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Review

Geopolymers: Ceramic-Like Inorganic Polymers

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Abstract

Geopolymers are ceramic-like inorganic polymers produced at low temperature, generally below 100 °C. They consist of chains or networks of mineral molecules linked with covalent bonds. The raw materials are mainly minerals of geological origin, hence the name "geopolymer". They comprise several molecular units for example: silico-oxide (Na,K)-(-Si-O-Si-O-) for (Na,K)-poly(silicate) or (Na,K)-poly(siloxonate), silico-aluminate (Na,K)-(-Si-O-Al-O) for (Na,K)-poly(sialate), ferro-silico-aluminate (Na,K)- (-Fe-O-Si-O-Al-O-) or (Na,K)-poly(ferro-sialate), alumino-phosphate (-Al-O-P-O-) for poly(alumino-phosphate), formed in a geopolymerization process. We focus here on the reactivity of calcined kaolinite, an aluminosilicate oxide $Si_2O_5Al_2O_2$, metakaolin, which led to the discovery of geopolymers 40 years ago. A distinction is made between two synthesis routes: alkaline medium (Na+, K+, Li+, Ca++, Cs+ and the like) and acidic milieu (phosphoric acid, organic carboxylic acids). The alkaline route is the most important, so far. NMR spectroscopy provides data on the molecular structure and polymeric character. The geopolymerization mechanism starts with polycondensation of oligomers into small ribbon-like molecules. This intermediary stage involves several Si-OH groups together with H_2O molecules. It is referred to as NASH or KASH by some cement scientists and generalized to the final geopolymer structure. The poly(sialate) final structure consists of well-polymerized individual elementary nanoparticles of 5 to 40 nm in size.

Keywords: Geopolymer, polymerization mechanism, applications, properties, molecular structure.

I. Introduction

Geopolymers are ceramic-like inorganic polymers produced at low temperature, generally below 100 °C. They consist of chains or networks of mineral molecules linked with covalent bonds. Because they are polymers, they should be referred to with polymer terminology, which is very different from the traditional terminology used by ceramicists. For example, the formula of one major clay mineral, kaolinite, is
- for a ceramicist $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$,
- for a chemist, $Si_2O_5Al_2(OH)_4$.

From a geopolymer standpoint, we write [≡Si-O-Al-(OH)$_2$]$_n$ with the covalent aluminum hydroxyl - Al-(OH)$_2$ side groups branched to the poly(siloxo) hexagonal macromolecule [≡Si-O-]$_n$. This polymeric approach has profound consequences with regard to a better understanding of the geopolymerization mechanisms. In particular, metakaolin results from the dehydroxylation of the -OH groups in kaolinite, according to the reaction:

$$Si_2O_5Al_2(OH)_4 \rightarrow Si_2O_5Al_2O_2 + 2H_2O$$
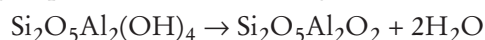
The reactive molecule consists of two different aluminosilicate oxides $Si_2O_5Al_2O_2$, namely:

$$[\equiv Si\text{-}O\text{-}Al=O]_n \text{ and } [\equiv Si\text{-}O\text{-}Al\text{-}O\text{-}]_n.$$

This suggests strong chemical reactivity, as opposed to the traditional way of writing $2SiO_2 \cdot Al_2O_3$. See the detailed chemical reaction mechanisms in the following sections.

The starting raw-materials are:
- rock-forming minerals, alumino-silicates,
- amorphous silica,
- and industrial by-products (alumino-silicates) like coal fly ash, blast furnace slag.

They chemically react within two different synthesis routes:
- in alkaline medium with (Na, K) hydroxides and soluble alkali-silicates, yielding poly(silicates), poly(siloxo), poly(silico-aluminates), poly(sialate) types and,
- in acidic medium (here with phosphoric acid), yielding poly(alumino-phospho) types.

Geopolymers comprise the following molecular units (or chemical groups) presently studied and implemented in several industrial developments:
- Si-O-Si-O- siloxo, poly(siloxo)
- Si-O-Al-O- sialate, poly(sialate)
- Si-O-Al-O-Si-O- sialate-siloxo, poly(sialate-siloxo)
- Si-O-Al-O-Si-O-Si-O- sialate-disiloxo, poly(sialate-disiloxo)
- (R)-Si-O-Si-O-(R) organo-siloxo, poly-silicone
- Al-O-P-O- alumino-phospho, poly(alumino-phospho)
- Fe-O-Si-O-Al-O-Si-O- ferro-sialate, poly(ferro-sialate)

Hardening, or setting, or geopolymerization, occurs at low temperature, below 100 °C, or at room temperature. The nature of the hardened geopolymer is either x-ray amorphous at ambient and medium temperatures, or

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x-ray crystalline at temperatures above 500 °C for Na-based, and above 1000 °C for K-based species respectively.

II. Historical Background

In the aftermath of various catastrophic fires in France between 1970 – 72, which involved common organic plastic, research on nonflammable and noncombustible plastic materials became my objective. In 1972, I founded the private research company Cordi SA, later called Cordi-Géopolymère.

In my pursuit to develop new inorganic polymer materials, I was struck by the fact that the same simple hydrothermal conditions governed the synthesis of some organic plastics in alkaline medium, as well as mineral feldspathoids and zeolites. Thus, phenol and formaldehyde polycondense into the famous Bakelite invented by Bakeland at the beginning of the 20th century, one of the oldest manmade plastics (Fig. 1a). On the other hand, aluminosilicate kaolinite reacts with NaOH at 100 – 150 °C and polycondenses into hydrated sodalite (a tectoaluminosilicate, a feldspathoid), or hydrosodalite (Fig. 1b).
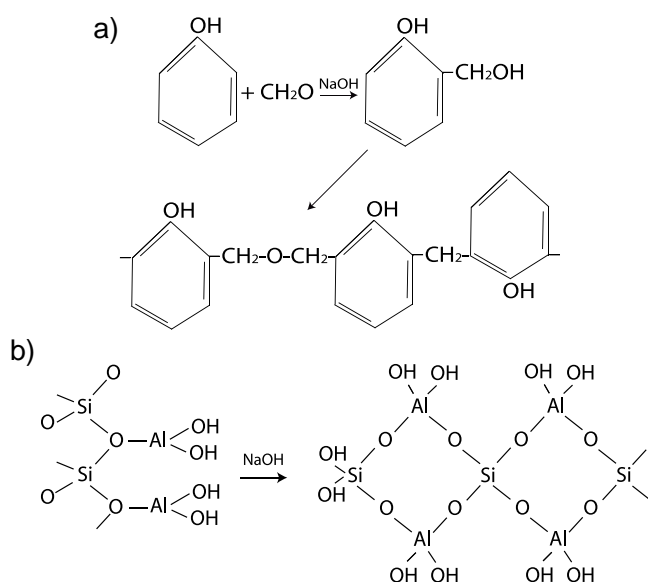

Fig. 1: a) left, Phenoplast polycondensation between phenol and formaldehyde, in alkaline medium. b) right, Polycondensation of kaolinite $Si_2O_5,Al_2(OH)_4$ in alkaline medium.

In 1972, the French ceramicist team Jean Paul Latapie and Michel Davidovics, working at the former ceramic tiles manufacturer Cerabati, confirmed that water-resistant ceramic tiles could be fabricated at temperatures lower than 450 °C, i.e. without firing. They had found this technical information in a literature survey carried out by the French ceramic institution *Société Française de Céramique*. One component of clay, kaolinite, reacted with caustic soda at 150 °C. In fact, the industrial application of this kaolinite reaction with alkali began in the ceramic industry with Niels Olsen (1934)[1] and was later reinvented in 1964 by Berg *et al.* (1970)[2], a Russian team, but without successful industrial implementation. Earlier, Flint *et al.* (1946)[3], at the National Bureau of Standards, had developed various processes for the extraction of alumina starting from clays and high-silica bauxites. One intermediary step in the extraction process involved the precipitation of a sodalite-

like compound. Borchert and Keidel (1949)[4] prepared hydrosodalite $Si_2Al_2O_8Na_2.H_2O$ by reacting kaolinite in a concentrated NaOH solution, at 100 °C. Howell (1963)[5] obtained a Zeolite A type, using calcined kaolin (metakaolin) instead of kaolinite, preventing the formation of hydrosodalite. In 1969, Besson, Caillère and Hénin at the French Museum of Natural History, Paris, carried out the synthesis of hydrosodalite from various phyllosilicates (kaolinite, montmorillonite, halloysite) at 100 °C in concentrated NaOH solution, (Besson *et al.*, 1969)[6].

From the study of the scientific and patent literature covering the synthesis of zeolites and molecular sieves — essentially in the form of powders — developed in the 1940s – 1950s (see in Fig. 2), it became clear that this geochemistry had so far not been investigated for producing mineral binders and mineral polymers. I proceeded therefore to develop amorphous to semi-crystalline, three-dimensional, silico-aluminate materials, which I call in French "géopolymères", geopolymers (mineral polymers resulting from geochemistry or geosynthesis).

