Joseph Davidovits

GEOPOLYMER

Chemistry & Applications

5th edition

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Professor Joseph Davidovits.

Professor Joseph Davidovits is famous for his pioneering work on geopolymers. He is an internationally renowned French materials scientist and archeologist, who was honored by French president Jacques Chirac with one of France's two highest awards, the Chevalier de l'Ordre National du Mérite, in November 1998. Born in 1935, he has a French Degree in chemical engineering and a German Doctorate Degree (PhD) in chemistry, was professor and founder of the Institute for Applied Archaeological Sciences at Barry university, Miami, Florida (1983-1989), Visiting professor at Penn State university, Pennsylvania (1989-1991) and Director of the Geopolymer Institute, Saint-Quentin, France (1979-present). He is a world expert in low-temperature geosynthesis as well as in archaeological science. He is the inventor in 1979 of geopolymers and the chemistry of geopolymerization. He has authored/co-authored hundreds scientific papers, reports, and dozen of books, holds more than 50 patents and has written in 2008 the reference book *Geopolymer Chemistry and Applications*, 5th edition issued in 2020. Since 2009, he is the Chairman of the annual international gathering: Geopolymer Camp.

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Part I

Polymers and Geopolymers

Chapter 1

Introduction

The discovery of a new class of inorganic materials, geopolymer resins, binders, cements and concretes, resulted in wide scientific interest and kaleidoscopic development of applications. From the first industrial research efforts in 1972 at the Cordi-Géopolymère private research laboratory, Saint-Quentin, France, until the end of 2019, thousands of papers and patents were published dealing with geopolymer science and technology. On August 31. 2005, the Geopolymer Institute (a non-profit scientific organization founded in 1979) was proud to announce in its News on line (www.geopolymer.org): "*Since 1997, 80000 papers have been downloaded by 15000 scientists around the world at the geopolymer.org website*". The extent of international scientific and commercial interest in geopolymers was evidenced by several large conferences. In France, the First European Conference on Soft Mineralurgy, organized by the Geopolymer Institute and sponsored by the European Economic Commission, was held at the University of Technology of Compiègne in June 1988 (*Geopolymer '88*). Eleven years later in June-July 1999, the Geopolymer Institute organized the Second International Conference *Geopolymere '99*, held in Saint-Quentin; the published proceedings included 32 papers presented to the 100 scientists from over 12 countries. The Third International Conference, *Geopolymer 2002* was held in Melbourne, Australia, in October 2002.

Since 2003, several national and international scientific institutions have organized "geopolymer sessions", "geopolymer seminars" and "geopolymer conferences". The Geopolymer 2005 World Congress was a tribute to the 26th anniversary of the creation of the Geopolymer Institute by J. Davidovits. The main topic of the world congress was *Geopolymer-chemistry and sustainable Development.* It gathered two major events in two different locations: the Fourth International Conference in Saint-Quentin, France, June-July, 2005, organized by the Geopolymer Institute; the International Workshop on Geopolymer Cements and Concrete in Perth, Australia, September 2005, chaired by V.J. Rangan, organized by Curtin University of Technology, Perth, the University of Alabama, USA, and sponsored by the National Science Foundation, USA. More than 200 scientists attended the congress and 85 international public and private research institutions presented a total of 75 papers. They cover a wide scope of topics ranging from geopolymer chemistry, industrial wastes and raw materials, geopolymer cements, geopolymer concretes (including fly ash-based geopolymers), applications in construction materials, applications in high-tech materials, matrix for fire/heat resistant composites, and applications in archaeology. The published proceedings (*Geopolymer 2005*) includes 60 selected papers and is titled: *Geopolymer, Green Chemistry and Sustainable Development Solutions.* In 2007, I started writing the 1rst edition of this book; the 2nd edition was published in 2008, the 3rd in 2011 and the 4th in 2015. In 2009, we agreed to propose every year two international events: a Geopolymer Symposium in January, at Daytona Beach, Florida, USA, within the frame of the International Conference on Advanced Ceramics and Composites, organized by the American Ceramic Society and Prof. W. Kriven from Illinois University, and a Geopolymer Camp in July, at Saint-Quentin, France, organized by the Geopolymer Institute. The 11th Geopolymer Camp 2019 was a tribute to the 40th anniversary of the creation of the Institut Géopolymère (Geopolymer Institute).

