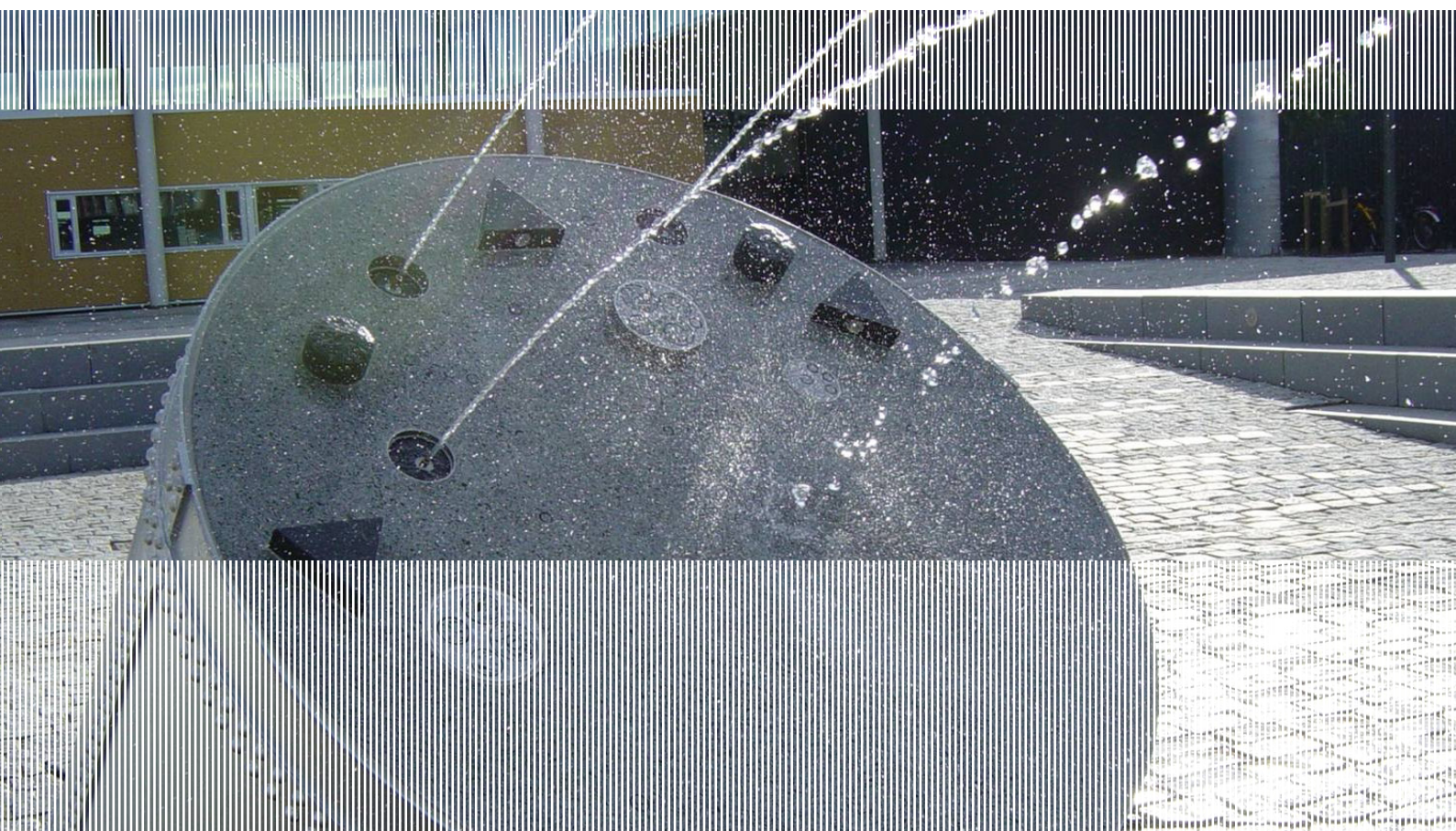


SINTEF Building and Infrastructure Klaartje De Weerd

Geopolymers – State of the art

COIN Project report 37 – 2011



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FA 1 Environmentally friendly concrete

SP 1.1 Low carbon-footprint binder systems

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Preface

This study has been carried out within COIN - Concrete Innovation Centre - one of presently 14 Centres for Research based Innovation (CRI), which is an initiative by the Research Council of Norway. The main objective for the CRIs is to enhance the capability of the business sector to innovate by focusing on long-term research based on forging close alliances between research-intensive enterprises and prominent research groups.

The vision of COIN is creation of more attractive concrete buildings and constructions. Attractiveness implies aesthetics, functionality, sustainability, energy efficiency, indoor climate, industrialized construction, improved work environment, and cost efficiency during the whole service life. The primary goal is to fulfil this vision by bringing the development a major leap forward by more fundamental understanding of the mechanisms in order to develop advanced materials, efficient construction techniques and new design concepts combined with more environmentally friendly material production.

The corporate partners are leading multinational companies in the cement and building industry and the aim of COIN is to increase their value creation and strengthen their research activities in Norway. Our over-all ambition is to establish COIN as the display window for concrete innovation in Europe.

About 25 researchers from SINTEF (host), the Norwegian University of Science and Technology - NTNU (research partner) and industry partners, 15 - 20 PhD-students, 5 - 10 MSc-students every year and a number of international guest researchers, work on presently eight projects in three focus areas:

- Environmentally friendly concrete
- Economically competitive construction
- Aesthetic and technical performance

COIN has presently a budget of NOK 200 mill over 8 years (from 2007), and is financed by the Research Council of Norway (approx. 40 %), industrial partners (approx 45 %) and by SINTEF Building and Infrastructure and NTNU (in all approx 15 %).

For more information, see www.coinweb.no

Tor Arne Hammer
Centre Manager

Summary

Geopolymers are produced by mixing aluminate and silicate containing minerals or aluminosilicates (e.g. fly ash or clays) with an activating highly alkaline solution. As a result a three dimensional network of silica and alumina tetrahedra sharing oxide bonds is formed. The mechanism of reactions is still disputed. It should be noted that a true geopolymer should be low in calcium in order to avoid formation of discrete compounds thereof.

The main reasons for the on-going research on geopolymers are partly environmental in order to reduced CO₂ emissions relative to Portland cement, and partly economical in particular when unexploited fly ash can be used as aluminosilicate source.

Good early strength can be achieved, in particular when heat cured, but the strength level is very sensitive to the balance between reactive Si/Al and the amount of alkalis. In terms of durability, geopolymers seems to have better heat and acid resistance than ordinary Portland cement.

Even though geopolymers appear to be one of the promising building materials for the future, there is still range of concerns that need to be addressed. Inherent variations in the chemical and physical composition of the raw materials can affect the final properties of the geopolymer (e.g. fly ash, calcined clay). When cured at ambient temperature problematic drying shrinkage has been observed. Chemical admixtures designed for Portland cement e.g. plasticizing admixtures do not necessarily work for geopolymers. The high alkaline solution complicates handling of the geopolymers and can also lead to extensive efflorescence on the surface leading to less aesthetic appearance.

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1 Introduction

Geopolymers are of interest as a building material. Owing to increased environmental concerns as well as diminishing natural resources geopolymers are spotted as a valuable alternative for Portland cement. Geopolymers can have similar cementing characteristics as Portland cement, but they can be produced out of by-products from other industry (e.g. fly ash) or less energy craving and CO₂-emitting materials (e.g. calcined clay, alkali activators).

The study of the alkali activation process of aluminosilicate sources (e.g. fly ash and calcined clay) as a method the synthesizing new cementitious materials is gaining relevance in the scientific community. The increasing number of scientific publications as well as international events dedicated to this topic is a proof of it. Currently, there are, however, not that many practical applications.

The report gives a brief introduction in geopolymers, and discusses the advantages and challenges met when using geopolymers as building materials.

1.1 Definition

A geopolymer is an inorganic binder. It is synthesized by mixing at ambient or higher temperatures (e.g. 90°C) a reactive aluminosilicate powder (e.g. fly ash, metakaoline, calcined clay) with an alkaline activator that contains alkali hydroxide, silicates, aluminates, carbonates or sulphates, or a combination thereof (see Figure 1). The reaction product is mainly an amorphous aluminosilicate glass phase built up of interlinked SiO₄⁴⁻ and AlO₄⁵⁻ tetrahedra forming a 3D-structure.

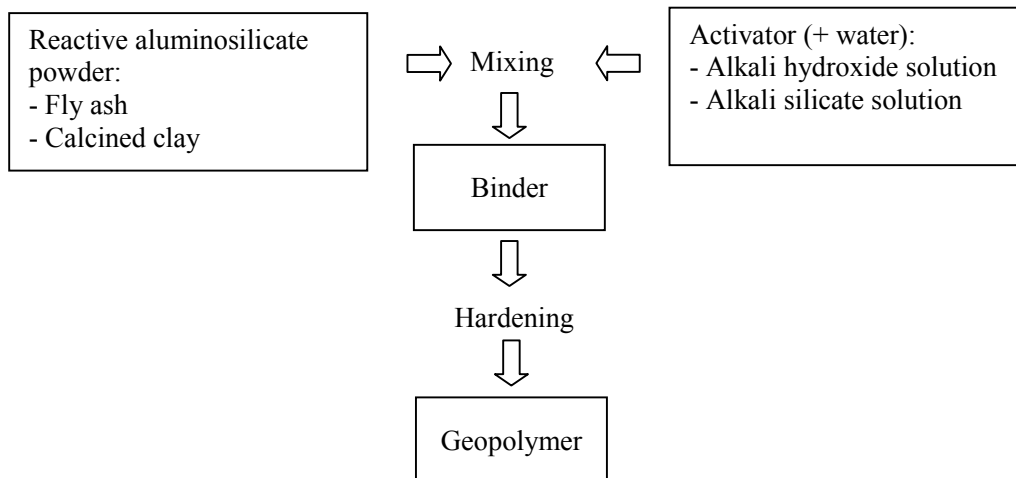


Figure 1: Production process of geopolymers.