	Zeolite molecular sieve	Alkali-activation (slag)	Hydrosodalite (kaolin)	Geopolymer
1930			1934 : Olsen (Netherland)	
1940		1940 : Purdon (Belgium)	1945 : US Bureau of Standard (USA)	
	1945 : Barrer (UK)		1949 : Borchert, Keidel (Germany)	
1950	1953 : Barrer, White (UK)	1953: Trief Cement (USA)		
	1956 : Milton (USA)	1957: Glukovsky (Ukraine) *soil-silicate concrete*		
1960			1963 : Howell (USA)	
			1964 : Berg *et al.* (USSR)	
			1969 : Besson *et al.* (France)	
1970		1972 : Davidovits (France) *Siliface Process*		1976 : Davidovits *(IUPAC terminology)*
				1979 : Davidovits (France) *Geopolymer*

Fig. 2: Milestones in alumino-silicate chemistry.

The first applications were building products developed in 1973 – 1976, such as fire-resistant chip-board panels, comprising a wooden core faced with two geopolymer nanocomposite coatings, in which the entire panel was manufactured in a one-step process (Davidovits, 1972)[7]. We coined the term "Siliface Process". An unusual feature was observed to characterize the manufacturing process: for the first time, the hardening of organic material (wood chips and organic resin based on urea-formaldehyde aminoplast) occurred simultaneously with the setting of the mineral silico-aluminate (Na—poly(sialate)/quartz nanocomposite, when the same thermosetting parameters were applied as for organic resin: 150 – 180 °C temperature (Davidovits, 1976)[8].

Independently of this ceramic-like geopolymer material development, it was discovered that alkalis such as NaOH or KOH would accelerate the setting of an industrial by-product, blast furnace slag. In the 1930s, this chemistry was originally used to determine if the slag would set

when added to Portland cement. In the course of studying the testing systems for slag, Belgian scientist Purdon (1940) [9] discovered that the alkali addition produced a new, rapid-hardening binder (see Fig. 2). Alkali-activated slag cements (called Trief cements) were used in the USA for large-scale construction as early as the 1950s. The usual activation required adding 1.5 % NaCl and 1.5 % NaOH to 97 % ground slag mix (U.S. Army Engineer Waterways Experiment Station, 1953). In 1957, Victor Glukhovsky, a scientist working in the Ukraine at the KICE (Kiev Institute of Civil Engineering in the USSR), investigated the problem of alkali-activated slag binders, and in the 1960s and 1970s made a major contribution in identifying both calcium silicate hydrates (CSH), and calcium and sodium alumino-silicate hydrates (NASH) as solidification products. Glukhovsky called the concretes produced with this technology "soil silicate concretes" (1959) [10] and the binders "soil cements" (1967) [11].

Raw materials used in the synthesis are mainly rock-forming minerals of geological origin, hence the name: *"geopolymer"* coined in 1979. An article published by the Commission of the European Communities in 1982 entitled *The Need to Create a New Technical Language for the Transfer of Basic Scientific Information*, outlines the reasons why the generic term *"geopolymer"* was chosen for this new chemistry [12].
Much of the original research into geopolymers was conducted on calcined kaolinitic clay precursors, an aluminosilicate oxide $Si_2O_5Al_2O_2$ better known under the generic term of metakaolin [13]. A distinction is made between two synthesis routes:

– in alkaline medium (Na^+, K^+, Li^+, Ca^{++}, Cs^+ and the like);
– in acidic medium with phosphoric acid and organic carboxylic acids.

The alkaline route is the most important in terms of R&D and commercial applications and will be described below. Details on the acidic route are outlined in the papers by Wagh (2004) [14], Perera *et al.* (2008) [15], Cao *et al.* (2005) [16].

III. Geopolymer ceramic-like synthesis in alkaline medium: poly(sialate) based on poly(silicone) terminology

(1) Ionic coordination or covalent bonding; chemical valence or coordination number?

In 1937, W.L. Bragg published a method for classifying all kinds of silicates and their crystal structures based on the concept of the ionic theory by Linus Pauling. The fundamental unit is a tetrahedral complex consisting of a small cation such as Si^{4+}, or Al^{3+} in tetrahedral coordination with four oxygens (Pauling's first rule). Many textbooks explain the geometry of the SiO^{4-} tetrahedron and other mineral structures as determined by the relative sizes of the different ions.
This ionic coordination representation is no longer adapted to the requirements of geopolymer chemistry as this is governed by covalent bonding mechanisms. The differences between the ionic concept (coordination) and the covalent bonding are profound. See Fig. 3.

The double tetrahedron structure (coordination) shares one oxygen anion O^{2-}, whereas in the Si-O-Si- molecular structure, the covalent bond is achieved through Si and O co-sharing one of their electrons. This results in stronger bond within the structure. The American mineralogist and geochemist G.V. Gibbs and his team [17] studied the polymeric bond Si-O-Si-O and stated in 1982 – 2000: "The successful modeling of the properties and structures of silica … lends credence to the statement that a silica polymorph like quartz can be viewed as a giant molecule bound together by essentially the same forces that bind the atoms of the Si-O-Si skeleton into a small siloxane molecule". The term "giant molecule" used by G.V. Gibbs is equivalent to the definition of *"geopolymer"* and the wording "small siloxane molecule" describes the organo-silicon polymer compounds.

single tetrahedron   *di-silicate ions double tetrahedron*

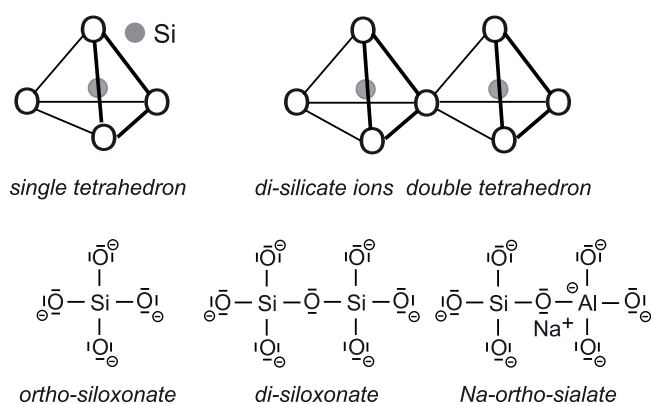*ortho-siloxonate*   *di-siloxonate*   *Na-ortho-sialate*

Fig. 3: Top, tetrahedron structure; bottom, covalent bonding.

There are direct structural analogies between poly(siloxonates) silicates, poly(sialates) silico-aluminates and poly(methylsiloxane) silicone molecules. Sialate is an abbreviated form for alkali silicon-oxo-aluminate, the alkali being sodium-potassium-lithium-calcium and the term poly(sialate) covers all geopolymers containing at least one (Na,K,Li,Ca)(Si-O-Al), (Na,K,Li,Ca)—sialate unit (Davidovits, 1976) [8]. What is important here is the exact identity in shape and structure between siloxonate-based molecules (alkali silicates), siloxane oligomers and sialate, silico-aluminate, oligomers. Fig. 4 shows the structures for monomers, dimers, trimers, tetramers and pentamers of poly(siloxonate), poly(methylsiloxane) and poly(sialate) respectively.
Because of its amphoteric character, the Al atom is either trivalent (in acidic medium) or tetravalent (in alkaline medium) according to the reaction

$$Al(OH)_3 + OH^- \Rightarrow [Al(OH)_4]^-$$

There is very often misunderstanding between the chemical tetravalence of Al and the tetra-coordination of Al with surrounding oxygens. Tetravalence describes a chemical mechanism (covalent or polar bonding), whereas tetra-coordination shows the crystallographic positions of the atoms, independently of the forces that govern their intra-connection: ionic, co-valent, van der Waals, hydrogen bonds (physical characteristic). The mix-up is due to the general tetrahedral representation after Bragg that does not differentiate between AlO_4 tetravalence

and IV-fold coordination with oxygen. According to the Bragg's method, the sialate network consists of SiO_4 and AlO_4 tetrahedra linked alternatively by sharing all the oxygens (Fig. 3).

Fig. 4: Molecular structures of poly(siloxonate), poly(methysiloxane) and poly(sialate) oligomers. The caption "No." for sialate oligomers refers to the molecules isolated in solution and displayed in Fig. 8.

In Fig. 5a, the Al atom in the kaolinite molecule is trivalent -O-Al-$(OH)_2$. After dehydroxylation into metakaolinite, it is still chemically trivalent but becomes tetra-coordinated with its surrounding oxygens and is chemically unstable. In Fig. 5b, alkalination of kaolinite produces a tetravalent, chemically stable Al unit. It is obvious that, in the latter case, Al is also tetra-coordinated with O and OH, but this physical characteristic does not play any major role in the chemical mechanism of geopolymerization.

Fig. 5: Trivalent and tetravalent Al atom.

Another point of concern are numerous scientific papers displaying a misleading structural representation of

metakaolin. See the incorrect model in Fig. 6. First, in the Al-O-Al layer, the Al^{3+} atom is represented as being chemically tetravalent (AlO_4), in the same way as the Si-O-Si network with its tetravalent Si^{4+} configuration. The oxygen atom is also trivalent O^{3-}, which is nonsense because it is actually chemically bivalent. This is a major error, namely the confusion between chemical valence and physical coordination. This confusing structural representation is copy-pasted in numerous publications dealing with metakaolin-based geopolymer. In fact, for metakaolin, the Al atom is trivalent Al^{3+}, but Al is tetracoordinated, Al(4), pentacoordinated, Al(5) and even hexacoordinated Al(6) to oxygens. Actually, the reactive molecule comprises two Al-oxide types (see later and in Fig. 16).

