH is able to continuously supply Ca$^{2+}$ to its interaction with alkali silicate until 72h in this sample.

For S24H-0.3, the same amount of CH was added to the system compared to S1H-0.3. However, the content of CH remaining in the system is much less than that in S1H-0.3 indicating more CH has been reacted in S24H-0.3 than that in S1H-0.3. This is caused by the different reactivity of the two
types of alkali silicates used in S1H-0.3 and S24H-0.3. The alkali silicate in S24H-0.3, which was made by reacting silica fume with 1mol/L of NaOH for 24 hours, is more reactive than the one used in S1H-0.3 which was obtained by reacting silica fume with 1mol/L of NaOH for 1 hours leading to a larger consumption of CH in S24H-0.3 than that in S1H-0.3. Hence, more CH is left in the system of S1H-0.3.

This confirms our hypothesis on explaining the oscillatory rheology results given in the previous subsection that it is the interaction between alkali silicate and calcium in S24H-0.3 generating much more structure development in S24H-0.3 than that in S1H-0.3.

For S1H-0.1 which had the same type of alkali silicate as S1H-0.3, less CH was added to it compared to S1H-0.3. As a result, less CH is found in the system compared to S1H-0.3.

For S24H-0.1, the same amount of CH was added to its system compared to S1H-0.1. Interestingly, the CH in S24H-0.1 is almost consumed at 1h indicating the rapid reaction rate of calcium with alkali silicate. Compared to S1H-0.1, this high reaction rate between alkali silicate and calcium confirms what we proposed by comparing S24H-0.3 and S1H-0.3, showing that the alkali silicate made by reacting silica fume with NaOH for 24 hours is more reactive when it reacts with calcium resulting in a larger consumption rate of CH.

5.3.2.3 Further Discussion

Based on the above results, clearly, two factors determine the content of CH remaining in the samples: the quantity of CH addition and the reactivity of alkali silicate. The more CH is added to the system; the more calcium is provided to react with alkali silicate. Therefore, more CH can be found unreacted in the system. The reactivity of alkali silicate is another factor determining the content of CH remaining in the system. The more reactive the alkali silicate is, the higher the reaction rate and consequently the less CH will be left in the system.

5.3.3 Evolution of Silicon-oxygen Networks

The evolution of the silicon-oxygen network in the system during the interaction of alkali silicate with calcium was studied with $^{29}\text{Si NMR}$. Based on the results of NMR, information about the silicon-oxygen network and its evolution can be investigated qualitatively and quantitatively. For the sake of convenience, the standard notation of $Q^n$ nomenclature [81], which has been introduced in detail in 4.3.3, is used for interpreting the NMR results.
5.3.3.1 Qualitative Analysis

According to the deconvolution results of the NMR spectra, typical Si species with their characteristic peaks can be assigned. In this way, the presence of different Si species can be obtained. The NMR spectra as well as the corresponding deconvolution results of S1H-0.1, S1H-0.3 and S24H-0.1 are given in Appendix B. The results of S24H-0.3 are presented in the following.

The NMR spectra of S24H-0.3 at different ages are given in Figure 5.19. The peaks shift downfield after the addition of CH.

![NMR spectra and corresponding deconvoluted curves of S24H-0.3 (24 hours, Ca/Si = 0.3).](image)

The alkali silicate slurry used in this sample is made by reacting silica fume with NaOH solution for 24 hours, the same as the one in S24H-0.1. Based on the results in 4.3.3, the silicon-oxygen networks present in the alkali silicate slurry of S24H-0.1 and S24H-0.3 are more complex and cross-
linked than the ones in S1H-0.1 and S1H-0.3. As shown in Figure 5.19, the silicon-oxygen network present in the alkali silicate slurry contain Q², Q³ and Q⁴. The peak with a center located at about -89 ppm is assigned to Q² having two bridging oxygens and two non-bridging ones. The shift of the center of this peak away from its usual position ranging from -79 ppm to -85 ppm, indicates that one of the non-bridging oxygens is connected with a proton [81] while the other may be connected with an alkali. The peak with a center located at about -100 ppm is assigned to Q³ having three bridging oxygens and one non-bridging one. The shift of the center of the peak assigned to Q³ to the upfield suggests that the non-bridging oxygen is connected with a proton as well. Moreover, the presence of unreacted silica fume is confirmed by the typical peak of Q⁴ with its center located at about -109 ppm.

1 hour after the addition of CH₃, significant changes can be noticed. The disappearance of the peak assigned to Q⁴ indicates the complete consumption of the unreacted silica fume by de-polymerization. The peak assigned to Q¹ having only one bridging oxygen and three non-bridging oxygens with other tetrahedrons, has its center located at about -78 ppm. Q¹ is usually present at the end of a chain or in a dimer as shown in Figure 5.20. It is clear that Q¹ is formed from the de-polymerization. The peak assigned to Q² with its center located at about -85 ppm indicates that one of the two non-bridging oxygens of a tetrahedron is connected with the incorporated calcium [81, 112]. The area under the peak assigned to Q² is larger than that is found in the alkali silicate slurry, suggesting the formation of Q². The peak with its center located at about -89 ppm is assigned to the cyclic Q³ [101, 113] which is indicated as Q³_cyc here and in Figure 5.19 and Figure 5.20. The possible structure is schematically shown in Figure 5.20. It is clear that this type of Q³ has a more complex and cross-linked silicon-oxygen network than the regular one. In the meantime, the peak assigned to the regular Q³ disappears. This infers that the original Q³ present in the alkali silicate slurry is completely consumed.

Figure 5.20: Schematic representation of Q¹ existing at the end of a chain or in a dimer and Q³_cyc.
24 hours after the addition of CH, further changes are noticed. The peak assigned to Q\(^1\) disappears and indicates the consumption of Q\(^1\) by its re-polymerization rather than its de-polymerization, since the typical peak of Q\(^0\) as the product of de-polymerization of Q\(^1\) is not found. The peak assigned to Q\(^2\) has its center located at about -85 ppm confirming the incorporation of calcium. The area under the peak assigned to Q\(^2\) is slightly larger than that found in the sample of 1h indicating the formation of Q\(^2\). This formation of Q\(^2\) is likely caused by the re-polymerization of Q\(^1\) rather than the de-polymerization of Q\(^3\).cyc. Because the area under the peak assigned to Q\(^3\).cyc in this sample hardly changes compared to the one found in the sample of 1h. It means little Q\(^3\).cyc has been neither consumed due to the de-polymerization to form Q\(^2\) nor formed due to the re-polymerization at the expense of Q\(^2\). It is possible that the de-polymerization and re-polymerization reach a dynamic equilibrium at this moment.

72 hours after the addition of CH, the area under the peak assigned to Q\(^2\) with its center located at about -85 ppm is slightly smaller than that of Q\(^2\) found in the sample of 24h. This suggests the slight consumption of Q\(^2\) by the re-polymerization rather than the de-polymerization, since the peaks belonging to Q\(^1\) and Q\(^0\) as the products of the de-polymerization of Q\(^2\) are not found. The peak assigned to Q\(^1\).cyc has its center located at about -89 ppm, consistent with the one found in the sample of 24h. Notably, the peak assigned to the regular Q\(^3\) re-appears 72 hours after the addition of CH. This is likely caused by the re-polymerization of Q\(^2\). Therefore, the silicon-oxygen network is undergoing the re-polymerization.

Based on the above results, the silicon-oxygen network contained in the system of S24H-0.3 goes through de-polymerization predominant stage and re-polymerization predominant stage in sequence. During this process, a cyclic Q\(^3\) is found. However, the mechanism of its formation needs further investigation.

Combining with the results given in Appendix B, the NMR spectra and the corresponding deconvolution results are summarized in Table 5.3.

Obviously, de-polymerization predominates at the early age before re-polymerization takes over and predominates at the later age.
Table 5.3: Summary of the NMR spectra and the corresponding deconvolution results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time</th>
<th>Q₁</th>
<th>Q₂_{Ca}**</th>
<th>Q₃</th>
<th>Q₄_{cyc}</th>
<th>Q⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(-62 ppm ~ -83 ppm) *</td>
<td>(-85 ppm)</td>
<td>(-91 ppm ~ -98 ppm)</td>
<td>(-89 ppm)</td>
<td>(-103 ppm ~ -115 ppm)</td>
</tr>
<tr>
<td>S1H-0.1</td>
<td>1h</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
</tr>
<tr>
<td></td>
<td>24h</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
</tr>
<tr>
<td></td>
<td>72h</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
</tr>
<tr>
<td>S1H-0.3</td>
<td>1h</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
</tr>
<tr>
<td></td>
<td>24h</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
</tr>
<tr>
<td></td>
<td>72h</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
</tr>
<tr>
<td>S24H-0.1</td>
<td>1h</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
</tr>
<tr>
<td></td>
<td>24h</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
</tr>
<tr>
<td></td>
<td>72h</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
</tr>
<tr>
<td>S24H-0.3</td>
<td>1h</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
</tr>
<tr>
<td></td>
<td>24h</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
</tr>
<tr>
<td></td>
<td>72h</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
<td>γ</td>
</tr>
</tbody>
</table>

* Range of the center of the deconvoluted peak.
** Q₂_{Ca} denotes the Q₂ having the connection with calcium.
5.3.3.2 Quantitative Analysis

With the deconvolution technique, the fractions of different Si species can be obtained. In this way, the evolution of the silicon-oxygen network present in the systems can be investigated quantitatively. In addition, a mean degree of connectivity can be calculated to characterize the state of polymerization of the silicon-oxygen network in the samples [114], as shown in Equation 5.14 where \( n' \) denotes the mean degree of connectivity, \( n \) and \( Q \) are the same as the standard notation of \( Q^n \) nomenclature [81].

\[
n' = \frac{\sum_n n \times Q^n}{\sum Q^n}
\]

Equation 5.14

(1) S1H-0.1

Based on the deconvolution analysis of the NMR spectra, the quantitative analysis about the silicon-oxygen network in this sample and the mean connectivity are shown in Figure 5.21. Considering the essential role of CH playing during the whole process, the results of 5.3.2 are briefly indicated as well.
Before the addition of CH, the alkali silicate slurry was obtained by reacting silica fume with 1mol/L of NaOH solution for 1 hour. Based on the results in Chapter 4, the silicon-oxygen network contained in this system is composed of 41.81% of Q⁴, 22.61% of Q³ and 35.58% of Q².

1 hour after the addition of CH, the fraction of Q⁴ decreases from 41.81% to 28.98%; the fraction of Q³ remains constantly at about 22.60%; the fraction of Q² increases from 35.58% to 48.42%. It is clear that the system is at the de-polymerization predominant stage. The more cross-linked specie like Q⁴ is consumed to form the less cross-linked specie like Q². Q³ is probably playing two roles as either the product of the de-polymerization of Q⁴ or the reactant of the de-polymerization to form Q². Both effects determine the fraction of Q³ present in the system at this moment. Therefore, the minor change of the fraction of Q³ indicates that the formation of Q³ by the de-polymerization of Q⁴ almost equals the consumption of Q³ by its de-polymerization to form Q² during this period.

24 hours after the addition of CH, the fraction of Q⁴ continuously decreases from 28.98% to 15.28%; the fraction of Q³ decreases from 22.60% to 19.98%; the fraction of Q² increases from 48.42% to 64.74%. Similar to the results of the sample of 1h, the system is also predominated by the de-
polymerization. The more cross-linked silicon-oxygen networks like $Q^4$ and $Q^3$ are consumed to form the less cross-linked silicon-oxygen network like $Q^2$. As the product of de-polymerization of $Q^4$ and the reactant of the de-polymerization to form $Q^2$, clearly, $Q^3$ is consumed slightly more than it is formed resulting in the decrease of its fraction.

72 hours after the addition of CH, $Q^4$ is completely consumed with its fraction decreasing from 15.28% to 0%; the fraction of $Q^3$ increases significantly from 19.98% to 88.92%; the fraction of $Q^2$ decreases from 66.74% to 11.07%. Presumably, the system during this period has experienced two stages. In the first stage, the continuous de-polymerization predominates the system resulting in the exhaustion of $Q^4$. In the second stage, the re-polymerization takes over and predominates the silicon-oxygen network in the system resulting in the formation of $Q^3$ at the expense of $Q^2$.

The above results quantitatively describe the evolution of silicon-oxygen network during the interaction between alkali silicate and calcium in S1H-0.1. The system experiences de-polymerization predominant process at the early age, and re-polymerization predominant stage at the later age. This is consistent with the evolution of the mean connectivity given in Figure 5.21, showing that it firstly decreases and increases in the end. In addition, the re-polymerization occurs after the consumption of CH.

(2) S1H-0.3

According to the deconvolution analysis of the NMR spectra, the quantitative analysis and the mean connectivity regarding the evolution of the silicon-oxygen network in S1H-0.3 are shown Figure 5.22. The presence of CH interpreted from the results of 5.3.2 is indicated as well.
Before the addition of CH, the silicon-oxygen network present in the alkali silicate slurry contain 41.81% of $Q^4$, 22.61% of $Q^3$ and 35.58% of $Q^2$.

1 hour after the addition of CH, the fraction $Q^4$ decreases from 41.81% to 21.70%; the fraction of $Q^3$ decreases slightly from 22.61% to 17.91%; the fraction of $Q^2$ increases significantly from 35.58% to 60.39%. It is clear that the system is undergoing a de-polymerization predominant stage. More polymerized species like $Q^4$ and $Q^3$ are consumed to form the specie like $Q^2$ with lower polymerization degree. $Q^3$ as the product of the de-polymerization of $Q^4$ as well as the reactant of the de-polymerization to form $Q^2$, therefore, can be considered as an indicator of the reaction rate of those two de-polymerization processes as shown in Equation B.1 (Appendix B). At this moment in particular, the decrease of the fraction of $Q^3$ and the significant increase of the fraction of $Q^2$ indicate the consumption of $Q^3$ by the de-polymerization to form $Q^2$ is slightly larger than the formation of $Q^3$ by the de-polymerization of $Q^4$.

24 hours after the addition of CH, $Q^4$ is completely consumed with its fraction dropping from 21.70% to 0%; the fraction of $Q^3$ increases significantly from 17.91% to 53.76%; the fraction of $Q^2$
decreases from 60.39% to 46.24%. It is clear that both de-polymerization and re-polymerization are ongoing during this period. Because the increase of the fraction of Q$^3$ is larger than the decrease of the fraction of Q$^4$ indicating the additional formation of Q$^3$ from the re-polymerization. Presumably, the de-polymerization is predominant in the first place resulting in the consumption of Q$^4$ and the formation of Q$^3$ and Q$^2$. Subsequently, the re-polymerization happens at the expense of Q$^2$ to form Q$^3$ leading to the significant increase of the fraction of Q$^3$ and the decrease of the fraction of Q$^2$.

72 hours after the addition of CH, the fraction of Q$^3$ increases from 53.76% to 75.80%; the fraction of Q$^2$ continuously decreases from 46.24% to 24.20%. Apparently, the re-polymerization predominates the silicon-oxygen network in the system at this moment. More and more Q$^3$ is formed at the expense of Q$^2$ by re-polymerization.

The above results quantitatively evaluate the evolution of silicon-oxygen network during the interaction between alkali silicate and calcium in S1H-0.3. The system is predominated by de-polymerization at beginning and subsequently predominated by re-polymerization, consistent with the trend of the mean connectivity shown in Figure 5.22. In addition, similar to the situation in S1H-0.1, the re-polymerization occurs after the complete consumption of CH.

(3) S24H-0.1

With the deconvolution analysis of the NMR spectra, the quantitative analysis and the mean connectivity of the silicon-oxygen network in S24H-0.1 are shown in Figure 5.23. The presence of CH is indicated as well.
Before the addition of CH, the silicon-oxygen network in alkali silicate slurry contains 29.59% of Q⁴; 57.4% of Q³ and 13.01% of Q². Compared to the ones present in S1H-0.1 and S1H-0.3, the silicon-oxygen network in this system is more complex and cross-linked according to the previous results given in Chapter 4.

1 hour after the addition of CH, the fraction of Q⁴ decreases from 29.59% to 17.73%; the fraction of Q³ decreases significantly from 57.4% to 14.34%; the fraction of Q² increases dramatically from 13.01% to 67.93%. Apparently, the silicon-oxygen network is at a de-polymerization predominant stage. The polymerized species like Q³ and Q⁴ are consumed by the de-polymerization to form the less polymerized specie like Q². According to the decrease of the fractions of Q³ and Q⁴ as well as the increase of the fraction of Q², it is clear that the rate of the consumption of Q³ by its de-polymerization to form Q² is much higher than that of the formation of Q³ by the de-polymerization of Q⁴, i.e. Q³ is consumed more than it is formed.

24 hours after the addition of CH, Q⁴ is completely consumed due to de-polymerization. Its fraction decreases from 17.73% to 0%. The fraction of Q³ significantly increases from 14.34% to 93.04%.
The fraction of $Q^2$ decreases from 67.93% to 6.96%. Clearly, both de-polymerization and re-polymerization occur during this period. Presumably, the de-polymerization predominates in the first period resulting in the consumption of $Q^4$. Subsequently, the re-polymerization takes over and predominates the silicon-oxygen network leading to the formation of $Q^3$ at the expense of $Q^2$.

72 hours after the addition of CH, the fraction of $Q^3$ slightly decreases from 93.04% to 92.01%, the fraction of $Q^2$ slightly increases from 6.96% to 7.99%. This little change of the fractions of $Q^3$ and $Q^2$ can be considered as a minor variation. Therefore, the system is at a stable state.

The above results quantitatively characterize the evolution of the silicon-oxygen network during the interaction between alkali silicate and calcium in S24H-0.1. Similar to the S1H-0.1 and S1H-0.3, the system firstly experienced a de-polymerization predominant stage and subsequently a re-polymerization predominant stage. The occurrence of the re-polymerization is after the complete consumption of CH.

(4) S24H-0.3

With the deconvolution analysis of the NMR spectra, the evolution of the silicon-oxygen network and the mean connectivity of the silicon-oxygen network in S24H-0.3 are obtained as shown in Figure 5.24. The presence of CH in the system is indicated as well.
FORMATION OF CALCIUM ALKALI SILICATE IN THE CHEMICAL MODEL SYSTEM

Figure 5.24. Quantitative analysis of the NMR results of S24H-0.3 (24 hours, Ca/Si = 0.3).

The silicon-oxygen network present in the alkali silicate slurry is the same as the one in S24H-0.1 containing 29.59% of $Q^4$; 57.50% of $Q^3$ and 13.01% of $Q^2$.

1 hour after the addition of CH, $Q^4$ representing the unreacted silica fume is completely consumed; the cyclic $Q^3$ ($Q^3_{\text{cyc}}$) appears with its fraction of 77.65%; the fraction of $Q^2$ increases from 13.01% to 18.65%; $Q^1$ appears with its fraction of 3.7%. On the one hand, the consumption of $Q^4$, the increase of the fraction of $Q^2$ and the appearance of $Q^1$ indicate the occurrence of the de-polymerization. The polymerized species are consumed to form the less polymerized species. On the other hand, the appearance of $Q^3_{\text{cyc}}$ suggests the re-polymerization is also ongoing, since the formation of such a type of complex silicon-oxygen network as shown in Figure 5.20 can only be realized by the re-polymerization of less polymerized species rather than de-polymerization. Therefore, the de-polymerization may occur simultaneously with the re-polymerization in the sample at this moment. During de-polymerization, the silicon-oxygen network of the polymerized species is destroyed to form species with less polymerization degree. During re-polymerization, species with lower polymerization
degree tend to interlink with each other to form the ones with higher polymerization degree. Presumably, due to the intensive de-polymerization promoted by the abundant presence of CH in the system, the concentrations of the less polymerized species (e.g. Q^2 and Q^1) are raised significantly. This stimulates their interlinkages to form the more polymerized species [95, 101] such as Q^{3_{cyc}} even during a de-polymerization process.

24 hours after the addition of CH, the fraction of the Q^{3_{cyc}} slightly decreases from 77.65% to 75.88%; the fraction of Q^2 increases from 18.65% to 24.12%; Q^1 is not found. On the one hand, due to the promotion effect by CH on de-polymerization [115, 116], Q^{3_{cyc}} is inevitably affected to form the less polymerized specie like Q^2 resulting in the decrease of the fraction of Q^{1_{cyc}} and the increase of the fraction of Q^2. On the other hand, the less polymerized species tend to interlink with each other to form the more polymerized species like Q^{3_{cyc}} and Q^2. This resulted in the consumption of Q^1 and the formation of Q^2.

72 hours after the addition of CH, the fraction of Q^{3_{cyc}} decreases from 75.88% to 72.71%; the fraction of Q^2 decreases from 24.12% to 21.03%; the regular Q^3 appears with its fraction of 6.26%. As indicated in Figure 5.24, the added CH has been consumed at this moment. Hence, the promotion effect on de-polymerization by CH ceased. Similar to the other samples (S1H-0.1, S1H-0.3 and S24H-0.1), the re-polymerization can take over as the predominant effect in the system. The less polymerized specie like Q^2 gets interlinked to form the more polymerized specie like Q^3 resulting in the decrease of the fraction of Q^2 and the increase of the fraction of Q^3. Concerning the reason for the formation of Q^3 rather than Q^{3_{cyc}} as the product of the re-polymerization of Q^2, perhaps, different mechanisms govern the re-polymerization processes occurring at the early age when Q^{3_{cyc}} is formed as the product and at the later age when Q^3 is formed as the product. It should be noted that, the decrease of the fractions of Q^{3_{cyc}} and Q^2 as well as the appearance of Q^3 imply that a minor de-polymerization occurs before the re-polymerization starts to predominate.

The above results characterize the evolution of the silicon-oxygen network during the interaction between alkali silicate and calcium in S24H-0.3. The system experiences a process during which the re-polymerization occurs simultaneously with the de-polymerization in the earlier age. Subsequently, the system goes through a re-polymerization predominant stage after the complete consumption of CH.

5.3.3.3 Influence of calcium

Fundamentally speaking, calcium can influence the interaction between alkali silicate and calcium in two ways. Firstly, calcium can interlink different alkali silicate to form calcium alkali silicate as shown in Equation 5.1 and Equation 5.2. As a result, calcium gets incorporated into the silicon-oxygen network.
Secondly, due to the incorporation of calcium into the interlayer space of the silicon-oxygen networks, the stability of the original structure of the silicon-oxygen network is weakened. As a result, the silicon-oxygen network is prone to rupture [50]. The rupture of those networks describes the depolymerization. Many studies have confirmed the promotion effect of calcium on the depolymerization [115-117].

It means that the more calcium is available for its interlinkage and incorporation into the silicon-oxygen network, the more silicon-oxygen network is prone to rupture and consequently the more depolymerization is going to happen.

In the light of this consideration, further analysis about the influence of calcium on the evolution of Si environment in S1H-0.1, S1H-0.3, S24H-0.1 and S24H-0.3 should be conducted.

(1) Comparison between S1H-0.1 and S1H-0.3

S1H-0.1 and S1H-0.3 have the same type of alkali silicate slurry which was obtained by reacting silica fume with 1 mol/L of NaOH solution for 1 hour. Therefore, the influence of calcium on the interaction between this type of alkali silicate and calcium can be investigated. The evolutions of the fractions of Q², Q³ and Q⁴ are given in Figure 5.25.

![Figure 5.25: Evolutions of the fractions of (a) Q², (b) Q³ and (c) Q⁴ in S1H-0.1 and S1H-0.3.](image)

As the indicators of de-polymerization, the evolutions of the fractions of Q² and Q⁴ shown in Figure 5.25 (a) and (c) clearly indicate the promotion effect of calcium on de-polymerization. The more calcium is added to the alkali silicate slurry, the more de-polymerization occurs. Accordingly, additional
Q\textsuperscript{2} as the product of de-polymerization is formed, while additional Q\textsuperscript{4} representing the unreacted silica fume is consumed.

The evolution of the fraction of Q\textsuperscript{3} is complicated due to its multiple roles during this process: the product of the de-polymerization of Q\textsuperscript{4}, the reactant of its de-polymerization to form Q\textsuperscript{2} and the product of the re-polymerization of Q\textsuperscript{2}. First, the more calcium is present in the system, the more Q\textsuperscript{4} can be de-polymerized to form Q\textsuperscript{3} leading to an increase of the fraction of Q\textsuperscript{3}. Second, the more calcium is present, the more Q\textsuperscript{3} is consumed by its de-polymerization to form Q\textsuperscript{2}. Thirdly, during the re-polymerization, Q\textsuperscript{3} forms at the expense of Q\textsuperscript{2}. It is clear that only the last process is not directly influenced by calcium. Notably, re-polymerization only happens after the depletion of calcium based on the results given in the previous subsection.