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 must get a polymer terminology, very different from the traditional way in use by ceramicists or cement scientists. 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 $[\equiv Si\text{-}O\text{-}Al\text{-}(OH)_2]n$ with the covalent aluminum hydroxyl $\text{-}Al\text{-}(OH)_2$ side groups branched to the poly(siloxo) hexagonal macromolecule $[\equiv Si\text{-}O\text{-}]n$.

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 alumino-silicate 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 $2SiO_2 \cdot Al_2O_3$. Metakaolin is not alumina Al_2O_3 ! See the detailed chemical reaction mechanisms in the following sections.
Other starting raw-materials are:

- rock-forming minerals, alumino-silicates,
- amorphous silica,
- and industrial by-products (alumino-silicates) like coal fly ashes, blast furnace slag.

They chemically react within two different synthesis routes:

- alkaline medium with (Na, K) hydroxides and soluble alkali-silicates yielding poly(silicates), poly(siloxo), poly(silico-aluminates), poly(sialate) types and,
- acidic medium (here with phosphoric acid) yielding poly(alumino-phospho) types.

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

How should we consider geopolymers? Are they a new material, a new binder or a new cement for concrete? Geopolymers are all of these. They are new materials for coatings and adhesives, new binders for fiber composites, waste encapsulation and new cement for concrete. The properties and uses of geopolymers are being explored in many scientific and industrial disciplines: modern inorganic chemistry, physical chemistry, colloid chemistry, mineralogy, geology, and in all types of engineering process technologies. 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, bio-technologies (materials for medicinal applications), foundry industry, cements and concretes, composites for infrastructures repair and strengthening, 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.

1.1 Historical background

My chemistry background had focused on organic polymer chemistry and 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 alkali 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 man-made plastic (Figure 1.1).

On the other hand, the alumino-silicate kaolinite reacts with NaOH at 100–150°C and polycondenses into hydrated sodalite (a tectoalumino-silicate, a feldspathoid), or hydroxysodalite (Figure 1.2).

From the study of the scientific and patent literature covering the synthesis of zeolites and molecular sieves — essentially in the form of powders — 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

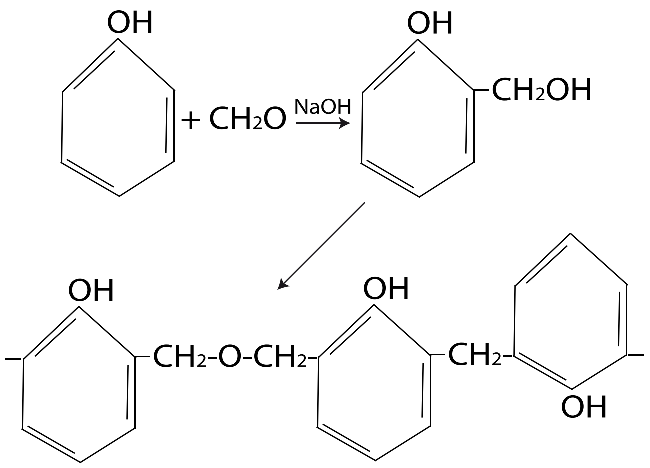


Figure 1.1: Phenoplast polycondensation between phenol and formaldehyde, in alkali medium.