Fig. 6: Wrong model for metakaolin structure: tetravalent aluminum and trivalent oxygen.

(2) Geopolymerization starts with oligomers

An important issue in sialate-based geopolymerization relates to its reaction mechanism. At the beginning of geopolymer research and afterwards, for at least 25 years, it was assumed that the geochemical syntheses occurred through hypothetical oligomers (dimer, trimer). Further polycondensation of these hypothetical building units provided the actual structures of the three-dimensional macromolecular edifice, see Fig. 7. Review papers published at the First Geopolymer Conference in 1988, and at the second, 11 years later, in 1999, could not present scientific details describing the actual reaction mechanism.

Fig. 7: Reaction mechanism for sialate and sialate-siloxo species, described as hypothetical by Davidovits in 1988 [18].

The most important contribution to this issue is the paper by North and Swaddle (2000) [19]. Using ^{29}Si and ^{27}Al NMR spectroscopy, they suspected the presence of solute

species with Si-O-Al sialate linkages in concentrated solutions. One major improvement in their research was that their study was carried out at low temperature, at 5 °C and below. Indeed, it was discovered that the polymerization of oligo-sialates was taking place on a time scale of around 100 milliseconds, i.e. 100 to 1000 times faster than the polymerization of ortho-silicate. At room temperature, or higher, the reaction is so fast that it cannot be detected with conventional equipment. They chose KOH over NaOH used in their previous study because concentrated KOH alumino-silicate solutions resist gelation longer than their NaOH analogs. Owing to the very weak signal of ^{29}Si, the NMR experiments had to be run up to three days long to get significant detailed spectra. They successfully detected five solute species, displayed in Fig. 8 below, namely two linear molecules and three cycles:

– one ortho-sialate $(OH)_3$-Si-O-Al$(OH)_3$ for Si:Al=1;
– one linear ortho(sialate-siloxo) $(OH)_3$-Si-O-Si$(OH)_2$-O-Al$(OH)_3$, one cycle ortho(sialate-siloxo), for Si:Al=2;
– two cycles ortho(sialate-disiloxo), for Si:Al=3.
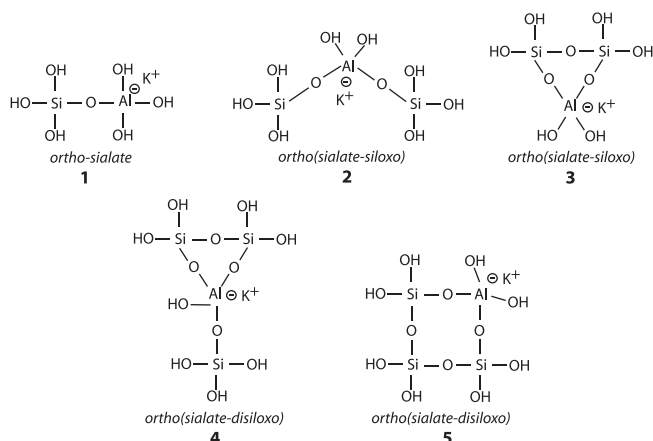
Fig. 8: Five ortho-sialate oligomers isolated in KOH solutions, after North and Swaddle (2000) [19].

The hypothetical oligomers set forth in geopolymer synthesis were no longer virtual molecules. As a matter of fact, they exist in soluble forms and are stable in concentrated solutions at high pH. Swaddle's study confirmed our polymerization mechanisms tentatively reported earlier with linear oligo-sialate, oligo(sialate-disiloxo) and rings or cycles, as starting geopolymer building units.

(3) Geopolymer 3D-frameworks, microstructure, nanoparticulates.

A polymer is a macromolecule with definite size and molecular weight. These two key values are established by several complementary physical methods working either in the solid state (electron microscopy) or in solution (light-scattering). A gel on the other hand designates an indefinite amorphous compound with unresolved dimension. Kriven *et al.* (2003) [20] used TEM (transmission electron microscopy) to investigate the microstructure of fully reacted potassium-poly(sialate-siloxo) type geopolymers. It consists of nanoparticulates ranging from 5 to 15 nm in dimension (50 to 150 Å) separated by nanoporosity, the features of which are of the order of 3 to 10 nm (Fig. 9).
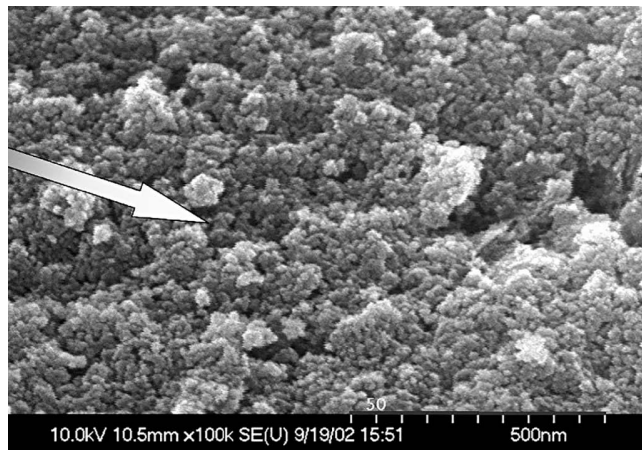
Fig. 9: Nano-particulate or geopolymeric micelle, point of arrow, after Kriven *et al.* (2003) [20].

Kriven's team found nanoporous, sponge-like microstructure characteristic of a fully reacted region of geopolymer. TEM/EDS analyses of these fully reacted regions indicated that the microchemistry frequently observed corresponds to a Si:Al ratio of 2:1, that is poly(sialate-siloxo). Then the room temperature samples were heated slowly over 4 h to 1000 °C. The nanosized microstructure was still stable after reaching 1000 °C and subsequent furnace stabilization to ≈ 990 °C. Selected area diffraction (SAD) indicated that the fully reacted regions are still amorphous. No evidence of sintering or "grain growth" was observed. The nano-particulates represent a characteristic feature of the geopolymer matrix and their dimensions suggest the presence of a macromolecule of definite size, and therefore, definite molecular weight.

Sindhunata *et al.* (2006) [21] studied the microstructure of fly-ash-based geopolymer matrix and found that its structure resembles aluminosilicate particulates of 5 – 20 nanometers in dimension, which are connected and form nano-channels and pores, as reported by Kriven *et al.* (2003) for K—poly(sialate-siloxo) geopolymer.

It is the accumulation of these nanoparticulates, or individual particulates, that forms the geopolymer matrix. They are sometimes called precipitated particles and their dimensions are similar to those of micelles made of surfactant molecules, which result from the self-aggregation of small surfactant molecules in water. However, the temperature stability of the geopolymer nanoparticulates strongly supports the presence of giant molecules. In other words, it is in favor of the polymeric model. Fig. 10 shows the very small dimension of this geopolymer nanoparticulate, when compared to other spherical structures, colloidal silica, silica fume and fly ash.

The core of these nanoparticulate geopolymers is made of aluminosilicate frameworks that are similar to those of rock-forming minerals. Yet, there are major differences. In 1994, we simulated a theoretical structure for K-poly(sialate-siloxo) (K)-(Si-O-Al-O-Si-O) that was consistent with the NMR spectra [22]. It is displayed in Fig. 11a and does not show the presence of water in the structure. This is demonstrated by the fact that ^{27}Al MAS-NMR spectroscopy of all (Na,K)-poly(sialate-siloxo) (Na,K)-(Si-O-Al-O-Si-O) showed ^{27}Al chemical shifts

in the range of 55 ppm from $[Al(H_2O)_6]^{3+}$ identical to the spectrum displayed in Fig. 11b, which indicates that the aluminum is of the $AlQ_4(4Si)$ type and is tetrahedrally coordinated, or more exactly tetravalent. The absence of any other resonance and the extremely narrow peak at 55 ppm, excludes any residual singular building units of low molecular weight such as dimers and trimers. (Na,K)-poly(sialate-siloxo) (Na,K)—(Si-O-Al-O-Si-O) are true three-dimensional framework silico-aluminates with polymeric building units.
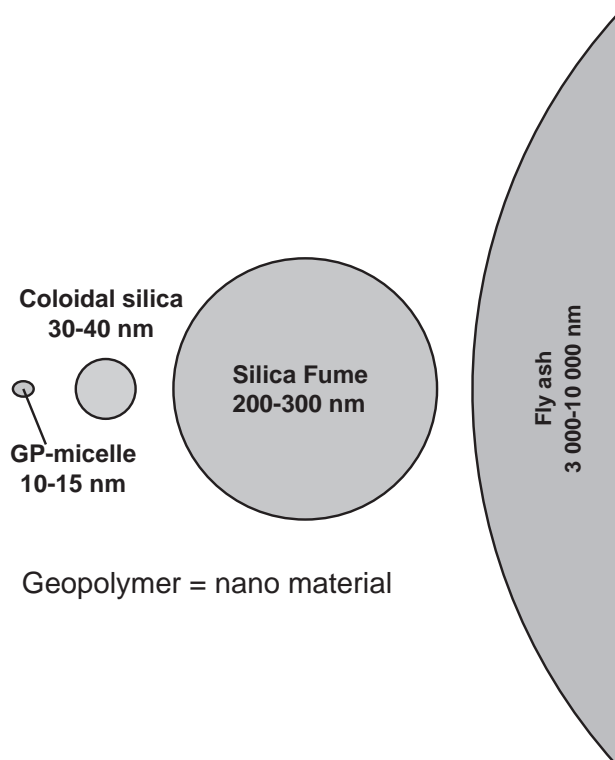
Fig. 10: Dimension of the geopolymeric micelle (particulate) compared to colloidal silica, silica fume and fly ash spheres.