It should be noted that alkali activated slag is not considered to be a geopolymer as slag is Ca rich material. In a Ca rich system another type of reaction products is formed, namely calcium silicate hydrates. In this type of phases, silicate tetrahedra are found in one-dimensional chains rather than in 3D structures as observed in geopolymers (see Figure 2). Another difference is that water is bound in the structure of calcium silicate hydrates, but not in geopolymers, resulting in superior chemical and thermal resistance of the geopolymers.

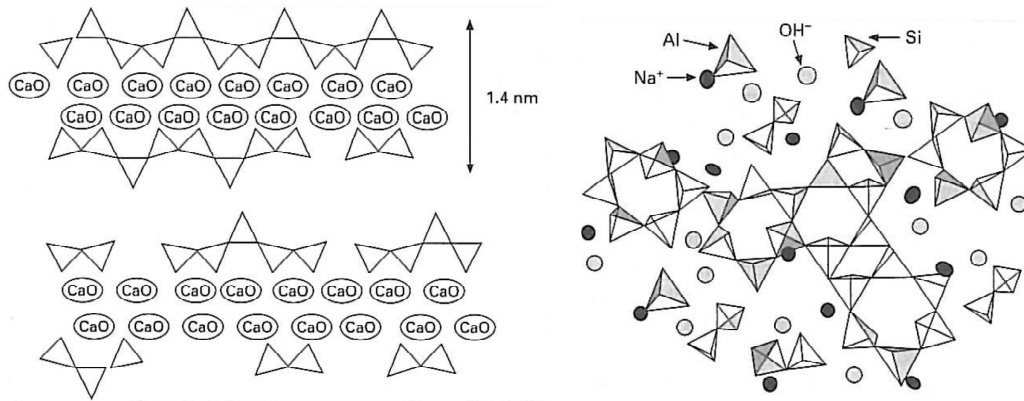


Figure 2: Left: The chemical structure of one-dimensional calcium silicate hydrates (Dreierketten); Right: The 3D-structure of geopolymers (image from Inés García Lodeiro).

1.2 Nomenclature

The term geopolymers was first used by Davidovits in the 1970's for alkali-activated alumina-silicate binders [1]. According to Davidovits, the “geo-“ part refers to the Greek Gaia which means earth, as geopolymers mainly exist of aluminium and silicon oxide which are the most common materials in the earth's crust (see Figure 3). Other authors attribute the prefix “geo” to the constitutive relationship of the binder to geological materials such as natural stone and/or minerals [2].

The “-polymer” part refers to the composition of the geopolymers which is a three dimensional network of monomers consisting of aluminate and silicate tetrahedra.

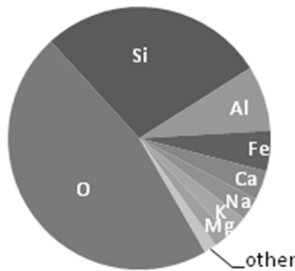


Figure 3: The elements present in the earth's crust.

Through history there has been discussion about the term geopolymer. Many other names have been used to indicate this kind of materials, examples are [3]:

soil cement, low-temperature aluminosilicate glass, alkali-activated cement, geocement, alkali-bonded ceramic, inorganic polymer concrete, hydroceramic.

However, now geopolymer has become an accepted and established term.

It should be mentioned that geopolymers have been referred to as zeolite precursors [4, 5]. This is due to the similarity in the chemical composition: both consist out of a 3D-network of silicate and aluminate tetrahedra. Their microstructure is however very different: zeolites have typical crystalline structures, whereas geopolymers have mainly an amorphous structure. Zeolites are generally produced at much higher water to solid ratios and are often cured at elevated temperatures and pressures (autoclaved) to enhance the formation of the crystalline structure. Crystalline zeolitic phases, e.g. hydroxysodalite and herchelite, have been observed to form over time within geopolymers [6]. The reaction process of geopolymers oriented towards the production of cementitious materials, can be considered as a zeolitisation process where the last stage of crystallisation is not reach or at least not completed [7]. A geopolymer is a not (fully) crystallized zeolites.

1.3 History

The use of alkali activated materials in construction is not new [8, 9]. Alkali-activated slag has for example been used since the 1940's in Belgium, from the 1950's in Ukraine, and during the 1980's it was used in Scandinavian countries, under product names such as Trief and F-cement.

However, the first thorough studies on low Ca alkali activated systems (i.e. geopolymers) date from the 1980s and mainly the 1990s.

The first publications dealt with the activation of metakaoline, calcined kaoline clay. Davidovits published his early work mainly in little revealing patent literature and at geopolymer '88 conference. During the 1990s, Palomo and Glasser [10] and Rahier et al. [11-13] published extremely valuable work which inspired many other researchers. The first publication on fly ash activated systems is according to [14] a conference paper from 1993 of Wastiels et al. [15].

Currently many research groups all over the world focused on this topic. Amongst them are: the group of Palomo, Fernandez-Jimenez, Alonso et al. in Spain; Kaps and Buchwald in Germany; Barbosa, MacKenzie et al. in New Zealand; van Deventer, Duxson, Provis et al. in Australia; Davidovits et al. in France; Grutzeck and Roy et al. in the US.

It should be noted that theories have been proposed regarding the use of geopolymers in ancient constructions such as the city of Ur and Cheops Pyramids [1, 8]. The debate whether the blocks of pyramids have been poured rather than chiselled, however, is still on-going.

2 Raw materials

In order to obtain a geopolymer with desired properties e.g. high rapid strength, low shrinkage, high acid resistance or low cost, a range of ratios need to be controlled:

- Si/Al ratio
- Na/Si and K/Si ratio
- water to solid ratio

It is therefore of major importance to characterize the aluminosilicate source (e.g. fly ash and calcined clay) and to determine their reactivity, in order to be able to estimate the amount silicates and aluminates reacting. It should be noted that the particles size distribution or fineness is of importance regarding the reactivity of the aluminosilicate source.

The mix can then be optimized by adjusting the type and the amount activators added.

2.1 Aluminosilicate source

There is a wide range of reactive aluminosilicate powders available which can be used for geopolymer production.

They can be divided into three main classes:

- by-products from other the industry
e.g. fly ash, low calcium slags [16] and mining waste [17]
- natural reactive aluminosilicate powders
e.g.: sedimentary diatomaceous earth formed from skeletons of microscopic organisms (mostly silica), volcanic glass and tuffs, diagenized silica gel from hot springs or acid environment [18] (mostly silica), and non-thermally activated clays [19, 20]
- activated aluminosilicates
e.g. calcined clays and especially metakaoline

All materials have in common that they contain reactive silica and alumina. In the following paragraphs fly ash and calcined clays are discussed in more detail as most of the research has been conducted on them.

2.1.1 Fly ash

Fly ash is by-product of coal fired power plants. The coal can be combusted in different ways at the power plants: dry-bottom boilers, wet-bottom boilers and cyclone furnaces. The most common type, fly ash, originates from dry-bottom boilers. The annual production of coal ash in 2010 was estimated to be about 800 million tonnes [5], of which fly ash constitutes about 500 million tonnes [21]. In average about 16% of the total amount of ash is used [21]. The disposal of the unused remainder has become a serious environmental problem.

At the coal fired power plants, coal is ground fine prior to combustion. It is then blown into an incinerator where it is heated up to 1600°C. During this process most of the carbon is burnt off. Coal deposits are often contaminated with for example shale, siltstone, sandstones or clay minerals. These minerals will melt upon combustion and form small spherical droplets (minimization free surface energy). After combustion the flue gases are rapidly cooled down, leading to the formation of spherical glassy particles, fly ash, which are collected from the flue gas using electrostatic precipitation. The size of the fly ash particles ranges between 1 µm to 150 µm, with an average particle size between 7-12 µm [22].

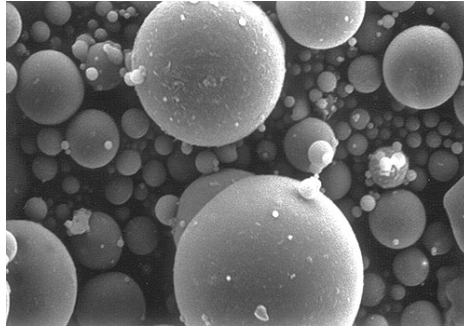


Figure 4: Secondary electron image taken by an electron microscope from fly ash particles.

The composition of the fly ash depends among other factors on the composition of the coal burned, and more precisely the composition of the inorganic contaminants present in the coal.

According to ASTM C 618 fly ash can be divided into two classes: low-calcium Class F derived from bituminous and anthracitic coals, and high-calcium Class C originating from lignitic or subbituminous coals. It should be noted that the ASTM C 618 classification is not necessarily logically based on the total $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ content and not on the CaO content.

The European classification system EN 450 differentiates between siliceous and calcareous fly ash. Siliceous fly ash needs to have a reactive CaO content lower than 10%. The SiO_2 is required to be higher than 25%, and the sum of SiO_2 , Al_2O_3 and Fe_2O_3 should be no less than 70%.

Class F and siliceous fly ashes are the classes relevant for geopolymer production.

The burning process of the coal and cooling rate of the flue gas also play an important role for the type of phases formed within the fly ash. Fly ash consists mainly (50-90%) of an amorphous aluminosilicate glass phase, considered to be the reactive phase of the fly ash. However, a part of the mineral melt crystallizes or separates upon cooling, forming phases such as mullite and minor amounts of quartz, and iron rich and calcium rich phases. The silicates and aluminates present in these phases are generally considered inert [23].