From 1 h to 24 h, the rate of the decrease of the fraction of Q\textsuperscript{3} in S1H-0.3 (Figure 5.25 (c)) is larger than that in S1H-0.1. This confirms the promotion effect by calcium, showing that the more calcium is added to the system, the more Q\textsuperscript{4} is de-polymerized. In the meantime, the rate of the increase of the fraction of Q\textsuperscript{2} in S1H-0.3 (Figure 5.25 (a)) is larger than that in S1H-0.1. From 1 h to 24h, the fraction Q\textsuperscript{2} in S1H-0.3 decreases while that in S1H-0.1 continues to increase. This indicates that the re-polymerization in S1H-0.3 starts to predominate the de-polymerization due to the abundant presence of the less polymerized silicate. The fraction of Q\textsuperscript{3} which is the product of the re-polymerization of Q\textsuperscript{2} increases accordingly. For S1H-0.1, the fraction of Q\textsuperscript{2} continuously increases until 24h when the content of CH in the system reaches an extremely low value. From 24h to 72h, the re-polymerization resulted in the decrease of the fraction of Q\textsuperscript{2} and increase of the fraction of Q\textsuperscript{3}. Notably, the fraction of Q\textsuperscript{3} in S1H-0.1 is higher than that in S1H-0.3 at that moment probably due to the minor promotion effect from the trace amount of CH present in S1H-0.3.

The above investigation provides explanation to the co-occurrence of the exhaustion of CH and the predominance of re-polymerization.

(2) Comparison between S24H-0.1 and S24H-0.3

S24H-0.1 and S24H-0.3 have the same type of alkali silicate slurry which was obtained by reacting silica fume with 1mol/L of NaOH solution for 24 hours. Hence, the influence of calcium on this type of alkali silicate slurry can be studied. The evolutions of the fractions of the related species are given in Figure 5.26.
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Figure 5.26: Evolutions of the fractions of (a) Q1 and Q2, (b) Q3 and Q3_cyc, (c) Q4 in S24H-0.1 and S24H-0.3.

Similar to the comparison between S1H-0.1 and S1H-0.3, the influence of calcium on the evolution of the silicon-oxygen network in S24H-0.1 and S24H-0.3 is also closely associated with de-polymerization and re-polymerization. Generally speaking, the more calcium is present for its interaction with alkali silicate, the more de-polymerization occurs and predominates the silicon-oxygen network. Once the content of CH reaches an extremely low value or exhausts, the re-polymerization starts to predominate the de-polymerization.

The presences of Q1 and Q3_cyc in S24H-0.3 are caused by the promotion effect of calcium. For the presence of Q1, clearly, the formation Q1 results from the intensive de-polymerization promoted by calcium. For the presence of Q3_cyc, a two-step process can be derived from the results mentioned in 5.3.3.2. Firstly, an intensive de-polymerization is promoted by the large amount of CH added to the system leading to a rapid increase of the concentration of the less polymerized Si species (like Q1 and Q2) in the system. This abundant presence of the less polymerized Si species can stimulate the re-polymerization [95]. As a result, a more complex and cross-linked silicon-oxygen network like Q3_cyc is formed. Secondly, once CH is consumed in the system, the relatively high concentration of the less polymerized Si species cannot be maintained due to its continuous consumption to form Q3_cyc and the slowing down of the formation of the less polymerized Si species. Consequently, the formation of Q3_cyc ceases since this reaction can only be activated under high concentration of the less polymerized Si species presumably. Meanwhile, because of the exhaustion of CH, re-polymerization starts to take over as the predominant effect in the system leading to the formation of Q3 at the expense of Q2.
The above analysis offers extensive explanation to the influence of CH on the alkali silicate slurry obtained by reacting silica fume with 1mol/L of NaOH for 24 hours. The formations of $Q^1$, $Q^3$ and $Q^{3cyc}$ as the most featured findings at this stage are emphasized.

By comparing the influence of calcium on the alkali silicate slurry obtained by reacting silica fume with NaOH solution for 1 hour and 24 hours, clearly, different types of alkali silicate slurry are also responsible for the different performances of the silicon-oxygen networks in the systems.

5.3.3.4 Influence of alkali silicate

As noticed in the previous subsections, the type of the alkali silicate slurry has a great influence on its interaction with calcium. In the following content, the influence of the type of alkali silicate slurry on the silicon-oxygen network during its interaction with calcium will be investigated.

(1) $Ca/Si = 0.1$

Considering S1H-0.1 and S24H-0.1 have the same amount of CH added to the system, the influence of the two types of alkali silicate obtained by reacting silica fume with NaOH solution for 1 hour and 24 hours on the silicon-oxygen networks at a Ca/Si of 0.1 can be studied. The fractions of $Q^2$, $Q^3$ and $Q^4$ in S1H-0.1 and S24H-0.1 are plotted in Figure 5.27 respectively.

![Figure 5.27](image)

Figure 5.27: Evolutions of the fractions of (a) $Q^2$, (b) $Q^3$ and (c) $Q^4$ from S1H-0.1 and S24H-0.1.

As stated before, the evolutions of the fractions of $Q^2$ and $Q^4$ can be considered as the indicators of the de-polymerization. As shown in Figure 5.27 (a) from 0h to 1h, the increase of the fraction of $Q^2$
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in S24H-0.1 is more significant than the one in S1H-0.1. Similar trend is found in Figure 5.27(b) for the evolution of the fraction of Q^3 during the same period. In the meantime, however, the decrease of the fractions of Q^3 due to de-polymerization are similar in both systems. This indicates that more de-polymerization induced by calcium was happening in S24H-0.1 than that in S1H-0.1; the formation of Q^2 mainly resulted from the de-polymerization of Q^3. It means the de-polymerization preferably happens on Q^3 [116], probably because its silicon-oxygen network is easier and more open for external influences.

From 1h to 24h, the fraction of Q^2 in S1H-0.1 continues to increase while that in S24H-0.1 decreases rapidly. At the same time, the fraction of Q^3 significantly increases in S24H-0.1 while that in S1H-0.1 slightly decreases. The fractions of Q^4 in both systems decrease, and the fraction of Q^4 in S24H-0.1 reaches zero indicating its complete consumption. This indicates that, on the one hand, the silicon-oxygen network in S1H-0.1 is still experiencing the de-polymerization resulting in the consumption of Q^3 and Q^4 to form Q^2. On the other hand, the silicon-oxygen network in S24H-0.1 firstly goes through the de-polymerization resulting in the complete consumption of Q^4 and subsequently experiences the re-polymerization leading to the formation of Q^3 at the expense of Q^2.

From 24h to 72h, little changes can be found for the silicon-oxygen network in S24H-0.1 indicating an equilibrium has been reached. In the meantime, the fraction of Q^2 in S1H-0.1 starts to decrease accompanied with the increase of the fraction of Q^3. The fraction of Q^4 reaches zero as well. This shows the re-polymerization prevails during this period in S1H-0.1.

Based on the above analysis, obviously, the silicon-oxygen network in S1H-0.1 experiences a delayed de-polymerization and re-polymerization compared to those in S24H-0.1. Because the silicon-oxygen network present in the alkali silicate slurry of S24H-0.1 is more vulnerable for the incorporation of calcium and so as the subsequent reactions, compared to that in S1H-0.1. Combining with the results given in Chapter 4, the silicon-oxygen network of the alkali silicate slurry obtained by reacting silica fume with NaOH solution for 24 hours is more complex and cross-linked than the one reacting for 1 hour. Therefore, the more complex and cross-linked the silicon-oxygen network is, the more vulnerable it is to the incorporation of calcium and the subsequent reactions. It means that, the alkali silicate slurry obtained by reacting silica fume with NaOH solution for 24 hours is more reactive than the one reacting for 1 hour during its interaction with calcium at a Ca/Si ratio of 0.1.

(2) Ca/Si = 0.3

Similarly, the evolutions of the silicon-oxygen network in S1H-0.3 and S24H-0.3 are plotted in Figure 5.28 Similar to the comparison between S1H-0.1 and S24H-0.1, both S1H-0.3 and S24H-0.3 have
the same amount of CH added to the system. In this sense, the influence of the type of alkali silicate slurry on the silicon-oxygen networks at a Ca/Si ratio of 0.3 can be studied.

As stated before, the de-polymerization can be indicated by the evolution of the fractions of Q² and Q⁴. As shown in Figure 5.28 (c), the fraction of Q⁴ in S24H-0.3 dramatically decreases to zero at 1h while that in S1H-0.3 decreases as well. In the meantime, the fraction of Q² in S1H-0.3 rapidly increases while that in S24H-0.3 slightly increases accompanied by the appearance of Q¹. This confirms the occurrence of the de-polymerization in both systems. The evolution of the fraction of Q³ is complicated due to its multiple roles as the product of the de-polymerization of Q⁴, the reactant of its de-polymerization to form Q² and the product of the re-polymerization. At 1h, the fraction of Q³ in S1H-0.3 slightly decreases indicating the de-polymerization was predominant in this system. Meanwhile, the appearance of Q³_cyc instead of the regular Q³ in S24H-0.3 implies the co-occurrence of the re-polymerization with the de-polymerization in the system at this moment. During the formation of Q³_cyc by the re-polymerization, Q² and Q¹ present in the system are consumed. This consumption offsets part of the fraction increases of both species caused by the intensive de-polymerization. This explains why the fractions of Q² and Q¹ only increase slightly during this period in S24H-0.3.

From 1h to 24h, a slight re-polymerization happened at the expense of Q¹ to form Q² while the fraction of Q³_cyc hardly changes. In the meantime, the re-polymerization started to take over as the predominant factor after the complete consumption of Q⁴ in S1H-0.3. This leads to the decrease of the fraction of Q² and the increase of the fraction of Q³.
From 24h to 72h, the re-polymerization continuously predominates the silicon-oxygen network in S1H-0.3 leading to the decrease of the fraction of Q$^2$ and the increase of the fraction of Q$^3$. In S24H-0.3, the re-polymerization results in the slight decrease of the fraction of Q$^2$ and the appearance of the regular Q$^3$. In the meantime, the fraction of Q$^3_{cyc}$ decreases a bit.

Based on above result, on the one hand, the comparison between S1H-0.3 and S24H-0.3 shares some similarities with that between S1H-0.1 and S24H-0.1. The silicon-oxygen network present in the alkali silicate slurry obtained by reacting silica fume with NaOH solution for 24 hours is much more reactive during its interaction with calcium than the one reacting for 1 hour. As a result, the silicon-oxygen network in S1H-0.3 goes through de-polymerization and re-polymerization with some delays compared to those in S24H-0.3. On the other hand, due to the large addition of CH, S24H-0.3 experiences a co-occurrence of de-polymerization and re-polymerization at the beginning, resulting in the formation of a more complex silicon-oxygen network of Q$^3_{cyc}$. The re-polymerization takes over as the predominant factor afterwards.

(3) Remarks

In this subsection, the influence of the type of alkali silicate slurry on the silicon-oxygen network during the interaction between alkali silicate slurry and calcium is investigated. Generally speaking, the more complex and cross-linked the silicon-oxygen network present in alkali silicate slurry, the more vulnerable this network is to the incorporation of calcium. Therefore, the de-polymerization is more intensive and the re-polymerization occurs earlier given a certain amount of calcium to react with. When large amount of CH is added to the system containing the more complex and cross-linked silicon-oxygen network, the de-polymerization is progressively encouraged to raise the concentration of the less polymerized Si species in the system. As a result, the occurrence of re-polymerization can be activated simultaneously with the de-polymerization leading to the formation of a featured specie of Q$^3_{cyc}$.

5.3.4 Microstructure Analysis

The evolution of the microstructure of the system during the interaction between alkali silicate and calcium was characterized with SEM-EDS measurements.

In the first part, qualitative analysis was carried out on the selected areas on different samples with BSE imaging and elemental mapping. This provides the information about the morphology of phases as well as the distribution of elements during the interaction between alkali silicate and calcium.
In the second part, with the help of grey scale level analysis based on BSE images, the capillary porosity of different samples was evaluated to offer quantitative information about the microstructure.

5.3.4.1 Qualitative Analysis

Considering the essential roles of calcium, silicon and sodium during the interaction between alkali silicate and calcium, these three elements were chosen for the elemental mapping on each area. Consequently, the distribution of those elements with time, which characterize the state and evolution of the system respectively, can be obtained.

(1) $S1H-0.1$

The BSE images and the corresponding elemental mapping of calcium, silicon and sodium of the samples collected from $S1H-0.1$ at 1h, 24h and 72h are given in Figure 5.29.

![BSE images and corresponding elemental mapping of S1H-0.1 (1 hour, Ca/Si = 0.1).](image)

1 hour after the addition of CH, as shown in the BSE image, the matrix of the sample contains different regions according to their different grey levels. This suggests that the presence of several different phases in the system. The particle with its diameter at about 80 µm is marked with the arrow No.1. It has the highest grey level in the BSE image. As shown in the elemental mapping of calcium and silicon, little calcium but abundant silicon is found in the interior of this particle indicating that this silicon-rich particle may be the unreacted alkali silicate present in the system considering the uniform distribution of sodium in this sample. In addition, small particles with a high concentration of calcium
are found to surround the silicon-rich particle. These calcium-rich particles, notably, contain much less silicon than the silicon-rich particle as marked. Actually, the concentration of silicon contained by these particles is almost the same with (if it is not lower than) the concentration of silicon in the matrix. This means these calcium-rich particles can be the unreacted CH or the formed calcium alkali silicate with an extremely high Ca/Si ratio.

24 hours after the addition of CH, the unreacted alkali silicate particle (in the center) is still present in the system but found to have a smaller size indicating its consumption by the interaction with CH. Besides, a considerable amount of calcium can be found in the interior of this silicon-rich particle indicating the penetration of calcium into the unreacted alkali silicate particle and the subsequent reactions to form calcium alkali silicate. More importantly, nearly all the calcium-rich particles contain a considerable amount of silicon at the same time. It means those calcium-rich particles are calcium alkali silicate formed from the interaction between alkali silicate and calcium, as marked with the arrow No.2. In addition, the distribution of calcium is more homogeneous than the sample of 1h suggesting the fully participation of calcium to its interaction with alkali silicate. As a result, the quantity of the unreacted CH remaining in the system should be accordingly low. This conclusion is confirmed by the XRD and TGA results, showing that the CH was almost completely consumed (0.65%).

72 hours after the addition of CH, according to the BSE image, the matrix of the sample is more homogeneous than the samples of 1h and 24h. This is caused by the continuous reactions in this calcium-alkali-silicate system. There are hardly any unreacted alkali silicate particles present in the system suggesting the complete consumption of alkali silicate. The calcium and silicon preset in the matrix of this sample are more uniformly distributed than the ones in the sample of 24h, indicating the re-organization of those elements during the continuous reactions in the system. The area marked with the arrow No.3 is another example of a group of the calcium alkali silicate.

(2) S1H-0.3

The BSE images and the corresponding elemental mapping of calcium, silicon and sodium are shown in Figure 5.30.
1 hour after the addition of CH, as seen in the BSE image, regions with different grey levels can be assigned to several phases present in the system. Similar to the situation in S1H-0.1, the particles with low calcium and high silicon concentrations are found with different size. These particles are the unreacted alkali silicate present in the system. Besides, large amount of calcium-rich particles prevail in the matrix of this sample. Compared to S1H-0.1, more calcium-rich particles can be found in Figure 5.30, because more CH is added to S1H-0.3. It is clear that little silicon can be found in the interior of the calcium-rich particles. This means those particles are mainly the unreacted CH present in the system, one of them is marked with the arrow No.1. This is consistent with the XRD and TGA results that, abundant CH is present in the system at this time. Therefore, 1 hour after the addition of CH, the system of S1H-0.3 contains both unreacted alkali silicate and unreacted CH.

24 hours after the addition of CH, compared to the sample of 1h, the silicon-rich particles assigned to the unreacted alkali silicate are rare. This confirms the consumption of alkali silicate by its continuous reactions with calcium. Besides, less calcium-rich particles assigned to the unreacted CH are found in this sample confirming the consumption of CH by its interaction with alkali silicate. An example of the unreacted CH is marked with the arrow No.2. These results are consistent with the XRD and TGA results, showing that unreacted CH are still present in the system.

72 hours after the addition of CH, the disappearance of both the unreacted alkali silicate and the CH suggests their consumption in this sample. This is consistent with the XRD and TGA results.
mentioned before. In addition, the distributions of calcium and silicon are more uniform than that in the sample of 24h confirming the interaction between alkali silicate and calcium.

(3) S24H-0.1

The BSE images and the corresponding elemental mapping of calcium, silicon and sodium are given in Figure 5.31.

1 hour after the addition of CH, two phases can be differentiated according to their different grey levels in the BSE image. The phase with higher grey level, as marked with the arrow No.1, contains more calcium than its neighbors while silicon and sodium are rare in its interior. This indicates that this particle is perhaps the unreacted CH present in the system. Notably, several exceptions can be found as marked with the arrow No.2 where high contents of both calcium and silicon are found in the interior of this particle. It means this particle is a calcium alkali silicate formed from the interaction between alkali silicate and calcium. This confirms the XRD and TGA results, showing that CH is almost entirely consumed 1 hour after its addition. The phase with lower grey level is generally uniform according to visual inspection. It contains silicon with a considerable quantity while rare calcium. This suggests this phase can be assigned to the unreacted alkali silicate which was well-dispersed in the matrix of this sample. This is probably due to the longer reaction time between silica fume and 1mol/L of NaOH in this sample compared to the ones in S1H-0.1 and S1H-0.3.
24 hours after the addition of CH, the matrix of the sample is more uniform compared to the sample of 1h. The phase with high grey level is found to contain both calcium and silicon in its interior suggesting the penetration of calcium to react with alkali silicate. Compared to the sample of 1 h, the distribution of calcium is more dispersed indicating the interaction between CH and alkali silicate. Notably, the calcium-rich particle assigned to unreacted CH is not found indicating the consumption of CH in this sample. This is consistent with the XRD and TGA results.

72 hours after the addition of CH, the matrix is more uniform compared to the sample of 24 h. This confirms the continuous microstructure evolution during this period. Most importantly, the distributions of calcium and silicon are uniform in the matrix of this sample suggesting the multiple reactions in this calcium-alkali-silicate system. Compared to the samples of 72h in S1H-0.1 and S1H-0.3, the distribution of calcium and silicon in this sample is much more homogeneous. This might be caused by the well-dispersed alkali silicate as mentioned before.

(4) S24H-0.3

The BSE images and the corresponding elemental mapping of calcium, silicon and sodium are given in Figure 5.32.

![BSE images and elemental mappings](image)

Figure 5.32: BSE images and the corresponding elemental mapping of S24H-0.3 (24 hours, Ca/Si = 0.3).

1 hour after the addition of CH, two phases can be differentiated according to their different grey levels in the BSE image. The phase with a high grey level contains more calcium and silicon than the other one. This phase can be assigned to calcium alkali silicate or unreacted CH present as groups. The
phase with a low grey level can be assigned to alkali silicate or calcium alkali silicate well-dispersed in the matrix of the sample. On the one hand, the large particles assigned to unreacted alkali silicate (e.g. the ones present in the sample of 1h in S1H-0.3) are not found in this sample indicating a good dispersion of alkali silicate. On the other hand, the large particles assigned to the unreacted CH (e.g. the ones present in the sample of 1h in S1H-0.3) are not found as well. The particles with high concentration of calcium are probably the formed calcium alkali silicate or the unreacted CH, one of them is marked with the arrow No.2. However, no matter these particles are assigned to which one, it is clear that less unreacted CH can be found according to the elemental mapping. Considering the same amounts of CH are added to S1H-0.3 and this sample (S24H-0.3), therefore, this finding suggests the consumption of CH in this sample is larger than that in S1H-0.3 based on the reduced presence of the large particles assigned to unreacted CH. This is consistent with the XRD and TGA results given in 5.3.2. The particle marked with the arrow No.1 is an example of calcium alkali silicate as the product of the interaction between alkali silicate and calcium.

24 hours after the addition of CH, the matrix is more uniform compared to that in the sample of 1h, indicating the continuous multiple reactions in the calcium-alkali-silicate system. The distributions of calcium and silicon present in the matrix of this sample are more uniform than the ones in the sample of 1h, indicating the interaction between alkali silicate and calcium. The calcium-rich particles, as marked with the arrow No.2, contain less calcium and silicon compared to those in the sample of 1h.

72 hours after the addition of CH, the matrix of the sample is progressively more homogeneous compared to the sample of 24h confirming the evolution of the microstructure during the continuous interaction between alkali silicate and calcium. Most importantly, calcium and silicon are more uniformly dispersed in the matrix of the sample confirming the multiple reactions in the system. In addition, neither the calcium-rich particle nor the silicon-rich particle, which is similar to the ones assigned to the unreacted CH in other samples, can be found in this sample. This confirms the XRD and TGA results, showing that CH is almost completely consumed in the system at this moment.

5.3.4.2 Quantitative Analysis

In order to quantitatively evaluate the evolution of the microstructure during the interaction between alkali silicate and calcium, the capillary porosity analysis was carried out based on the grey level analysis of the BSE images of each sample [111]. The results are given in Figure 5.33.
Generally speaking, the capillary porosity of all the samples decreases with the reaction time due to the continuous development of microstructure during the interaction between alkali silicate and calcium to form calcium alkali silicate.

For S1H-0.1, its porosity experiences a plateau in the first 24 hours at about 9%. Subsequently, it decreases to about 5% 72 hours after the addition of CH. This means that the development of microstructure resulting in the decrease of porosity is more pronounced at the later age than that at the earlier age. Presumably, at the earlier age, the formation of calcium alkali silicate in such a system is not enough to improve the microstructure. At the later age, the accumulation of calcium alkali silicate as well as further physico-chemical reactions, e.g. the interaction between calcium alkali silicate and alkali silicate [53], favors the development of microstructure.

For S1H-0.3, its highest porosity was reached at about 13% 1 hour after the addition of CH. Till 24h, the porosity decreases to about 7%. Eventually, it reaches at about 3% 72 hours after the addition of CH. Compared to S1H-0.3, more CH is added to the alkali silicate slurry of this system. However, the additional CH added to the system does not contribute significantly to the development of microstructure by reacting with alkali silicate to form calcium alkali silicate at the earlier age. This indicates that, the microstructure development is limited by the properties of alkali silicate, especially its reactivity of interacting with CH at the beginning. As this interaction carried on, more and more calcium alkali silicate is formed and accumulated to densify the matrix of this sample at later age. Till this time, the additional CH added to the system might benefit the development of microstructure by fully interacting with alkali silicate. Considering the addition of CH to 1mol/L of NaOH solution at a
liquid to solid mass ratio of 3, the more CH is added, the more solution is introduced to the system. As a result, the additional introduced solution can have a dilution effect to increase the measured porosity, especially when the formation and accumulation of calcium alkali silicate are not sufficient enough to offset this diluting effect at this moment. This is why the porosity of this sample has a high value at 1h.

For S24H-0.1, its porosity decreases from about 5.0% at the beginning to about 2.5% in the end at a constant rate. This indicates the continuous microstructure development is ongoing due to the formation of calcium alkali silicate. Compared to S1H-0.1 having the same amount of CH addition, the silicon-oxygen network contained in the alkali silicate slurry of S24H-0.1 is more complex and reactive based on the results in Chapter 4. As a result, more calcium alkali silicate is formed by the interaction between alkali silicate and calcium. Accordingly, the porosity of this sample is lower than that of S1H-0.1.

For S24H-0.3, it has the lowest porosity of all the samples throughout the measurement. Its porosity decreases from about 3.6% to about 1.5% at a relatively constant rate. This suggests the most microstructure development is generated by the formation of calcium alkali silicate in this sample. Compared to S24H-0.1, more CH is added to this sample providing more calcium available for its interaction with alkali silicate. As a result, more microstructure development is generated in S24H-0.3 than that in S24H-0.1. Compared to S1H-0.3, more complex and reactive silicon-oxygen network is present in the alkali silicate slurry of S24H-0.3. Accordingly, more calcium alkali silicate is formed from the interaction between alkali silicate and calcium to generate microstructure development in S24H-0.3 than that in S1H-0.3.

5.4 Further Discussion on Structure Development

As one of the most critical findings of the present study, the structure development induced by the interaction between alkali silicate and calcium hydroxide has been investigated through multiple approaches. Various factors associated with this process have been studied. Accordingly, this process is illustrated from the rheological, physico-chemical, nano and micro structural points of view. Nevertheless, how the development of the structure and its properties are influenced by those various factors comprehensively has not been addressed. Therefore, further analysis and discussion will be given in this section aiming at providing a comprehensive and fundamental mechanism about the interaction between alkali silicate and calcium.

In general, the influencing factors can be classified into two groups regarding their operational mode: the physical factor like capillary porosity; the chemical factor like the re-organization of silicon-
oxygen network during de-polymerization, re-polymerization and incorporation of calcium as shown in Figure 5.34. In this sense, the comprehensive influences of these two factors on the structure development during the interaction between alkali silicate and calcium can be studied.

![Diagram of varied factors' contribution to the structure development]

Figure 5.34: Schematic representation of varied factors’ contribution to the structure development.

### 5.4.1 Physical Factor

The structure development consisting of the coagulation and rigidification processes is highly influenced by the solid volume fraction in the sample. As the solid volume fraction increases, more and more collisions and inter-particle forces will be generated [109, 118] and therefore, benefit the structure development.

Basically, the solid volume fraction describes the quantity of solid phase present in the system. Therefore, any process associated with the volume change of solid, e.g. the consumption of the solid reactants and the formation of the solid products, can affect the structure development. In the present study, notably, the unreacted silica fume and alkali silicate are dispersed in the slurry as particles. The changes of their quantity due to multiple reactions do affect the solid volume fraction. More importantly, the formation of calcium alkali silicate might have the most significant influence on structure development. Because this process alters not only the quantity of solid phases but also their way of organization.