Water is present only at temperatures below 150 °C – 200 °C, essentially in the form of -OH groups associated with $SiQ_3(3Si,1OH)$ and $SiQ_2(2Si,2OH)$ species (Fig. 12).

These -OH groups are located essentially on the surface of the nano-particulates, and each particulate is surrounded with some physically bonded water and some siloxonate hydrate molecules.

Nevertheless, scientists working on low-temperature applications, such as cements and waste management, try to pinpoint cation hydration and water molecules like for Portland cement. One model first proposed by Barbosa *et al.* (2000) [23] and Rowles (2004) [24] only shows incompletely reacted geopolymer. The geopolymerization mechanism shown in Fig. 13 starts with oligomer condensation into a ribbon-like small molecule. This intermediary stage involves several Si-OH groups together with H_2O molecule and also free NaOH resulting from the geopolymerization. It is coined NASH (sodium-alumino-silicate-hydrate) or KASH (potassium-aluminum-silicate hydrate) by some cement scientists and generalized to the final geopolymer structure, which is wrong. The free NaOH is fully consumed during the polycondensation step into the 3D network.
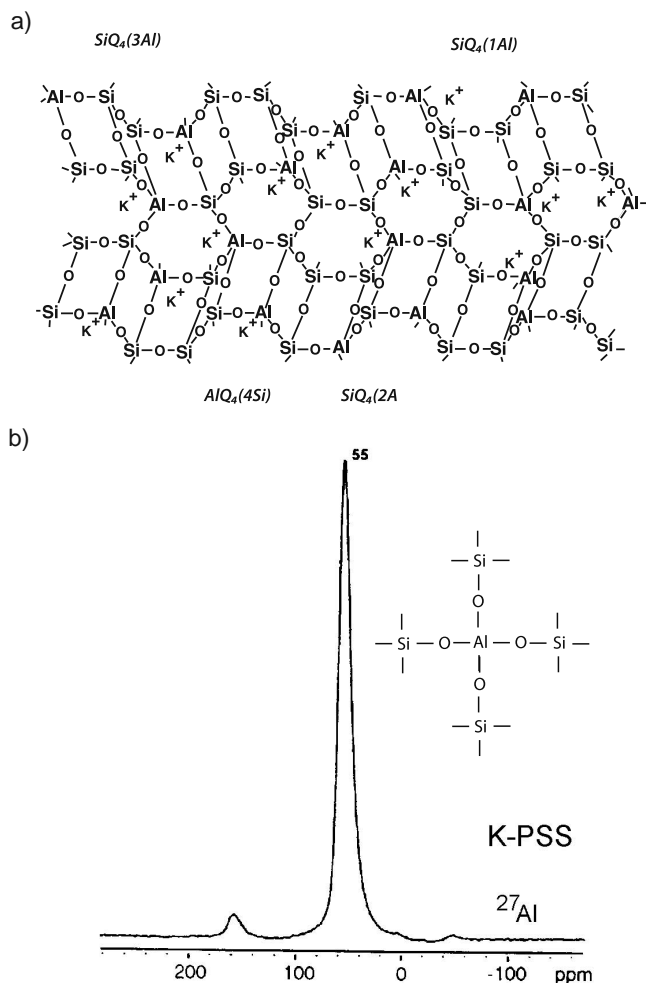
Fig. 11: a) left, 3D-structural model for fully reacted K—poly(sialate-siloxo), Davidovits (1994) [22]. b) right, ^{27}Al MAS-NMR spectra for K—poly(sialate-siloxo) K—PSS (Davidovits, 1988) [18].

The reasoning of the cement scientists is only valid for the first stage of alkalination (which they call alkali-activation) as exemplified by the Al NMR spectra shown in Fig. 14a. The major resonances at 74/65 ppm in alkali-activated slag (no MK-750 added) can be assigned to $AlQ_2(2Si,2OH)$ and $AlQ_3(3Si,OH)$ species. With the addition of 30 parts MK-750, the resonance is narrower at 58 ppm suggesting three-dimensional networking of the type $AlQ_4(4Si)$. The Al spectrum demonstrates that, in opposition to alkali-activated slag, the Al in (Ca,K) geopolymers is entirely chemically connected, i.e. the cations Na+ and K+ are trapped within the structure, with no -OH group inside the particulates, providing long-term stability and corrosion resistance. To call them NASH (sodium-alumino-silicate-hydrate) or KASH (potassium-alumino-silicate-hydrate) is inappropriate and generates confusion.

Fig. 14b shows the Al spectrum for MK/slag/fly ash-based cement. The ^{27}Al NMR spectrum for the original ash contains two signals, one centered at 50 ppm for Al(IV) configuration and a second at -4 ppm assigned to Al(VI). They are mainly associated with the presence of mullite. In both cases, MK-750/slag and NaOH-based, geopolymerization shifts the first resonance to higher values (56 ppm) with Al(4Si) environment, characteristic of well condensed sialate networks in geopolymers.
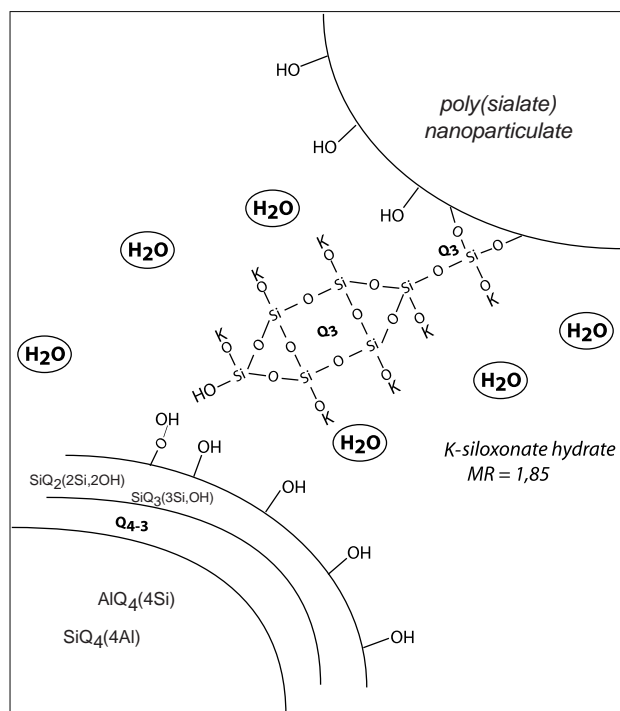
Fig. 12 : Simplified structure of K—nano-poly(sialate) particulates with siloxonate molecule between the particulates.
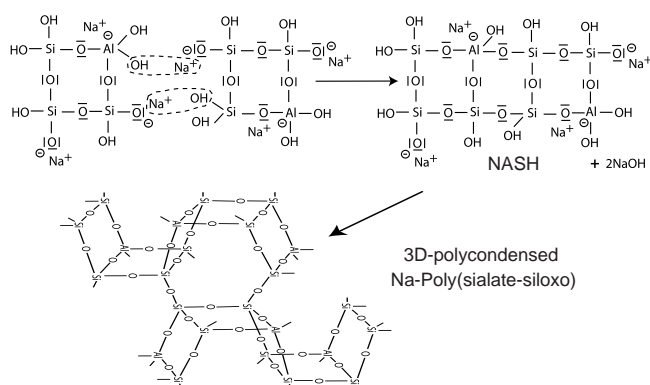

Fig. 13: Geopolymerization with intermediary oligo-sialate-hydrate formation, top part right, wrongly called NASH/KASH by cement scientists. This hydrated molecule polycondenses into a fully reacted 3D geopolymer network.