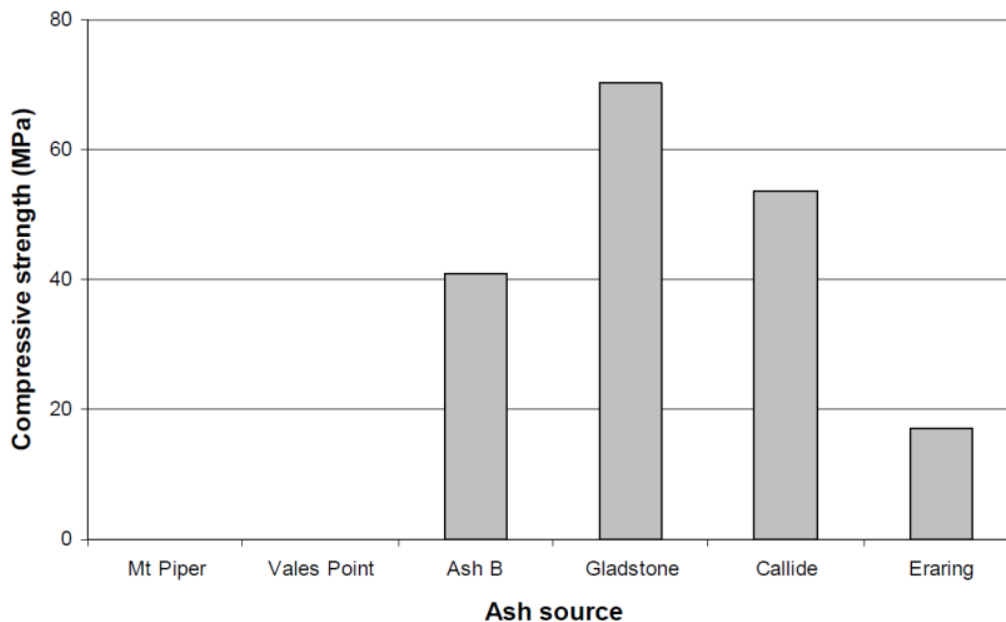


Figure 5: Compressive strength of geopolymers produced with 6 different Australian fly ashes [24].

Fly ash is a very heterogeneous material. First of all, one fly ash particle may contain different phases. Secondly, the composition of the fly ash varies from particle to particle, as the composition of the fine ground coal particles varies. Thirdly, the fly ash composition varies not only from power plant to powder plant, but also the production from one single power plant varies in composition as natural coal deposits are inhomogeneous.

Fly ash is a challenging product to use for precisely designing geopolymers, due to the variations in composition (see Figure 5).

However, the fact that large quantities are produced as a by-product, and that the major part is dumped into landfills, make it an attractive raw material for geopolymer production both from an environmental and an economical point of view.

2.1.2 Calcined clay

Clays are hydrous aluminium phyllosilicates or aluminium sheet silicates with various amounts of iron, magnesium, alkali metals, alkali earths and other cations. Clays are weathered products and are therefore inherently strained and ultrafine grained. They are built up by tetrahedral sheets mainly consisting of silica and octahedral sheets consisting of alumina. Clays built out of a tetrahedral sheet combined with an octahedral sheet are referred to as 1:1 clays where examples are kaolinite and serpentine. The ones consisting of an octahedral sheet sandwiched between two tetrahedral sheets are called 2:1 clays, e.g. illite and smectite. Figure 6 shows as an example the structure of the clay mineral kaoline.

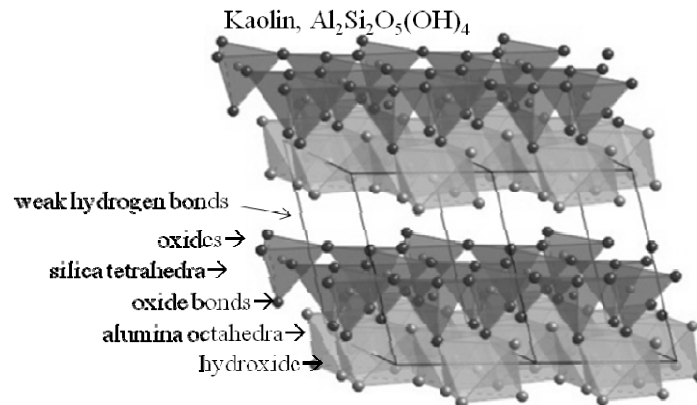


Figure 6: The structure of kaoline.

During calcinations the clay is heated up to 500-900°C. During this process the free water evaporates. In addition, a dehydroxilation takes place, resulting in a loss of the long range order of the alumina and silica layers and rendering the powder X-ray amorphous. Another important structural change is that much of the alumina transforms from an octahedral coordination to a tetrahedral coordination upon calcination [25]. These changes results in a distortion of the structure and thereby renders the clay more reactive [26].

The reactivity of the calcined clay depends on the composition of the clay used and its calcination temperature. This is illustrated in Figure 7. It should be mentioned that most clay deposits consist of blends of different types of clays. In addition, clays can contain inert phases such as crystalline quartz.

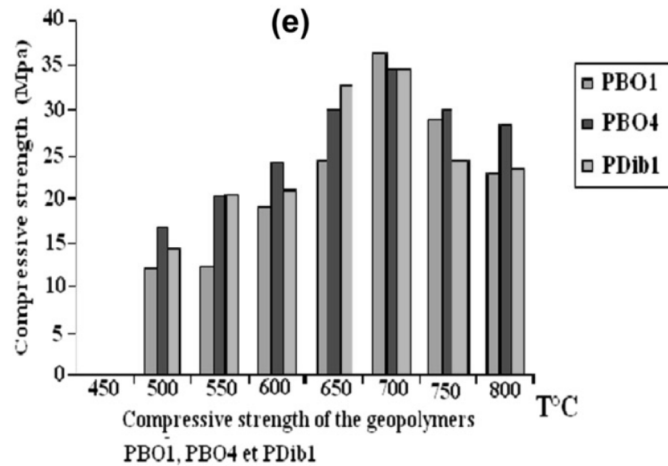


Figure 7: The compressive strength of geopolymer paste prepared with three different kinds of blue clay from Cameroon each calcined at 7 different temperatures [27].

The term geopolymer was first applied by Davidovits on materials synthesized with calcined kaoline, also called metakaoline [1]. Pure metakaoline has often been used as a reference material to study the process of geopolymerisation. Kaoline is however a valuable mineral for several applications. Hence, for commercial production of geopolymers e.g. as a construction material, calcined blue clays (impure/blended clays) are more of interest as they are cheap and widely available.

The drawback of calcined clay based geopolymers is the very high specific surface and the irregular shape of the particles, resulting in a high water demand [28]. This in turn can cause problems regarding drying shrinkage and consequently cracking.

Clays contain variable amounts of alkali in their structure. Therefore, geopolymers based on calcined clay can be more prone to efflorescence than fly ash based geopolymers [28].

2.2 Alkaline activator

Besides a reactive aluminosilicate source one also needs an alkaline activator to produce a geopolymer. The most common alkaline activators used are alkali hydroxide solutions and alkali silicates. In addition to these a couple of other activators will be briefly discussed.

It should be noted that a range of studies has been performed using calcium hydroxide as an activator with or without additional alkali. However as the focus of this report is on low-Ca systems, these studies are not within the scope.

2.2.1 Alkali hydroxide solutions

The most commonly used alkali hydroxide activator is NaOH and KOH as they are both widely available. Other less readily available alkali hydroxides such as LiOH, RbOH and CsOH are rarely used as activators for the production of geopolymers [29].

Sodium is less expensive than potassium. However, NaOH has some disadvantages compared to KOH. First of all, its dramatic loss of solubility with decreasing temperatures (30 wt% at 0°C and 50 wt% at 25°C), which can lead to precipitation of NaOH when used at lower temperatures. The solubility of KOH is not that temperature dependent. Secondly, NaOH solutions tend to be more viscous than KOH solution for similar concentrations, giving rise to impaired rheological properties of the fresh mix.

It has been shown that an increasing concentration of the activator results in enhanced compressive strength [5, 30] (see Figure 8).

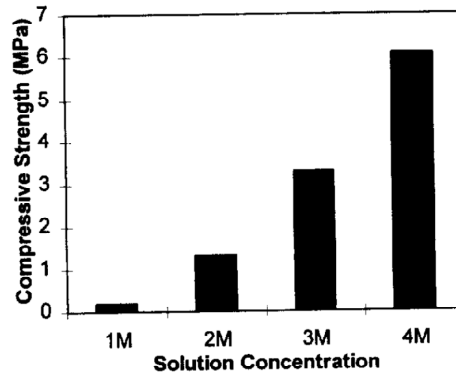


Figure 8: Effect of the NaOH concentration on the compressive strength after curing for 7 days at 90°C (water/fly ash = 0.80) [30].

Both KOH and NaOH give rise to the formation of crystalline zeolitic structures [5, 31]. The crystallization appears most rapid for NaOH. This crystallization has been associated with strength loss, however whether it is the direct cause, is still up for discussion [29].

It should be noted that alkali hydroxide activation can be considered to be not so user friendly due to the highly corrosive nature of the alkali hydroxide activators and the high heat release associated with their dissolution to form concentrated solutions (preparation of 10M NaOH heats the solution up to 90°C). Hence, silicate activation might be preferred. Another practical disadvantage can be the increase in viscosity of the alkali hydroxide solution with increasing concentration (> 1M) [29]. Finally, the use of highly concentrated alkali hydroxide solutions can lead to efflorescence where excess alkali react with the CO₂ present in the atmosphere to precipitate as salts on the surface [29, 32].

2.2.2 Alkali silicate solutions

Alkali silicate solutions consist of a blend of Na₂O or K₂O, Si₂O and water. They are also referred to as water glass. In these solutions silica polymerizes to different species (see Figure 9). It is however complicated to identify these different species. The most common technique to this is ²⁹Si NMR which will be discussed more in detail later on.

It should be noted that this dissolved silica is slightly acidic. Monomeric silica, Si(OH)₄, is for example also known as orthosilicic acid, and behaves as a weak acid under alkaline conditions. The pH of silicate activating solutions is therefore buffered to approximately 11-12.