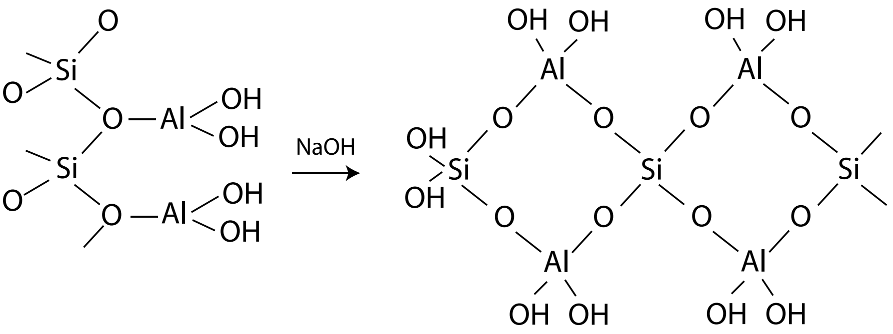


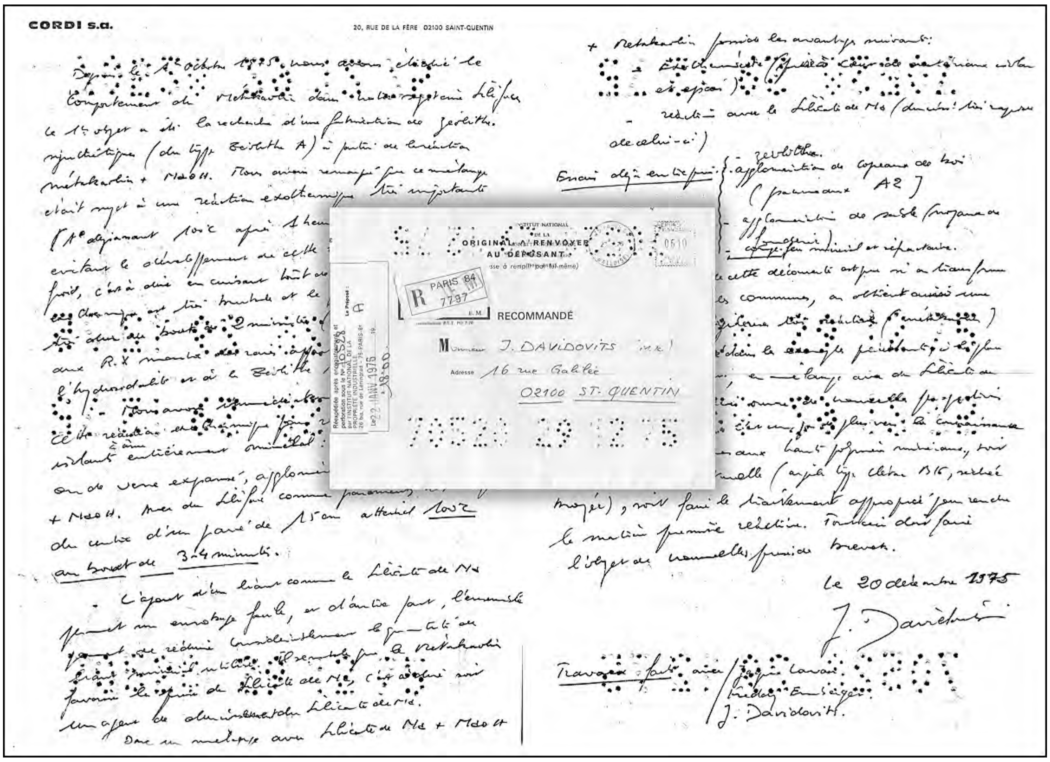
Figure 1.2: Polycondensation of kaolinite $Si_2O_5,Al_2(OH)_4$ in alkali medium.

three-dimensional silico-aluminate materials, which I call in French "géopolymères", geopolymers (mineral polymers resulting from geochemistry or geosynthesis).

The first applications were building products developed in 1973–1976, such as fire-resistant chip-board panels, comprised of a wooden core faced with two geopolymer nanocomposite coatings, in which the entire panel was manufactured in a one-step process (Davidovits, 1973). We coined it "*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 applying the same thermosetting parameters as for organic resin: 150–180°C temperature (Davidovits, 1976).

1.1.1 The invention of the first mineral resin, October 1975

Since 1972, we were involved in applying a methodology based on the transformation of kaolinitic clays. The material was wet clay and could only be processed through compression or extrusion. We did not have at our disposal a fluid binder, so far. The real breakthrough took place when, in 1975, we discovered at the CORDI laboratory a geopolymeric liquid binder based on metakaolin and soluble alkali silicate. I recognized the potential of this discovery and presented an *Enveloppe Soleau* for registration at the French Patent Office (Figure 1.3). Here is the English translation of the hand written text:



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RECOMMANDÉ

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Adresse 16 rue Galilée

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70528 29 12 75

le 20 décembre 1975

J. Davidovits

Figure 1.3: *Enveloppe Soleau* filed on 29/12/1975

Text of the Enveloppe Soleau filed on 29/12/1975, number 70528, at Institut National de la Propriété Industrielle, INPI, Paris. English translation from French:

"Since October 1, 1975 we study the behaviour of metakaolin in our Siliface system. The first goal was to find a process for the manufacture of synthetic zeolites (type Zeolite A) by reacting metakaolin + NaOH. We noticed that this mixture was prone to a very important exothermic reaction [t° exceeding 100°C after 1 hour of storage in a bag]. If we do not let this exothermic reaction to start at room temperature, namely if we cure immediately the mixture, then the exothermic reaction becomes very powerful and the product obtained is very hard after 2 minutes at 120°C; X-ray diffraction shows picks attributed to hydrosodalite and to Zeolite A. We immediately planed to use this exothermic reaction in the manufacturing of insulating blocks consisting entirely of a mineral core made of expanded shale or expanded glass spheres, agglomerated with metakaolin + NaOH. In a panel covered with a Siliface facing, the temperature in the center of a 15 cm thick core reaches 100°C after only 3–4 minutes. The addition of a binder such as Na-Silicate leads to a liquid coating, and allows reducing the quantity of mineral binder used in the process. It seems that metakaolin behaves as a hardener for Na-Silicate.

Consequently, a mixture involving Na-Silicate + NaOH + Metakaolin has the following advantages:

- Exothermicity (hardening to the heart of thick material);
- Reaction with Na-Silicate (very fast hardening of the liquid binder).

Tests already undertaken on: - zeolites; - agglomeration of wood chips (A2 panels); - sand agglomeration (foundry cores); - mineral and refractory fire barrier.

Another consequence of this discovery is that one can treat common clays at 500–600°C, to obtain a very reactive argillaceous raw material (metakaolin type) being able to be used in the preceding examples in place of pure metakaolin, together with Na-Silicate, or alone. This opens very interesting new prospects. It is a step towards more knowledge on the specific reactions involving mineral polymers, either by using natural raw materials for example standard clay like Clérac B16, dried, ground, or by performing the suitable treatment to transform them into reactive raw material. New patent filings will sanction all these discoveries. On December 20, 1975, J. Davidovits" *End of translation.*

It was the first mineral resin ever manufactured. The title of the patent, *Mineral polymer*, was self evident (Davidovits, 1979). The commercial product, coined Geopolymite™, was a good fire resistant alternative to organic resin. Then, Neuschäffer (1983) at the licensed German Company Dynamit Nobel (later Hüls Troisdorf AG) discovered the high reactivity of silica and alumina fumes, by-products of the manufacture of high-tech ceramics.

In early 1983, the Chairman of Lone Star Industries Inc., at this time the leading cement manufacturer on the American continent, was traveling in Europe and learned about our new geopolymeric binders. Lone Star Industries and Shell Oil Company had just announced the formation of a corporation to develop, produce, and market a new class of materials that were expected to have a wide-ranging impact on construction, architectural, and engineering applications. These materials were made from mineral aggregates combined with organic polymers and monomers. In other words, it was an "organic polymer concrete". Shell Oil supplied the chemical expertise in organic polymers, while Lone Star supplied the mineral aggregates. By enlisting our new inorganic geopolymers, Lone Star took the opportunity to challenge Shell Oil's chemical expertise. In August 1983, with James Sawyer as Head of Lone Star's research laboratory in Houston, Texas, I started to develop early high-strength geopolymeric binders and cements based on both geopolymeric and hydraulic cement chemistries. Within one month, Lone Star Industries Inc. formed the development company, Pyrament, which was exclusively dedicated to the implementation of this new class of cement. A few months later, Lone Star separated from the Shell Oil deal. It was discovered that the addition of ground blast furnace slag, which is a latent hydraulic cementitious product, to the poly(sialate) type of geopolymer, accelerates the setting time and significantly improves compressive and flexural strength. The first Davidovits and Sawyer (1985) patent was filed in Feb. 22, 1984, and titled "Early High-Strength Mineral Polymer" (US Patent). The corresponding European Patent, filed in 1985, is titled "Early High-Strength Concrete Composition" and these patents disclose our preliminary finding from the research carried out in August-September of 1983. Geopolymer cements are acid-resistant cementitious materials with zeolitic properties that can be applied to the long-term containment of hazardous and toxic wastes.