IV. Metakaolin-based geopolymer ceramic-like materials

Forty years ago, in October 1975, in our CORDI laboratory (later Cordi-Géopolymère) in Saint-Quentin, France, we were testing a new French metakaolin brand named Argical® supplied by the company A.G.S. (now Imerys). It was manufactured with an advanced technology in a flash calciner instead of being roasted in a rotary kiln or a vertical multiple-hearth oven. We discovered that this metakaolin was reacting very well with soluble alkali silicates. We recognized the potential of this discovery and presented an "Enveloppe Soleau" for registration at the French Patent Office. The hand-written text was filed on 29/12/1975, number 70528, at, INPI, Paris. It describes how metakaolin was reacting very well with soluble alkali silicates. It is reproduced with the English translation from French in Chapter 1 of the reference

book by J. Davidovits, *Geopolymer Chemistry and Applications,* since the 3rd edition, 2011 onwards [27]. The link to the free download PDF file of this Chapter 1 is located at <http://www.geopolymer.org/shop/product/geopolymer-chemistry-applications/>. The patent was filed with the self-evident title "Mineral polymer" (Davidovits, 1979) [28].
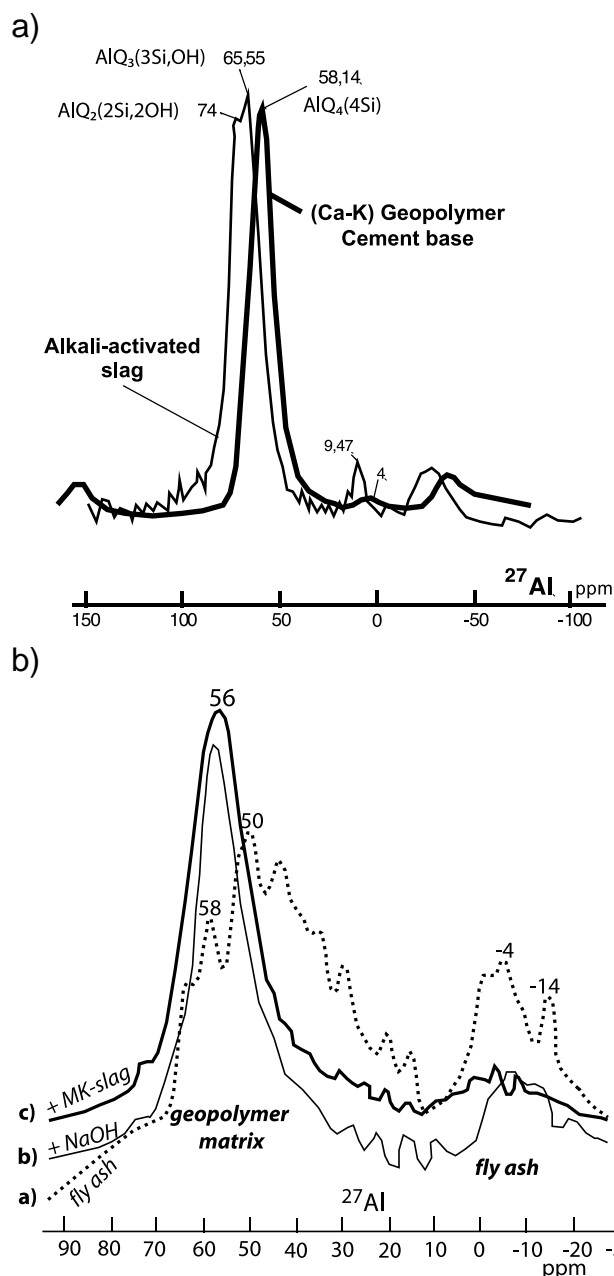

Fig. 14: a) left, ^{27}Al NMR spectrum of hardened geopolymeric Cement Base, evolution from alkali-activated slag towards geopolymer cement. Left curve, no MK-750 added; right curve, with 30 parts MK-750 (Davidovits *et al.*, 1999) [25]. b) right, ^{27}Al NMR spectroscopy for a) original fly ash, b) pure NaOH geopolymerization, c) MK-750/slag method after Davidovits (2000) [26].

Our first contact with flash-calcined metakaolin in 1975 was very exciting. We had prepared a mixture of 1 kg powder with 0.3 kg NaOH solution 12 M and let it mature in a plastic bag for a while. After 1 h, we were surprised by the high amount of water vapor and condensation seeping outside of the bag, with a temperature exceeding 100 °C, and a polyethylene bag that had been totally destroyed.

We had discovered one of the major properties of this metakaolin, namely its powerful exothermicity and reactivity in alkaline medium.

The introduction of MAS-NMR spectroscopy in the study of silicates by Lipmaa *et al.* (1980) [29] and Müller *et al.* (1981) [30] transformed our view and our knowledge of silicate structures. The most important contribution for our study was made in 1985 by MacKenzie's team from New Zealand. The first paper by Meinhold, MacKenzie and Brown (1985) [31] describes the presence of a *"chemical shift intermediate between tetrahedral and octahedral"*. This chemical shift intermediate will be later assigned to pentahedral aluminum sites Al(5). But, in their second paper, MacKenzie *et al.* (1985) [32], the authors could not claim to have discovered this new Al(5). It was against the view of the main stream of scientists at that time. Three years later, the paper by Sanz *et al.* (1988) [33] confirmed the presence of Al(4) and Al(5), in addition to Al(6). They applied MAS-NMR to follow the kaolinite-mullite transformation with temperature, from 20 °C to 1200 °C. The obtained spectra are displayed in Fig. 15. The ^{27}Al MAS-NMR spectrum for raw kaolinite (20 °C) contains one resonance at 0 ppm characteristic of Al(6). When the sample is heated, the intensity of this line decreases up to 980 °C, then increases again at 1055 °C (transformation to mullite). In the medium temperatures above 400 °C, that is during the dehydroxylation phases of kaolinite, two new lines appear at 55 – 60 ppm, assigned to Al(4) and at 25 – 30 ppm, assigned to Al(5). The intensity of the Al(5) line increases with temperature from 450 °C to 850 °C, then it decreases and disappears at 980 °C. The maximum intensity is spread 700 – 850 °C, hence the name MK-750 for this reactive metakaolin. The Al(4) line remains with the same intensity
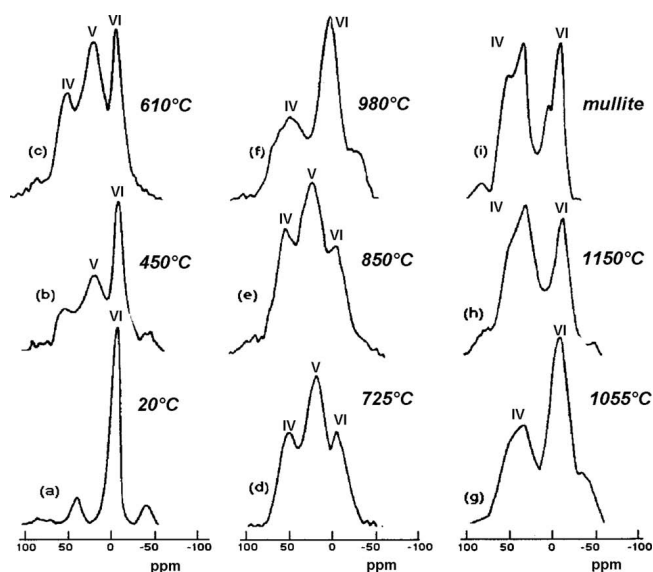

Fig. 15: ^{27}Al MAS-NMR spectra of kaolinite samples treated at different temperatures, with coordination numbers IV, V, VI, after Sanz *et al.* (1988) [33].

The reactivity and exothermicity are closely related to the calcination method of the raw kaolinitic clay source. The standard parameters set at the Geopolymer Institute and in our industry partner's laboratories involve the grinding of

the clay, and calcining in an electric oven, in air, at 750 °C for 3 h; the heating time from 20 °C up to 750 °C is 1 h 30 min, the cooling time 1 h 30 min, totaling 6 h in the furnace. What we find in the literature is totally different, so that it is hard to compare any results derived from these researches.

(1)   *Dehydroxylation mechanism of kaolinite with three different Al sites*

We know now that calcination produces two different Al oxides, one with Al(4) coordination, the second with Al(5). In addition, we still have a certain amount of remaining -OH groups with Al(6).

(a)   *Al oxide with the Al-O-Al-O sequence*

In the case of the first oxide with Al(4), water is expelled by dehydroxylation of two neighboring -Al(OH)$_2$ groups with the creation of the covalent sequence Al-O-Al-O as shown in Fig. 16a. The Al atoms remain chemically trivalent and are electronically neutral and stable.

(b)   *Al oxide with the alumoxyl Si-O-Al=O sequence*

The intra-dehydroxylation in the same Al atom produces the formation of the Al(V) oxide -Al=O as shown in Fig. 16b. It may be termed alumoxyl with reference to the C=O carboxyl group in organic chemistry. In the early stage of development of silicone chemistry, it was also thought that intra-dehydroxylation might occur within the -OH group of the same Si atom with formation of the -Si=O oxide (Kiping, 1927) [34]. Yet, this has not been proven, so far (McGregor, 1955 [35]; Noll, 1968 [36]). In silicones, dehydroxylation would exclusively occur between two neighboring Si(OH)$_2$ silanols. What happens for Si chemistry may not necessarily be true for Al. The steric arrangement in Fig. 17 shows that the V-fold coordination of Al results from the existence of this particular covalent Si-O-Al=O sequence [37]. It is characteristic of the highly strained 5-fold coordinated Al^{3+} polyhedron, which contains a double bond with oxygen [57].
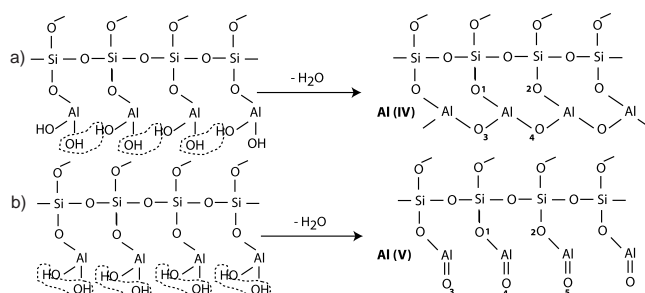

Fig. 16 : a): Inter-dehydroxylation of kaolinite and creation of the Al(IV) oxide with the Al- O-Al-O sequence. b): Intra-dehydroxylation of kaolinite and creation of the Al(V) alumoxyl with the Si-O-Al=O sequence.