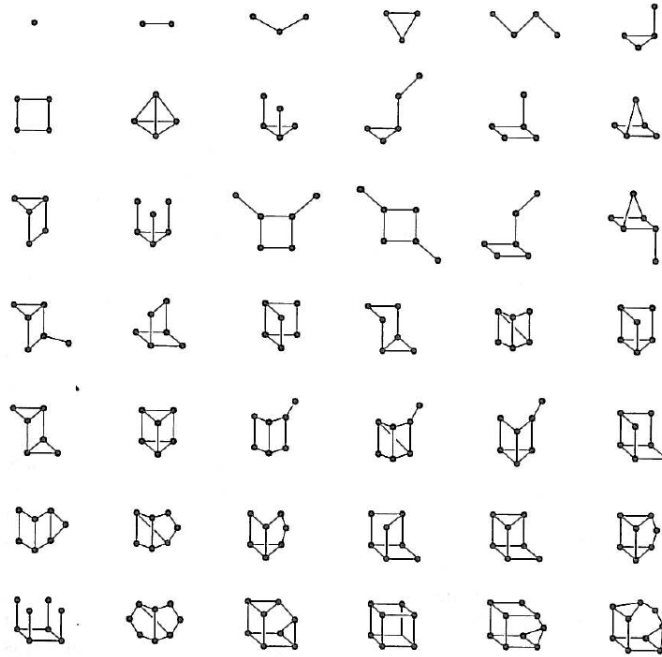


Figure 9: Species identified by ^{29}Si NMR of alkaline silicate solutions. Dots are SiO_4 tetrahedra and lines represent Si-O-Si bonds shared between neighbouring tetrahedra. All Si sites are tetrahedral and hydroxyl groups are not shown. From [29] based on [33].

From Figure 10, it can be seen that the viscosity of the alkali silicate activator increases significantly with increasing Si/Na ratio. The graph is made by Provis [29] based on results reported by Vail [34]. Note that the y-axis is logarithmic. Once more, the potassium variant shows to be less viscous than the sodium water glass. For more information the reader is referred to [29].

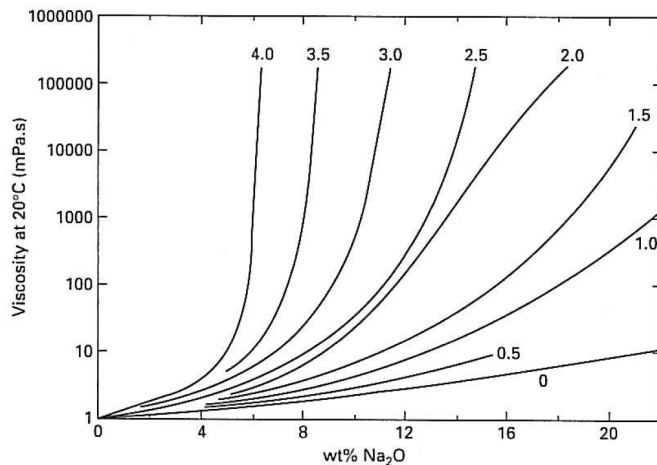


Figure 10: Viscosity of sodium silicate solutions with mass ratio $\text{SiO}_2/\text{Na}_2\text{O}$ marked. From [29] based on data from [34].

It has been observed by Criado et al. [31] that less zeolitic phases are formed when alkali silicate activators are used compared to alkali hydroxide activators. The content of zeolites formed tends to decrease with increase Si/alkali ratio of the activator [31].

2.2.3 Other activators

To the author's knowledge only a few studies have been performed using activators other than calcium hydroxide (not in the scope of this study), alkali hydroxides or alkali silicates.

Fernández-Jiménez and Palomo [5] investigated the effect of combining NaOH with Na₂CO₃ to activate fly ash. The presence of the carbonates resulted in the formation of more porous reaction products and hence lower compressive and flexural strength. The authors attributed the impaired strength to, reduced reactivity of the fly ash caused by the formation of sodium carbonate which acidifies the system.

Another activator which has been reported is sodium aluminate [35]. This might be recommended when reacted powder source is low in alumina e.g. geothermal silica [18].

3 Synthesis and composition

Besides discussing the synthesis and composition of geopolymers, also a brief overview of commonly used techniques to study geopolymers is given.

3.1 Synthesis

The reaction mechanisms taking place when going from the blended ingredients to the final hardened geopolymer product (see Figure 1) are very complex and are still not fully understood.

The process of geopolymerisation is similar to the zeolitisation process except for the full crystallization [5]. Murayama et al. [36] describes the zeolitisation, first by a dissolution of Si^{4+} and Al^{3+} from the reactive aluminosilicate, followed by a condensation step of silicate and aluminate ions where the aluminosilicate gel precipitates, and finally crystallisation of the zeolite occurs. In geopolymers, this full crystallisation is slowed down dramatically due to the relatively low water to solid ratio and the high concentration of OH^- .

The first model was proposed by Glukhovsky in the 1950's. The model divides the whole process into three stages [37]: (1) destruction-coagulation; (b) coagulation-condensation; (c) condensation-crystallization.

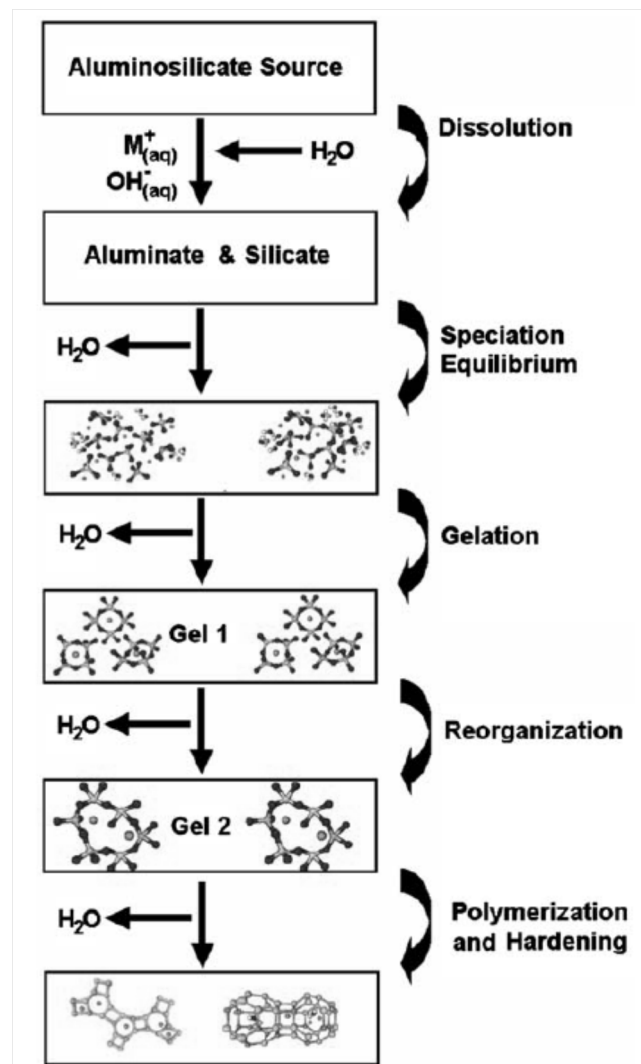


Figure 11: Conceptual model for geopolymerisation [3].

In a state of the art paper written by Duxson et al. [3] a more elaborated model is presented. The process is explained using the different reaction mechanisms as shown in Figure 11. Though presented linearly, the different processes are coupled and occur concurrently.

During the dissolution process, the high concentration of OH^- in the system is responsible for the breakdown of the Si-O-Si, Si-O-Al and Al-O-Al bonds from the vitreous glass phase of the aluminosilicate source, and Si-OH and Al-OH groups (most likely monomeric) are formed. This process is called alkaline hydrolysis. It should however be noted that this process has never been confirmed in the highly alkaline and poorly diluted systems which are the case in geopolymer synthesis.

Once in the solution, a complex mixture of silicate, aluminate and aluminosilicate species is formed. Monomers interact to form dimers, which in turn interact with another monomer to form trimers, tetramers and so on.

The solution quickly over-saturates, due to the fast dissolution of the glass at high pH. This leads to the formation of a gel, as the oligomers condensate and form a large network. The first gel type formed (Gel 1 in Figure 11) is rich in aluminium. This can be attributed to higher aluminium concentration in the solution during the first hours as Al-O bonds are weaker than Si-O in the reactive aluminosilicate powder [38]. As the reaction continues more Si-O of the initial source go into solution, raising the silicon concentration in the solution and in the gel phase, Gel 2.

The water which was used during the dissolution is released during the gelation. Hence, water plays the role of reaction medium and resides within the pores of the gel.

During the reorganisation process, the system continues to rearrange and reorganize, and the connectivity of the gel network increases. This results in the formation of a 3D aluminosilicate network.

The entire process from dissolution to reorganization as shown in Figure 11, cover the two first steps of the model of Glukhovsky.

The final process of polymerization and hardening determine the microstructure and the pore distribution of the hardened geopolymer, which is crucial for the physical properties of the resulting cement [39].

3.2 Composition

A geopolymer is build up out of AlO_4^- and SiO_4^- tetrahedra, each of which are linked in the four (or less) corners with other tetrahedra by bridging oxygen atoms and hence a 3D structure is formed. The structure of the geopolymer is mainly amorphous, but may contain some traces of crystalline zeolitic phases as mentioned in the paragraph discussing the synthesis of geopolymers.

The presence of aluminum is essential for the solidification of the geopolymer. Highly concentrated solutions of alkaline silicate are generally metastable. Hence, soluble silica is in itself not sufficient to produce a chemically hardened material. Compounds formed of silicates re-dissolve in water. Alkaline aluminosilicates on the other hand have a very low solubility.

The distribution of silicate tetrahedra and aluminate tetrahedra results in Si-O-Si and Si-O-Al bonds, while Al-O-Al bonds are not formed as they are energetically not favored. Therefore the Si/Al ratio of the geopolymer is minimum 1 [2]. However, sufficient aluminum has to be present in order to have stable aluminosilicate network. If the idea would be that each silicate

tetrahedra needs at least one aluminate tetrahedral neighbor, the maximum Si/Al ratio would be 4 [2].

Alkali ions contribute to the dissolution of the alumina and silica from the aluminosilicate source by increasing the pH of the solution and giving rise to high OH⁻ concentration. In addition, they also have a crucial role in the structure of the geopolymers. The alumina tetrahedron (AlO₄⁵⁻) can substitute silicate tetrahedron (SiO₄⁴⁻) in the structure. However, when linked to four neighboring tetrahedra the aluminate tetrahedron possess a negative charge. It is this negative charge that is counterbalanced by the positive charge of alkalis and/or earth alkalis. Hence, the alkalis from the activation solution are part of the network.