The porosity of the sample obtained from a large number of image analysis represents the surface area fraction of the visible voids, which can represent the solid volume fraction of that surface. Accordingly, the influence of the porosity on the structure development can be explored. The results of porosity and structure development at 1h are combined and shown in Figure 5.35.
As shown in Figure 5.35, the relationship between the porosity and the structure development defined by $G'_\text{max}$ and $G'_\text{min}$ is clear: the increase of porosity leads to the decrease of the structure development and vice versa. In particular, S1H-0.3 has the highest porosity and the smallest structure development defined by its $G'_\text{max}$ and $G'_\text{min}$. S24H-0.3 has the lowest porosity and the largest structure development defined by its $G'_\text{max}$ and $G'_\text{min}$. S1H-0.1 has a higher porosity than S24H-0.1, accordingly the structure development of S1H-0.1 is smaller than that of S24H-0.1.

Therefore, a hypothesis about the influence of porosity on structure development can be proposed and illustrated as follows. On the one hand, the porosity obtained by the image analysis represents the volume fraction of pores and voids on a cross section of the sample. On the other hand, the solid volume fraction of the sample describes the volume fraction of solid in the whole sample. Hence, the porosity can characterize the solid volume fraction in a way. The physical meaning of the porosity obtained from image analysis is schematically shown in Figure 5.36. As long as the number of the images used for acquiring porosity by image analysis is large enough to ensure its representativity for the whole sample, the porosity obtained from image analysis can be used as an indicator of solid volume fraction of the sample.
In this sense, as the porosity decreases, the solid volume fraction increases. It means more solid phases are present in the sample leading to the increase of the collisions and inter-particle forces benefiting the structure development. This is why a strong correlation between porosity and structure development can be found in Figure 5.35. Notably, using porosity obtained from image analysis to characterize solid volume fraction of the whole sample should be critically conducted to ensure the reliability [111, 119].

5.4.2 Chemical Factor

The re-organization of the silicon-oxygen network during the interaction between alkali silicate and calcium inevitably influences the structure development [104]. As stated in the previous sections, the silicon-oxygen network can be affected by two phenomena: incorporation of calcium and re-organization of silicon-oxygen network.

5.4.2.1 Incorporation of Calcium

Calcium plays two roles during and after its incorporation into silicon-oxygen network. On the one hand, calcium can act like a bridge to link two alkali silicate groups. As shown in Equation 5.1 and Equation 5.2, the calcium provided by the added CH is incorporated into the silicon-oxygen network creating the interlinkages. In this sense, this type of connections are continuously generated resulting in the re-organization of the network. On the other hand, the silicon-oxygen network can be weakened by the incorporation of calcium leading to the rupture of the network which promotes the depolymerization of the silicon-oxygen network in the system. Both of the two effects are able to change the organization of the groups and particles present in the system and therefore, affect the structure development.
In the light of this consideration, it is possible to investigate their influences by correlating the consumption of CH from 0.05h to 1h and the content of CH at 1h as well as the structure development defined by $G'_\text{max}$ and $G'_\text{min}$ are shown in Figure 5.37. The reversible structure development is defined by Equation 5.13.

![Figure 5.37: Consumption of CH from 0.05h to 1h, content of CH at 1h and reversible structure development.](image)

It is extremely important to know that the consumption of CH due to its interaction with alkali silicate from 0h to 0.05h is not taken into account in this study. This has a great influence on the following qualitative investigation particularly for the samples (S24H-0.1 and S24H-0.3) containing the highly reactive alkali silicate (24h).

S1H-0.1 and S1H-0.3 have the same type of alkali silicate slurry, which was obtained by reacting silica fume with 1 mol/L of NaOH solution for 1 hour, reacting with different amount of CH. Compared to S1H-0.3, S1H-0.1 has larger $G'_\text{max}$, $G'_\text{min}$ and the reversible structure development. It seems that less addition of CH benefits the structure development. However, this does not conflict with what we previously propose regarding the influence of calcium on the structure development. Because it is the quantity of the reacted CH rather than the added CH which influences the structure development.
Furthermore, other factors could have influences as well. The consumption of CH from 0.05h to 1h in S1H-0.1 is almost the same as that in S1H-0.3 indicating the structure development generated by the interaction between alkali silicate and calcium in S1H-0.1 and S1H-0.3 are similar. Meanwhile, the quantity of CH remaining in the system of S1H-0.3 is much more than that in S1H-0.1 (even more than 3 times). This unreacted CH present in the system can only act as “temporarily inert” particles dispersed in the system without contributing to the structure development. These inert particles and additional NaOH solution introduced at the same time result in a dilution effect to the structure as stated in the previous section. Therefore, less structure development can be found in S1H-0.3 compared to that in S1H-0.1.

S24H-0.1 and S24H-0.3 have the same type of alkali silicate slurry, which was obtained by reacting silica fume with 1 mol/L of NaOH solution for 24 hours, reacting with different amount of CH. Compared to S24H-0.1, S24H-0.3 has a larger $G'_\text{max}$, $G'_\text{min}$ and structure development. This is consistent with the hypothesis we propose that, the more CH is added, the more structure development can be generated. The consumption of CH from 0.05h to 1h in S24H-0.1 almost equals that in S24H-0.3. This is different from the comparison in the previous paragraph. To explain this, the comparison between S1H-0.3 and S24H-0.3 needs to be taken into account. Same amounts of CH are added to S1H-0.3 and S24H-0.3. However, the CH remaining in the system of S1H-0.3 is about 6 times more than that in S24H-0.3 at 1h, while the consumptions of CH from 0.05h to 1h in both systems are similar. This indicates that, most of the CH added to S24H-0.3 is consumed from 0h to 0.05h which is out of the evaluation. Therefore, it means that the real consumption of CH due to its interaction with alkali silicate is the sum of its consumption from 0h to 0.05h and the consumption from 0.05h to 1h. This explains why the structure development in S24H-0.3 is larger than that in S24H-0.1 when their consumptions of CH are similar. Therefore, the influence of calcium on the structure development in S24H-0.1 and S24H-0.3 is consistent with our hypothesis, notifying that the more calcium reacts with alkali silicate, the more structure development can be generated.

5.4.2.2 Re-organization of Silicon-oxygen Network

As previously stated, the re-organization of silicon-oxygen network is caused by de-polymerization and re-polymerization. During the de-polymerization, the siloxane bonds in silicon-oxygen network are destroyed resulting in the breakage of the whole network. During the re-polymerization, siloxane bonds are created by condensation leading to the re-construction of the silicon-oxygen network, as given in Equation 5.15 [102]. Notably, the re-polymerization can be catalyzed by the incorporated calcium [114]. Of course, such a process of re-organization of the silicon-oxygen network will change the properties of calcium alkali silicate, which is the most important
product determining the structure development of the system during the interaction between alkali silicate and calcium.

\[(\text{Si} - \text{O} \ldots \text{Ca} \ldots \text{O} - \text{Si}) + \text{H}_2\text{O} \rightarrow (\text{Si} - \text{O} - \text{Si}) + \text{Ca}^{2+} + 2\text{OH}^-\quad \text{Equation 5.15}\]

In the light of this consideration, the influence of the re-organization on the structure development can be investigated. Considering the duration of the oscillatory measurement, this analysis is limited within the range from 0.05h to 1h. However, in order to provide a comprehensive information for this investigation, the prior and subsequent states of these silicon-oxygen network are also given. In this way, the structure development defined by \(G'_{\text{max}}\) and \(G'_{\text{min}}\) is correlated with the corresponding state of the silicon-oxygen network, as shown in Figure 5.38.
Figure 5.38: Influence of silicon-oxygen network on structure development.
For the comparison between S1H-0.1 and S1H-0.3, as shown in Figure 5.38, the structure development in S1H-0.1 is slightly higher than that in S1H-0.3. This result can be attributed to two reasons. Firstly, it is clear that the silicon-oxygen networks in both S1H-0.1 and S1H-0.3 at 1h are experiencing a de-polymerization predominant process. It means the connectivity of the system is decreasing due to the breakage of siloxane bonds. Accordingly, less and less bonds in silicon-oxygen network at the micro scale are available to produce the structure development at the macro scale. Secondly, there is a large number of unreacted CH present in S1H-0.3 at 1h according to the results given in 5.3.2. Considering the role of calcium as a catalyst for de-polymerization, therefore, the more calcium is contained in the system, the more de-polymerization is going to happen. In this sense, the de-polymerization occurred in S1H-0.3 is much more than that in S1H-0.1 at 1h. It means more siloxane bonds are under attack in S1H-0.3 at 1h compared to S1H-0.1. Accordingly, less bonds are available to generate structure development in S1H-0.3 than that in S1H-0.1.

For the comparison between S24H-0.1 and S24H-0.3, the structure development in S24H-0.3 is larger than that in S24H-0.1. Two reasons are responsible for this result. Firstly, it is clear to find out that the silicon-oxygen network in S24H-0.1 are experiencing a de-polymerization predominant process at 1h, while the de-polymerization in S24H-0.3 occurs simultaneously with the re-polymerization at this moment according to the results in 5.3.3. It means that the bonds in S24H-0.1 are undergoing breakage while the bonds in S24H-0.3 are experiencing breakage and generation at the same time. The final state of the silicon-oxygen network in S24H-0.3 at this moment is determined by both de-polymerization and re-polymerization. Secondly, the presence of $Q^3_{\text{cyc}}$ in S24H-0.3 at 1h is believed to be one the most important reasons for the structure development. A silicon-oxygen network containing such a complex and cross-linked Si specie is expected to be able to contribute more to the structure development compared to the one containing regular $Q^3$.

Notably, as shown in Figure 5.38, the Si-environment compositions of S1H-0.3 and S24H-0.1 at 1h are comparable while their structure developments are completely different. However, this does not mean the structure developments are independent from the influence of the silicon-oxygen networks in these two systems. Actually, this is highly affected by the physical factor as previously stated in 5.4.1 that, a large number of unreacted CH is present in S1H-0.3 as “temporary inert” particles which cannot contribute considerably to the structure development. In addition, the additional solution introduced at the same time also has an adverse effect on the structure development in S1H-0.3. Moreover, those unreacted CH in S1H-0.3 ensured the continuousness of the de-polymerization. While the de-polymerization in S24H-0.1 is almost at its end according to the extremely low content of unreacted CH present in the system (5.3.2) as well as its subsequent state of silicon-oxygen network at 24h.
Accordingly, the state of the silicon-oxygen networks in S24H-0.1 at 1h also favors the structure development.

5.5 Summary

This chapter investigates the interaction between alkali silicate and calcium hydroxide from multiple points of view. The rheological, chemical, nano and micro structural properties of the calcium alkali silicate as the product of this interaction are characterized with various methods. Based on the above results and discussion, the following findings can be obtained:

1. The interaction between alkali silicate and calcium hydroxide results in a structure development which consists of coagulation and rigidification leading to the formation of a rigid structure.

2. As the trigger of the interaction resulting in the structure development, calcium hydroxide plays essential roles to influence the silicon-oxygen network of calcium alkali silicate. The more calcium hydroxide is added to the alkali silicate slurry with higher reactivity; the more structure development can be generated from the multiple physico-chemical reactions. In addition, the more calcium hydroxide is added to the alkali silicate slurry with lower reactivity; the less structure development can be generated.

3. The silicon-oxygen network present in the alkali silicate slurry have huge influence on the structure development. Its reactivity predominantly determines the structure development: the more reactive those networks are, the more structure development can be generated and vice versa.

4. The polymerization degree of the silicon-oxygen network in the system evolves with the interaction between alkali silicate and calcium hydroxide. At the earlier age when calcium hydroxide is abundantly present in the system, the de-polymerization prevails leading to the breakage of the siloxane bonds to generate a less cross-linked system; in the later age when calcium hydroxide is consumed or with a trace amount in the system, the re-polymerization starts to take over as the predominant process in the system resulting in the formation of a more cross-linked and complex silicon-oxygen network.

5. The structure development generated during the interaction between alkali silicate and calcium hydroxide is highly influenced by both the physical factor and chemical factor.

6. $Q^{cyc}$ is considered to be responsible for the significant structure development in S24H-0.3.
These findings provide comprehensive and fundamental information about the interaction between alkali silicate and calcium hydroxide. Combining with the results of Chapter 4 where the information about the interaction between reactive silica and NaOH solution has been provided, a panoramic view of the multiple interactions among reactive silica, alkaline solution and calcium can be obtained. Based on this, an original fundamental mechanism about the generation and evolution of the reaction rim which is closely related with the interior expansive force in ASR can be proposed, as given in Chapter 6.
After investigating the multiple interactions among the reactive silica, alkaline solution and calcium hydroxide in Chapter 4 and Chapter 5, a mechanism about the formation and evolution of the reaction rim in ASR is proposed in this chapter. Extensive discussion of applying this mechanism to explain other phenomena in ASR is provided as well.
6.1 Foreword

As stated in Chapter 2, the multiple interactions among reactive silica, alkaline solution and calcium hydroxide during the chemical process of the formation of the reaction rim in ASR can be classified into two steps: the interaction between reactive silica and alkaline solution to form alkali silicate comes first, the interaction between alkali silicate and calcium to form calcium alkali silicate comes second. The former has been studied in Chapter 4 and the latter has been investigated in Chapter 5.

In Chapter 4, the influence of the reaction time on the properties of alkali silicate has been studied. The reactivity of the alkali silicate during its interaction with calcium can be predicted. In Chapter 5, the structure development generated from the interaction between alkali silicate and calcium is explored. The influences of the reactivity of alkali silicate and quantity of the added calcium on the structure development are emphasized.

In this way, the information to obtain a better understanding about the two steps concerning the formation and evolution of reaction rim are provided. By coordinating the findings from previous chapters, an original mechanism dedicated to explaining the formation and evolution of the reaction rim can be proposed. Afterwards, the mechanism is extrapolated to demonstrating several typical phenomena of ASR.

6.2 Formation and Evolution of Alkali Silicate in Chemical Model System and Concrete

In this section, the chemical model system used in Chapter 4 is compared to the cementitious system where the reactive silica present in aggregates reacts with alkalis and hydroxyls present in the pore solution of cement paste. Afterwards, the findings of Chapter 4 are extrapolated to the cementitious system to provide a fundamental understanding about the formation and evolution of alkali silicate in the first step of generating reaction rim.

In the cementitious system where ASR occurs, as soon as the reactive silica from the aggregate comes into contact with the pore solution of the cement paste, Si-O-Si of silica, also known as siloxane, is attacked by hydroxyl (OH\(^{-}\)) to generate Si-OH (silanol) leading to the hydrolysis of silica. As OH\(^{-}\) continually attacks siloxanes, the network of tetrahedral silica breaks down. Alkali silicate forms after the incorporation of alkalis (Na\(^{+}/\) K\(^{+}\)) to counter balance the negative charges on the surface of the silicates. Thereafter, once Ca\(^{2+}\) comes into contact with the alkali silicate, calcium alkali silicate forms from the interaction between alkali silicate and calcium [104]. This process can be considered as a
pozzolanic reaction [11, 51]. Nevertheless, the formation of calcium alkali silicate may not occur immediately after alkali silicate is released into the solution due to the lack of calcium [83]. This local shortage of calcium is caused by its interaction with alkali silicate at the early age. As a result, the alkali silicate present in the system can interlink with each other by condensation [30] leading to an increase of the polymerization degree of numerous silicon-oxygen networks in the system [51, 52]. It means that, once the alkali silicate accumulates in the system without reacting with calcium, further evolution like polymerization will occur and alter its nano structure and consequently its properties. In this sense, the polymerization degree of the alkali silicate present in the cementitious system largely depends on how long it remains in the system: it is less complex and polymerized when it stays shortly in the system until its reaction with calcium; it is more complex and polymerized when it stays in the system for a long time.

In the chemical model system given in Chapter 4, the alkali silicate slurry is obtained by reacting silica fume with 1mol/l of NaOH solution for 1 hour or 24 hours. According to the results of Chapter 4, those two chemical model systems with different reaction times contain the silicon-oxygen networks with low and high polymerization degree, respectively. In particular, the chemical model system obtained from the interaction for 1 hour simulates the system where the alkali silicate does not undergo further evolution after it is formed; the chemical model system obtained from the interaction for 24 hours simulates the system where the alkali silicate has experienced further evolution of polymerization since it is formed. Combining with what has been stated in the previous paragraph, those two types of alkali silicate slurry can represent the systems containing the alkali silicate with and without experiencing polymerization since it is formed.

Based on the conclusion of Chapter 4, the alkali silicate slurry that experienced further evolution contains more complex silicon-oxygen network and more hydroxyl groups compared to the one that does not undergo the evolution. Those properties have a huge impact on the reactivity of the alkali silicate during its interaction with calcium.

6.3 Formation and Evolution of Calcium Alkali Silicate in Chemical Model System and Concrete

In this section, the chemical model system used in Chapter 5 is compared to the cementitious system where the alkali silicate reacts with calcium in the pore solution of cement paste. Subsequently, the findings of Chapter 5 are extrapolated to the cementitious system to give a comprehensive description about the formation and evolution of calcium alkali silicate in the second step of the formation of reaction rim.
As stated in Chapter 2, the main calcium source in cementitious system is CH. As one of the products of cement hydration, CH is originally generated in the cement paste leading to its abundant presence there. The dissolution of CH will occur to compensate for the decreased concentrations of OH\(^-\) and Ca\(^{2+}\) once they are consumed by the interaction with silica and the interaction with alkali silicate, respectively. Hence, the free CH can act as a buffer to maintain a high pH level and the saturation of Ca\(^{2+}\) in the pore solution of the cement paste [36]. In this sense, the content of calcium available for any further reactions is determined by the quantity of CH: the more CH is contained in concrete, the more calcium can be provided for further reactions. It should be noted that the calcium provided by other components (e.g. calcium silicate hydrate) in concrete is ignored here. In addition, CH can be found rarely in the aggregates. Therefore, the availability of calcium is different from place to place: the closer to the cement paste, the more calcium can be provided; the closer to the aggregate, the less calcium can be found. Accordingly, in the other way around, the content of calcium which can be provided for the interaction with alkali silicate depends on the location. Moreover, as stated in the previous section, the availability of calcium for further reactions also depends on the consumption of calcium during the interaction with alkali silicate occurring at the early age.

In the light of this consideration, the additions of CH to the alkali silicate slurry at the Ca/Si ratio of 0.1 and 0.3 can simulate the interaction between alkali silicate and calcium under the conditions where little calcium and abundant calcium is present, respectively. The conclusions of Chapter 5, therefore, can be extrapolated to the cementitious system with respect to the availability of calcium to the interaction with alkali silicate.

**6.4 System Representation**

As stated above, the alkali silicate slurries obtained by reacting silica fume with NaOH solution for 1 hour simulates the system containing the alkali silicate which is formed immediately after the attack of alkaline solution on reactive silica without undergoing further evolution; the alkali silicate slurries obtained by reacting silica fume with NaOH solution for 24 hours simulates the system containing the alkali silicate which has experienced further evolution of polymerization in the system. In addition, different amounts of calcium available for further reactions also represent different scenarios in cementitious system.

In this way, the four systems studied in Chapter 5 can simulate certain conditions in the cementitious system:
6.5 Mechanism of Formation and Evolution of the Reaction Rim

After clarifying the conditions represented by the four systems studied in Chapter 5, the mechanism of the formation and evolution of the reaction rim can be proposed based on the conclusions of Chapter 4 and Chapter 5:

(1) The formation of alkali silicate: once the reactive silica in aggregates meets the pore solution of cement paste, alkalis and hydroxyls will attack and destroy the siloxane bonds in the silicon-oxygen network of reactive silica to form silanol bonds leading to the formation of alkali silicate. This is schematically shown in Figure 6.1.
Once alkali silicate is formed from the interaction between reactive silica and alkaline solution, it will immediately react with the calcium nearby to form calcium alkali silicate. It is reasonable to believe that, the content of CH at this place is relatively high assuming that its interaction with alkali silicate does not start. Therefore, it is the alkali silicate without undergoing further evolution of polymerization reacting with the calcium which is abundant in this stage. Obviously, it is rational to use S1H-0.3 (1 hour, Ca/Si = 0.3) to simulate this situation where the alkali silicate slurry obtained by reacting reactive silica with NaOH solution for 1 hour interacts with relatively abundant CH.

Based on the results of Chapter 5, little structure development is generated at the early age of this process. It means the formed structure constituting calcium alkali silicate is not rigid but flexible, making it possible to migrate from the location where it forms to the capillary pores and voids in the matrix of cement paste around this reaction site, given a considerable driving force. This process is schematically shown in Figure 6.2.
As the reaction between alkali silicate and calcium continues, the calcium present at this region is consumed leading to the reduction of its content, so that less and less CH is available for its interaction with alkali silicate. Rationally, SiH-0.1 (1 hour, Ca/Si = 0.1) can be used for simulating this situation that the alkali silicate without undergoing further evolution of polymerization reacts with relatively rare CH.

According to the results of Chapter 5, similar to the situation in the previous stage, little structure development can be generated from this process at the early age as well. Similar to that formed in Stage 2, the structure is also flexible and prone to migration to the neighborhood. This is shown in Figure 6.3.
(4) Apparently, on the one hand, the calcium present in this region is limited compared to its abundance in the cement paste. Accordingly, the continuous interaction between alkali silicate and calcium will inevitably result in the local depletion of calcium. On the other hand, the formation of alkali silicate from the interaction between the reactive silica in aggregates and the pore solution of cement paste can proceed continuously due to the abundant availability of both reactants. This results in the local accumulation of alkali silicate which tends to interlink with each other to form another type of alkali silicate with a higher polymerization degree, as stated previously. As a result, the alkali silicate experiences further evolution. This transition process is shown in Figure 6.4. Notably, the interaction between the existing calcium alkali silicate with the constituents of the pore solution is out of our scope for this moment.

![Evolution of alkali silicate in Stage 4](image)

Figure 6.4: Schematic representation of Stage 4.

(5) As the alkali silicate accumulates and evolves, the volume of this phase will increase. Once the evolved alkali silicate enters a new region where abundant calcium is present, this type of alkali silicate will interact with the abundant calcium to form calcium alkali silicate. Obviously, this situation can be simulated by S24H-0.3 (24 hours, Ca/Si = 0.3), where the alkali silicate which has experienced further evolution of polymerization reacts with abundant CH. Notably, this abundant calcium can also be supplied by the migration or penetration of calcium [37]. According to the results of Chapter 5, huge structure development can be generated from this interaction. It means a rigid structure can be established in a short time at the place where the polymerized alkali silicate comes into contact with the abundant calcium, as shown in Figure 6.5. Obviously, this rigid structure will stay at the location where it forms and covers the reaction site where alkali silicate is formed and accumulated, i.e. it is too rigid to be forced to migrate.
(6) Similar to the situation in Stage 3, the continuous interaction between alkali silicate and calcium results in the reduction of the content of calcium present at this place. As a result, less CH is available for its interaction with the evolved alkali silicate. This situation can be simulated by S24H-0.1 (24 hours, Ca/Si = 0.1) where the alkali silicate which experienced further evolution of polymerization interacts with rare CH.

According to the results of Chapter 5, a considerable number of structure development is generated from this interaction at the early age. The structure generated in this stage is more rigid than those in S1H-0.1 and S1H-0.3 while less rigid than that in S24H-0.3. Moreover, based on the process mentioned above, this structure should be located between the rigid structure formed in Stage 5 and the aggregate surface. Therefore, the rigid structure formed in Stage 5 can grow with the help of this process leading to the coverage the space where alkali silicate accumulates. This process is schematically shown in Figure 6.6.
(7) Notably, as long as alkali silicate is continuously formed and accumulated from the interaction between reactive silica and alkaline solution, the polymerization of alkali silicate can be activated and maintained. The polymerized alkali silicate, thereafter, can be continuously supplied to the reactions in Stage 5 and Stage 6 leading to the continuous formation of the rigid structure until the complete coverage of the place where alkali silicate forms and accumulates. Till that time, the aggregate is completely packed by the rigid structure as the reaction rim did according to Ichikawa [37, 78]. This process is shown in Figure 6.7.

![Figure 6.7: Schematic representation of Stage 7.](image)

### 6.6 Further Discussion on Various Phenomena of ASR

After the proposal of the mechanism of the formation and evolution of the reaction rim, extensive discussion will be given by utilizing the proposed mechanism on explaining several typical phenomena of ASR.

#### 6.6.1 Reaction Rim Theory

##### 6.6.1.1 Boundary Conditions For the Formation of Reaction Rim

It is widely accepted that the reaction rim does not occur in every concrete affected by ASR. However, the interaction between the reactive silica in aggregates and the pore solution of cement paste to form alkali silicate as well as the interaction between the formed alkali silicate and the calcium from cement paste to form calcium alkali silicate, as the prior steps to form the reaction rim, cannot be avoided whatever the reaction rim is spotted in the affected concrete or not. This implies that the
formation of reaction rim should meet certain conditions under which the interaction between reactive silica and pore solution as well as the interaction between alkali silicate and calcium is able to generate such a rigid structure to stop the migration of alkali silicate and provide a mechanical constraint on the reaction site as proposed by Ichikawa [37, 78]. Based on the mechanism proposed above, the necessary conditions for the occurrence of the reaction rim can be illustrated as follows.