(c)   *Dehydroxylation with Al-O-Al-OH sequence*

The remaining untouched hydroxyls Al-OH kaolinite unit with Al(6) is displayed in Fig. 17. For example, we may have a succession of two untouched hydroxyls Al-OH and two oxides Al-O- or, to simplify, formation of the Al-O-Al-OH sequence.

In Fig. 17, the Al-O-Al-O- sequence has IV-fold coordination between Al and the oxygens, numbered 1 to 4, generates three covalent bonds between Al and oxygen No. 1, No. 3 and No. 4, and one van der Waals bond between Al and oxygen, No. 2, located in the sialate Si-O-Al- sequence. In the Al-O-Al-OH sequence, the VI-fold coordination is between Al and the oxygens, hydroxyls, numbered 1 to 6. It generates three covalent bonds between Al and oxygen No. 1, hydroxyls No. 2 and No. 5, and three van der Waals bond between Al and oxygens No. 3, No. 4 and No. 6. The formation of the -Al=O alumoxyl species provides a satisfactory explanation of the structural mechanism of the Al(V) coordination with surrounding oxygens. The oxygens involved in V-fold coordination are numbered 1 to 5. The Al(V) configuration consists of two covalent bonds between Al and oxygens No. 1 and No. 4, and three van der Waals links between Al and oxygens No. 2, No. 3 and No. 5.
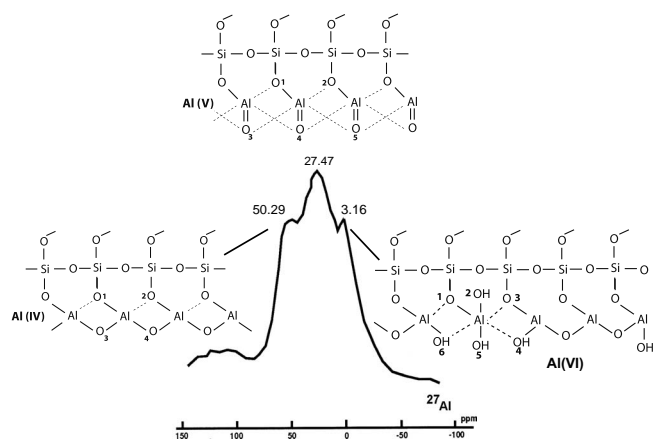
Fig. 17: Three sequences constituting metakaolin (MK-750) molecular structure, dotted line for coordination links, full line for chemical valence links. The numbers for oxygen and hydroxyl atoms provide the Al(IV), Al(V) and Al(VI)coordination parameters [37].

(2) Reaction mechanism in alkaline milieu

The calcination of kaolinite does not destroy the lamellar structure of the tabular-shaped metakaolinite pellets shown in Fig. 18. Electron microscopy studies by German scientist Eitel showed, as early as 1939, that kaolinite particles retain their hexagonal outline far above the dehydration temperature, up to 750 °C.

The alkaline attack starts on the outer faces of the metakaolinite particle. It continues, layer by layer, from the edges to the inside. This is a very important feature, which induces two different geopolymerization mechanisms. We discovered the implications of this structural parameter by chance.
Our PhD student M. Zoulgami (1997–2000) prepared a MK-750-based Na—poly(sialate-siloxo) geopolymer (with Si:Al=2) dedicated to biomaterial applications. This implied a drastic diminution of the pH from pH 10.5–11 to a neutral value in the range of 7.5, by heat treatment at 750 °C. In the paper by Zoulgami *et al.* (2002) [38], x-ray diffraction of the dried geopolymer showed two major crystalline phases: nepheline ($NaAlSiO_4$), Si:Al=1, and albite ($NaAlSi_3O_8$), Si:Al=3. These two phases are coexist-

ing in the ratio 50/50 and the bulk reactional mix corresponds to the formula

$Na_{4.5}Al_{4.5}Si_{9.04}O_{27.11}$, i.e. $NaAlSi_2O_6$ or Si:Al=2

The EDS analyses performed on this geopolymer treated at 750 °C show that the bulk chemical composition is equal to $NaAlSi_2O_6$. This means that both geopolymer phases, namely nepheline and albite detected with x-ray diffraction, are in two distinct phases on the nano scale. Duxson *et al.* (2005) [39] also noticed for temperature above 500 °C the formation of nepheline with Na and of a not well-defined component similar to albite. One geopolymerization generates the formation of a Si:Al=1 geopolymer, the second a Si:Al=3 geopolymer, with an overall value Si:Al=2.
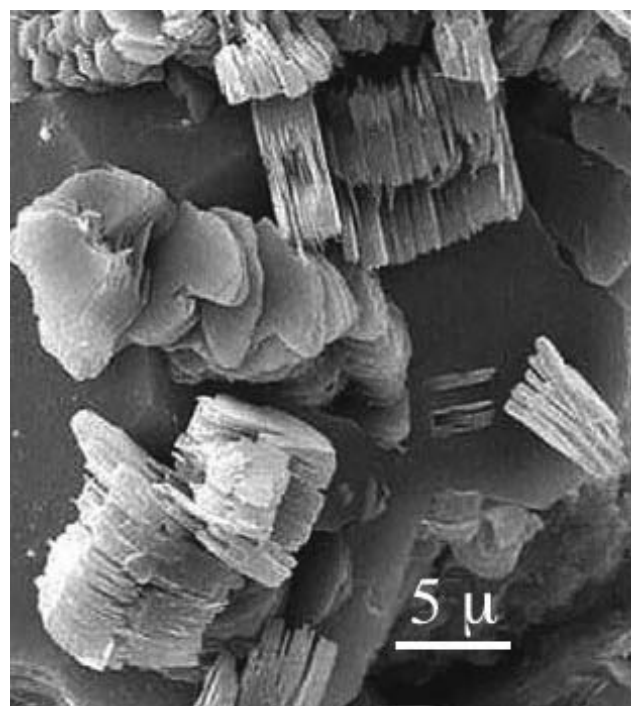

Fig. 18: Metakaolinite pellets.

As recognized by MacKenzie's team in the Zhang *et al.* (2009) [40] paper, MK-750-based geopolymer binders and cements are different from the simple alkali activation with NaOH, published by several authors. This NaOH simple alkali-activation of metakaolin generates products of the type Zeolite A. For the authors, a geopolymer cement or a geopolymer binder implies the reaction of MK-750 with soluble (Na, K) alkali silicates. The authors suggest that the various silicate units (Q_0, Q_1, Q_2, Q_3) present in the alkali-silicate solution have a templating function during geopolymerization.

Rowles and O'Connor (2009) [41] calcined metakaolin at 750 °C for 24 h. SEM imaging of the resulting geopolymer revealed the presence of a two-phase microstructure; the matrix phase being the fully formed geopolymer with Si:Al=3, while the grain phase was reminiscent of, but chemically dissimilar to, the MK precursor with Si:Al=1. The problem is that the authors did not recognize that these two phases were due to the initial layered arrangement of the tabular shaped metakaolin particulates shown in Fig. 18 above. It is strange that this unique structural property of metakaolinite is ignored or not taken into

consideration by the majority of scientists who try to explain the geopolymerization of MK-750-based geopolymers [42,43].

The relatively recent papers by Favier *et al.* (2013, 2015) [44,45] are the most important papers so far, dealing with this evident structural parameter. Their elastic modulus study on MK-750-based geopolymer suspensions confirms the 2-step reaction mechanism mentioned above. At the very early stage of the reaction (less than 15 min after the beginning of mixing), aluminosilicate molecules with Si:Al ratio in the range of 2 to 3 are formed at the grain boundaries, while the rest of the solution is still mainly composed of silicate/siloxonate oligomers of type Q_0, Q_1, Q_2 and also Q_3. In the second phase, the geopolymer hardens with a second rapid increase of the elastic modulus. This fast increase indicates that a new chemistry is taking over, with Si:Al=1, which does not involve any siloxonate molecules, only NaOH. As the geopolymerization progresses, at the scale of dozens to hundreds of nanometers, different sialate species coexist as a distribution of solid solutions between Si:Al=1 to Si:Al=4, more specifically poly(sialate) of the nepheline type, Si:Al=1, together with poly(sialate-disiloxo) of the albite type, Si:Al=3, and others. In their second study, the authors provide strong evidence for a heterogeneous formation and a two-step mechanism. They focused on the solid/liquid heterogeneous suspension. Using static liquid-phase NMR they could specifically monitor the chemical speciation of the mobile species in the suspending liquid (ions, oligomers or small gel particles). It is also one of the rare works of research that takes into account the exact molecular composition of the alkali-silicate solution, namely the simultaneous presence of highly depolymerized species, isolated ortho-silicate Q_0, as well as polymerized silicate oligomers, with silicon speciation Q_1, Q_2, Q_3. The paper by Zhang *et al.* (2009) [40] stresses the same importance for the molecular structure of the various silicate units (Q_0, Q_1, Q_2, Q_3) present in the alkali-silicate solution. They suggest that they have a templating function during geopolymerization.
Accordingly, the geopolymerization of MK-750 with (Na,K)-silicates results from two reaction mechanisms, illustrated in Fig. 19 below, taking place in the following order [37,42,43]:

– phase 1: outer faces/edges reaction involving Na^+, K^+, OH^- and Q_0, Q_1, Q_2 and Q_3 siloxonates; resulting geopolymer with atomic ratio Si:Al between 1 and 4;
– phase 2: inner particulate reaction with only Na^+, K^+, OH^-; resulting geopolymer with atomic ratio Si:Al=1.