In the 1980's Davidovits introduced the sialate nomenclature to describe the aluminosilicate structures [1]. The Si-O-Al was called the sialate bond, and Si-O-Si the siloxo bond. The composition of the geopolymers was hence described by their Si/Al ratio. The different structure were described using the following formula: M_n[-(Si-O)_z-Al-O]_n · wH₂O. Where z (= 1, 2 or 3) stands for the Si/Al ratio and n is polymerisation degree. There are 3 possible monomeric units which are depicted in Figure 12 are then called for poly(sialate) for z = 1, poly(sialate-siloxo) for z = 2 and poly(sialate-disiloxo) for z = 3.

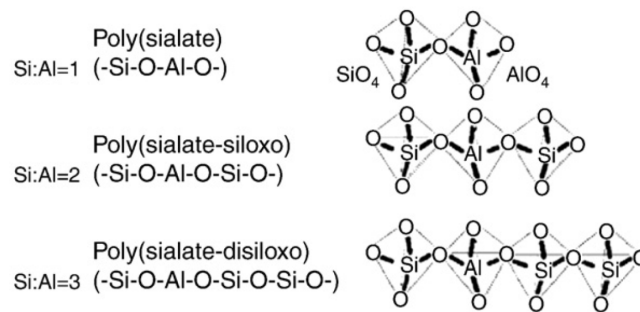


Figure 12: Monomeric units from geopolymer gel as suggested by Davidovits [1].

Unfortunately, the term sialate had already been used since the 1950s to describe salts of sialic acid, a nine-carbon monosaccharide. In addition, this system of nomenclature implies certain aspects of the geopolymer gel system which do not correspond to reality. First of all, it is a one-dimensional description of the 3D structure, and secondly, it only describes integer Si/Al ratios [14].

3.3 Techniques to analyse the composition and structure of geopolymers

A range of techniques have been used to study geopolymers. Some techniques can be used to follow the kinetics of the reacting geopolymer paste at early age e.g. calorimetry, rheology, FTIR and EDXRD. Whereas techniques such as MAS-NMR, XRD and SEM, but also FTIR are used on hardened samples. A brief description and some results of the different techniques are shown in the following paragraphs.

3.3.1 Calorimetry and rheology

Changes in the heat emitted by, and the rheology of the reacting geopolymer give an indication of the on-going reactions [12, 40, 41].

During the different chemical reactions, heat is emitted. The heat emitted gives an indication of the rate and degree of reaction. Figure 13 shows the Quasi-isothermal DSC curves for different reacting geopolymers [41]. The presence of two peaks, indicate that two types of reactions are taking place, e.g. dissolution and polymerisation.

The loss in workability of the geopolymer paste can be related to the build up of structure in the geopolymer gel [12, 40] and so will probably also direct measurement of gel-strength.

However, in order to explain the changes observed using these techniques additional experiments as will be described in the following paragraphs are needed.

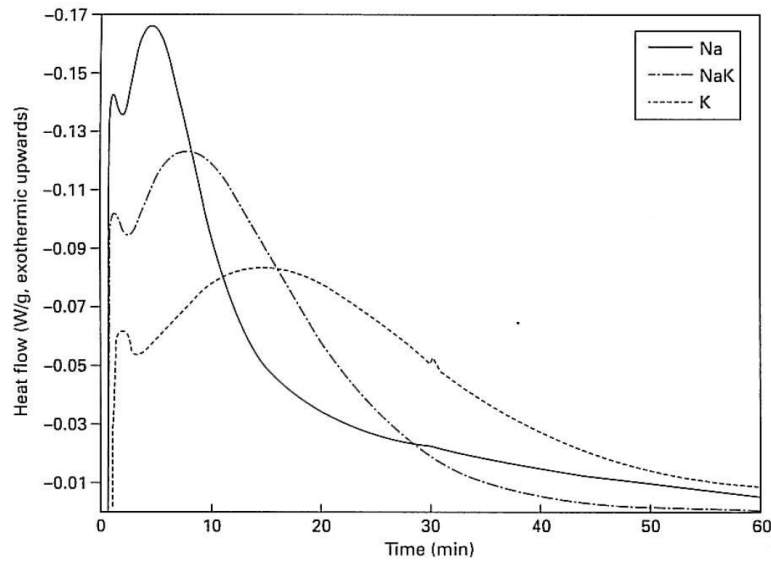


Figure 13: Quasi- isothermal DSC data for the reaction of alkali silicate solutions with metakaoline at 40°C, for different alkalis as marked [41].

3.3.2 FTIR

Fourier transformed infrared spectroscopy (FTIR) gives formation about bonds between atoms. The Si-O-T bonds where T is tetrahedral Si or Al, are the bonds of interest.

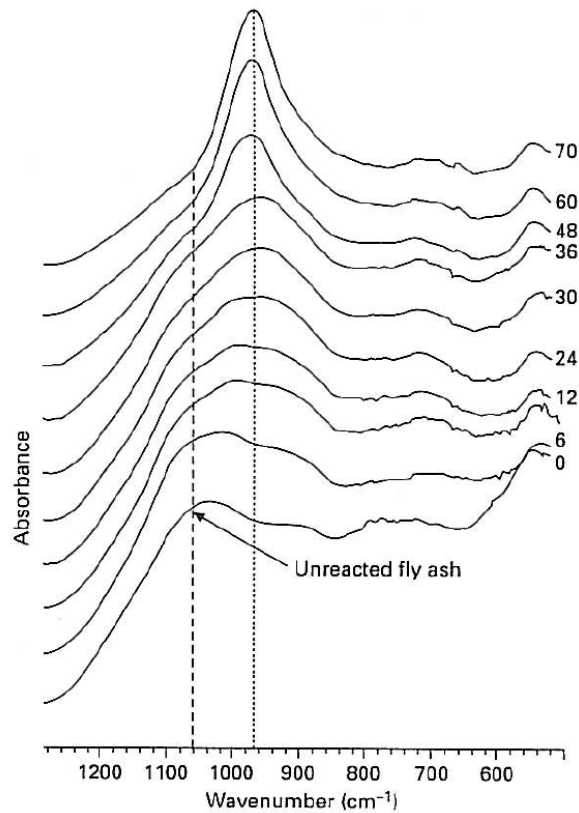


Figure 14: FTIR spectra of geopolymer development for samples activated with 6M NaOH. Numbers represent curing time in hours [41, 42].

Figure 14 shows the FTIR spectra of a reacting geopolymer at different curing times. The shoulder on the geopolymer spectra at 1055 cm⁻¹ is attributed to the main Si-O-T asymmetric

stretching band for unreacted fly ash. A clear reduction of the intensity of this band can be observed as the fly ash reacts over time. The band at approximately 960 cm^{-1} is associated with geopolymer network. It can be seen that this band gains in intensity after an “induction” period of about 40 hours.

It has been observed that when silicate containing activators are used, the dissolved silicates exhibit strong stretching bonds in the same region as the final geopolymer network [42]. This technique is therefore more adequate for geopolymers activated with alkali hydroxides.

3.3.3 EDXRD

Energy dispersive X-ray diffractometry (EDXRD) is a special diffraction technique which is able to distinguish phases with a low range of order, and can hence make a distinction between the precursor (e.g. fly ash) and the geopolymer gel formed. A set-up with a high-energy, high brilliance X-ray source and low-angle detector is required [43].

Figure 15 shows EDXRD spectra for a reacting geopolymer. Based on these results the degree of reaction can be calculated.

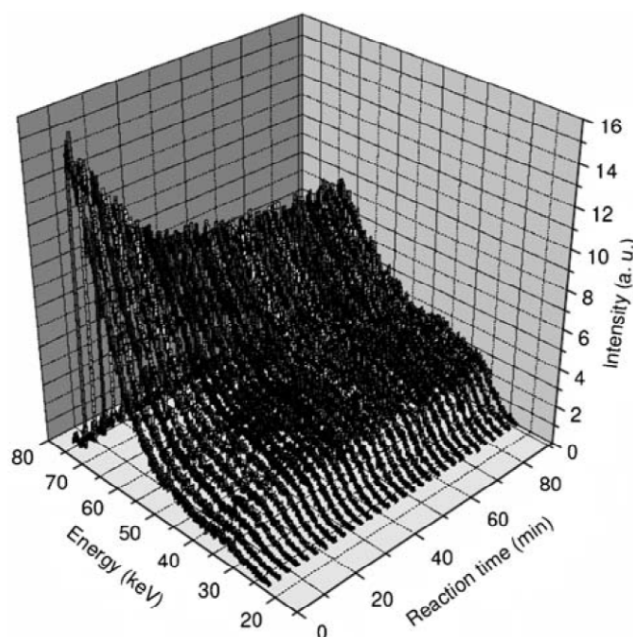


Figure 15: The smoothed and normalised EDXRD data for the system with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.0$ [43].

3.3.4 MAS NMR

MAS NMR (Magic Angle Spinning Nuclear Resonance Spectrometry) is commonly used to assess the structure of geopolymers. A solid sample is submitted to an external electromagnetic field and electromagnetic waves within radio frequency. At a certain frequency the spin of the nuclei of the atom of interest resonates. The electromagnetic signal emitted by the sample at this resonance frequency gives information about the coordination of the atom. The two types of NMR used in the study of geopolymers are ^{29}Si MAS NMR and ^{27}Al MAS NMR.

^{29}Si NMR gives an insight into the coordination of silica in the geopolymer. In order to describe this, a special notation is used. Tetrahedral sites within silicate species are denoted Q^n , where n is the number of bonds to other tetrahedral sites; so a silicate monomer $\text{Si}(\text{OH})_4$ is denoted Q^0 , and a fully coordinated site is Q^4 (see Figure 16).

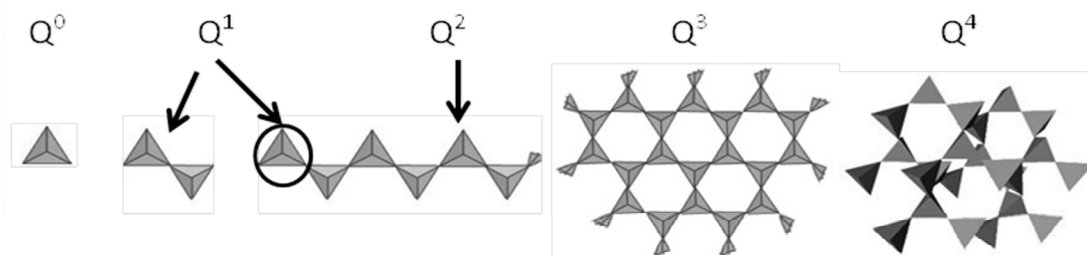


Figure 16: Illustration of the different coordinations of silica tetrahedra and their notation.