At Lone Star, in 1984, Richard Heitzmann and James Sawyer likewise blended Portland cement with geopolymer. Their purpose was to take advantage of the good properties of geopolymeric cement along with the low manufacturing cost of Portland cement. The resulting Pyrament® Blended Cement (PBC) was very close to alkali-activated pozzolanic cement. It comprised 80 % ordinary Portland cement and 20 % of geopolymeric raw materials (Heitzmann *et al.*, 1989). Pyrament PBC was recognized in the construction industry for its ability to gain very high early strength quite rapidly (US Army

Corps of Engineers, 1985). It was the ideal material for repairing runways made of concrete, industrial pavements, and highway roads. In the case of a runway, a 4–6 hours hardening is enough to allow the landing of an Airbus or a Boeing. The geopolymeric cement reaches a compression strength of 20 MPa after 4 hours, whereas plain concrete gets to this strength after several days. As of fall 1993, Pyrament concrete was listed for over 50 industrial facilities and 57 military installations in the USA, and 7 in other countries, and for nonmilitary airports. In 1994 the US Army Corps of Engineers released a well-documented study on the properties of Pyrament Blended Cements based concretes, which are performing better than had ever been expected for high-quality concretes.

In the field of so-called high-tech applications, since 1982, the French aeronautic company Dassault Aviation (Vautey, 1990) has used geopolymer molds and tooling in the development of French Airforce fighters (Davidovits *et al.* 1991). More than a hundred tooling and other items have been delivered for aeronautic applications and SPF Aluminum processing. In 1994 the American Federal Aviation Administration (FAA) with R. Lyon, initiated a cooperative research program to develop environmentally friendly, fire resistant matrix materials for aircraft composites and cabin interior applications. The Geopolymer composites were selected by FAA as the best candidate for this program (Lyon, 1997).

Environmentally-driven geopolymer applications are based on the implementation of (K,Ca)–poly(sialate-siloxo) / (K,Ca)–poly(sialate-disiloxo) cements. In industrialized countries (Western countries) emphasis is put on toxic waste (heavy metals) and radioactive waste safe containment. On the other hand, in emerging countries, the applications relate to sustainable development, essentially geopolymeric cements with very low CO_2 emission. Both fields of application are strongly dependent on politically driven decisions. Heavy metal waste encapsulation with geopolymer started in 1987, in Canada, with the financial support of CANMET Ottawa, Ontario Research Foundation, Toronto, and Comrie Consulting (Davidovits and Comrie, 1988). The safe containment of uranium mine tailings and radioactive sludge started in 1994 within the European research project GEOCISTEM, funded by the European Union. The GEOCISTEM project was aimed at manufacturing cost-effectively new geopolymeric cements (Geocistem, 1997). It was experimented on two important uranium-mining locations of Wismut, former East Germany, with the collaboration of BPS Engineering, Germany. Our results clearly show that solidification with geopolymeric cement (K,Ca)–poly(sialate-siloxo) is a prime candidate to cost-efficiently fill the gap between conventional concrete technology and vitrification methods (Hermann *et al.*, 1999).

Major efforts were dedicated to greenhouse CO_2 mitigation with the development of low CO_2 geopolymer cements. My research on this very important geopolymer application started in 1990 at Penn-State University, Materials Research Laboratory, USA. The production of 1 tonne of kaolin based-geopolymeric cement generates 0.180 tonnes of CO_2, from combustion carbon-fuel, compared with 1 tonne of CO_2 for Portland cement, i.e. six times less. Fly ash based-geopolymeric cement has attracted intensive research world-wide because it emits even less CO_2, up to nine times less than Portland cement. This simply means that, in newly industrializing countries, six to nine times more cement for infrastructure and building applications might be manufactured, for the same emission of green house gas CO_2 (Davidovits, 1993). One particular project, GEOASH, dealt with the study of European fly ashes and the implementation of user-friendly processes (GEOASH, 2004–2007). However, new global-warming concerns are no longer supporting the implementation of fly ash-based cement technologies. The Geopolymer Institute recommends instead the development of Ferro-sialate geopolymer cements. See our recent article on the subject titled "*A continent is on fire: stop promoting fly ash based geopolymer cements,* as well as in Chapter 13 and Chapter 26, section 26.3.3.2 (Davidovits, 2020).

1.2 The scope of the book

Although review articles and conference proceedings cover various aspects of the science and application of geopolymers, a researcher or engineer is still at a loss to readily obtain specific information about geopolymers and their use. It is this void that we hope to fill with this book.

There are two main purposes in preparing this book: it is an introduction to the subject of geopolymers for the newcomer to the field, for students, and a reference for additional information. Background details on structure, properties, characterization, synthesis, chemistry applications are included.

Each chapter is followed by a bibliography of the relevant published literature including patents. There are many examples in geopolymer science where an issued patent is either a primary reference or the only source of essential technical information. Excerpts from the more important patents are included in some chapters.