(3) Applications

MK-750-based ceramic-like geopolymers have a variety of applications. These include new binders and resins for coatings and adhesives, fiber composites, waste encapsulation and new cement for concrete. The wide variety of applications includes: fire-resistant materials, decorative stone artefacts, thermal insulation, low-tech building materials, low-energy ceramic tiles, refractory items, thermal shock refractories, bio-technologies (materials for medical applications), foundry industry, cement and concretes, composites for infrastructure repair and reinforcement,

high-tech composites for aircraft interiors and automobiles, high-tech resin systems, radioactive and toxic waste containment, arts and decoration, cultural heritage, archaeology and history of sciences.
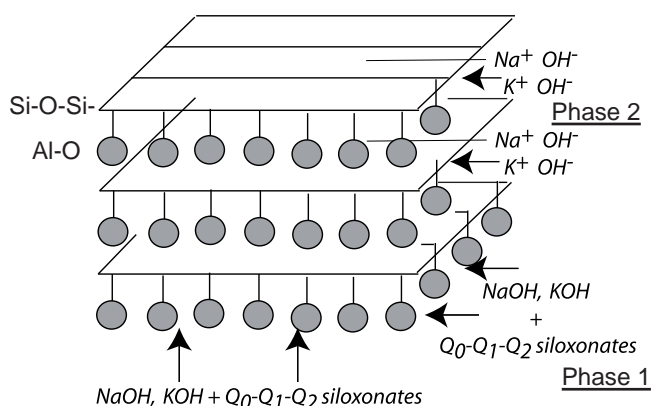

Fig. 19: Schematic representation of the chemical attack on MK-750 layered particles with Phase 1 and Phase 2 [37,42,43]. The interval between each layer is 7.5 Å.

The route to high-temperature ceramics via MK-750 geopolymerization was pioneered by W. Kriven and her team at the University of Illinois at Urbana-Champaign, USA. They converted fully condensed MK-750-based K-poly(sialate-siloxo) geopolymer into highly valuable leucite ceramic $KAlSi_2O_6$. This demonstrated an alternative route in the production of these highly valuable refractory ceramics, without the necessity for expensive equipment, long processing times, and costly precursors (Kriven *et al.*, 2003, 2006) [46,47]. One paper by Kriven *et al.* (2005) [48] was presented at the Geopolymer 2005 Conference. Later on, Dechang Jia and his team at Harbin Institute of Technology, China, also focused their research on this geopolymer route. When compared to hydrothermal methods, geopolymer technology is advantageous with regard to its low cost and short fabricating time; with the proper processing procedure, geopolymer can be directly converted into the final structural leucite, kalsilite or pollucite ceramic [49].

He *et al.* (2010) [50] stressed how the geopolymer route is of great interest. They discovered that the addition of cesium stabilized the geopolymeric leucite. The cesium substitution for potassium was effective in stabilizing the cubic polymorph of leucite to room temperature. In the paper by He *et al.* (2011) [51], they used MK-750 containing a certain amount of silica (quartz). They obtained the transformation into leucite at a temperature as low as 800 – 900 °C instead of 1050 – 1100 °C with pure kaolin and ceramic firing. Contrary to Kriven's paper, which produces fully reacted geopolymer, here, the method is not 100 % satisfactory. Indeed, owing to the existence of unreacted metakaolin, K-geopolymer was inhomogeneous at the molecular level. Higher energy was thus required for the structural rearrangement during the change from amorphous to crystallized phase. On the other hand, W. Kriven and her team continued to improve the crystallized geopolymer route to make ceramic powders and ceramics (see under references [57–64]).

V. Geopolymer cements and concretes

We have geopolymer resins and binders as well as geopolymer cements. From a terminology point of view, cement is a geopolymer binding system that hardens at room temperature, like regular Portland cement. If a geopolymer compound requires heat setting, it may not be called geopolymer cement. Creating geopolymer cement requires an alumina silicate material, a user-friendly alkaline reagent, sodium or potassium soluble silicates with a molar ratio MR $SiO_2:M_2O>1.45$, M being Na or K, and water. Room temperature hardening relies on the addition of calcium cations, essentially iron blast furnace slag.

(1) Portland cement chemistry vs Geopolymer cement chemistry

Fig. 20 compares the two systems: on the left, the hardening of Portland cement through simple hydration; in the center the hardening (setting) of Geopolymer cement through polycondensation; on the right, the corresponding ^{29}Si NMR spectra. ^{29}Si NMR spectra clearly show the difference in molecular structure. For Portland, in the hydrated CSH, the silicon unit is of the type $Si(Q_0)$ for calcium silicate monomers, with also some amount of calcium silicate oligomer of types $Si(Q_1)$ and $Si(Q_2)$. By contrast, for geopolymer, the structure is polymerized into a silico-aluminate, three-dimensional network of the type K—poly(sialate-siloxo) wherein the silicon unit is of the type $Si(Q_4)$.
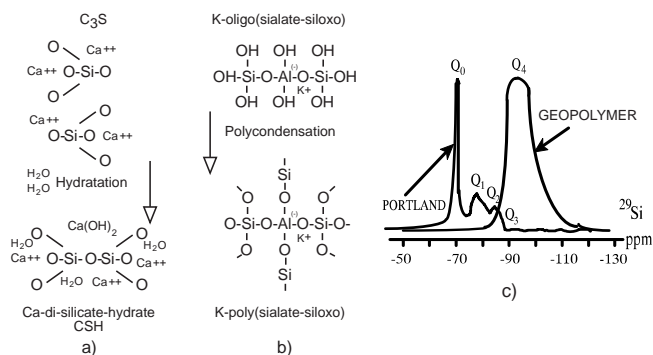
Fig. 20: Portland cement chemistry vs Geopolymer cement chemistry: a) Hardening of Portland cement through simple hydration of Calcium Silicate into Calcium Di-Silicate hydrate (CSH) and lime $Ca(OH)_2$; b) Hardening (setting) of Geopolymer cement through poly-condensation of Potassium Oligo-(sialate-siloxo) into Potassium poly(sialate-siloxo) cross linked network; c) ^{29}Si NMR spectra.

Geopolymer cements cure more rapidly than do Portland-based cements. They can gain most of their strength within 24 hours. However, they set slowly enough that they can be mixed at a batch plant and delivered in a concrete mixer. Geopolymer cement also has the ability to form a strong chemical bond with all kinds of rock-based aggregates.

(2) Geopolymer cement is not alkali-activated cement

Geopolymer cement is sometimes mixed up with alkali-activated cement and concrete, or alkali-activated-material. Despite more than 50 years of development in Eastern Europe (Glukhovsky [10, 11]; Tailing and Brandstetr [52])

and China (Shi *et al.*[53]), alkali-activated materials were not manufactured separately and not sold to third parties as commercial cement. On the contrary, its chemistry was used only in the making of alkali-activated concretes. Geopolymer technology was from the start aimed at manufacturing binders and cements for various types of applications. Lone Star Industries introduced the first industrialized geopolymer cement in USA in 1986. Named Pyrament®, it resulted from the research developments carried out by Davidovits and Sawyer (1985) [54]. Geopolymer cements of the Davya types were sold for laboratory testing by the French company Cordi-Géopolymère until 2009. The Davya 20, Davya 30 and Davya 60 were (K,Ca)—poly(sialate-siloxo) MK-750-based geopolymer cements.

Because Portland cement concretes can be affected by the deleterious alkali-aggregate reaction, referred to as AAR or alkali-silica reaction termed ASR, the wording alkali-activation has a bad impact on civil engineers. Nevertheless, several cement scientists continue to promote the idea of alkali-activated materials or alkali-activated geopolymers. These cements called AAM encompass the specific fields of alkali-activated slags, alkali-activated coal fly ashes, alkali-activated blended Portland cement. It is interesting to mention the fact that geopolymer cements do not generate any of these deleterious reactions.