According to the above mechanism, the decisive steps to form the rigid structure are Stage 4 and Stage 5. Obviously, two conditions should be matched. Firstly, the alkali silicate formed from the interaction between reactive silica and pore solution must undergo further evolution in such a system to have a complex and polymerized silicon-oxygen network. Secondly, this polymerized alkali silicate must come into contact and react with a large number of calcium. In this way, a significant structure development can be generated resulting in the formation of a rigid structure which can be considered as the reaction rim.

Therefore, the necessary conditions for the formation of the reaction rim are: the formation of the polymerized alkali silicate and the abundant calcium to interact with. If the alkali silicate present in the system is less polymerized, the system will follow the theme of Stage 2 when calcium is abundant or Stage 3 when calcium is rare. Certainly, no rigid structure and therefore no reaction rim can be found. Or, if there is completely no calcium present in the system, the system will keep undergoing Stage 1 and Stage 4. Of course, no rigid structure will be generated. Only if calcium meets and reacts with the polymerized alkali silicate, a considerable rigid structure can be built. However, this structure might be not rigid enough to act like the reaction rim does at the very beginning of its formation. Deficiencies like incomplete coverage of the aggregate, limited constraint and so on can be encountered.

6.6.1.2 Mechanical Constraint Around Aggregate

According to Ichikawa’s theory [37, 78], the reaction rim should be able to apply a constraint around the aggregate until it is destroyed by the accumulated expansive force between the reaction rim and the aggregate surface.

The rigid structure generated in Stage 5 and Stage 6 might be able to provide the mechanical constraint when the aggregate is completely covered by the rigid structure, as shown in Figure 6.7. However, further information about the mechanical properties of the rigid structure needs to be disclosed.
6.6.2 Migration of ASR Gel

It is well known that, ASR gel can migrate from the region where it forms to the voids and capillary pores located in the matrix of the cement paste in the vicinity of an aggregate [27, 75, 120, 121]. Based on the above mechanism, the flexible structure which is composed of the calcium alkali silicate formed from Stage 2 and Stage 3 might be able to migrate. Notably, the structure which is composed of the calcium alkali silicate formed from Stage 5 and Stage 6 is probably too rigid to migrate and penetrate into the pores and voids. This process is shown in Figure 6.8.

![Figure 6.8: Schematic representation of migration of ASR gel to voids and pores, the sizes of an aggregate and the solid phase of cement paste are adjusted for shown.](image)

6.6.3 Interior or Exterior of Aggregate?

ASR gel is usually found at two places in concrete: the interface between the aggregate and the matrix of cement paste and the interior of a micro crack in an aggregate. However, the cracking due to ASR always starts in the interior of an aggregate rather than at the interface. It seems that the presence of ASR gel at the interface between the aggregate and the matrix of cement paste does not contribute to the cracking due to ASR. Little work has been dedicated to this point. And Ichikawa’s model cannot explain this phenomenon unless two prerequisites, i.e. the reaction rim has a higher tension force than the aggregate and the bond between the reaction rim and the aggregate can withstand higher tensile forces than the reaction rim itself, are matched. Unfortunately, both
prerequisites are almost impossible. In this subsection, why the cracking only starts in the interior of an aggregate is addressed based on the mentioned mechanism in 6.5.

Based on the proposed mechanism, the complete coverage of the reaction site where alkali silicate forms and accumulates is much easier in the interior of an aggregate (e.g. a micro crack, pores) than that on the interface. For the situation on the interface between the aggregate and the cement paste, it takes long time for the rigid structure (reaction rim) to completely cover the surface of an aggregate by following the process of the proposed mechanism. Moreover, the necessary conditions for the formation of reaction rim are difficult to be matched on the whole aggregate surface. In contrast, those conditions can be more easily matched at the opening of the interior of an aggregate as shown in Figure 6.9. It means that the reaction rim is easier to be formed at the opening of the interior of an aggregate compared to its formation around an aggregate.

Meanwhile, the interior of the aggregate is weakened by the continuous attack by alkalis and hydroxyls to generate alkali silicate. As a result, the aggregate is prone to cracking when alkali silicate is accumulated in the interior of the aggregate. In this sense, no wonder ASR is observed more often in the interior of an aggregate than that at the interface between aggregate and cement paste.

![Figure 6.9: Schematic representation of reaction rim formed on the aggregate surface and in a micro crack of an aggregate.](image)

6.6.4 Calcium Content of ASR Gel

As one of the most controversial issues of ASR, the calcium content of ASR gel varies widely [12, 74]. This variation can be caused by many factors including the characterization method [51].
Based on the proposed mechanism, if the measurement is conducted on the area where the products from Stage 2 and Stage 5 are present, the ASR gel with a relatively high Ca/Si ratio can be found. If the measurement is carried out on the area where the products from Stage 3 and Stage 6 are present, the ASR gel with a relatively low Ca/Si ratio can be found. If the measurement is conducted on the area where the products from Stage 1 and Stage 4 are present, no calcium can be found in the ASR gel there. It means that the calcium content of ASR gel really depends on the location where it is formed and measured. Notably, the further interaction between the products and the pore solution afterwards is not taken into account.

6.7 Summary

In this chapter, an original mechanism about the formation and evolution of the reaction rim based on the conclusions of the previous chapters is proposed. An application of the proposed mechanism on explaining several typical phenomena of ASR is provided.
PART III

FORMATION AND EVOLUTION OF

CALCIUM ALKALI SILICATE

AT AN INTERFACE
In this chapter, the formation of the reaction rim is simulated in a calcium-alkali-silicate system which simulates the interaction between the reactive silica in aggregates and the pore solution of cement paste at their interface. The chemical composition, transport properties and microstructure of the simulated reaction rim are investigated to provide comprehensive information about how it is formed and operates in such a system.

Parts of this chapter have been published in Materials, 2016 [122, 123].
7.1 Background

The formation of reaction rim in ASR-affected concrete consists of two steps: the formation of alkali silicate from the interaction between reactive silica in aggregates and the pore solution of cement paste; the formation of calcium alkali silicate from the interaction between the formed alkali silicate and the calcium. Based on the mechanism proposed in Chapter 6, the formation of calcium alkali silicate from the interaction between alkali silicate and calcium is one of the decisive steps for the formation, evolution and operation of the reaction rim. Moreover, the interface between the reactive silica in aggregate and the pore solution of the cement paste is the very place where the formation and evolution of the reaction rim take place. However, the heterogeneous conditions on such an interface makes it extremely difficult to understand the reaction rim in concrete, not mentioning the influences from other constituents in concrete. It means the mechanism proposed in Chapter 6 cannot be directly extrapolated to concrete.

In light of this consideration, in the present chapter, a chemical model system is created to simulate the multiple interaction among silica, alkaline solution and calcium at the interface between the reactive silica in aggregates and the pore solution of cement paste during the formation and evolution of the reaction rim in real concrete. With the help of such a chemical model system, the formation of calcium alkali silicate from the interaction between alkali silicate and calcium on their interface was simulated to illustrate the formation and evolution of the reaction rim, providing information for a better understanding about the reaction rim and the mechanisms of ASR in real concrete.

7.2 Materials and Methods

7.2.1 Raw Materials

In order to simulate the interaction between the reactive silica and the constituents in the pore solution to generate alkali silicate in the first step of the formation of the reaction rim with an accelerated reaction rate, a type of silica fume (Elekem Microsilica Grade 940U, Oslo, Norway) instead of reactive silica was used in this study. The composition of the silica fume expressed as oxides and XRD pattern are given in Chapter 3. A 1 mol/L NaOH solution was used as the source of alkali and hydroxyl throughout this study. This solution was obtained by dissolving pellets of NaOH in distilled and CO₂-free water. The slurry of Ca(OH)₂ was obtained by adding a certain amount of powdered Ca(OH)₂ to the 1 mol/L NaOH solution with the liquid to solid mass ratio of 3. The Ca(OH)₂ slurry was to simulate the calcium source in concrete that is present both in the pore solution of the cement paste in the form of Ca²⁺ and in the
vicinity of the aggregate surface predominantly in the form of free portlandite. The reason for the addition of NaOH solution during the preparation of Ca(OH)$_2$ slurry was to maintain the liquid to solid ratio and the pH level of the whole system at a relatively constant level. The Ca(OH)$_2$ slurry was kept mixing on the rotary mixer to maintain its homogeneity until its use. The pellets of NaOH and powder-like Ca(OH)$_2$ were both reagent grade.

**7.2.2 Preparation of Alkali Silicate Slurry and Calcium Alkali Silicate**

The alkali silicate slurry, as the simulated product of the alkaline attack on reactive silica, was prepared by adding the 1 mol/L NaOH solution to the silica fume, sealed in a polypropylene bottle filled with N$_2$ and mixed with a rotary mixer at a speed of 60 rpm at room temperature. The liquid to solid mass ratio was set to 3 to simulate the partial silica dissolution in ASR [83]. The mixing was stopped after 24 h. Subsequently, the mixture was left at rest for another 24 h. This allows the stratification of the mixture leading to a stable system with a clear liquid layer at the top and a black slurry layer at the bottom (Figure 7.1 (a)). This state simulates the situation near the surface of reactive silica during the formation of the reaction rim in ASR where unreacted silica, dissolved and undissolved alkali silicate coexist. After the desired standing period, the Ca(OH)$_2$ slurry was added softly to the top of the mixture without any shaking or stirring to avoid disturbance of the layered structure (Figure 7.1 (b)). The amount of added calcium was set to make the calcium to silica mole (Ca/Si) ratio of the whole system as 0.3 to ensure excess presence of Ca(OH)$_2$ near the interface. This step is to simulate the contact of alkali silicate with the calcium source which is present as either Ca$^{2+}$ or Ca(OH)$_2$ in the second step of the formation of the reaction rim. Afterwards, the mixture was sealed again to avoid contamination and left at rest for another one day (1 d), four days (4 d) and seven days (7 d) to let the reactions continue and the structure evolve before the collection of samples.

![Figure 7.1: The appearance of the mixture: (a) before Ca(OH)$_2$ addition; and (b) after the addition of Ca(OH)$_2$.](image-url)
7.2.3 Sample Collection and Treatment

After the desired standing period, paste-like sample (Figure 7.2 (a)), sheet-like sample (Figure 7.2 (b)) and slurry-like sample (Figure 7.2 (c)) were collected from Location I, Location II and Location III, respectively, of the system, as shown in Figure 7.1. The state of the system when the samples were collected will be introduced in the next section.

![Figure 7.2: The appearance of the samples from different positions: (a) paste-like sample from the middle layer; (b) sheet-like sample from the hard layer; and (c) slurry-like sample from the slurry layer.](image)

All the fresh samples were immediately immersed in isopropanol for seven days to arrest further reactions. Isopropanol was renewed every day. After the desired immersion period of seven days, the samples for the XRD analysis, the TGA/DTA analysis and the X-Ray Fluorescence (XRF, NEX CG, Rigaku, Tokyo, Japan) analysis were taken out of isopropanol and dried under vacuum at room temperature for 2 days (enough for the samples with a small amount). The sheet-like samples for the Environmental Scanning Electron Microscope (ESEM, Philips XL30, Philips, Amsterdam, The Netherlands, as shown in Figure 7.3) equipped with Energy-dispersive X-ray spectroscopy (EDS, EDAM 3 EDS system, EDAX, Tilburg, The Netherlands) measurements were taken out of the isopropanol, dried in a desiccator filled with N₂ for 2 weeks to avoid any damage during vacuum drying. Portlandite and silica gel were also present in the desiccator for removing any possible CO₂ and moisture. Thereafter, the sheet-like samples were impregnated in an epoxy platform vertically (see Figure 7.4) to expose their cross sections. Notably, in order to preserve the original morphology of the sheet-like sample for the ESEM-EDS analysis, the adhesives attached to the sheet-like samples were not removed. Afterwards, the fixed samples were stored in a desiccator filled with N₂ during the hardening of epoxy for one day. The polishing step was followed according to the procedure proposed by Stuzman [106] to ensure accurate EDS results [124]. The moulds for impregnation and the instrument for polishing are as the same as the ones used in Chapter 5.
Figure 7.4. The sheet-like sample fixed vertically in an epoxy.

For the sheet-like samples, for $^{29}$Si solid-state cross-polarization (CP)/Magic angle spinning (MAS) nuclear magnetic resonance (NMR, Agilent Technologies Inc., Santa Clara, CA, USA) analysis, additional steps of sample preparation were followed and described as follows. After the sheet-like sample was collected from the system and immersed in isopropanol, the adhesives attached to the sheet-like sample were removed with a brush. Subsequently, the sample was immersed in isopropanol for seven days to cease further reactions. Afterwards, the sample was dried for 48 h under vacuum. Eventually, the sheet-like sample was crushed and ground into powder. This step was carried out in a glove box filled with N$_2$ to avoid contamination.
7.2.4 Characterization Methods

XRD measurements were carried out to identify crystalline phases by using a Thermo Scientific ARL X’Tra Diffractometer equipped with a Peltier cooled detector at a scan rate of 0.8 °/min. TGA/DTA were carried out to identify specific phases by quantifying the mass loss at different temperatures. During the measurements of TGA/DTA, the samples were heated from room temperature to 1000 °C at a rate of 10 K/min under N₂ atmosphere to avoid any contamination. XRD, TGA/DTA and XRF tests were carried out at Department of Inorganic and Physical Chemistry, Ghent University, Ghent, Belgium. The instruments for XRD and TGA/DTA analysis have been described in Chapter 5. The ESEM-EDS analysis was conducted at Microlab, Faculty of Civil Engineering & Geosciences, Delft University of Technology, The Netherlands. The information about the parameters for NMR tests can be found in Chapter 4.

7.3 Results and Discussion

7.3.1 System State Description

Twenty-four hours after calcium was added, according to the observation during the collection of samples from different places of the system, the appearance of the layered system is schematically shown in Figure 7.5. At the top, there is a liquid layer. Beneath, the middle layer, where the paste-like sample (Figure 7.2 (a)) was taken from, is wrapped by a white thin hard layer (the hard layer, where the sheet-like sample (Figure 7.2 (b)) was taken from) separating the middle layer from the liquid layer above and the slurry layer (where the slurry-like sample (Figure 7.2 (c)) was taken from) beneath as well. In general, the samples were collected from three locations: the middle layer, the hard layer and the slurry layer.

![Schematic representation of the layered mixture.](image-url)
7.3.2 XRD Results

The XRD patterns of the sample collected from the middle layer are shown in Figure 7.6. Obviously, the XRD patterns of the sample either from the system reacted for one, four or seven days are similar. This indicates that the different reaction periods did not have significant influence on the types of phases in the middle layer. The characteristic peaks at around 18° (2θ), 28.5° (2θ), 34° (2θ), 47° (2θ) and 50° (2θ) confirm the presence of Ca(OH)$_2$. The peaks from the calcite as the sign of carbonation in the middle layer are noticed as well. In addition, it seems that calcium alkali silicate was probably not present in the middle layer since its typical broadened and weak peaks were not found.

![XRD patterns of the sample collected from the middle layer](image)

Figure 7.6: XRD patterns of the sample collected from the middle layer (1, portlandite; 2, calcite).

The XRD patterns of the sample collected from the slurry layer are shown in Figure 7.7. Similar to the trend mentioned in the previous paragraph, the storage period has hardly any influence on the types of phases in the slurry layer as well. Particularly, the broadened peak centered around 21° (2θ) indicates the presence of unreacted silica fume or alkali silicate. Moreover, there are no characteristic peaks from Ca(OH)$_2$ and calcite indicating the absence of these phases in the slurry layer. The absence of the typical broadened peaks from calcium alkali silicate suggests that there is little or even no calcium alkali silicate present in this layer.
7.3.3 TGA Results

The TGA results of the samples from the middle layer are shown in Figure 7.8. The content of Ca(OH)$_2$ and calcite present in the middle layer can be calculated based on the mass loss. The method of calculation is provided elsewhere [110]. Apparently, the consistency among the results of the samples reacted for one, four and seven days confirms the trend observed by the XRD that the storage period indeed had no significant influence on the types of phases in the middle layer. More particularly, the significant mass loss located between 400°C and 500°C verifies the abundant presence of Ca(OH)$_2$. The mass loss due to calcite is also clear between 650°C and 800°C. However, the presence of calcium alkali silicate is uncertain since the curves have extremely low but non-negligible slopes ranging between 100°C and 400°C. The mass loss within this range can be attributed to the dehydration of calcium alkali silicate or alkali silicate [110].
The TGA results of the samples collected from the slurry layer are shown in Figure 7.9. The disappearance of the typical mass loss contributed by either Ca(OH)$_2$ or calcite confirms the XRD results that the slurry layer contained neither Ca(OH)$_2$ nor calcite. Combing with the XRD results, the significant mass loss located between 100 °C and 400 °C is due to the dehydration of alkali silicate rather than calcium alkali silicate since the typical broadened peaks from calcium alkali silicate were not found in the XRD results shown in Figure 7.7.

Figure 7.8: Mass loss of the sample from the middle layer determined by TGA.

Figure 7.9: Mass loss of the sample from the slurry layer determined by TGA.
7.3.4 XRF Results

The XRF results of the samples from either the middle layer or the slurry layer with different reaction periods are summarized and plotted in Figure 7.10. Notably, the mole ratio of the elements including (O, Al, Fe, Mg and so on) are not given individually in this chart to avoid confusion.

![Figure 7.10: Mole fraction of calcium and silicon in the middle layer (ML) and the slurry layer (SL). For example, 1 D ML = the middle layer collected from the sample reacted for one day; 1 D SL = the slurry layer collected from the sample reacted for one day.](image)

Obviously, regardless of the storage period, calcium is abundant in the middle layer while rare in the slurry layer; and the silicon is rare in the middle layer while abundant in the slurry layer. Particularly in the middle layer, the mole fraction of silicon is no more than 1% with respect to that of calcium, which is more than 20%. The abundance of the calcium is consistent with the XRD and TGA results showing that portlandite and calcite were present in the middle layer. In addition, the content of alkalis (Na and K) is slightly higher in the slurry layer than in the middle layer regardless of the storage period. This is perhaps due to the fact that more alkalis were bonded by alkali silicate in the slurry layer. This also infers that the contents of alkalis present in the middle layer and the slurry layer are similar.

In the middle layer, where Ca(OH)$_2$ is abundantly present, any silicate reacts with the excess Ca(OH)$_2$ to form calcium alkali silicate. Hence, the weak signal of silicon detected in the middle layer came from a trace amount of calcium alkali silicate. This confirms the suspicious presence of calcium alkali silicate, which was not detected by XRD and TGA in the middle layer due to its extremely low concentration.

In the slurry layer, regardless of the storage period, the mole fraction of calcium is lower than 0.1% while that of silicon is higher than 10%. This indicates that, on the one hand, no additional calcium
arrived in the slurry layer considering the original mole fraction of calcium in the silica fume. On the other hand, silicon prevailed in the slurry layer, which is consistent with the XRD results shown in Figure 7.7 showing that the slurry layer was composed of unreacted silica fume or alkali silicate.

7.3.5 Existence of a Transport Barrier

Based on the XRD, TGA and XRF results mentioned in the previous sections, some remarks need to be clarified before we continue. In the middle layer, the excess Ca(OH)$_2$ present in this layer enabled the reaction between calcium and silicate to proceed as long as both of them were present in this area. However, the least amount of silicon detected by XRF as well as the evidence of excess portlandite present in this area suggests that, the reaction ceased due to a lack of sufficient reagent, i.e., silicate. Therefore, it is reasonable to believe that no additional silicate coming from the slurry layer arrived in the middle layer. The trace amount of silicate detected was perhaps from the dissolved silicate originally present in the liquid layer at the top, though the transport of trace amount of silicate cannot be absolutely excluded based on these results. However, this possible migration or supply of silicate was supposed to be limited, otherwise the excess Ca(OH)$_2$ present in the middle layer can react with any silicate to form calcium alkali silicate resulting in an expected observation of the typical broadened peaks from calcium alkali silicate in the XRD results shown in Figure 7.6 as well as a higher silicon content in the XRF results shown in Figure 7.10. Hence, it is rational to conclude that the further migration of silicate from other positions, especially from the slurry layer beneath, to the middle layer was somehow prevented leading to an insufficient supply of silicate for its reaction with calcium in the middle layer. This implies that a transport barrier exists between the silicate source (the slurry layer) and the calcium source (the middle layer) to prevent the migration of silicate from the slurry layer to the middle layer against the great silicate concentration gradient. It should be noted that this transport barrier was indeed playing a similar role of the reaction rim as proposed by Ichikawa [37, 78].

A similar situation happened in the slurry layer, a transport barrier was able to prevent the migration of calcium coming from other places, especially from the middle layer, to the slurry layer. Otherwise if any additional calcium was present in the slurry layer, it could react with abundant alkali silicate there to generate calcium alkali silicate resulting in an expected observation of the typical broadened peaks in the XRD results shown in Figure 7.7 as well as a higher calcium content in the XRF results shown in Figure 7.10.
With respect to alkalis, there are only slight differences between their concentrations in the middle layers and the slurry layers from different samples. This infers the migration of alkalis was not influenced by such a transport barrier.

Based on the above results and discussion, this transport barrier preventing the penetration of both calcium and silicate can only be located between the middle layer, which was the calcium source at the top, and the slurry layer, which was the silicate source at the bottom. Considering the layered appearance of this system as shown in Figure 7.5, the hard layer physically separated the middle layer and the slurry layer. Therefore, the hard layer was identified as the transport barrier preventing the migration of calcium and silicate. Accordingly, further emphasis will be cast on the hard layer itself to investigate its properties and explore its functioning mechanism as a transport barrier. It needs to be noted that, even though the transport barrier found in this study had comparable functions as the reaction rim, we will keep addressing it as transport barrier rather than reaction rim considering the simplified chemical model system used in this study.

### 7.3.6 BSE Imaging

BSE images of samples with storage periods of one, four and seven days are shown in Figure 7.11 (a)–(c), respectively. The directions of the images are shown as well.

![Impregnated sample](image)

Figure 7.11: BSE images for the samples reacted for: (a) one day; (b) four days; and (c) seven days.

As shown in Figure 7.11, the BSE images of all the samples share some similarities. First, obviously, three regions with different grey levels can be found. According to the direction of the sample
placement, these three regions can be assigned to the three phases found on the samples: adhesives from the middle layer on the upper surface of the hard layer; the hard layer itself; adhesives from the slurry layer on the lower surface of the hard layer. In particular, Region I was located at the upper surface of the hard layer belonging to the adhesives from the middle layer; Region II was the hard layer; and Region III was located at the lower surface of the hard layer belonging to the adhesives from the slurry layer.

Obviously, compared to the other two regions, the region of the hard layer had the highest grey level indicating it was the most densified phase. The region of the adhesives from the slurry layer was relatively more uniform than the other two regions. The region with the adhesives from the middle layer contained fragmental particles with different size.

The border between the adhesives from the middle layer and the hard layer as indicated with the blue arrows in Figure 7.11, were not as clear as the ones between the hard layer and the adhesives from the slurry layer as indicated with orange arrows in Figure 7.11. In addition, several cracks can be noticed in all the BSE images in Figure 7.11. However, no products can be found in the interior of these cracks. This indicates the cracks did not form until the sample preparation. These cracks probably formed during the drying treatment.

7.3.7 EDS Results

In order to investigate the elemental composition of the hard layer, EDS area-scanning was carried out on the selected areas of each sample. As shown in Figures 7.12–7.14 for the sample reacted for one, four and seven days, respectively, the locations of the areas selected for EDS area-scanning are marked with rectangles. For the sake of convenience, the elemental composition of each area analyzed by EDS was expressed as Ca/Si ratio and alkali to silica mole ((Na+K)/Si) ratio. The averaged Ca/Si ratios and (Na+K)/Si ratios as well as their corresponding deviations of the areas from each column were plotted according to its relative position as indicated in the BSE images.
Figure 7.12: Changes of Ca/Si ratio and (Na+K)/Si ratio of the areas from the sample reacted for one day. The red curve represents the change of Ca/Si ratio, the yellow curve represents the change of (Na+K)/Si ratio.

The EDS results of the sample that reacted for one day are shown in Figure 7.12. Based on the results of Ca/Si ratio, two regions can be differentiated: the first region containing the six columns on the left having a low value of Ca/Si ratio; the second one containing the first column on the right having a high value of Ca/Si ratio. The Ca/Si ratios of the areas from the second region, in particular, were about 1.60 on the mean, while the Ca/Si ratios of the areas from the first region were lower than about 0.40.

Interestingly, the Ca/Si ratio dropped dramatically from about 1.60 to about 0.40 within a distance of 204 µm between the first and second columns from the right, confirming the existence of the border of the hard layer with the adhesives from the middle layer between the first and the second columns as marked with a blue arrow in Figure 7.11 (a). The huge decrease of the Ca/Si ratio across the border indicates that the hard layer was able to keep large amount of calcium outside of its territory. It should be noted that either the decreasing amount of calcium or the increasing amount of silicon present in these areas can cause the decrease of Ca/Si ratio. However, for the situation here on the border of the hard layer with the adhesives from the middle layer where abundant Ca(OH)₂ was present, the decreasing amount of calcium should be the dominant effect since the concentration of silicate in these areas was expected to be low. On the contrary, such a significant decrease of Ca/Si ratio was not found across the border of the hard layer with the adhesives from the slurry layer, as indicated with an orange arrow in Figure 7.12. The Ca/Si ratio dropped from about 0.25 for the areas...
located on the hard layer to about 0.14 for the areas located on the adhesives from the slurry layer. This minor decrease was probably attributed to the abundant presence of silicate near the lower surface of the hard layer in contact with the slurry layer beneath. In other words, the relatively high concentration of silicate as well as the relatively low concentration of calcium limited the change of the Ca/Si ratio in this area.