In alumina silicate structures, the notation is also extended to describe the number of Si-O-Al bonds; $Q^n(mAl)$, with n the polymerization degree and m the number of Al neighbours per silicate tetrahedral, and both n and $m \in (0,1,2,3,4)$. For example, a $Q^3(2Al)$ site hosts two Si-O-Al bonds, one Si-O-Si bond and one Si-O-H bond. Figure 17 shows the ^{29}Si MAS NMR spectra of typical metakaoline and metakaoline based Na-geopolymer. The spectra of the geopolymer is deconvoluted to the spectra of the different Si coordinations.

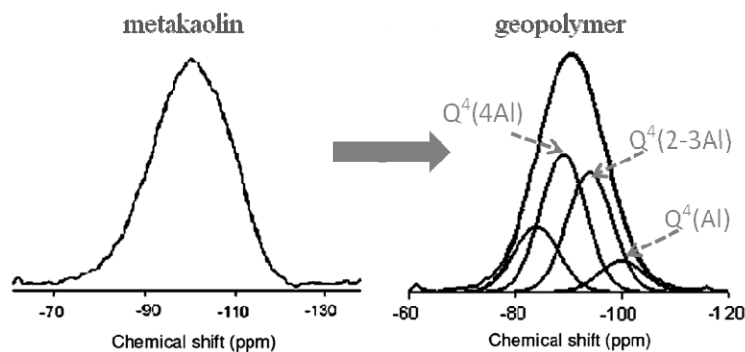


Figure 17: ^{29}Si MAS-NMR spectra of: left: typical metakaoline; right: metakaoline based Na-geopolymer [3].

^{27}Al MAS NMR on the other hand gives an indication of the coordination of Al. It is, however, more complex than the Si variant. The general consensus is that Al can replace Si in essentially all positions. This technique can however be used for another purpose, namely, to evaluate the degree of reaction of the aluminosilicate powder as demonstrated in Figure 18. In the geopolymeric reaction product, aluminium is tetrahedrally coordinated. In the reactive powder (e.g. fly ash or calcined clay), however, aluminium can be found in other coordinations e.g. octahedral alumina Al(VI) or bipyramidal alumina Al(V). The reduction in Al(V) and Al(VI), gives an idea of the degree of reaction of the raw material [3].

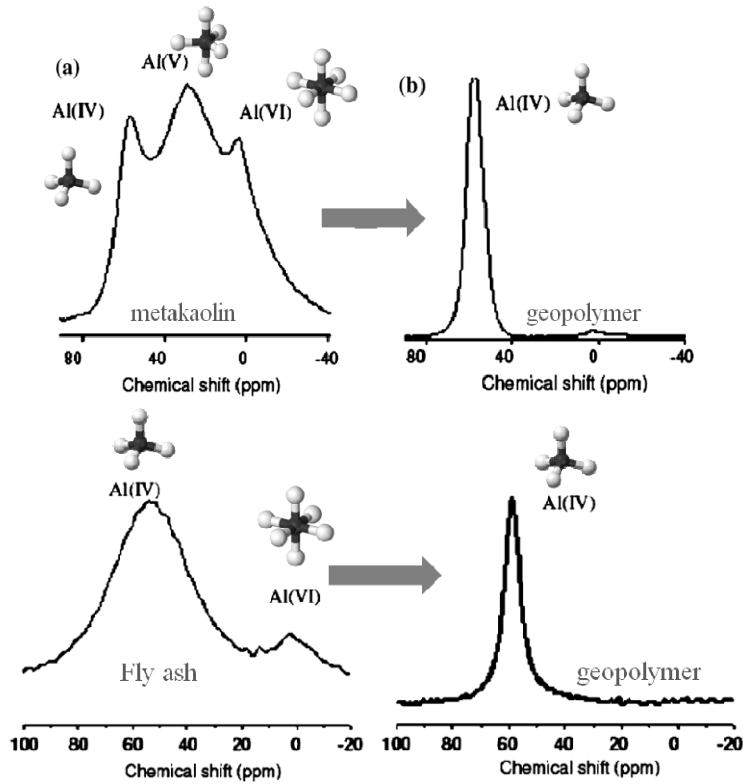


Figure 18: ^{27}Al MAS NMR spectra showing the different coordinations of Al in (a) typical metakaoline, (b) metakaoline-based Na-geopolymer from metakaoline with Si/Al ratio 2.15, (c) typical fly ash, and (d) Na-geopolymer from NaOH activation of fly ash (20h, 85C) [3].

3.3.5 XRD

XRD (X-ray diffraction) is used to detect crystalline phases. Even though the main hydration product of geopolymers is amorphous aluminosilicate, crystalline phases can be present. Either crystalline phases which are present in the raw material, for example quartz or mullite in fly ash, or crystalline reaction products such as zeolitic phases.

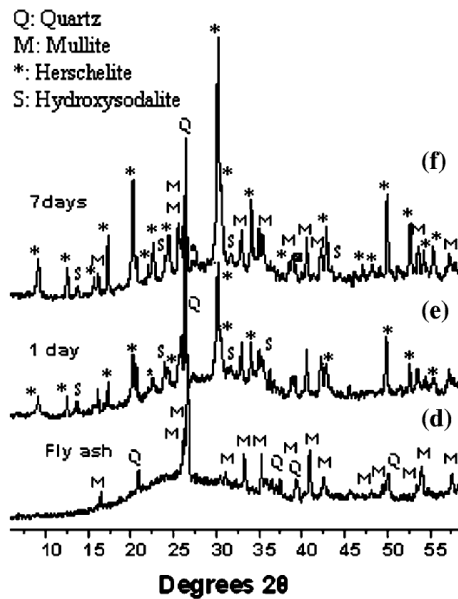


Figure 19: XRD diffractograms of (d) typical fly ash, (e) inorganic polymer from fly ash after 20 h at 85°C and (f) after 7 days at 85°C [3].

Figure 19 shows the X-ray diffractograms of the unreacted fly ash, and the inorganic polymer from the fly ash after 20 h at 85°C and after 7 days at 85°C [3]. In the unreacted fly ash mullite and quartz are present. Additionally, one can see broad hump, which is due to the presence of amorphous materials. Upon reaction, the mullite and quartz do not change, however, additional crystalline phases can be observed, such as herchelite and hydroxysodalite which are zeolitic phases.

3.3.6 SEM and TEM

SEM (Scanning electron microscopy) and TEM (transmission electron microscopy) can be used to study the microstructure of geopolymers. Both techniques shoot at the sample with an electron beam. With SEM a thick sample is used and the reflected signals are analysed, whereas with TEM very thin sections are prepared (5 nm - 2µm) and the transmitted signals are analysed. The signal analysed with SEM originates from a much larger volume (e.g. 1µm³) than with in the case of TEM. The resolution of TEM is therefore higher than SEM. Figure 20 shows TEM micrographs of geopolymers synthesized with metakaoline and fly ash [3].

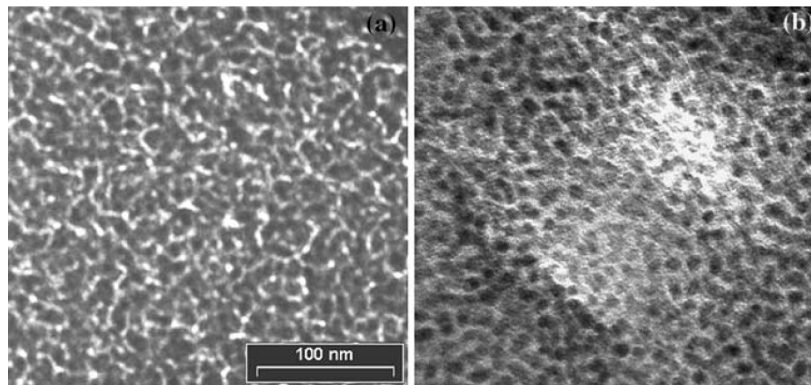


Figure 20: TEM micrographs of geopolymers synthesized by alkali-silicate activation of (a) metakaoline and (b) fly ash [3].

Information about the topography of the broken surface of a hydrated sample can be obtained using the SEM in SE-mode (secondary electron), an example is shown in Figure 21.

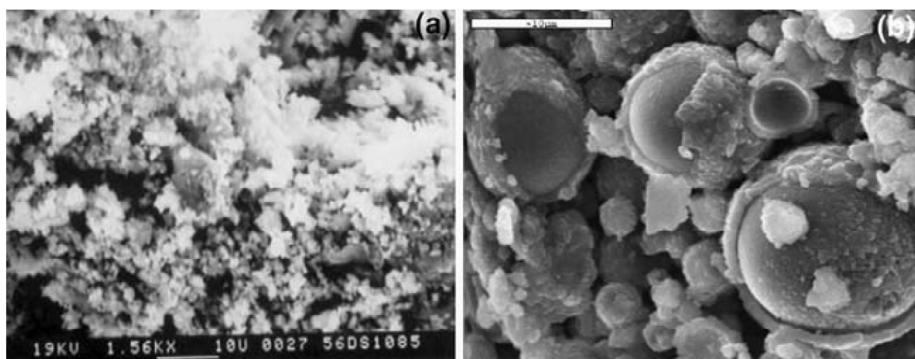


Figure 21: SEM-SE micrographs of (a) metakaoline and (b) fly ash activated with 8 M NaOH [3].

Analysing the backscattered electrons (BSE), information about the composition of a polished section can be obtained as heavier elements reflect the electron more strongly, and appear brighter in the image. Figure 22 shows SEM BSE micrographs of reacted metakaoline and fly ash geopolymers [3].