With pure alkali-activated slag, the compressive strength is 80 MPa after 28 days and it goes down to 50 MPa with a 50:50 mixture of slag/MK-750. The addition of MK-750 seems to be less efficient than thought since the strength decreases. But, we must take into account that what is required for a modern cement is long-term stability. However, the latter is a function of the molecular structure. The mechanism is summarized in Fig. 21. Alkali-activated slag provides higher strength but poor physicochemical properties because, in the chemical structure of its hydroxylated oligomer, the Na^+ or K^+ cations are located on the edge of the cyclic oligomer (K,Ca)—cyclo-ortho(sialate-disiloxo) with $Si(Q_2)$. They can easily migrate in contact with water and be leached out. This unstable phase is called NASH or KASH by cement scientists for sodium/potassium-alumino-silicate-hydrate, and generalized to the final geopolymer matrix, which is wrong. In geopolymer cement with its three-dimensional networking, hardening results from the polycondensation of the ribbon bidimensional polymers Ca—poly(sialate) Si:Al=1, and (Na,K)—poly(sialate- disiloxo) Si:Al=3, with $Si(Q_3)$ towards more stable reticulated 3D geopolymers with $Si(Q_4)$. This mechanism provides long-term stability because the Na^+ or K^+ cations are fixed and trapped inside the frameworks of the types Ca-anortite, Na-albite or K-orthoclase (as in natural feldspar or plagioclase) [55]. In fact, by varying the ratio slag/MK-750, end-users can choose between high compressive strength and low stability (danger for alkali-activated slag), or optimal strength with long-term durability and corrosion resistance for geopolymer cements.
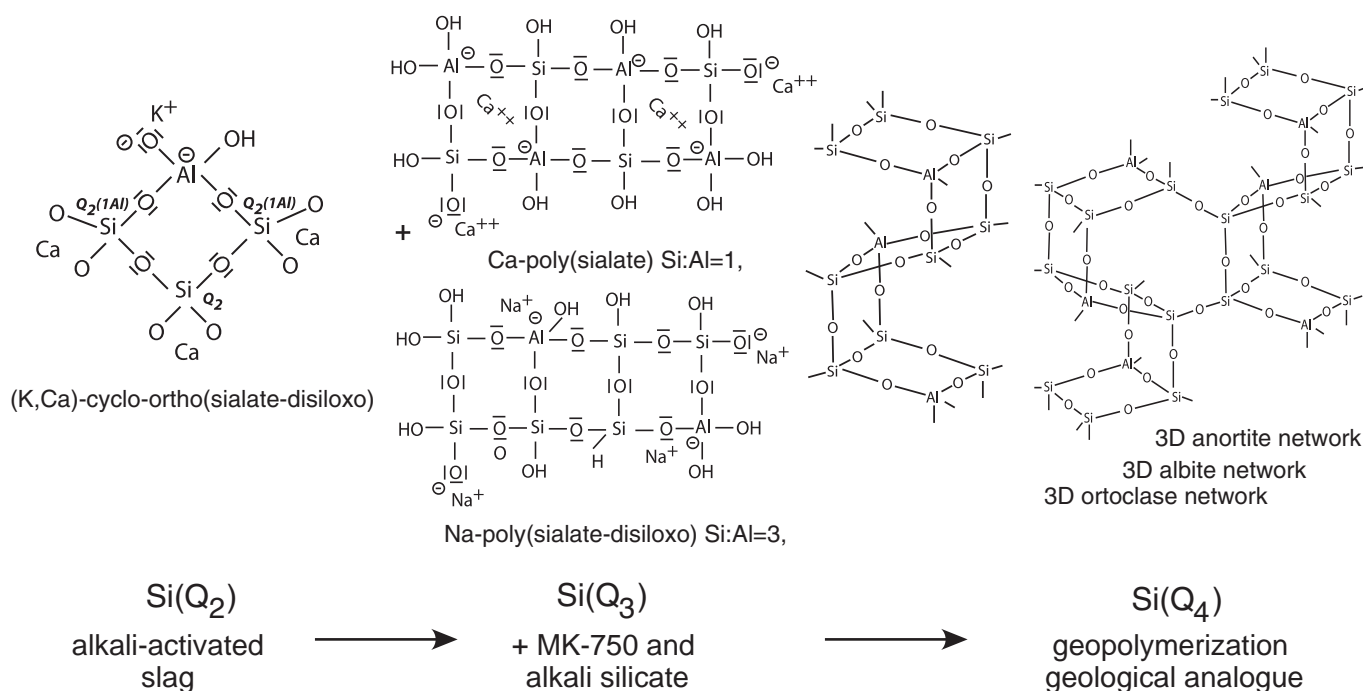
Fig. 21: From alkali-activated slag to stable 3D geopolymer network resulting from the addition of MK-750. From left to right, structural changes from unstable cyclic oligomer Si(Q_2) obtained by alkali activation of blast furnace slag, through ribbon bidimensional polymers Si(Q_3) towards stable reticulated 3D geopolymers with Si(Q_4).

(3) Geopolymer cement categories

The categories comprise [56]:
– Slag-based geopolymer cement.
– Rock-based geopolymer cement.
– Slag/fly-ash-based geopolymer cement.
– Ferro-sialate-based geopolymer cement.

Slag-based geopolymer cement

Manufacturing components:
Metakaolin MK-750 + blast furnace slag + alkali silicate (user-friendly).
Geopolymeric make-up:
Si:Al=2; in fact solid solution of Si:Al=1, Ca-poly(disialate) (anorthite type) + Si:Al=3, K-poly(sialate-disiloxo) (orthoclase type) and CSH Ca-disilicate hydrate.

The first geopolymer cement developed in the 1980s was of the type (K,Na,Ca)-poly(sialate) (or slag-based geopolymer cement) [54].

Rock-based geopolymer cement

The replacement of a certain amount of MK-750 with selected volcanic tuffs yields geopolymer cement with better property and lower CO_2 emissions than the simple slag-based geopolymer cement.
Manufacturing components:
Metakaolin MK-750, blast furnace slag, volcanic tuffs (calcined or not calcined), mine tailings and alkali silicate (user-friendly).
Geopolymeric make-up:
Si:Al=3; in fact solid solution of Si:Al=1 Ca-poly(disialate) (anorthite type) + Si:Al=3 – 5 (Na,K)-poly(silate-multisiloxo) and CSH Ca-disilicate hydrate.

Slag/fly ash-based geopolymer cement

Presently two types based on Class F fly ashes:
*Type 1: alkali-activated fly ash geopolymer (user-hostile):*In general, requires heat hardening at 60 – 80 °C and is not manufactured separately and becomes part of the resulting fly-ash-based concrete. NaOH (user-hostile) + fly ash: fly ash particles embedded in an alumino-silicate gel with Si:Al= 1 to 2, zeolitic type (chabazite-Na and sodalite).
Type 2: slag/fly.ash-based geopolymer cement (user-friendly): Room-temperature cement hardening. User-friendly silicate solution + blast furnace slag + fly ash: fly ash particles embedded in a geopolymeric matrix with Si:Al=2, (Ca,K)-poly(sialate-siloxo).

Ferro-sialate-based geopolymer cement

The properties are similar to those of rock-based geopolymer cement but involve geological elements with high iron oxide content. The geopolymeric make up is of the type poly(ferro-sialate) (Ca,K)-(-Fe-O)-(Si-O-Al-O-). This user-friendly geopolymer cement is in the development and pre-industrialization phase.

VI. Conclusions

A geopolymer is a mineral macromolecule having a well-defined size and molecular structure. We have seen how (Na,K)-poly(sialate) and (Na,K)-poly (sialate-siloxo) type geopolymers consisted of individual elementary nanoparticles of 5 to 40 nm in size (50 to 400 Å) separated by a nanoporosity ranging from 3 to 10 nm. This microstructure is formed at ambient temperature and is still stable at temperatures well above 1000 °C. This nanoparticulate microstructure measuring 5 to 40 nm in size is also found in fly-ash-based geopolymer cement. It is therefore an essential characteristic of silicoaluminate geopolymers.

It is the result of a very precise chemical mechanism involving covalent bonding and promoting the formation and production of ceramic-like materials.

Yet it is the arrangement of these nanoparticulates that forms the geopolymer matrix. It governs the chemical, physical and mechanical properties of ceramic-like materials found in a wide variety of uses. Some geopolymer applications are still in development while others are already industrialized and marketed. The following areas may be mentioned:

– treatment and containment of toxic, radioactive and nuclear waste and mine tailings;

– high-tech geopolymer resins and binders for paints, coatings and grouts resistant to corrosion and temperature;

– fire- and temperature-resistant compounds for the manufacture of prototypes and toolings;

– biotechnology and medical applications;

– high-tech composites made of carbon fiber and others resistant to fire and heat for aeronautics and automotive, for the repair and reinforcement of civil engineering infrastructures.

– geopolymer cements and concretes with low-CO_2 greenhouse gas emission and low energy demand;

– geopolymer ceramics and manufacturing techniques with low-CO_2 greenhouse gas emission and low energy demand.

The wide variety of potential applications includes: fire-resistant materials, decorative stone artifacts, thermal insulation, low-tech building materials, low-energy ceramic tiles, refractory items, thermal shock refractories, biotechnologies (materials for medical applications), foundry industry, cement and concretes, composites for infrastructures repair and reinforcement, high-tech composites for aircraft interior and automobile, high-tech resin systems, radioactive and toxic waste containment, arts and decoration, cultural heritage, archaeology and history of sciences.

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