Moreover, for the areas located within the territory of the hard layer, their Ca/Si ratio slightly decreased from about 0.45 to about 0.25 as getting away from the border of the hard layer with the adhesives in a distance of about 800 µm. This implies the hard layer was even capable of preventing migration of calcium and silicate within its territory. In addition, the changes of the (Na+K)/Si ratio had a smaller variation ranging from 0.20 to 0.30 indicating the weak interaction between the hard layer and the alkalis.

![Figure 7.13: Changes of Ca/Si ratio and (Na+K)/Si ratio of the areas from the sample reacted for four days. The red curve represents the change of Ca/Si ratio, the yellow curve represents the change of (Na+K)/Si ratio.](image)

The EDS results of the analyzed areas of the sample that reacted for four days are shown in Figure 7.13. Similar to the sample that reacted for one day, two regions can be differentiated with respect to the values of Ca/Si ratio: the region containing the first column from the right with a high value of Ca/Si ratio; the region containing the other seven columns on the left with a low value of Ca/Si ratio. Based on the observation from the BSE image shown in Figure 7.11 (b), the region with high value of Ca/Si ratio was located on the adhesives from the middle layer; the region with the second column to the
seventh column on the right was located on the hard layer itself; the first column on the left was located on the adhesives from the slurry layer.

Comparably, a dramatic decrease of the Ca/Si ratio was noticed from the first column on the right to the second one. The Ca/Si ratio dropped from about 1.80 to about 0.40 within a distance of 380 μm suggesting the existence of the border between the hard layer with the adhesives from the middle layer as indicated with a blue arrow in Figure 7.11 (b). Such a high value of Ca/Si ratio implies the presence of Ca(OH)₂ in this region. Besides, the dramatic drop of Ca/Si ratio confirms the ability of the hard layer to stop the penetration of calcium into its matrix. With respect to the border of the hard layer with the adhesives from the slurry layer as indicated with an orange arrow in Figure 7.11 (b), the Ca/Si ratio dropped from about 0.24 to about 0.08 across the border. This decrease of Ca/Si ratio was mainly attributed to the significantly increasing concentration of silicate rather than the decreasing concentration of calcium confirming the hard layer was able to stop the transport of silicate as well. Moreover, the (Na+K)/Si ratio did not show significant changes across these regions consistent with the results of the sample that reacted for one day.

![Figure 7.14](image)

Figure 7.14: Changes of Ca/Si ratio and (Na+K)/Si ratio of the areas from the sample reacted for seven days. The red curve represents the change of Ca/Si ratio, the yellow curve represents the change of (Na+K)/Si ratio.

In Figure 7.14, the EDS results of the sample that reacted for seven days are given. Compared to the samples with the reaction periods of one day and four days, a similar trend of Ca/Si ratio variation across the borders has been found. A significant decrease of Ca/Si ratio was noticed across the border.
of the hard layer with the adhesives from the middle layer from about 1.20 to about 0.47 within a distance of 376 µm. Meanwhile, the Ca/Si ratio experienced another considerable decrease across the border of the hard layer with the adhesives from the slurry layer from about 0.25 to about 0.10. This is consistent with the results from the other two samples that the hard layer was indeed able to prevent the transport of calcium and silicate across its borders. Furthermore, for the areas in the interior of the hard layer, their Ca/Si ratios slightly dropped from about 0.47 to about 0.25, suggesting the hard layer was also capable of preventing the migration of calcium and silicate in its interior. In addition, (Na+K)/Si ratio experienced a minor variation ranging from 0.21 to 0.25 consistent with the results of the other two samples.

With the help of the above results, the areas located at the hard layers itself from different samples can be identified. Thereafter, the Ca/Si ratio of these areas are plotted against their corresponding (Na+K)/Si ratio to reveal the elemental composition of the hard layer, as shown in Figure 7.15. The results appeared to be relatively concentrated implying the similarity among the samples with different storage periods. The Ca/Si ratio of calcium alkali silicate found on the hard layers was roughly ranging between 0.22 and 0.53; the (Na+K)/Si ratio was ranging between 0.20 and 0.26. This is different from the previous studies that the reaction rim found in real concrete was with either high Ca/Si ratio [74] or low Ca/Si ratio [76]. This is perhaps due to the relatively pure chemical model system used in this study compared to the heterogeneous conditions in real concrete. Moreover, the areas located closer to the lower surface of the hard layer which was in contact with the slurry layer, had a lower Ca/Si ratio; the ones located closer to the upper surface of the hard layer which was in contact with the middle layer, had a higher Ca/Si ratio. Interestingly, the Ca/Si ratios of all the areas located close to the lower surface of the hard layer in contact with the slurry layer were around 0.20. It seems this is the lowest Ca/Si ratio for the calcium alkali silicate to form the hard layer.

Figure 7.15: Elemental compositions of the analyzed areas on the hard layers from the samples with the storage period of one day (1 D), four days (4 D) and seven days (7 D).
7.3.8 NMR Results

The powdered samples from the hard layer with different reaction periods were analyzed with $^{29}$Si NMR. For the sake of convenience, the standard notation of Q$^n$ nomenclature to interpret the NMR spectra [81] is given in Chapter 4. With the help of this nomenclature, the processes of polymerization and de-polymerization can be defined. The polymerization describes a process of interconnection between different tetrahedron with an increasing amount of Q$^3$ or Q$^4$ at the expense of Q$^1$ or Q$^2$. The de-polymerization describes an opposite process to the polymerization that the amount of Q$^1$ or Q$^2$ increases at the expense of Q$^3$ or Q$^4$.

The assignment of the peaks shown in Figure 7.16 was obtained by deconvolution. As shown in Figure 7.16, the powdered samples of the hard layers from different systems were mainly composed of Q$^2$ with a chemical shift ranging between −79 ppm and −85 ppm and Q$^3$ with a chemical shift ranging between −91 ppm and −98 ppm. The absence of the signal from Q$^4$ in these spectra suggests there was no unreacted silica present in the hard layers. For the sample that reacted for one day (Figure 7.16 (a)), aside from the typical peaks of Q$^2$ at −85 ppm and Q$^3$ at −94.1 ppm, a peak centered at −83.2 ppm was found. This was attributed to the altered environment of Q$^2$ by its linkage with a proton and so presence as a bridging tetrahedron [125]. This altered Q$^2$ is named Q$^2$(L) here and later on. Similarly, for the samples those reacted for four days and seven days, the resonance of Q$^2$ slightly shifted downfield, leaving a minor shoulder next to the main peak of Q$^3$.

![Figure 7.16](image_url): $^{29}$Si nuclear magnetic resonance (NMR) spectra of the hard layer in the system reacted for: (a) one day; (b) four days; and (c) seven days. The solid lines are the experimental spectra, the dashed lines are the deconvoluted spectra.

Based on the deconvoluted spectra shown in Figure 7.16, the fraction of each type of silica tetrahedron can be obtained according to the percentage of the area under its deconvoluted spectrum. As shown in Table 7.1, the fraction of Q$^2$(L) decreased and that of Q$^1$ increased with the
increase of the reaction period. In other words, the polymerization degree of the calcium alkali silicate from the hard layer increased with the increase of the storage period. In the meantime, however, the fraction of $Q^3$ experienced an increase from one day to four days and a decrease from four days to seven days. It should be noted that the observed increase of $Q^3$ and decrease of $Q^2_{(l)}$ with the storage period does not necessarily mean that $Q^3$ was formed at the expense of $Q^2_{(l)}$ as usual. This polymerization can also be caused by the interlinkage of the alkali silicate externally from the slurry layer with the calcium alkali silicate in the hard layer near its lower surface [53]. Meanwhile, on the contrary, the interaction between Ca(OH)$_2$ present in the middle layer and the calcium alkali silicate in the hard layer near its upper surface would unavoidably cause the de-polymerization of the calcium alkali silicate [50, 115], given the previous results that the content of calcium increased near the upper surface of the hard layer. Therefore, the polymerization degree of the hard layers was determined by polymerization and de-polymerization happening on either surface of the hard layer.

Table 7.1: Area percentages of the deconvoluted components in the $^{29}$Si nuclear magnetic resonance (NMR) spectra.

<table>
<thead>
<tr>
<th>Storage Time</th>
<th>$Q^2_{(l)}$ (%)</th>
<th>$Q^2$ (%)</th>
<th>$Q^3$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>One day</td>
<td>86.2</td>
<td>5.5</td>
<td>8.3</td>
</tr>
<tr>
<td>Four days</td>
<td>79.2</td>
<td>7.1</td>
<td>13.7</td>
</tr>
<tr>
<td>Seven days</td>
<td>65.4</td>
<td>5.8</td>
<td>28.8</td>
</tr>
</tbody>
</table>

Therefore, an assumption can be made based on the results shown in Table 7.1 and given as follows. Based on the increasing amount of $Q^3$, the polymerization dominated the de-polymerization in the system. The rate of the de-polymerization caused by the interaction of calcium with calcium alkali silicate near the upper surface of the hard layer should be much lower than that of the polymerization happening near the lower surface of the hard layer.

### 7.3.9 Self- Thickening Process and Evolution of the Transport Barrier

Based on the above results and discussion, the evolution mode of the hard layer from a thin layer of calcium alkali silicate formed at the interface between the alkali silicate slurry and the CH paste to
the hard layer which fully operates as a transport barrier, can be realized by a self-thickening process. This process can be visualized by a reasoning process shown schematically in Figure 7.17 and illustrated as follows.

Figure 7.17: Schematic representation of the self-thickening process: (a) prior to the formation of the hard layer, the migration of minor Ca$^{2+}$ and alkali silicate through a thin layer of calcium alkali silicate formed at the interface between alkali silicate slurry and CH paste; (b) interaction between Ca$^{2+}$ and alkali silicate on the either side of the layer of calcium alkali silicate which separates the alkali silicate slurry and CH paste; (c) formation and accumulation of calcium alkali silicate on the layer of calcium alkali silicate; and (d) the formation of the hard layer and the extension of the borders of the hard layer by the accumulation of calcium alkali silicate.

If any free calcium with a considerable amount is present on the lower “temporary” surface of the layer of calcium alkali silicate formed at the interface between alkali silicate slurry and CH paste, it can immediately react with the abundant alkali silicate present there to form calcium alkali silicate leading to the thickening of the layer of calcium alkali silicate until the concentration of calcium is too low to trigger this interaction. For example, in this study, such a threshold of Ca/Si ratio for enabling the formation of such a solid phase of calcium alkali silicate is about 0.20 according to the EDS results of the areas located at the border of the hard layer with the slurry layer. Alternatively, if any alkali
silicate is present on the upper “temporary” surface of the layer of calcium alkali silicate which is in contact with the middle layer, it can react with abundant Ca(OH)₂ to form calcium alkali silicate leading to the thickening of the layer of calcium alkali silicate until the amount of silicate is too low to trigger this interaction as well. This self-thickening process, as a result, enables the growth of the layer of calcium alkali silicate towards either the middle layer for the upper surface at the top or the slurry layer for the lower surface at the bottom. In other words, the migration of calcium and silicate is completely prevented as soon as this process stops, i.e. the layer of calcium alkali silicate is thick enough to prevent the transport of both calcium and silicate. At that moment, the hard layer acting as a transport barrier is formed. Moreover, if any new transport path of calcium and silicate such as a micro crack is generated across the hard layer, the interaction mentioned above can “heal” this “wound” until the path is fully blocked.

7.3.10 Extrapolation to Calcereous Aggregate

In the chemical model system of this study, the pore solution is assumed to be the only source of calcium, consistent with the situation for the aggregates like opal, chert and sandstone where little calcium is present around the reactive silica in the aggregates. This leads to the formation of a continuous phase of alkali silicate. For the aggregates coming from calcereous rock, calcium is abundantly contained in the calcium carbonate surrounding the reactive silica. However, this type of calcium cannot be considered as active as the one provided by the pore solution. Because calcium carbonate has an extremely low solubility in water at room temperature (about 13 mg/L, $K_{sp} = 3.3 \times 10^{-9}$) compared to calcium hydroxide with its solubility at about 1.7 g/L ($K_{sp} = 5.5 \times 10^{-6}$). Therefore, this type of calcium is actually “locked” in the calcium carbonate which surrounds the reactive silica in the calcium-rich aggregates. Accordingly, the calcium carbonate can be considered as an inert phase which separates or even isolates the reactive silica in aggregates. In this sense, a continuous phase of alkali silicate will be altered into various regions of alkali silicate separated by the calcium carbonate phase, as shown in Figure 7.18. Notably, each region of alkali silicate can still be considered as a continuous phase of alkali silicate at a smaller scale.

It should be mentioned that the above situation with calcereous aggregate also applies to the aggregates containing other minerals by knowing that, all aggregates contain various minerals.
7.3.11 Extrapolation to ASR Occurring in Crack

Notably, for the situation where the damage of ASR happens within the aggregate, the reaction rim (the hard layer in this study) can form at the opening of the crack to the cement paste and behave similarly. It means that the alkali silicate present in the interior of the crack interacts with the calcium coming from the pore solution of cement paste to form calcium alkali silicate blocking the opening of the crack to the cement paste, as shown in Figure 7.19 (a)-(c). The sidewall of the crack can be considered to be equal to the sidewall of the bottle as shown in Figure 7.5. Notably, this extrapolation should be critically conducted.

7.3.12 Interaction Sequence
Combining all these results, it is possible to depict an image of what is happening at the interface between alkali silicate and calcium in a calcium-alkali-silicate system. Based on this, further understanding about the formation and evolution of the reaction rim can be provided.

(1) The formation of alkali silicate: after the reactive silica meets the NaOH solution, the silica tetrahedral networks are destroyed to form alkali silicate.

(2) The formation of calcium alkali silicate: alkali silicate can interlink with calcium to form calcium alkali silicate once they meet with each other.

(3) The accumulation of calcium alkali silicate: the formation of calcium alkali silicate will continue as long as both alkali silicate and calcium are present and can come into contact with each other.

(4) The formation of the transport barrier: the accumulation of calcium alkali silicate near the interface between alkali silicate and Ca(OH)$_2$ physically separates these two phases.

(5) The thickening and evolution of the transport barrier: as long as additional calcium or silicate can penetrate the interface which is composed of the previously formed calcium alkali silicate to reach the other reactant to react with, this barrier can be thickened by the newly formed calcium alkali silicate.

(6) Once calcium or silicate exhausts near the interface of the transport barrier either with alkali silicate (e.g., the lower surface of the hard layer in this study) or with Ca(OH)$_2$ (e.g., the upper surface of the hard layer in this study), the isolation of alkali silicate and Ca(OH)$_2$ is reached. Thereafter, the transport of calcium and silicate are prevented.

(7) Whenever a disturbance opens a new path (e.g., micro cracks) to let alkali silicate or calcium pass through, additional interaction between alkali silicate and calcium will be triggered again until the products “heal” the breakage.

As a consequence, depletion of Ca$^{2+}$, further polymerization of alkali silicate and even the accumulation of alkali silicate due to the continuous interaction of reactive silica with the alkaline solution, as reported by other researches [51, 52, 83], are likely to be realized in the region of the slurry layer. Once the interior expansive force exceeds the strength of the transport barrier, typical deterioration due to ASR occurs.
7.4 Summary

In this chapter, the chemical interaction of reactive silica, alkaline solution and calcium on the interface between the reactive silica in aggregates and the pore solution of cement paste is simulated in an original simplified calcium-alkali-silicate system. The emphasis was led on the interaction between alkali silicate and Ca(OH)$_2$ to provide information and inspiration about the formation and evolution of the reaction rim in real concrete from a fundamental chemical point of view. The following remarks are found:

- A transport barrier located on the interface between alkali silicate and Ca(OH)$_2$ was found. It separated these two phases and prevented the transport of both calcium and silicate through itself leading to a layered system.

- This transport barrier was composed of calcium alkali silicate with a Ca/Si ratio ranging from 0.22 to 0.53 and a (Na+K)/Si ratio ranging from 0.20 to 0.26.

- The calcium alkali silicate from the transport barrier was mainly composed of the silicon–oxygen organization of Q$^2$ and Q$^3$, its polymerization degree increases with the storage period.
In this chapter, the elastic modulus of the reaction rim formed in a calcium-alkali-silicate system has been investigated. The relationship between the elastic modulus and calcium to silicon ratio of the calcium alkali silicate present at the indented place is given.

Parts of this chapter have been published in Materials, 2016 [123].
8.1 Background

In the prior work given in Chapter 7, the existence of a transport barrier similar to the reaction rim has been demonstrated. The transport barrier is also called the hard layer based on the findings. According to the conclusions of Chapter 7, this transport barrier with a thickness of around 1 mm is located at the interface between the alkali silicate slurry and the Ca(OH)$_2$ paste in a calcium-alkali-silicate system which simulates the formation of the reaction rim around the reactive aggregate in concrete. Comparable to the reaction rim proposed by Ichikawa et al. [37], this transport barrier was able to prevent the transport of calcium and silicate, separate the system into layers and allow the penetration of alkalis. Based on the findings, it is rational to believe that the formation and evolution of the reaction rim proposed by Ichikawa et al. [37, 78] has been realized in our chemical model system. Notably, although the hard layer found in our prior work was acting as a transport barrier which had a similar role as the reaction rim, we will keep addressing it as the hard layer or the transport barrier in study of this chapter, since we investigated a chemical model system, not real concrete.

According to Ichikawa [37, 78], besides acting as a semi-permeable membrane, the reaction rim should be able to apply a mechanical constraint in response to the expansive force generated by the accumulation of alkali silicate before its breakage. Elastic modulus, as one of the key factors needed to evaluate the behaviour of a material under stress, is of great relevance in linking the mechanical performance of the reaction rim under the expansive force due to ASR with the intrinsic properties of the calcium alkali silicate constituting the reaction rim. In the light of this consideration, the elastic modulus of the calcium alkali silicate constituting the transport barrier formed at the interface between alkali silicate and calcium is investigated with nano-indentation in this work. Thereafter, the relationship between the elastic modulus of the calcium alkali silicate and its elemental composition is studied. In addition, the influence of capillary porosity on the elastic modulus of the indented areas is explored.

8.2 Materials and methods

8.2.1 Materials

The materials and the instruments for preparing the alkali silicate slurry are the same as the ones in Chapter 7, detailed introduced is given in Chapter 4.
8.2.2 Sample Preparation

To simulate the first step of the formation of the reaction rim, which is the formation of alkali silicate from the interaction between the reactive silica in aggregates and the pore solution of cement paste, the alkali silicate slurry as the product of this process was obtained from the interaction of the silica fume with 1 mol/L NaOH solution. The detailed process is the same as the one in Chapter 7 and introduced briefly as follows: (1) 1 mol/L NaOH solution was added to 20g of silica fume at a liquid to solid mass ratio of 3 to simulate partial silica dissolution in ASR [83]; (2) the mixture was sealed in a polypropylene bottle and rotated using a rotary mixer at a speed of 60 rpm for 24 hours at room temperature; (3) the mixture was taken off the mixer and left at rest for another 24 hours for stratification. These steps simulated the situation near the surface of reactive silica particle where unreacted silica, dissolved and undissolved alkali silicate co-exist.

Afterwards, the CH paste was added softly to the top of the alkali silicate slurry without shaking or stirring to avoid disturbance. Subsequently, the mixture was sealed again and left at rest for another 7 days for further evolution. This is enough for the system to reach the equilibrium according to the results of our prior studies. This step simulated the contact of the calcium present in the form of both Ca²⁺ and free CH with the dissolved and undissolved alkali silicate at the interface between the alkali silicate and calcium near an aggregate surface. The amount of the CH paste added to the system was set to 1g, 5g and 10g to simulate the different situations near the aggregate surface during the formation of the reaction rim in a sense that different amounts of calcium may be available for its interaction with alkali silicate. Notably, the availability of calcium near the aggregate surface is associated with the distance to the aggregate surface: more calcium is present close to the cement paste while less calcium is present close to the aggregate. With this consideration, three systems created in this study are introduced as follows:

(1) the system under the condition that the amount of calcium is extremely low due to the consumption by its interaction with alkali silicate at an earlier time [83]. In this study, this shortage of calcium results in formation of calcium alkali silicate which is not sufficient to completely cover the surface of the alkali silicate slurry;

(2) the system under the condition that a moderate amount of calcium leading to a complete coverage of the surface of the alkali silicate slurry in this study;

(3) the system under the condition that an excess amount of CH is present when the surface of the alkali silicate slurry is completely covered in this study. This situation usually happens at the location close to the pore solution of the cement paste where abundant CH is present.
These systems, after the addition of the CH paste, are shown in Figure 8.1 and illustrated as follows:

(1) For the sample with a CH paste addition of 1g (S1), the added portlandite precipitated at the top surface of the alkali silicate slurry without covering its whole surface enabling the free transport of alkali silicate from the uncovered surface;

(2) For the sample with a CH paste addition of 5g (S2), the added Ca(OH)$_2$ precipitated and just covered the whole surface of alkali silicate slurry;

(3) For the sample with a CH paste addition of 10g (S3), the added Ca(OH)$_2$ not only covered the surface of alkali silicate slurry but also precipitated more on top of that, the thickness of the sediment is about 2-3 mm.

Figure 8.1: The appearance of the mixture after the CH paste addition of 1g, 5g and 10 g in S1, S2 and S3, respectively.

After 7 days of storage, samples from different systems were collected. According to the observation during the sample collection, the appearance of the system is similar with the one in Chapter 7 shown in Figure 7.4. From top to bottom, there were four layers in this system: (1) the liquid layer at the top; (2) the middle layer where excess CH precipitated (only for S3); (3) the hard layer separating the precipitated CH from (4) the alkali silicate slurry layer. The location of the samples collected for the investigation in this study is marked in Figure 7.4 as well. The appearance of the original sample (the hard layer) is shown in Figure 8.2 (a).
The hard layer was collected from three systems and immediately immersed in isopropanol for 7 days to remove the water and therefore, to stop any reaction. Isopropanol was renewed every day. Meanwhile, the adhesives on the surface of the samples were carefully removed with a brush during the isopropanol immersion. After 7 days of immersion, the samples were transferred to a desiccator with silica gel and portlandite and left there for 2 weeks to dry. Afterwards, the samples were impregnated vertically in an epoxy to expose the surface of their cross section as shown in Figure 8.2 (b) and Figure 8.2 (c). After the impregnation (wet potting to avoid the damage from vacuum) and polishing by following the procedures proposed by Stutzman [106], the samples were ready for analysis. The moulds for impregnation and the instrument for polishing are the same with the ones used in Chapter 7.

![Image](image.png)  
(a) Original sample  
(b) Plan view after impregnation  
(c) Side view after impregnation

Figure 8.2: Sample before and after impregnation.

### 8.2.3 Nano-indentation Testing

Nano-indentation is a micromechanical test. Its principle and measuring procedure are similar to the hardness test but at a micro scale. With the help of nano-indentation, local mechanical properties including elastic modulus and hardness of the tested points can be determined [126]. However, it has to be emphasised that the obtained measurement of nano-indentation is highly sensitive to the surface roughness of the tested surface [127]. As a consequence, micromechanical properties obtained by various researchers have a wide variation range and therefore, should be critically analysed.

In this study, Agilent Nano Indenter G200 (Agilent Technologies, California, USA, as shown in Figure 8.3) was used for nano-indentation [128, 129] at the Microlab, Faculty of Civil Engineering & Geosciences, Delft University of Technology, to investigate the elastic modulus of the cross section of the hard layer which was located at the interface of the alkali silicate slurry and the CH paste. A Berkovich tip was used as the indenter of nano-indentation and both the loading and unloading rate
were set at 0.001 mN/s. The indentation depth was 2000 nm. Particularly, the grid for S1 with a CH paste addition of 1g was set to consist of 5 rows with 15 indents per row, the grid for S2 with a CH paste addition of 5g was set to consist of 3 rows with 20 indents per row, the grid for S3 with a CH paste addition of 10g was set to consist of 7 rows with 10 indents per row. The distance between neighbouring indents was 40 µm. Continuous Stiffness Method (CSM) was applied for testing [130].

8.2.4 Scanning Electron Microscope Imaging and Elemental Composition Analysis

Back-scattered electron (BSE) and secondary electron (SE) images of the indented region of each sample were obtained by using Scanning Electron Microscope (SEM) of JEOL JSM 5600 (JEOL, Tokyo, Japan). Notably, the samples for BSE-EDS analysis need to be coated with carbon. The instruments for SEM-EDS analysis and carbon coating are the same as the ones used in Chapter 5. The BSE images were used for qualitatively checking the capillary porosity of the samples. During the elemental composition analysis with the Energy-dispersive X-ray Spectroscopy (EDS) within the SEM, the SE images were used for locating the indentation imprint. The area-scanning of EDS analysis was carried out on each indentation imprint. The size of the area of each indentation imprint selecting for EDS analysis was set
to be the largest indentation imprint of all the indentations on each sample to avoid errors introduced by the different size of the indentation imprint.