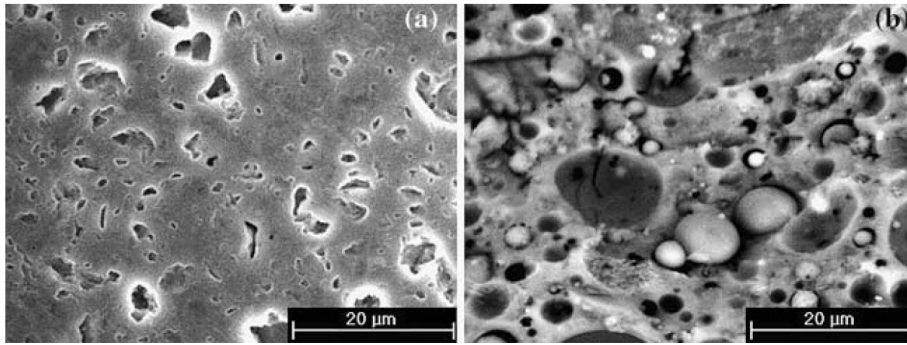


Figure 22: SEM BSE micrographs of inorganic polymers synthesized from (a) metakaoline and (b) fly ash.

EDS (energy dispersive spectrometry) or WDS (wave length dispersive spectrometry) are used for elemental analysis of for example reaction products.

4 Properties

In this chapter a brief overview over range of properties associated with geopolymers is given.

4.1 Resistance against acids

Geopolymers have shown to possess better acid resistance properties than ordinary Portland cement pastes. An example of this is shown in Figure 23 [44, 45].

The severe deterioration of OPC samples in acidic environments is connected to the high calcium content of the material, either as $\text{Ca}(\text{OH})_2$ or CSH of high molar C/S. The deterioration mechanism of geopolymers in acid environments is attributed to the replacement of exchangeable cations (Na, K) with proton or hydronium (H^+ and H_3O^+), and a dealumination process of the geopolymer gel.

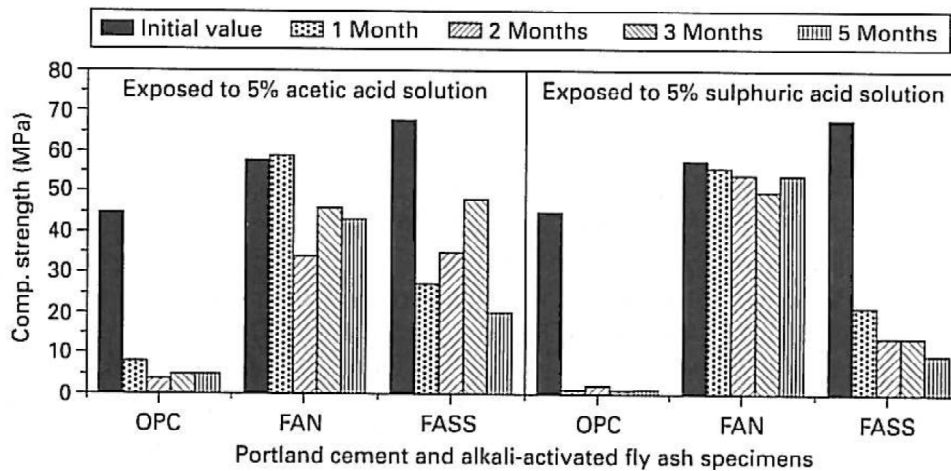


Figure 23: Compressive strength evolution of Portland cement and alkali activated fly ash (with NaOH (FAN) and sodium silicate (FASS)) specimens exposed to 5% acetic acid solution and 5% sulphuric acid solution from [44] based on data from [45].

4.2 Resistance to alkali-aggregate reaction

As concentrated alkali activators are used to produce geopolymers one might wonder about the alkali-aggregate reaction (AAR) in geopolymer concrete.

Studies performed by Garcia-Lodeiro, Fernandez-Jimenez and Palomo [44, 46, 47] have shown that geopolymers produced of activated fly ash are less susceptible to alkali silica reaction than OPC. This has been attributed to the absence of calcium in the geopolymer system which results in a less expansive AAR product.

Figure 24 compares the expansion of OPC mortar prisms with alkali activated fly ash geopolymers mortar prisms (AAFA), when immersed in a 1M NaOH solution at 85°C (ASTM C1260-94). The OPC prisms, and the prisms with a geopolymer activated with water glass (AAFAW) exceed the maximum expansion after 16 days. The geopolymer activated with NaOH (AAFAN) on the other hand reaches the 16 day limit after approximately 4 months. The fact that both geopolymers eventually expand was attributed to the formation of ASR gel albeit in small amounts and zeolite crystallization [44].

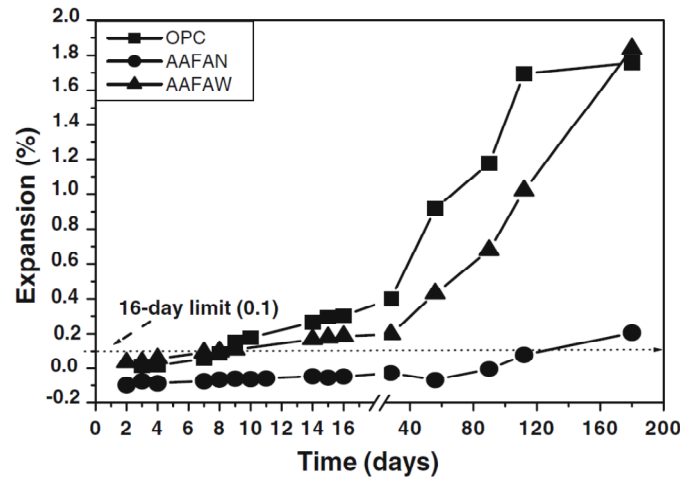


Figure 24: Alkali-silica reaction-induced expansion determined by the accelerated test based on ASTM C1260-94 [47].

4.3 Resistance against elevated temperatures

Geopolymers have been reported to possess improved resistance against elevated temperatures compared to binders made with Portland cements [2]. This is attributed to the fact that the water present in the aluminosilicate gel is not structurally bound, contrary to the water present in calcium silicate hydrates formed during Portland cement hydration. However, crystallization of aluminosilicate gel might lead to volume loss at elevated temperatures. A high content of water glass and unbound alkali can on the other hand lead to swelling (melting phase formation) at higher temperatures.

4.4 Immobilizing hazardous waste and radioactive waste

Geopolymers have shown to be able to immobilize hazardous materials [48] such as lead [49, 50], boron [51] and arsenic [52, 53]. The former two can not be stabilized in a Portland cement based system as they tend to retard or even inhibit cement hydration. Chromium on the other hand can not be stabilized in alkali activated fly ash matrices as soluble salts are formed, but Cr(III) can be stabilized as Ca_2CrO_4 in Portland cement systems [49].

Geopolymers also can be used to stabilize/solidify intermediate-level radioactive waste such as Cs, Mo and Sr [48, 54-56]. This immobilisation is attributed to the fact that these elements are part of the solid structure. It appears that geopolymers act like zeolites in retaining certain cations [55].

4.5 Strength and permeability

The early age and ultimate strength, together with the permeability depend strongly on the “mix design” of the geopolymer (Si/Al, alkali concentration, water to solid ratio, use of water glass) and the reactivity of the components (e.g. metakaoline versus fly ash).

Duxson et al. [57] varied the Si/Al ratio of a geopolymer system by adding different amounts of water glass, and keeping the $\text{Al}_2\text{O}_3/\text{Na}_2\text{O} = 1$. From Figure 25 it can be seen that the compressive strength increased with increasing Si/Al ratio. This strength increase was attributed to the fact that the microstructure became denser with increasing Si/Al ratio (see Figure 26) as less crystalline zeolitic phases formed (confirmed with XRD) [57].

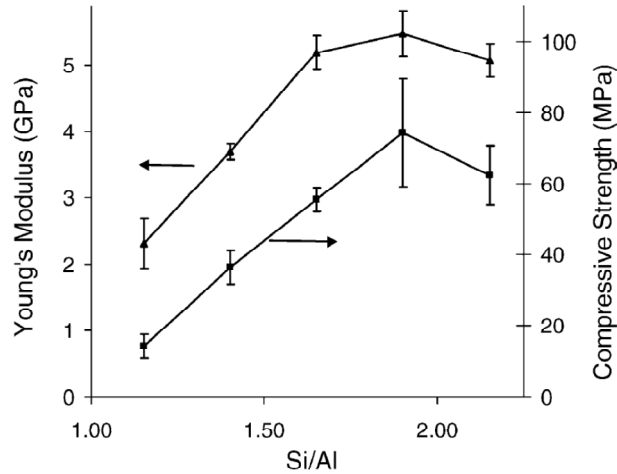


Figure 25: Young's moduli and ultimate compressive strengths of geopolymers with varying Si/Al ratio [57].

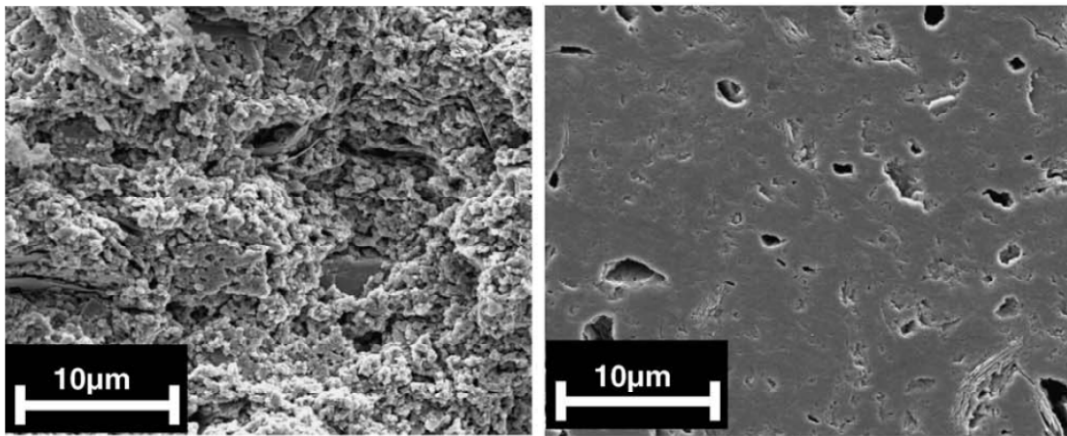


Figure 26: SEM micrographs of Na-geopolymers with Si/Al ratio of 1.15 and 1.90 respectively left and right [57].