8.3 Results and Discussion

8.3.1 Nano-indentation Measurements

Areas where the indentations were performed are marked with a rectangle in the BSE images of each sample, as shown in Figure 8.4 (a), Figure 8.5 (a) and Figure 8.6 (a) for S1, S2 and S3, respectively. The elastic modulus of each area measured by nano-indentation was plotted according to its position (X-Y) to give an elastic modulus map, as shown in Figure 8.4 (b), Figure 8.5 (b) and Figure 8.6 (b) for S1, S2 and S3, respectively.

Figure 8.4: (a) The BSE image of S1 with a CH paste addition of 1g; (b) the corresponding elastic modulus.

According to the BSE image of sample S1 with a CH paste addition of 1g as shown in Figure 8.4 (a), the surface of the cross section of the hard layer was generally uniform except for some areas with higher grey scale level. These brighter areas were thought to have more products which reflect the electron beams from the SEM. As shown in Figure 8.4 (b), most of the indented areas of this sample had elastic moduli ranging from 4 GPa to 8 GPa while several areas located on the right had elastic moduli below 4 GPa. Notably, the three areas marked with circles are the invalid indents due to surface defect. Apparently, the elastic modulus of the areas composed of the calcium alkali silicate found in this sample (S1) was much lower than those reported in the literature ranging from about 20 GPa to about 30 GPa [131]. This was probably because too little calcium was available in the system to form a stiffer calcium alkali silicate, since a higher calcium content usually leads to formation of a calcium alkali silicate with a higher elastic modulus [132]. This calcium alkali silicate with low calcium content
may form directly by the interaction of alkali silicate with calcium, or by the further interaction of alkali silicate with existing calcium alkali silicate [53], given the abundant presence and free transport of alkali silicate through the uncovered surface in S1.

Figure 8.5: (a) The BSE image of S2 with a CH paste addition of 5g; (b) the corresponding elastic modulus.

As shown in Figure 8.5 (a), the whole region of hard layer in specimen S2 can be divided into three parts according to their different grey scale levels: (1) the dark part at the top (P1) where rare product was available to reflect electron beams: this part was located at the region of the CH paste attached to the hard layer; (2) the intermediate part (P2), which was located at the transition zone of the bright part (the hard layer) with the dark part (the adhesives); (3) the bright part, completely located at the hard layer, at the bottom (P3) where large amounts of calcium alkali silicate were present. Therefore, combining with the location of the hard layer shown in Figure 6, P1 was from the CH paste; P2 was located at surface of the hard layer in contact with the CH paste; P3 was completely located at the hard layer closer to the slurry layer than the others. The grid of indentations on this sample is indicated with the rectangle in Figure 8.5 (a).

The nano-indentation results of the areas in S2 are shown in Figure 8.5 (b). The first row of indents, located near the border between the hard layer and the region of adhesive, had low elastic moduli ranging from 8 GPa to 12 GPa, indicating that the calcium alkali silicate present at this place was either weak or rare. The second row had, in general, higher values of elastic moduli compared to the first
row, ranging from 12 GPa to 16 GPa. This was possibly caused by a more densified structure present in the second row. The third row had slightly higher values of elastic moduli ranging from 12 GPa to 20 GPa. This was probably caused by the formation of a stiffer calcium alkali silicate at this location, since this region appeared to be as equally densified as the second row according to their similar grey scale levels from the BSE images. The area marked with a circle corresponds to an invalid indent.

![Figure 8.6: (a) The BSE image of S3 with a CH paste addition of 10g; (b) the corresponding elastic modulus.](image)

The BSE image of S3 with a CH paste addition of 10g is shown in Figure 8.6 (a). Obviously, three parts can be differentiated according to their grey scale level. (1) P1 has the lowest grey scale level, suggesting that it is porous. Furthermore, the large difference in appearance between P1 and the other parts, as well as the observation during sample collection indicates that, P1 was located at the region of the adhesive from the alkali silicate slurry. Its border with the hard layer is marked with an arrow in Figure 8.6 (a). (2) P2 was located at the hard layer. An increasing amount of calcium alkali silicate appeared as groups constituting a less porous but disorganized structure in this region. This disorganized appearance of calcium alkali silicate in groups (the largest is indicated in Figure 8.6 (a) by “G”), as the product of the interaction between alkali silicate and calcium, confirmed our hypothesis that neither alkali silicate nor calcium was well dispersed at their interface given that no shaking or stirring was applied to the mixture. (3) P3 was located at the region of the hard layer, further away from the border of the hard layer and the adhesives than the other two parts. Obviously, P3 contained the most calcium alkali silicate among these three parts leading to the formation of a more densified structure. Unlike the appearance of P2, the calcium alkali silicate in P3 was present as a continuous phase rather than as groups, implying the availability of alkali silicate and calcium was sufficient enough to ensure the development of such a continuous phase of calcium alkali silicate. Pores were still visible in P3 but with a decreased amount and size compared to P2. Interestingly, the groups of calcium alkali silicate in P2, particularly the one marked with “G” in Figure 8.6 (a), had a comparable
grey scale level to that of the continues phase in P3. This implies the porosity of the areas from P2 and P3 were almost the same. Therefore, combining with the location of the hard layer given in Figure 7.4, P1 was located at the adhesives from the slurry layer; P2 was located at the hard layer in contact with the alkali silicate slurry; P3 was located at the hard layer and further away from the alkali silicate slurry than the others.

The nano-indentation results of S3 with a CH paste addition of 10g are shown in Figure 8.6 (b). The grid of indents was located within the P2 and P3. Based on the results shown in Figure 8.6 (b), three layers can be differentiated from left to right according to their variation in elastic moduli. (1) The first layer from the left, located within the region of P2, had values of elastic modulus ranging from 4 GPa to 8 GPa. As shown in the BSE image, the region where the first layer was located had a porous structure resulting in low values of the elastic modulus. However, the group of calcium alkali silicate marked with “G” had a higher elastic modulus ranging from 12 GPa to 16 GPa than its neighbors in P2. (2) The second layer from the left with the values of elastic modulus ranging from 8 GPa to 12 GPa was located at an intermediate place between P2 and P3, where more calcium alkali silicate was present and less pores were found. (3) The third layer was fully within the territory of P3 which was the most densified region of this sample having values of elastic moduli ranging from 12 GPa to 20 GPa. The two areas marked with circles are the invalid indents.

This distribution of the elastic modulus suggested the possible relationship between elastic modulus and the grey scale level and the local porosity. Indeed, the higher the grey scale level, the lower the local porosity of the indented areas resulting in a higher value of elastic modulus. In other words, it seems that the local porosity dominantly determined the elastic moduli of the areas composed of calcium alkali silicate in this sample.

8.3.2 Elemental Composition Analysis

The elemental composition of each indented area measured by EDS was expressed as the calcium to silica mole (Ca/Si) ratio and the alkali to silica mole ((Na+K)/Si) ratio. Thereafter, the Ca/Si ratio of each indented area were plotted against its position (X-Y):

(a) Figure 8.7 (a) for S1 (with a CH paste addition of 1g);

(b) Figure 8.8 (a) for S2 (with a CH paste addition of 5g);

(c) Figure 8.9 (a) for S3 (with a CH paste addition of 10g).
Besides, the Ca/Si ratio and (Na+K)/Si ratio of all the indented areas were plotted in Figure 8.7 (b), Figure 8.8 (b) and Figure 8.9 (b) to reveal the elemental composition of the calcium alkali silicate from S1, S2 and S3 respectively.

![Figure 8.7: (a) The Ca/Si ratio variation of the indented areas from S1; (b) The elemental composition of the indented areas.](image)

The Ca/Si ratio variation of the indented areas of S1 is shown in Figure 8.7 (a). Most of the indented areas show a Ca/Si ratio less than 0.30 except two, which had a higher Ca/Si ratio ranging from 0.30 to 0.40 and whose locations are indicated with arrows in Figure 8.7 (a). Regardless of these two areas, nearly half of the areas had a Ca/Si ratio ranging from 0.10 to 0.20 and the others had a Ca/Si ratio ranging from 0.20 to 0.30. The locations of three invalid indents are marked with three circles, the elemental compositions of these areas were excluded from the results accordingly. Similar to its corresponding nano-indentation results given in Figure 8.4, the distribution of the Ca/Si ratio does not show any typical pattern indicating a generally homogeneous distribution of calcium and silicon in the hard layer of S1.

As shown in Figure 8.7 (b), the indented areas of S1 had the Ca/Si ratio ranging from 0.12 to 0.33 and the (Na+K)/Si ratio ranging from 0.05 to 0.45. Moreover, most of the areas (81%) had the Ca/Si ranging from 0.15 to 0.25 and 86% of the indented areas had the (Na+K)/Si ratio ranging from 0.20 to 0.30. This elemental composition of the calcium alkali silicate was comparable to the ASR product found within the crack of an aggregate [12] where silicate is abundant while little calcium can be expected. Actually, considering the surface of the alkali silicate slurry in the system of S1 not being completely covered by the added calcium shown in Figure 8.1, the free transport of alkali silicate can be expected to ensure the availability of silicate to react with the added calcium as much as possible.
As shown in Figure 8.8 (a) for S2 with a CH paste addition of 5g, most of the areas near the border of the hard layer with the adhesives at the top were with high values of Ca/Si ratio ranging from 0.40 to 0.60 except for two areas with the Ca/Si ratio of around 0.72 and 2.15 which are indicated with an arrow in Figure 8.8 (a). The areas from the second and the third rows of indents had a lower Ca/Si ratio ranging from 0.20 to 0.40. This decreasing trend of Ca/Si ratio when getting away from the border of the hard layer and the adhesives was caused by the presence of CH in the region of the adhesives. The location of this CH was expected to be near the area with a Ca/Si ratio of 2.15, since calcium alkali silicate alone cannot give such a high value of Ca/Si ratio [133]. Clearly, the presence of additional CH near the surface of the hard layer can increase the amount of calcium available for its interaction with alkali silicate to form a calcium alkali silicate with a high Ca/Si ratio. This is the reason for the areas from the first row to show a higher Ca/Si ratio than the others. Notably, the influence of this effect faded as the areas getting further away from the adhesives containing CH, resulting in the decreased Ca/Si ratio of the areas in the second and the third rows. The location of the invalid indent is marked with a circle.

As shown in Figure 8.8 (b), most of the areas (93%) had a Ca/Si ratio ranging from 0.30 to 0.50 and 83% of the areas had a (Na+K)/Si ratio ranging from 0.30 to 0.40. Comparing with the results of S1,
clearly the areas from S2 had generally a higher Ca/Si ratio resulting from the addition of more calcium or more specifically, the presence of Ca(OH)$_2$ in the adhesives.

![Ca/Si ratio variation](image)

Figure 8.9: (a) The Ca/Si ratio variation of the indented areas from S3; (b) The elemental composition of the indented areas.

The Ca/Si ratio variation of the indented areas from S3 is shown in Figure 8.9 (a). Generally speaking, the distribution of Ca/Si ratio of the indented areas did not show any typical pattern except several “islands” with a higher Ca/Si ratio as well as the areas near the border of the hard layer and the adhesives having a lower Ca/Si ratio. Notably, the location of the area indicated with “G” in Figure 8.9 (a) having a higher Ca/Si ratio than its neighbors are consistent with the one indicated with “G” in Figure 8.6 having a higher elastic modulus and higher grey scale level than its neighbors. This indicates that both a higher Ca/Si ratio and a more densified structure in this region contributed to a higher elastic modulus of this region. The location of the invalid indent is marked with a circle.

According to Figure 8.9 (b), most of the analyzed areas (84%) had a Ca/Si ratio ranging from 0.20 to 0.30, some areas had higher Ca/Si ratio ranging from 0.30 to 0.40 while one area had a Ca/Si ratio of about 0.44; 84% of the areas had the (Na+K)/Si ratio varying from 0.30 to 0.40. Comparing all the results with the ones of Brouxel [74], the calcium alkali silicate constituting the hard layer from S1 in this study had a similar Ca/Si ratio and (Na+K)/Si ratio with the reaction rim which was located at about 50 μm from the aggregate surface; the calcium alkali silicate constituting the hard layer from S2 had a similar Ca/Si ratio and (Na+K)/Si ratio with the reaction rim which was located at about 80 μm from the aggregate surface; the calcium alkali silicate constituting the hard layer from S3 had a similar Ca/Si ratio and (Na+K)/Si ratio with the reaction rim which was located at about 60 μm from the aggregate surface. Besides, for the ASR gel [36], the one formed at the place closer to the
cement paste than the aggregate has higher Ca/Si ratio; the one formed at the place closer to the aggregate than the cement paste has lower Ca/Si ratio. So presumably, the calcium alkali silicate from S1 can be considered as the product formed close to the aggregate surface; the calcium alkali silicate from S2 can be considered as the product formed close to the cement paste; the calcium alkali silicate from S3 can be considered as the product formed at an intermediate place between the former ones.

Regarding the situation in S2 and S3, notably, the hard layer from S2 (less calcium was added) was composed of calcium alkali silicate with a higher Ca/Si ratio; while the hard layer from S3 (more calcium was added) was composed of calcium alkali silicate with a lower Ca/Si ratio. However, this cannot be considered as a contradictory since the region from S2 was located close to the CH paste where CH was abundantly present while the region from S3 was located close to the alkali silicate slurry where little CH was present. Therefore, the Ca/Si ratio of the hard layer was more influenced by its location after the complete coverage of the alkali silicate slurry, i.e. higher Ca/Si ratio when it is close to the calcium, lower Ca/Si ratio when it is close to the alkali silicate.

8.3.3 Elastic Modulus vs Elemental Composition

The elastic modulus and Ca/Si ratio of all the indented areas are plotted in Figure 8.10 to investigate their relationship.

![Figure 8.10: The relationship between elastic modulus and Ca/Si ratio.](image)
As shown in Figure 8.10, the general relationship between the elastic modulus and the Ca/Si ratio of the indented areas from all the samples was consistent with the previous research [132, 134] stating that the elastic modulus increased with the increase of Ca/Si ratio. This was due to the formation of a more complex and interlinked silica network of calcium alkali silicate [135] encouraged by an increased amount of calcium. In S1, calcium was too sparse to ensure its continuous interaction with alkali silicate to form the calcium alkali silicate with a high Ca/Si ratio and elastic modulus, especially given that alkali silicate was sufficiently supplied through the uncovered surface of the slurry layer (shown in Figure 8.1) for its interaction with existing calcium alkali silicate as well [53]. In S2, due to the more CH was present in the adhesives attached to the hard layer, more calcium was available to be incorporated into the silicate network and form a calcium alkali silicate with a higher Ca/Si ratio and elastic modulus.

However, it should be noted that the influence of Ca/Si ratio on elastic modulus is different from sample to sample. Therefore, ANCOVA analysis was performed to evaluate the influence of other factors, e.g. porosity, on the relationship between Ca/Si ratio and elastic modulus within each sample and for all the samples. A level of significance of 0.05 was used. The results of the analysis for all the samples show that, the amount of diversity of the elastic modulus determined by Ca/Si ratio is 62.7%, the rest is determined by other factors including porosity. For the analysis of each sample, the amount of diversity of the elastic modulus determined by Ca/Si ratio in S1 is 0.5%. For S2, the amount of diversity of the elastic modulus determined by Ca/Si ratio is 46.4%, while for S3 it is 27.7%. This indicates that, the influence of other factors on the relationship between elastic modulus and Ca/Si ratio is the highest in S1 and lowest in S2. This featured phenomenon can be explained as follows.

As shown in Figure 8.5 (b) and Fig. 8.8 (b) for S2, the areas with the Ca/Si ratio higher than 0.40 were located near the interface of the hard layer with its adhesives where a porous and weak structure was expected. Hence, the elastic moduli of these areas were low even though the calcium alkali silicate here had a higher value of Ca/Si ratio. Simply stated, it was the porosity that predominantly determined the elastic modulus in this region rather than the Ca/Si ratio. At the same time, as shown in Figure 8.6 (b) and Figure 8.9 (b) for S3, the areas with higher Ca/Si ratio of about 0.30 having a densified structure were located far away from the border of the hard layer with its adhesives. Hence, these areas had higher elastic moduli resulting from the higher Ca/Si ratio and the lower local porosity. Moreover, the relatively concentrated points from S1 in Figure 8.10 inferred that the pore distribution is uniform and that a similar porous structure can be speculated in the whole region, given a concentrated distribution of Ca/Si ratio.
It should be noted that the variation between the depth of indentation and the interaction volume of SEM [136] could influence the results of this study by knowing that, the material measured by nanoindentation could be different with the one measured by SEM-EDS.

Besides, the impregnation of epoxy filling the capillary pores of the samples during the preparation of the samples for nano-indentation and SEM-EDS analysis could also have some influence. Because the elastic modulus of epoxy is about 3 GPa which overlaps with other data point as indicated in Figure 8.10. However, without impregnation, it would be very difficult to investigate the mechanical properties of the samples obtained from the simulated calcium-alkali-silicate system in this study.

### 8.3.4 Discussion on Elastic Modulus of the Hard Layer and Expansive Pressure in ASR

As stated in 8.3.2, the calcium alkali silicate constituting the hard layers from the three systems can represent the calcium alkali silicate formed at different places, where different amounts of calcium are available for interaction with alkali silicate resulting in the different Ca/Si ratio of the formed calcium alkali silicate: the calcium alkali silicate with a low Ca/Si ratio obtained from S1 can be considered to be formed close to the aggregate surface, where little calcium while abundant alkali silicate are present; the calcium alkali silicate with a high Ca/Si ratio obtained from S2 can be considered to be formed close to the cement paste, where abundant calcium while little alkali silicate are present; the calcium alkali silicate with a moderate Ca/Si ratio obtained from S3 can be considered to be formed at an intermediate place.

Figure 8.11: Schematic representation of the reaction rim formed at different locations (D1 < D2 < D3).

Based on the results of the present study, the calcium alkali silicate with a low Ca/Si ratio from S1 had a low value of elastic modulus. It implies that this type of calcium alkali silicate can make up the reaction rim which is formed close to the aggregate surface where large amount of alkali silicate is
present, as shown in Figure 8.11 (a). Alternatively, the calcium alkali silicate with a high Ca/Si ratio from S2 had a high value of elastic modulus. It implies that this type of calcium alkali silicate can make up the reaction rim which is formed close to the cement paste when little alkali silicate is present, as shown in Figure 11 (c). Furthermore, the calcium alkali silicate with a moderate Ca/Si ratio from S3 had a moderate value of elastic modulus, implying the formation of the reaction rim at an intermediate position compared to the former situations shown in Figure 11 (b).

8.3.5 Origination of the Rigid Structure

Based on the above results in this chapter, it is clear that the calcium alkali silicate generating from the interaction between alkali silicate and calcium has various levels of elastic moduli according to the location and the availability of calcium. Nevertheless, why and how the formed calcium alkali silicate is able to have such a featured properties cannot be answered with the findings in this chapter. Combining with the mechanism proposed in Chapter 6, remarkably, the origination of the rigid calcium alkali silicate can be explained as follows.

Bearing in mind, the alkali silicate slurry prepared for the investigation in this chapter has experienced 24 hours of mixing and another 24 hours of storage. It means that the silicon-oxygen networks present in this type of alkali silicate slurry had long time for their further evolution of polymerization. Therefore, a relatively polymerized silicon-oxygen networks can be expected to be present in this type of alkali silicate slurry. According to the conclusions of Chapter 5, significant structure development resulting in the formation of rigid structure can be stimulated and generated from the interaction between this type of alkali silicate and the calcium with a considerate amount. In the calcium-alkali-silicate system of Chapter 7 and Chapter 8, this structure development leads to the formation of the hard layer separating the alkali silicate slurry and the calcium hydroxide paste. However, unlike the situation mentioned during the proposal of the mechanism in Chapter 6, the equilibrium of the system in Chapter 7 and Chapter 8 cannot be destabilized by further formation and accumulation of alkali silicate once the hard layer is formed. As a result, the process following the mechanism proposed in Chapter 6 ceases after the formation of the hard layer. By extrapolating this finding to the cementitious materials suffering from ASR, it means once the continuous formation and accumulation of alkali silicate stop, no further expansive force can be generated and therefore no deterioration will happen, even if the reaction rim has already formed. This conclusion is consistent with our common knowledge about ASR in concrete.
8.4 Summary

After chemically realizing the formation of the reaction rim at the interface of alkali silicate and Ca(OH)$_2$ in a chemical model in Chapter 7, the elastic modulus of the calcium alkali silicate constituting this idealized reaction rim was investigated in this chapter, following conclusions can be drawn:

- The elastic modulus of the calcium alkali silicate constituting the reaction rim (the hard layer in this study) varied from 5 GPa to 20 GPa.

- The elastic modulus increased with the increase of Ca/Si ratio. The more calcium was available for its interaction with alkali silicate to form calcium alkali silicate, the higher the Ca/Si ratio was and consequently the higher the elastic modulus of the formed calcium alkali silicate.

- The formation of the rigid calcium alkali silicate having various levels of elastic modulus can be explained with the mechanism proposed in Chapter 6.

- These findings will enable a better understanding about the mechanical properties of the calcium alkali silicate formed at the interface between alkali silicate and Ca(OH) in a chemical model of ASR. Any extrapolation of these findings to real concrete should be critically conducted.
In this chapter, the interaction between the synthetic calcium alkali silicate and sodium hydroxide solution has been investigated. XRD and TGA are used.

*Parts of this chapter have been published in the conference proceedings of 14th International Congress on the Chemistry of Cement (ICCC 2015), held in Beijing, China, 13-16 October 2015 [39].*
9.1 Background

As the trigger of ASR, siloxane bond (Si-O-Si linkage) of reactive silica is firstly attacked by hydroxyl ions to form silanol bond (Si-O-H linkage), leading to the formation of dissolving silicates which are negatively charged at high pH. The dissolution rate depends on the pH solution [24] that the higher pH is in the solution, the faster and the more silica dissolves [137]. The negatively charged dissolving silicates are counter balanced mainly by alkalis (Na⁺/K⁺), leading to the formation of alkali silicate gel. By combining with calcium ions in solution, alkali silicate is converted into calcium alkali silicate [138]. Due to the similarity between the synthesis process and the ASR process in concrete, the synthetic gel has been reasonably chosen as a simplified model of the ASR gel which formed during ASR process and leading to ASR expansion.

Bearing in mind, once ASR gel is formed from a series of physico-chemical reactions in cementitious system, it could interact with other components present there, e.g. Ca²⁺, Na⁺, K⁺ and OH⁻ (other components including aluminum are out of the scope of this research). These interactions will inevitably change the composition and microstructure of ASR gel. As a result, its properties will change accordingly. In the light of this consideration, the interaction between the synthetic ASR gel and alkaline solution with different concentrations is investigated in this study.

9.2 Materials and Methods

9.2.1 Materials

The silica fume and NaOH solution used in the present study are the same as the ones used in Chapter 4.

9.2.2 Sample Preparation

The sampling process of this study contains two parts: gel synthesis and alkaline solution exposure. The mix design for gel synthesis is shown in Table 9.1.
Table 9.1: The mix of synthetic gels.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Targeted Ca/Si</th>
<th>Na/Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS01</td>
<td>0.1</td>
<td>0.19</td>
</tr>
<tr>
<td>MS05</td>
<td>0.5</td>
<td>0.28</td>
</tr>
<tr>
<td>MS10</td>
<td>1.0</td>
<td>0.39</td>
</tr>
</tbody>
</table>

9.2.3 Gel Synthesis

Calcium alkali silicate with the targeted Ca/Si ratio were synthesized by adding a certain amount of 1 mol/L NaOH solution into the mixture of silica fume and calcium hydroxide with different Ca/Si ratios. The slurry was sealed in a polypropylene bottle filled with argon gas to avoid carbonation and mixed by a rotary mixer at a speed of 60 rpm at room temperature. Liquid and solid mass ratio in this step was set as 3 to simulate partial silica dissolution which is the usual case of ASR in reality [83]. After the desired storage period, the slurry was filtered through a vacuum funnel and washed with distilled water to remove excess NaOH. Notably, the duration of the washing process should be critically limited to avoid further interaction between calcium alkali silicate and water. Thereafter, in order to stop reactions, the residue was immersed in isopropanol for 6 hours before it was dried at room temperature in a vacuum desiccator for 24 hours.

9.2.4 Alkali Hydroxide Solution Exposure

After the drying process, the synthetic calcium alkali silicate was immersed in the NaOH solutions with the concentrations of 0.1, 0.5 or 1.0 mol/L respectively, the samples were labelled according to the preparation process, e.g. MS0101 means a synthetic gel of MS01 was immersed in NaOH solution with a concentration of 0.1mol/L. Afterwards the samples were sealed and mixed in the same way as the synthesis process for 7 days. After filtration and drying, the samples were sent for analysis.

9.2.5 Characterization methods

The instruments for XRD, XRF and TGA analysis are the same with the ones used in Chapter 5 and Chapter 7 at the Department of Inorganic and Physical Chemistry, Ghent University.
9.3 Results and Discussion

9.3.1 XRD Results

The silica fume used in this study is amorphous as verified by the XRD pattern given in Chapter 3 with a broadened peak centered about 22° (2θ). The absence of other peaks indicates there are no other crystalline phases in the raw material.

The XRD patterns of the synthetic ASR gel samples are shown in Figure 9.1. The broadened peaks assigned to calcium alkali silicate [139] are found from the XRD patterns of MS05 and MS10. It needs to be noted that the broadened peaks from calcium alkali silicate in MS01 cannot be confirmed due to its overlaps with other phases [140]. Nevertheless, this is in agreement with the result from Hou [141] and enough for us to conclude that the gel synthesis in such a simulated system is successful.

Besides, the appearance of the XRD patterns changes with the addition of portlandite. The more portlandite is added, the less significant signal from silica fume can be found. The broadened peak assigned to the amorphous silica in silica fume centered at 22° (2θ) disappears when the Ca/Si ratio equals 1. In addition, the characterization peaks from unreacted portlandite can be recognized indicating the presence of excess portlandite in the system, even the peak is weak. This indicates the consumption of both silica fume and Ca(OH)_2 to form calcium alkali silicate [83]. Similar in MS05, the characterization peaks assigned to unreacted portlandite can be found co-existing with the presence of silica fume. This means, presumably, the multiple interactions among silica fume, alkaline solution and CH are still ongoing. This is consistent with the results from Leemann [83] where unreacted CH can be found in a similar calcium-alkali-silicate system with the Ca/Si ratio of 0.4.

The peaks assigned to calcite in MS10, as the product of carbonation, are observed at about 23° (2θ), 36° (2θ), 39° (2θ), 43° (2θ), and 49° (2θ), though the strongest characteristic peak occurring at 29° (2θ) overlaps with the featured peak from calcium alkali silicate at that position. Most of the carbonation happened during the XRD measurement. Notably, the peaks assigned to calcite are more significant in this sample. Presumably, most of the calcite in this sample is mainly generated from the carbonation of the unreacted CH. Because it is much easier for carbonation to happen in CH than calcium alkali silicate under usual conditions.
Figure 9.1: XRD patterns of synthetic calcium alkali silicate with different calcium hydroxide addition (a, calcium alkali silicate; b, calcium hydroxide; c, calcite)

The XRD patterns of different samples after alkali exposure are shown in Figure 9.2, Figure 9.3 and Figure 9.4.

As shown in Figure 9.2, the broadened peak assigned to the amorphous silica in silica fume disappears as alkaline concentration increases, indicating silica fume present in the samples was consumed due to its reaction with NaOH. The broadened peaks assigned to calcium alkali silicate become more and more significant as the disappearance of the peak from silica fume. The peaks assigned to the unreacted \( \text{CH} \) are found in the XRD patterns before and after alkaline exposure (Figure 9.4 and Figure 9.5). This result alone cannot provide any evidence about whether additional \( \text{CH} \) has combined with the newly formed alkali silicate. Besides, the presence of calcite are also confirmed by the peaks at around 23°(2θ), 36°(2θ), 39°(2θ), 43°(2θ) and 49°(2θ) from the XRD patterns before and after alkaline exposure.

Figure 9.2: XRD patterns of calcium alkali silicate with Ca/Si ratio of 0.1 after alkaline exposure.
Figure 9.3: XRD patterns of calcium alkali silicate with Ca/Si ratio of 0.5 after alkaline exposure.

Figure 9.4: XRD patterns of calcium alkali silicate with Ca/Si ratio of 1.0 after alkaline exposure.

9.3.2 TGA results

TGA results for the synthetic calcium alkali silicate with Ca/Si ratios of 0.1, 0.5 and 1.0 and the calcium alkali silicate after alkaline exposure are presented in Table 9.2. In order to exclude the impact of evaporation from trace amount of free water, the initial weight of the sample to calculate the mass loss was taken at 80°C.
Table 9.2: Mass loss determined by TGA.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Mass loss below 400°C [%]</th>
<th>Total mass loss [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS01</td>
<td>7.32</td>
<td>8.87</td>
</tr>
<tr>
<td>MS05</td>
<td>8.72</td>
<td>10.14</td>
</tr>
<tr>
<td>MS10</td>
<td>10.43</td>
<td>11.53</td>
</tr>
<tr>
<td>MS0101</td>
<td>7.34</td>
<td>9.37</td>
</tr>
<tr>
<td>MS0105</td>
<td>8.80</td>
<td>12.02</td>
</tr>
<tr>
<td>MS0110</td>
<td>13.06</td>
<td>17.53</td>
</tr>
<tr>
<td>MS0501</td>
<td>14.23</td>
<td>17.19</td>
</tr>
<tr>
<td>MS0505</td>
<td>14.09</td>
<td>17.14</td>
</tr>
<tr>
<td>MS0510</td>
<td>14.66</td>
<td>17.97</td>
</tr>
<tr>
<td>MS1001</td>
<td>13.61</td>
<td>19.71</td>
</tr>
<tr>
<td>MS1005</td>
<td>13.47</td>
<td>20.61</td>
</tr>
<tr>
<td>MS1010</td>
<td>16.49</td>
<td>21.65</td>
</tr>
</tbody>
</table>

The results show that the total mass loss increases with the increase of Ca/Si ratio, consistent with the results from Leemann [83]. This additional mass loss might come from the extra calcium alkali silicate formed from the multiple interactions between silica fume, alkaline solution and calcium. However, for the calcium alkali silicate with the Ca/Si ratio of 0.5 and 1.0, this additional mass loss can also come from the dehydration of unreacted CH present in the system. Notably, the unreacted silica fume is consumed during the alkaline exposure indicating the continuous interaction between silica fume and alkaline solution during the alkaline exposure process.

9.3.3 XRF Results

The XRF results investigating the changes of Ca/Si ratio and Na/Ca ratio of calcium alkali silicate before and after the alkaline exposure are given in Figure 9.5 (a) and Figure 9.5 (b) respectively.

![Figure 9.5 (a) Ca/Si ratio of calcium alkali silicate before and after alkaline exposure.](image)

![Figure 9.5 (b) Na/Si ratio of calcium alkali silicate before and after alkaline exposure.](image)
Although some variations exist according to the results presented in Figure 9.5, the synthesis of calcium alkali silicate with the targeted Ca/Si ratios is generally successful. The analyzed Ca/Si ratios are lower than the targeted Ca/Si ratios for MS01 and MS05, while MS10 has a larger Ca/Si ratio than the targeted one. These variations are mainly due to the presence of unreacted CH present in the solid sample, as confirmed by the XRD results. Considering that the samples are washed with water several times during preparation, sodium present in residue can be regarded as bound sodium. The washing can also cause calcium leaching leading to the variations of Ca/Si ratio. The amount of bound sodium increases with the increase of the targeted Ca/Si ratio. This perhaps results from the attack of additional OH\(^-\) provided by extra CH on silica fume. Meanwhile, more alkalis can be incorporated into the silicon-oxygen network of calcium alkali silicate. This is consistent with the results from Hong and Glasser [142] stating that the alkali binding ability improves as the Ca/Si ratio increases.

For the samples of calcium alkali silicate after alkaline exposure, the Ca/Si ratios of MS01 increases slightly after alkaline exposure, while the Ca/Si ratios of MS05 and MS10 drop dramatically after alkaline exposure. Moreover, the Ca/Si ratio increases as alkaline concentration increases from 0.1 mol/L to 1 mol/L. This implies that the Ca/Si ratio of calcium alkali silicate is determined by two factors: further attack of OH\(^-\) on silicon-oxygen network and ion exchange during alkaline solution exposure. After calcium alkali silicate meets alkaline solution, unreacted silica fume will react with alkalis and hydroxyls in the alkaline solution resulting in the formation of alkali silicate. As part of the formed alkali silicate enters the solution, the content of silicon contained by the calcium alkali silicate decreases leading to the increase of Ca/Si ratio. Meanwhile, Na\(^+\) exchanges with the incorporated calcium in silicon-oxygen network [38] leading to the decrease of the calcium content in samples and the increase of the sodium content. These two factors both contribute to the change of Ca/Si ratio and Na/Ca ratio. When the calcium alkali silicate with Ca/Si ratio of 0.1 is immersed in a 0.1 mol/L, 0.5 mol/L and 1.0 mol/L of NaOH solution, silica dissolution is the predominant factor determining the Ca/Si ratio of calcium alkali silicate which causes the increase of Ca/Si ratio. For the calcium alkali silicate with the Ca/Si ratio of 0.5, the attack on the existing silicon-oxygen network predominates the situation in the 0.1 mol/L of NaOH; the ion exchange effect predominates the situations in 0.5 mol/L of NaOH and 1.0 mol/L of NaOH solutions. For the calcium alkali silicate with the Ca/Si ratio of 1.0, the attack of NaOH on the silicon-oxygen network is the most significant, resulting in the considerable decrease of Ca/Si ratio for all the samples. This is probably due to the increase of Ca/Si ratio, influencing the microstructure of calcium alkali silicate making it more vulnerable to the attack from NaOH solution. These findings are confirmed by the results of Na/Si ratio in Figure 9.5 (b).
9.4 Summary

In this chapter, the influences of sodium hydroxide solution with different concentrations on the calcium alkali silicate with various Ca/Si ratios have been studied. Following conclusions can be drawn:

- The synthesis calcium alkali silicate with silica fume, sodium hydroxide solution and calcium hydroxide is successful, though variations between the measured Ca/Si ratio and the targeted Ca/Si ratio can be noticed.

- Two effects determine the variation of Ca/Si ratio and Na/Si ratio during the alkaline solution exposure: the attack of alkalis and hydroxyls on the existing silicon-oxygen networks resulting in the increase of Ca/Si ratio and Na/Si ratio; the ion exchanging effect between the incorporated calcium in calcium alkali silicate and the alkalis provided by the alkaline solution resulting in the decrease of Ca/Si ratio and increase of Na/Si ratio.
PART IV

CONCLUSIONS
Chapter 10 provides a summary of the thesis. The findings from previous chapters and the corresponding conclusions are given. The contributions of this thesis are clarified. Suggestions for further research are given in the end.
10.1 Foreword

Considering the complexity and heterogeneity of the physico-chemical reactions in ASR, in this study, most of the chemical reactions in ASR are idealized in a calcium-alkali-silicate system with the aim of investigating the chemical mechanism of the formation and evolution of reaction rim, which is closely associated with the generation and accumulation of the expansive interior force leading to deterioration in the concrete affected by ASR.

With the help of this calcium-alkali-silicate system, the interaction between reactive silica and alkaline solution to form alkali silicate as well as the interaction between alkali silicate and calcium to form calcium alkali silicate, as the two prior steps of the formation of reaction rim have been studied. The following findings and conclusions can be made.

10.2 Main Research Findings

10.2.1 Interaction Between Reactive Silica and Alkaline Solution

The attack of the alkalis and hydroxyls on the reactive silica contained in aggregates is the first step of ASR. Any other subsequent physico-chemical reactions of ASR are based on this interaction, especially the alkali silicate as the product of this interaction. In the light of this consideration, the formation of alkali silicate as well as its further evolution in such a system, has been studied in Chapter 4.

It is found that the interaction between the reactive silicate in aggregates and the pore solution of cement paste can be simulated in the chemical model system given in Chapter 4. During this interaction, de-polymerization and polymerization predominate the silicon-oxygen networks present in the system in sequence. At the early age of this process, the de-polymerization prevails leading to the breakage of the siloxane bonds in silicon-oxygen networks. At the later age of this process, the polymerization takes over and prevails in the system resulting in the re-construction of the siloxane bonds to form a more complex silicon-oxygen networks. In addition, other properties of the alkali silicate also change accordingly.

After extrapolating these findings to the ASR-affected concrete, the alkali silicate formed from the interaction between the reactive silica in aggregates and the pore solution of cement paste will also experience the de-polymerization and polymerization processes in sequence as long as it stays in such a system. In this sense, the alkali silicate present in the systems at different ages has completely
different properties. As a consequence, the interaction between alkali silicate and calcium, as the subsequent reaction in ASR, will be heavily affected by these differences.

10.2.2 Interaction Between Alkali Silicate and Calcium

As the most decisive step for the formation of reaction rim, the interaction between alkali silicate and calcium near the aggregate surface is simulated in a calcium-alkali-silicate system and studied in Chapter 5 by reacting two types of alkali silicate with different amounts of calcium.

It is found that a structure development can be generated from the interaction between alkali silicate and calcium resulting in the formation of a rigid structure. The alkali silicate which has experienced polymerization generates more structure development compared to the one which has not undergone polymerization, given the same amount of calcium addition. For the alkali silicate which has experienced polymerization, the more calcium is added to the system, the more structure development can be found. And consequently, more rigid structure can be generated. For the alkali silicate which has not experienced polymerization, the more calcium is added, the less structure development can be generated.

Moreover, it is found that the silicon-oxygen networks present in the system evolves during the interaction between alkali silicate and calcium. The de-polymerization prevails at the early age while the re-polymerization predominates at the late age. The presence of unreacted Ca(OH)$_2$ is found to be the decisive factor determining the predominant process in the system: when CH is present in the system, the de-polymerization is largely encouraged; when CH is exhausted, the re-polymerization takes over and predominates.

Most importantly, the structure development is found to be closely associated with the fraction of the Si species in the silicon-oxygen networks and the process they are undergoing. The more complex and polymerized the silicon-oxygen networks are, the more structure development forms and consequently the more rigid structure can be generated, and vice versa. Besides, more structure development can be found if the re-polymerization is the predominant process in the system, while less structure development can be found if the de-polymerization prevails in the system.

After extrapolating these findings to the ASR-affected concrete, an original mechanism about the formation and evolution of the reaction rim is proposed in Chapter 6. According to the mechanism, the occurrence of the reaction rim in the concrete affected by ASR is fundamentally resulting from the structure development during the interaction between alkali silicate and calcium which causes the
formation of a rigid structure. The structure development is determined by two factors: the polymerization of alkali silicate and the availability of calcium. Only the interaction between the alkali silicate which has experienced polymerization and the calcium with a considerable quantity can stimulate the formation of a considerable rigid structure constituting the reaction rim. Moreover, several featured phenomena of ASR, e.g. migration of ASR products, role of calcium and so on, have been explained with this mechanism.

10.2.3 Multiple Interactions Between Reactive Silica, Alkaline Solution and Calcium on An Interface

The interface between the reactive silica in aggregates and the pore solution of cement paste is the very place where the formation and evolution of reaction rim take place. In the light of this consideration, a calcium-alkali-silicate system is created to simulate the multiple interactions among reactive silica, alkaline solution and calcium happening on such an interface.

In Chapter 7, the calcium alkali silicate generated from the interaction between alkali silicate and calcium is found to be able to form a rigid structure on their interface. This rigid structure can prevent the penetrations of calcium and silicate through itself resulting in a layered system where the unreacted CH as the supplier of Ca\(^{2+}\) and the unreacted alkali silicate as the supplier of silicate are completely separated. It is found that, the Ca/Si ratio of the calcium alkali silicate constituting the rigid structure is ranging from 0.22 to 0.53, the (Na+K)/Si ratio is ranging from 0.20 to 0.26. The silicon-oxygen networks contained in the calcium alkali silicate are mainly composed of Q\(^2\) and Q\(^3\) indicating the presence of layers and chains.

After verifying that the existence of the rigid structure can act as a transport barrier similar to the reaction rim on the interface between alkali silicate and calcium, the elastic moduli of the selected regions on the rigid structure from various systems are investigated with the aim of exploring the mechanical properties of the rigid structure to be the reaction rim applying a constraint on the reaction site. It is found in Chapter 8 that the elastic moduli of the measured regions on the rigid structure varies from about 5 GPa to about 20 GPa. Meanwhile, the elastic modulus generally increases with the increase of the corresponding Ca/Si ratio indicating the influence of calcium on the mechanical properties of the calcium alkali silicate forming the rigid structure. The formation of such a rigid structure between alkali silicate and calcium hydroxide can be explained with the mechanism proposed in Chapter 6.
The findings of Chapter 7 and Chapter 8 confirm the formation of a rigid structure from the interaction between the polymerized alkali silicate and calcium hydroxide. This phenomenon verifies the mechanism proposed in Chapter 6.

10.2.4 Influence of Sodium Hydroxide Solution On the Synthetic Calcium Alkali Silicate

The interaction between NaOH solutions with various concentrations and the synthetic calcium alkali silicate with various Ca/Si ratios has been studied in Chapter 9. It is found that the continuous attack of alkalis and hydroxyls from NaOH solution on the silicon-oxygen networks of calcium alkali silicate raises the Ca/Si ratio. The exchanging effect between sodium present in the NaOH solution with the incorporated calcium in calcium alkali silicate reduces the Ca/Si ratio. This provides information about further evolution of calcium alkali silicate in the matrix of concrete once it is formed during the process of ASR. Further research is necessary to fulfil this research.

10.3 Preliminary Study On the Influence of Lithium (Appendix C)

10.4 Preliminary Idea on Extrapolation to the Pozzolanic Reaction (Appendix D)

10.5 Contribution of this work

In this study, a calcium-alkali-silicate system is developed to idealize the multiple interactions among reactive silica, alkalis, hydroxyls and calcium in the concrete affected by ASR. With such a chemical simplified model system, the factors beyond the research scope are excluded. In this way, it is possible to focus only on the chemical aspect of the interactions of ASR.

As the product of the interaction between reactive silica in aggregates and alkaline solution, alkali silicate is synthesized in the developed chemical model system mentioned above. The developments of various properties including the silicon-oxygen networks, content of hydrated site and specific surface area of the alkali silicate during its formation and further evolution in such a chemical model system, have been examined. This information has been used for further characterization about the formation of calcium alkali silicate.

As one of the most essential products of ASR, calcium alkali silicate is synthesized in the chemical model system. The generation of a rigid structure from the interaction between alkali silicate and
calcium is observed. The causes of the formation of such a rigid structure have been explored from both physical and chemical points of view. In this way, the link between the chemical reactions at the micro scale and the structure development at the macro scale during the interaction between alkali silicate and calcium has been established. Notably, the silicon-oxygen networks are believed to be one of the most decisive factors influencing the structure development leading to the formation of a rigid structure.

Based on the mentioned results, a novel mechanism about the formation and evolution of reaction rim in the concrete affected by ASR is proposed. The necessary conditions for the formation of reaction rim are given. The migration of ASR gel from the neighborhood of aggregates to the voids and pores in the cement paste is explained. The role of calcium during the occurrence and evolution of ASR is clarified.

With the help of the chemical model system and the proposed mechanism, the formation of calcium alkali silicate on the interface between alkali silicate and calcium is realized. The prevention of the penetration of calcium and silicate through the rigid structure located on the interface is observed. The elemental composition and silicon-oxygen networks of the calcium alkali silicate constituting the rigid structure are studied. The elastic modulus of the rigid structure is evaluated to provide information about the mechanical properties of the calcium alkali silicate formed on such an interface.

Interaction between the synthetic calcium alkali silicate with different Ca/Si ratios and the sodium hydroxide solution with various concentration is investigated.

### 10.6 Future Research

Based on the present study, recommendations for further study can be listed as follows:

- In the future, the influence of different alkalis including sodium, potassium and lithium on the dissolution of reactive silica, formation of alkali silicate and its subsequent interaction with calcium to form calcium alkali silicate should be studied. The emphasis will be laid on the micro structure and properties of the alkali silicate and calcium alkali silicate.

- The construction process of the rigid structure by the nucleation and growth of calcium alkali silicate at the micro scale needs to be disclosed. The internal forces among calcium alkali silicate particles, unreacted alkali silicate, unreacted silica and calcium hydroxide should be clarified.
• The development of the mechanical and transport properties of the formed calcium alkali silicate in the long term should be evaluated. The interaction between the existing calcium alkali silicate with other components in the cement paste should be taken into account as well.

• In the future, the dynamic process during which the interior expansive force generates and accumulates with the formation and evolution of the reaction rim needs to be explored to obtain more insight about the chemical reactions of ASR and its consequent expansion and cracking. Simulation and modelling are preferred on this topic.

• A model combining the dynamic processes of accumulation and migration of ASR gel can be established based on the results and the proposed mechanism in the present study, with the aim of characterizing the expansive force responsible for deterioration of ASR.

• Additional work is necessary for the extrapolation of the present study from a chemical model system to the cementitious system. The influences of multiple factors in real concrete on the formation and evolution of ASR gel will be taken into account.

• The research on exploring the relationship between ASR and pozzolanic reaction will be extended in the future. Further approaches on improving pozzolanic reactivity of materials can be conducted based on the findings of the present study.
References


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Appendix A

The following content presents the results about the evolutions of the storage modulus and loss modulus in the buildup and breakage stages of S1H-0.3, S24H-0.1 and S24H-0.3, supplementary to the results of S1H-0.1 given in 5.3.1.1.

(1) S1H-0.3

As shown in Figure A.1, the evolution of the storage modulus of S1H-0.3 is given. The time sweep of the buildup stage and the strain sweep of the breakage stage are indicated as well as the maximum storage modulus of the buildup stage from 1800 s to 2400 s and the minimum storage modulus from 3000 s to 3600 s.

![Figure A.1: Evolution of the storage modulus of S1H-0.3 (interaction between alkali silicate (1 hour) and CH at Ca/Si = 0.3) during the buildup stages.](image)

The evolution of the storage modulus of S1H-0.3 during the buildup stages is presented in Figure A.1. Similar to S1H-0.1, the storage modulus increases dramatically within each buildup stage indicating the continuous development of the structure. The maximum storage modulus as indicated in Figure A.1 slightly increases as a function of time. This indicates that more and more bonds between particles are generated.
Figure A.2: Evolution of the loss modulus of S1H-0.3 (interaction between alkali silicate (1 hour) and CH at Ca/Si = 0.3) during the buildup stages.

The evolution of the loss modulus of S1H-0.3 during the buildup stages is given in Figure A.2. The strain sweep for the breakage stage and the time sweep for the buildup stage are indicated. Clearly, within each buildup stage, the loss modulus increases significantly indicating the increase of the viscosity of the sample. This is caused by the physico-chemical reactions between alkali silicate and calcium.
Figure A.3: Evolutions of $G'$ and $G''$ of S1H-0.3 during the breakage stages.

In order to evaluate the effectiveness of the strain sweep on the breakage of weak bonds, $G'$ and $G''$ during the strain sweep are plotted against the strain amplitude and shown in Figure A.3. Both $G'$
and $G''$ continuously decrease throughout each breakage stage. Eventually, they intersect with each other at a certain value of strain amplitude which is called the critical strain amplitude. Before the critical amplitude point, $G'$ is larger than $G''$ indicating the system is solid-like; after the critical amplitude point, $G''$ is larger than $G'$ indicating the system is liquid-like. These results confirm the effectiveness of the strain sweep used for destroying the weak bonds present in the structure.

(2) S24H-0.1

The evolution of the storage modulus of S24H-0.1 during the buildup stages is shown in Figure A.4. The strain sweep for the breakage stage as well as the time sweep for the buildup stage is indicated. In addition, the maximum storage modulus of the buildup stage from 1800 s to 2400 s and the minimum storage modulus from 3000 s to 3600 s are indicated as well.

![Figure A.4: The evolution of the storage modulus of S24H-0.1 (interaction between alkali silicate (24 hours) and CH at Ca/Si = 0.1) during the buildup stages.](image)

As shown in Figure A.4, the evolution of the storage modulus of S24H-0.1 shares some similarities with S1H-0.1 and S1H-0.3, though differences can be found as well. The storage modulus increases continuously within each buildup stage, suggesting the significant development of structure during the buildup stages. The maximum storage modulus of each buildup stage, as indicated in Figure A.4, increases as a function of time. This indicates that more and more structure is generated during the buildup stages. The evolutions of the maximum storage modulus and minimum storage modulus during the buildup stages will be specially emphasized in the next section.
As shown in Figure A.5, the continuous and significant increase of loss modulus within each buildup stage confirms the increase of the viscosity of the sample induced by the physico-chemical reactions between alkali silicate and calcium. Notably, the maximum loss modulus which is reached at the end of each buildup stage is getting larger and larger from the 1\textsuperscript{st} buildup stage to the 6\textsuperscript{th} buildup stage. This is consistent with the trend of the maximum storage modulus found in Figure A.4.

In order to evaluate the effectiveness of the strain sweep for destroying the weak bonds, the evolutions of $G'$ and $G''$ during the breakage stages are given in Figure A.6.
As shown in Figure A.6, the critical strain amplitude of the sample has been reached in all the breakage stages. As a consequence, the weak bonds between particles associated with the reversible
mechanical process of coagulation has been destroyed as required. This will benefit further analysis about the formation of the strong bonds between particles which is associated with the irreversible mechanical process of rigidification.

(3) S24H-0.3

The evolution of the storage modulus of S24H-0.3 during the buildup stages is shown in Figure A.7. The strain sweep for breakage and the time sweep for buildup are indicated as well as the maximum storage modulus of the buildup stage from 1800 s to 2400 s and the minimum storage modulus from 3000 s to 3600 s.

![Figure A.7: Evolution of the storage modulus of S24H-0.3 (interaction between alkali silicate (24 hours) and CH at Ca/Si = 0.3) during buildup stages.](image)

According to Figure A.7, the storage modulus dramatically increases within each buildup stage. Unlike the previous samples, the storage modulus within the 1st buildup stage from 60 s to 600 s increases at a completely different rate. During this period, the storage modulus increases at an extremely high rate, indicating that the development of structure in the system progresses rapidly. This is probably caused by the rapid physico-chemical reactions between alkali silicate and calcium in S24H-0.3. In addition, the maximum storage modulus of the buildup stages increases in the first two buildup stages and slightly decreases in the rest of the buildup stages. Perhaps, because of the high reaction rate in the first two buildup stages, large amounts of reactants (alkali silicate and calcium) of the physico-chemical reactions are consumed at the early age resulting in the slowing down of these reactions.
reactions at the later age. As a result, the structure development decreases in the following buildup stages.