4.6 Carbonation and corrosion

Activated fly ash mortars have shown to be able to passivate steel reinforcement to a similar extent as Portland cement mortars, however the stability of the passivation in changing environmental conditions (e.g. relative humidity) appeared to depend strongly on the activator used [44, 58]. The effect of chlorides on the corrosion rate of the reinforcement is similar for geopolymer mortar and Portland cement mortar [58].

Geopolymer cement and concretes carbonate very slowly under wet conditions, but will carbonate quickly under dry conditions [33]. This carbonation can lead to a reduction of the pH level and can therefore slow down the reaction rate and as a consequence also the strength development [59].

The surface of geopolymers can be stained by a layer of alkali carbonates that form at room temperature when alkali leach out and react with CO_2 in the air [33]. This phenomenon is referred to as efflorescence.

4.7 Rheology

There is only a limited amount of studies reporting rheology of geopolymer concrete and the use of superplasticizers in these concretes [40, 60-62].

The workability of geopolymers depends strongly on the type of aluminosilicate source used e.g. fly ash has a lower water demand than metakaoline, but also on the type and concentration of the activator used. For instance will concentrated water glass render the geopolymer paste more viscous than sodium hydroxide [1, 40, 63].

The rheological behaviour of Portland cement paste and alkali activated fly ash paste was compared by Criado et al. [61]. The pastes showed a considerably differed rheological behaviour and interaction with plasticizing admixtures such as melamine, lignosulphonates and polycarboxylates as shown in Figure 27.

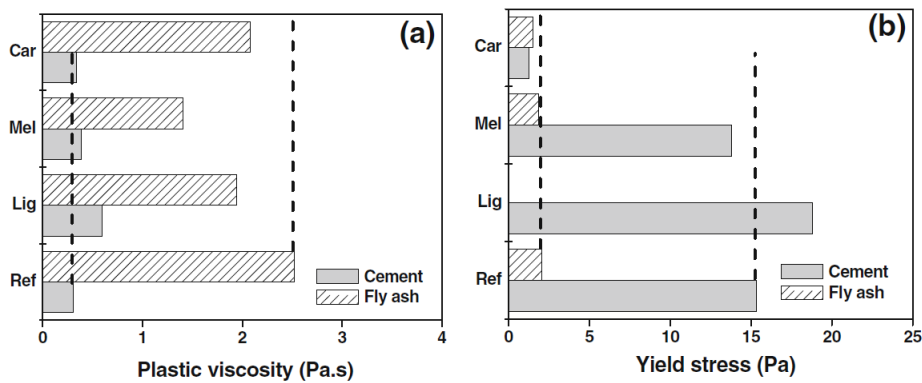


Figure 27: Bingham parameters (a) plastic viscosity and (b) yield stress of cement and activated fly ash paste without plasticizing admixture (ref), or with polycarboxylate (Car), melamine (Mel) or lignosulphonate (Lig) based plasticizing admixtures [61].

Palacios and Puertas observed changes in the chemical structure of commonly used superplasticizer types such as polycarboxylates and melamine except for naphthalene when they were dissolved in high alkaline media (NaOH solution pH 13.6 or water glass pH 13.4) using FTIR spectroscopy [60]. These changes did not occur when the admixtures were dissolved in a $\text{Ca}(\text{OH})_2$ solution (pH 12.4), as most admixtures are designed to form complexes with dissolve Ca^{2+} ions.

Hence, the study and development of plasticising admixtures for alkali activated systems is challenge to be dealt with.

4.8 Volume stability

Good volume stability of geopolymers has been reported in several reviews. Even though it is possible to obtain it through good proportioning and curing, this is not an inherent property of geopolymers.

Figure 28 shows the drying shrinkage of a fly ash geopolymer concrete which has been heat cured for 24 hours at 60°C , and the shrinkage of the same concrete when cured at ambient temperature [34]. It should be noted that the drying shrinkage of Portland cement concrete is in the range of 500-800 microstrain [1]. Hence, heat cured geopolymers can have superior properties regarding chemical shrinkage, whereas drying shrinkage appears to be a challenge for geopolymers cured at ambient temperature.

Kuenzel et al. [64] even states that drying shrinkage of metakaoline geopolymers is of major concern regarding applicability of the material. The potential of high chemical shrinkage of geopolymers is attributed to the high water demand of metakaoline geopolymers to achieve sufficient workability and the limited amount of this water which can be considered chemically bound (see resistance against high temperatures). Hence, much of the water held in the aluminosilicate gel can be released over longer time upon drying at ambient temperatures. Similar observations regarding drying shrinkage have been made for slag activated systems [60]. The chemical shrinkage can however be reduced by for example adding an inert filler and optimizing the particle packing [64].

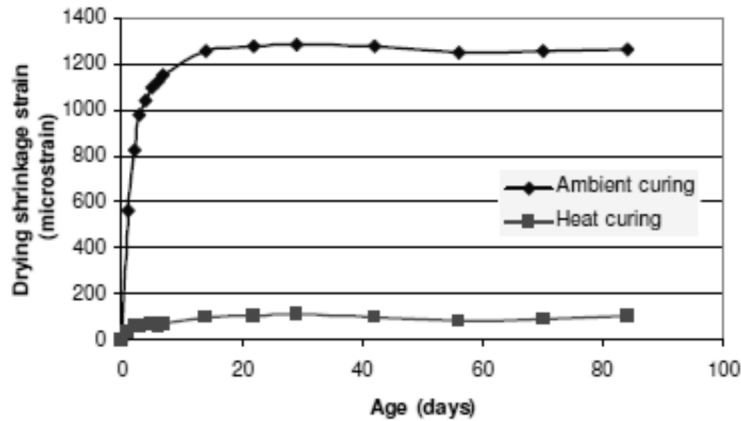


Figure 28: Drying shrinkage of heat-cured and ambient-cured specimens [34].

4.9 Ecological advantages

The fact that geopolymers can be made out of by products of other industries (e.g. fly ash or mining wastes), and thereby avoiding dumping in landfills, is an obvious ecological advantage of geopolymers.

Several researchers have compared the CO₂ emissions of geopolymers with cement production and have estimated a potential reduction from 20 to 80% [65-67].

However, to come with a reliable judgement regarding the ecological advantages one should perform a life cycle analysis, taking in account different the emissions, consumption of resource during the production, use and disposal of the structure. For further information on this the reader is referred to a publication of Weil, Dombrowski and Buchwald [68].

5 Applications

Geopolymers have been used for niche application such as [1]:

- tooling and molds
- fiber composites as heat resistant components or shields
- fiber composites for external strengthening of existing concrete structures
- geopolymer foam as heat insulation material
- solidification or stabilization of hazardous waste

However, only a few examples were found of large scale applications of geopolymers as construction materials:

1. An attempt for mass production geopolymer cement was undertaken during the 1990's, under the brand name Pyrament. The production was, however stopped after 4 years due to bankruptcy of the holding [1].

2. A recent large scale project where geopolymers were used was for the production of railway sleepers. A report published by Palomo et al. showed superior performance of the geopolymer regarding dimensional stability, early strength and contact between the matrix and the pre-tensioned wires [69].

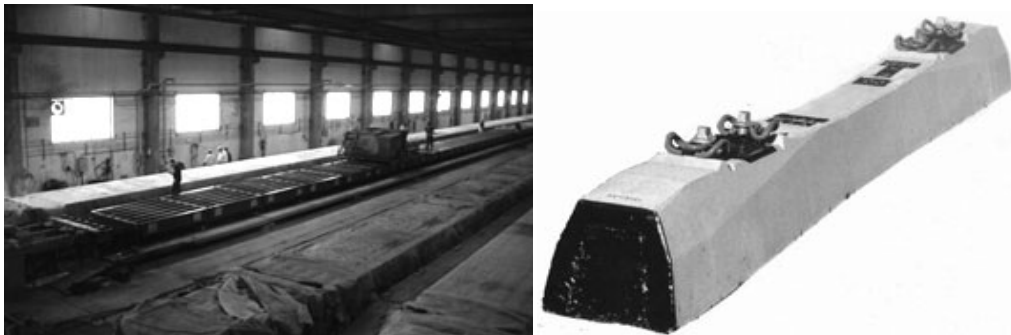


Figure 29: Production of railway sleepers using geopolymer concrete [69].

3. Currently, there is a commercial geopolymer concrete producer in Australia, namely The Zeobond Group, founded by Prof. Jannie van Deventer [67, 70]. They sell pre-mixed and pre-cast geopolymer concrete called E-crete for the construction of e.g. footpaths, driveways, house-slabs and wall elements. They claim that the CO₂-emission related to their geopolymer concrete is 50-80% less than for conventional concrete. In addition, they have documented that the geopolymer concrete has an improved fire resistance.



Figure 30: Geopolymer concrete used for paving.

In Northern Ireland, recently founded (November 2008) Banah UK Ltd. aims at commercially producing low-carbon cement based on a geopolymeric binder system, geopolymer concrete and lightweight geopolymer masonry units [71]. Suggested applications for the geopolymer concrete are e.g. foundations, precast floors, cills, lintels, wall panels, drains and railway sleepers.

From the examples given it can be seen that geopolymers are suited for certain niche markets, but not to take over the general OPC market. The few examples of large scale production of geopolymer concrete confirm the need of pilot projects in order to launch this technology for real.

6 Conclusion

Geopolymers are synthesized out of reactive aluminosilicate powder (e.g. fly ash or calcined clay) which is activated with an alkaline activator (alkali hydroxide or alkali silicate solution) at ambient or slightly elevated temperature. They have a 3D dense amorphous microstructure, built out of interlinked SiO_4 and AlO_4 tetrahedra, and contain charge balancing alkali.

Geopolymers possess mechanical properties which are comparable with materials based on OPC, and they have superior performance regarding heat resistance and acid resistance.

Geopolymer production is generally associated with lower CO_2 emissions than OPC production, turning them into a valid alternative from an environmental point of view. However, there are still some challenges to be met before geopolymers can go into mass production e.g. curing, volume stability, rheology, efflorescence and high pH. Hence, there is a need for further research and pilot projects in order to launch this technology for real.

7 References

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