The evolution of the loss modulus of this sample during the buildup stages is given in Figure A.8. The time sweep for the structure development and strain sweep for the structure breakage are indicated accordingly.

![Figure A.8: Evolution of the loss modulus of S24H-0.3 (interaction between alkali silicate (24 hours) and CH at Ca/Si = 0.3) during buildup stages.](image)

As shown in Figure A.8, the loss modulus generally increases within each buildup stage. The storage modulus evolves in a different way during the 1st and 2nd buildup stages compared to the other stages. This is consistent with the evolution of the storage modulus in the same period. In the sense, the properties of the sample including structure development and viscosity are highly influenced by the physico-chemical reactions. Notably, an unexpected variation (marked with a circle) which is probably caused by some unexpected disturbance to the measurement, can be found in the 2nd buildup stage.

The evaluation of destroying the weak bonds during the breakage stages is shown Figure A.9.
Figure A.9: Evolutions of $G'$ and $G''$ of S24H-0.3 during breakage stages.
As shown in Figure A.9, it is clear that the critical strain amplitude has been reached in all the breakage stages. Therefore, the complete destruction of the weak bonds, which is associated with the reversible mechanical process of coagulation, can be guaranteed.
Appendix B

The following content presents the NMR spectra and the corresponding deconvolution results of S1H-0.3, S24H-0.1 and S24H-0.1, supplementary to the results of S24H-0.3 given in 5.3.3.1.

(1) S1H-0.1

![NMR spectra and deconvoluted curves](image)

As shown in Figure B.1, generally, the peaks which are assigned to different Si species shift to the left (downfield) after the addition of CH and with the increase of reaction time.

Before the addition of CH, the alkali silicate and the unreacted silica fume contained in the alkali silicate slurry are the materials containing silicon-oxygen networks. Although the silicon-oxygen network of this mixture has been studied in 4.4.3, a brief analysis will be provided here for its
convenient comparison with other samples. The silicon-oxygen network present in the alkali silicate slurry contains $Q^2$, $Q^3$ and $Q^4$. The peak with a center at about -90 ppm is assigned to $Q^2$ which has two bonded oxygen to other tetrahedrons and two non-bonded oxygen. According to the shift of the center of the peak from its usual position ranging from -79 ppm to -85 ppm, one of the two non-bonded oxygens is connected with a proton [81] while the other one may connect with an alkali. The peak with a center at about -99 ppm is assigned to $Q^3$ which has three bonded oxygens to other tetrahedrons and one non-bonded oxygen. The non-bonded oxygen is connected with a proton according to its slight shift to the upfield than its usual position ranging from about -91 ppm to about -98 ppm. In addition, the peak with a center at about -110 ppm is assigned to $Q^4$ having four bonded oxygens with other tetrahedrons. Once CH is added to the system, the silicon-oxygen network of the system changes accordingly.

1 hour after CH’s addition, the peaks shift to the downfield showing that the de-polymerization of the silicon-oxygen network is ongoing. The sample of 1h contains $Q^2$, $Q^3$ and $Q^4$. Particularly, the center of the peak assigned to $Q^2$ is located at about -85 ppm, which is located at the downfield compared to that of the $Q^2$ present in the alkali silicate slurry. This means one of the two non-bonded oxygens of a tetrahedron is connected with the incorporated calcium [81, 112]. This finding confirms the incorporation of calcium into the silicon-oxygen network. The peak with its center at about -98 ppm is assigned to $Q^3$, whose non-bonded oxygen is thought to be connected with an alkali. The presence of the peak assigned to $Q^3$ suggests the presence of unreacted silica fume in this sample.

24 hours after CH’s addition, the peaks continue to shift to the downfield suggesting the continuous occurrence of the de-polymerization. Compared to the sample of 1h, the centers of the peaks of $Q^2$ and $Q^3$ do not shift neither to the downfield nor the upfield indicating there were little changes happening on the incorporated calcium and alkali. For the peak assigned to $Q^4$ which represents the unreacted silica fume, the area under it is smaller than that under its peak found in the sample of 1h. This shows the continuous consumption of unreacted silica due to de-polymerization. The de-polymerization is predominant at this age.

72 hours after CH’s addition, the peak assigned to $Q^4$ disappears indicating the exhaustion of the unreacted silica fume due to de-polymerization. The area under the peak assigned to $Q^3$ is larger than that is found in the sample of 24h indicating an increase of the fraction of $Q^3$. This increase can be caused by the de-polymerization of the more cross-linked specie like $Q^4$ or the re-polymerization of the less cross-linked species like $Q^2$ and $Q^3$, or even both as shown in Equation B.1. In addition, the area under the peak assigned to $Q^2$ is much smaller than that is found in the sample of 24h indicating some $Q^2$ is consumed by the re-polymerization to form $Q^3$. Notably, this consumption of $Q^2$ unlikely
results in the formation of $Q^1$ or $Q^0$ by de-polymerization, since the typical peaks of $Q^1$ and $Q^0$ are not found in the NMR spectra as shown in Equation B.2. Therefore, it is clear that the predominant effect at 72h is the re-polymerization.

$$
Q^4 \xrightarrow{\text{De-polymerization}} Q^3 \xrightarrow{\text{Re-polymerization}} Q^2 \text{ or } Q^1
$$  \hspace{1cm} \text{Equation B.1}

$$
Q^3 \xrightarrow{\text{De-polymerization}} Q^2 \xrightarrow{\text{Re-polymerization}} Q^1 \text{ or } Q^0
$$  \hspace{1cm} \text{Equation B.2}

Based on the above results, the silicon-oxygen network in S1H-0.1 firstly experiences a de-polymerization predominant stage at the early age, subsequently undergoes a re-polymerization predominant stage.

\(2\) S1H-0.3

As shown in Figure B.2, the NMR spectra and the corresponding deconvoluted curves of the sample collected from S1H-0.3 at different ages are given.

Figure B.2: NMR spectra and corresponding deconvoluted curves of S1H-0.3 (1 hour, Ca/Si = 0.3).
Similar to the results of S1H-0.1, the peaks shift to the downfield after the addition of CH and with the increase of reaction time. The alkali silicate slurry used for preparing this sample is the same as the one used in S1H-0.1. Hence, it is not necessary to give an introduction about the silicon-oxygen network present in this type of alkali silicate slurry. Detailed information and analysis can be found either in the previous subsection or 4.4.3.

1 hour after CH’s addition, the peaks shift to the downfield indicating that the de-polymerization is triggered by the addition of CH. The peak assigned to Q² with a center located at about -85 ppm confirms the incorporation of calcium in the silicon-oxygen network during this process. Notably, this area under the peak of Q² is much bigger than the one of Q² found in the alkali silicate slurry indicating the formation of Q² by the de-polymerization of Q³ and Q⁴. This formation of Q² is unlikely caused by the re-polymerization of Q⁰ and Q¹ since the typical peaks assigned to Q⁰ and Q¹ are not found in the NMR results as shown in Equation B.2. The peak assigned to Q³ has its center located at about -97 ppm. This area under the peak is slightly smaller than the one found in the alkali silicate slurry indicating the consumption of Q³ during this process. In addition, the peak assigned to Q⁴ confirms the presence of the unreacted silica fume in this sample. Based on the above results, it is not hard to find out that the de-polymerization prevailed in the first hour after the addition of CH.

24 hours after CH’s addition, the peaks continuously shift to the downfield compared to the sample of 1h indicating the de-polymerization is still ongoing. The disappearance of the peak assigned to Q⁴ suggests the complete consumption of the unreacted silica fume 24 hours after CH is added to the system. The peak assigned to Q³ has a center locate at about -98 ppm. The area under the peak assigned to Q² is smaller than the one found in the sample of 1h. This is perhaps due to the re-polymerization of Q² to form Q¹, since the peaks assigned to Q¹ and Q² as the products of the de-polymerization of Q² are not found (Equation B.2). In a word, evidence of both de-polymerization and re-polymerization can be found in the results of this sample.

72 hours after CH’s addition, further changes can be noticed. The peak assigned to Q² with its center at about -85 ppm is smaller than that of Q² found in the sample of 24h. This indicates the consumption of Q² by re-polymerization to form Q³, since the typical peaks assigned to Q¹ and Q⁰ as the products of de-polymerization (Equation B.2) cannot be found in the NMR results. The area under the peak assigned to Q³ is much larger than that of Q³ found in the sample of 24h suggesting the formation of Q³ due to re-polymerization. Because Q⁴ which can provide Q³ by its de-polymerization has been consumed 24 hours after CH’s addition. Therefore, Q³ can only be formed by re-polymerization (Equation B.1). In this way, it is rational to believe that it is the re-polymerization predominating the silicon-oxygen network at this stage.
Similar to S1H-0.1, the silicon-oxygen network in this sample experiences the de-polymerization predominant stage, and subsequently goes through the re-polymerization predominant stage.

(3) 1S24H-0.1

The NMR spectra and the corresponding deconvoluted curves of S24H-0.1 at different ages are given in Figure B.3.

As shown in Figure B.3, the peaks shift to the downfield after the addition of CH and with the increase of reaction time.
Before the addition of CH, the alkali silicate slurry is made by reacting silica fume with NaOH solution for 24 hours. Based on the results in 4.3.3, the silicon-oxygen network present in the alkali silicate slurry of S24H-0.1 and S24H-0.3 are more complex and cross-linked than the ones in S1H-0.1 and S1H-0.3.

1 hour after the addition of CH, all the peaks shift to the downfield indicating that the de-polymerization is predominant at this moment. The peak assigned to Q² is found to have its center located at about -85 ppm confirming the incorporation of calcium in the silicon-oxygen network. In the meantime, the area under the peak of Q² is much larger than the one found in the alkali silicate slurry. This suggests the formation of Q² by the de-polymerization. The area under the peak assigned to Q³ is found to have its center located at about -95 ppm. The area under the peak of Q³ is much smaller than the one found in the alkali silicate slurry. This suggests the consumption of Q³ by the de-polymerization rather than its re-polymerization to form Q⁴. Because in the meantime, the content of Q⁴ present in the system is less than it is found in the alkali silicate slurry indicating a consumption of Q⁴ by de-polymerization. Therefore, the sample at this age is experiencing a de-polymerization predominant process.

24 hours after the addition of CH, further changes are noticed. The disappearance of the peak assigned to Q⁴ indicates the complete consumption of the unreacted silica fume due to de-polymerization. The peak assigned to Q² has its center located at about -85 ppm confirming the incorporation of calcium in the silicon-oxygen network. The area under this peak is smaller than that of Q² present in the sample of 1h suggesting the consumption of Q² by the re-polymerization to form Q³ rather than the de-polymerization to form Q¹ and Q⁰. Because the peaks assigned to Q¹ and Q⁰ as the products of the de-polymerization of Q² are not found (Equation B.2). The peak assigned to Q³ has its center located at about -94 ppm. The area under the peak assigned to Q³ is much larger than the one found in the sample of 1h, indicating the formation of Q³. Notably, this formation of Q³ is contributed by both the de-polymerization of Q⁴ and the re-polymerization of Q² since the contents of the both species are smaller than those found in the sample of 1h according to the reduction of the areas under the peaks assigned to Q² and Q⁴. Therefore, it can be assumed that the silicon-oxygen network present in this sample firstly experiences a de-polymerization and a re-polymerization afterwards, or both processes at the same time.

72 hours after the addition of CH, little changes can be found compared to the sample of 24h indicating an equilibrium has been reached at this moment. The peak assigned to Q² has its center located at about -85 ppm confirming the incorporation of calcium in the silicon-oxygen network. The areas under the peaks assigned to Q² and Q³ are comparable with the ones found in the sample of 24h.
respectively. This suggests the fractions of Q² and Q³ hardly change from 24h to 72h. Therefore, it can be concluded that the silicon-oxygen network in this system reaches an equilibrium.

Based on the above results, following conclusion can be drawn. The system of S24H-0.1 firstly experiences a de-polymerization predominant stage until 1h. Subsequently, the system goes through a re-polymerization stage from 1h to 24h. Eventually, the system reached an equilibrium 72 hours after the addition of CH.
Appendix C

Preliminary Study On the Influence of Lithium

Mitigating ASR in concrete by using lithium salt has been widely acknowledged [143]. Many theories and models have been proposed to explain the role of lithium on mitigating ASR during the physico-chemical reactions of ASR [32, 63, 64, 144-146]. As an extensive utilization of the mechanism proposed in Chapter 6, the influence of lithium on the structure development generated from the interaction between alkali silicate and calcium is studied and illustrated with the aim of providing a novel explanation to the role of lithium on mitigating ASR in concrete.

The sample preparation is similar to the one used in Chapter 4 and Chapter 5, but the 1 mol/L of NaOH solution was replaced with 1 mol/L of LiOH solution which was made by dissolving lithium hydroxide monohydrate in the distilled and CO2-free water. 1 mol/L of LiOH solution was also used in preparation of the Ca(OH)2 paste. The oscillatory rheology measurement is conducted to evaluate the structure development generated from the interaction between alkali (lithium) silicate and calcium. The results are given in Figure C.1 where Na-24h-0.3 denotes the sample using NaOH solution to react with silica fume for 24 hours before the addition of the CH paste at a Ca/Si ratio of 0.3; Li-24h-0.3 denotes the sample using LiOH solution to react with silica fume with 24 hours before the addition of the Ca(OH)2 paste at a Ca/Si ratio of 0.3 and so on.

Figure C.1: Total structure development ($G'_{max}$), irreversible structure development ($G'_{min}$) and reversible structure development ($G'_{max}$-$G'_{min}$) of the sample affected by lithium.
As shown in Figure C.1, it is clear that $G'_{\text{max}}$ of Li-24h-0.3 is lower than that of Na-24h-0.3 throughout the measurement indicating that less total structure development was generated from the interaction between alkali (lithium) silicate and calcium compared to that from the interaction between alkali (sodium) silicate and calcium. Notably, the total structure development of Li-24h-0.3 starts to decrease after the second buildup stage. This can be attributed to the slowing down of the physico-chemical reactions between alkali (lithium) silicate and calcium. The total structure development generated in the system of Li-24h-0.1 is much lower than that of Na-24H-0.1. The above results suggest that the interaction between alkali (lithium) silicate and calcium generates much less structure development compared to the interaction between alkali (sodium) silicate and calcium.

The irreversible structure development ($G'_{\text{min}}$) generated from this interaction confirms the above trend that much less irreversible structure development has been generated from Li-24h-0.3 compared to Na-24h-0.3. Besides, rare irreversible structure development has been generated from Li-24h-0.1. The deceleration of the generation of irreversible structure development after the second buildup stage is consistent with that of total structure development. The results of reversible structure development given in Figure 10.1 confirm the above findings.

Based on the above results, several remarks can be made. (1) Similar to the situation given in Chapter 5, structure development can be generated from the interaction between alkali (lithium) silicate and calcium. (2) The more calcium is added to the system to react with, the more structure development can be generated. (3) Rare structure development can be generated from the system containing lithium compared to that containing sodium.

Combining these preliminary findings with the mechanism proposed in Chapter 6, following extrapolations can be drawn:

- It is relatively difficult for the interaction between alkali (lithium) silicate and calcium to generate a rigid structure compared to the system containing sodium.

- Based on the proposed mechanism, the mitigation of ASR by lithium is probably due to the prevention of the formation of a rigid structure which acts as the reaction rim. As a result, all the products are flexible to be expelled into the pores and voids in the matrix of cement paste near the aggregate. In this sense, it is impossible for the alkali silicate to locally accumulate before the generation of expansive force leading to expansion and cracking in ASR.

- Further studies are necessary to verify this assumption.
Appendix D

Preliminary Idea on Extrapolation to the Pozzolanic Reaction

The term “pozzolan” comes from the description of the volcanic ash mined at Pozzuoli, a village near Naples [147]. Since Roman time, the pozzolanic reaction has been closely related with the cementitious materials for construction. Nowadays, utilization of the pozzolanic reaction is one of the most promising approaches to improve the sustainability of concrete. The materials with pozzolanic reactivity include fly ash, granulated blast-furnace slag, metakaolin and silica fume etc. [148]. This type of material contains large amount of silicon which is usually present in the form of amorphous silica resulting in its high reactivity during the interaction with the pore solution of cement paste.

During the pozzolanic reaction, the reactive silica contained in the pozzolanic minerals reacts with multiple components in the cement paste including Ca\(^{2+}\), Na\(^+\), K\(^+\) and OH\(^-\) to generate calcium silicate hydrate [149, 150]. Obviously, the chemical reactions contained in pozzolanic reaction are similar to those in ASR, i.e. they share similar reactants: reactive silica from either pozzolanic minerals or aggregates, Ca\(^{2+}\), Na\(^+\), K\(^+\) and OH\(^-\) from the pore solution of the cement paste. Notably, other components like alumina contained in the pozzolanic minerals are out of the consideration here.

Those similarities between pozzolanic reaction and ASR was firstly reported by Urhan in 1987 [151] and recently by Diamond in 2004 and others [27, 152, 153]. However, completely different consequences are caused by those similar reactions: the products of pozzolanic reaction can act as a replacement of the hydration products to densify the matrix of concrete which is beneficial for various properties of concrete, while the products of ASR cause the generation of expansive force leading to the deterioration of concrete.

No wonder a question arises out of these opposite situation asking why similar chemical reactions end up with completely opposite consequences: products of pozzolanic reaction are beneficial while the ones of ASR are detrimental for concrete. Based on the mechanism proposed in Chapter 6, a descriptive model based on the following three scenarios with the aim of answering this question is given. Bearing in mind that this is a preliminary hypothesis.

It needs to be noted beforehand, both the pozzolanic material and the reactive aggregate can be considered as a reactive silica particle for simplification.

(1) Degree of Curvature and the Pattern of Product Formation
**Scenario 1**

The surface of a reactive silica particle where multiple interactions among reactive silica, alkaline solution and calcium happen is usually assumed to be flat, the products formed on such a surface are shown in Figure D.1 (a).

![Schematic representation of the products present at different places](image)

Figure D.1: Schematic representation of the products present at different places: (a) on the flat surface; (b) on the surface curving inward; (c) in the crack of an aggregate.

For a flat surface of a reactive silica particle, the products from the multiple interactions among reactive silica, alkaline solution and calcium tend to accumulate on its surface, and expand to the neighboring area as the reactions continue, as shown in Figure D.2.

![Schematic representation of the products form and accumulate on a flat surface of a reactive silica particle](image)

Figure D.2: Schematic representation of the products form and accumulate on a flat surface of a reactive silica particle.

**Scenario 2**

When the surface of the particle curves inward, the presence of the products formed there is shown in Figure D.1 (b). As the surface curves inward more significantly, a crack can be realized as shown in Figure D.1 (c). In this case, the products are trapped and tend to accumulate in the place at the interior of the aggregate, if there is not any force expelling those products from the interior. Obviously, this situation describes the occurrence of ASR in the interior of a crack in an aggregate.
The above situations can be characterized with the degree of curvature of the particle surface which is denoted with $D_c$. When the surface is flat, $D_c = 0$. When the surface curves inward the aggregate, $D_c < 0$. The narrower and deeper the crack is, the more negative $D_c$ is; the broader and shallower the crack is, the less negative $D_c$ is.

For a surface curving inward, the products tend to form and accumulate in the concave space. As long as the interactions continue, the products continuously accumulate until the concave space is fully filled. This process is schematically shown in Figure D.3. Under this condition, the more significant the surface curves inward, the more negative the degree of curvature is and consequently the easier the products will be trapped in the concaved space given the lack of driving force which expels the products. Obviously, this situation describes the occurrence of ASR in a crack of an aggregate.

![Figure D.3: Schematic representation of the products form and accumulate in a crack of a reactive silica particle.](image)

**Scenario 3**

On the opposite, if the surface curves outward the particle, the presence of the products on such a surface can be represented by the situation given in Figure D.4 (b). As the surface curves outward more significantly, the surface of the aggregate can be represented by a circle as shown in Figure D.4 (c), where the products tend to surround it once formed.

![Figure D.4: Schematic representation of the products form and accumulate in a crack of a reactive silica particle.](image)
Figure D.4: Schematic representation of the products present at different places: (a) on the flat surface; (b) on the surface curving outward; (c) around an aggregate.

Similarly, these situations can be described by introducing the degree of curvature. When the surface curves outward an aggregate, $D_c > 0$. The more it curves outward, the larger $D_c$ is; the less it curves outward, the smaller $D_c$ is.

For a surface with its degree of curvature approaching $+\infty$, it can be considered as a sphere. Under this condition, the products from multiple interactions among reactive silica, alkaline solution and calcium tend to form around the particle itself. As the interactions continue, the reactive silica is continuously consumed resulting in the formation of the products accumulating and surrounding the particle until the reactive silica is completely consumed eventually. This process is schematically illustrated in Figure D.5. It should be especially pointed out that, the reactive silica particle is actually acting as a nuclei for the products to nucleate around it.

Figure D.5: Schematic representation of the products form and accumulate around a reactive silica particle.

Therefore, the change of the particle surface with the change of its degree of curvature can be summarized in Figure D.6. The particle surface changes from a concave style to a flat one when $D_c$ increases from $-\infty$ to 0; the surface changes from a flat style to a convex one when $D_c$ increases from 0 to $+\infty$. Notably, when $D_c$ approaches $-\infty$, the particle surface curves inward so much that it can be considered as an infinitely narrow and deep crack; when $D_c$ approaches $+\infty$, the particle surface curves outward significantly and can be considered as a sphere.
Figure D.6: Schematic representation of the change of particle surface with degree of curvature. The solid line represents the surface of a particle.

(2) Size Effect

For a particle with an extremely small size, the degree of curvature of its surface is approaching $-\infty$. As stated above, the reactive silica particle is going to act as a nuclei for the nucleation and growth processes resulted from the continuous product formation. Notably, this is coincident with the behavior of pozzolanic minerals during its interactions with cement paste. Most importantly, it is extraordinarily difficult for the products to generate the expansive force under this condition. Because the reactive silica particle is so small that it will be consumed rapidly before an accumulation of products occurs. The smaller the particle is, the faster it will be consumed. This conclusion explains two phenomena in either pozzolanic reaction or ASR, ignoring the change of chemical reactivity by changing particle size: the reactivity of the pozzolanic minerals increases with the decrease of its particle size and vice versa [154, 155]; the pessimum effect depresses ASR by reducing the particle size of aggregates [78, 156, 157].

For a particle with an extremely large size, its surface can be considered flat with its degree of curvature of zero. The products are going to form and accumulate on the flat surface. Considering the flat surface is infinite, therefore, the growth of the products due to accumulation can only follow the direction away from the particle surface as indicated with a black solid arrow in Figure 10.3, given the reactive silica located at different places is equally reactive. In this way, the layers of products formed at different time simultaneously grow into the environment without interfering with each other. As a result, neither expansive force nor constraint can be generated during this process. This hypothesis also explains the mitigation of ASR with the pessimum effect by increasing the particle size of aggregates [78, 157].
For the particle containing the concaved surfaces as shown in Figure D.3, as stated in Chapter 6, it is easy for the products to accumulate in the concaved space resulting in the generation of expansive force locally once the products are continuously accumulated there. It should be noted that, compared to the mentioned two situations with extremely small and large particles size, this case only describes the local geometric property of the surface of a particle, its connection with particle size is weak. It means that this situation varies from case to case.

(3) Further discussion

Bearing in mind that any surface of a particle can be dissociated into a combination of the above three situations at different proportions, therefore, the influence of the pattern of the formation and accumulation of products on the possibility of having pozzolanic reaction or ASR could be characterized by the proportion of the above three situations taking on the surface. For example, it can be expressed in Equation D.1 where S denotes the surface of a particle, α denotes the fraction of the surface given in Scenario 1, β denotes the fraction of the surface given in Scenario 2, λ denotes the fraction of the surface given in Scenario 3.

\[ S = \alpha \cdot (\text{Scenario 1}) + \beta \cdot (\text{Scenario 2}) + \lambda \cdot (\text{Scenario 3}) \]

Equation D.1

As stated above, the larger the particle is, the larger the fraction of the surface given in Scenario 1 (α) is and the smaller the fraction of the surface given in Scenario 3 (λ) is. Under this condition, both pozzolanic reaction and ASR are hard to occur. Alternatively, the smaller the particle is, the smaller the fraction of the surface given in Scenario 1 (α) is and the larger the fraction of the surface given in Scenario 3 (λ) is. Under this condition, both pozzolanic reaction and the chemical reaction of ASR are enhanced. However, the deterioration of ASR is unlikely to happen due to the lack of pressure accumulation. The fraction of the surface given in Scenario 2 is thought to be associated with particle size. The smaller the particle is, the less possible for such a concave surface to be located and so on. This mechanism might fundamentally govern the pessimum effect in ASR and the size effect in pozzolanic reaction. However, additional evidence needs to be disclosed by further studies.
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A1
Kunpeng Zheng, Mladena Lukovic, Geert De Schutter, Guang Ye, Luc Taerwe (2016). Elastic Modulus of the Alkali-Silica Reaction Rim in a Simplified Calcium-Alkali-Silicate System Determined by Nano-indentation, Materials 9, 787

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