The industrial applications of geopolymers with engineering procedures and design of processes is also covered in this book.

1.3 Early observations

In the 1930s, alkalis, such as sodium and potassium hydroxide, were originally used to test iron blast furnace ground slag 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) discovered that the alkali addition produced a new, rapid-hardening binder (see Table 1.1). Alkali-activated slag cements (called Trief cements) were used in large-scale construction as early as the 1950s. The usual activation called for 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) developed alkali-activated slag binders and in the 1960s and 1970s made major contribution in identifying both calcium silicate hydrates, and calcium and sodium alumino-silicate hydrates as solidification products. He also noted that rocks and clay minerals react during alkali treatment to form sodium alumino-silicate hydrates , confirming earlier work carried out on clay reactivity (see below). Glukhovsky called the concretes produced with this technology "soil silicate concretes" (1959) and the binders "soil cements" (1967). More recently, cement scientists coined these products AAM, alkali-activated-materials and also claimed that geopolymer cements were AAM, generating confusion. Alkali-activated-materials are not geopolymers because they are not polymers, only hydrates of the types NASH and KASH (see for more details in Chapter 26, section 26.1.2 and the video series *Why AAM are not geopolymers*).

Earlier, Flint *et al.* (1946), at the National Bureau of Standards were developing various processes for the extraction of alumina starting from clays and high-silica bauxites. One intermediary step of the extraction process involved the precipitation of a sodalite-like com-

Table 1.1: Milestones in alumino-silicate chemistry.

	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*

pound. Borchert and Keidel (1949) prepared hydrosodalite (Na–PS) by reacting kaolinite in a concentrated NaOH solution, at 100°C. Howell (1963) obtained a Zeolite A type, using calcined kaolin (metakaolin) instead of kaolinite, preventing the formation of hydrosodalite.

In 1972, the ceramicist team Jean Paul Latapie and Michel Davidovics confirmed that water-resistant ceramic tiles could be fabricated at temperatures lower than 450°C, i.e. without firing. 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) and was later on reinvented in 1964 by Berg *et al.* (1970), a Russian team, but without any successful industrial implementation.

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).

In 1972, at CORDI laboratory in Saint-Quentin, we developed a technology based on this geosynthesis, which has been disclosed in various patents issued on the applications of the so-called "Siliface-Process" (Davidovits and Legrand, 1974). To a natural kaolinite/quartz blend (50/50 weight ratio) was added and mixed solid NaOH in the proportion of 2 moles or less of NaOH for 1 mole Al_2O_3 of the contained kaolinite, and water (1–1.5 g water for 1 g NaOH). The resulting granules were cold-pressed at 15 MPa into a green body, which was then hot-pressed (thermosetting process) in a mold equipped with a porous layer for water evaporation.

The thermosetting parameters were:

- Temperature: 130°C to 180°C;
- Applied hydraulic pressure: higher than the saturated vapor pressure of water, for the selected temperature, i.e. 10 to 30 bars;
- Time: one minute per millimeter thickness at 150°C or 10 minutes for a 10 millimeters thick plate. 65 to 75 % of the total time is devoted to degassing water.

The setting time is relatively short. In the absence of any pervious device, i.e. when degassing is not working, the polycondensation into hydrosodalite occurs very rapidly in a time as short as 15–20 seconds per millimeter thickness, at 180°C and 40 kg/cm^2 hydraulic pressure. Yet, due to the high internal pressure of water and the danger of explosion, the press must be equipped with safety devices (see for more details in Chapter 7). Otherwise, it is recommended to wait until the item has cooled down to room temperature before opening the press.

1.4 Phosphate-based geopolymer

Phosphate ceramics are synthesized at room temperature and they set rapidly like conventional polymers. They contain naturally occurring mineral phases, notably apatite. They represent another variety of mineral geopolymer, where Si is totally or partially replaced by P. They are formed by an acid-base reaction between a metal oxide and an acid phosphate. Virtually any divalent or trivalent oxide that is sparingly soluble may be used to form these phosphate geopolymers.

They have found a wide range of applications such as dental cements, construction materials, oil well cements, and hazardous and radioactive waste stabilization. The main difference between the silicate based geopolymers and phosphate geopolymers, however, is their syntheses. Poly(sialate) geopolymers and their derivates are synthesized in alkaline environment, but phosphate geopolymers are fabricated by acid-base reactions.

1.4.1 Phosphate geopolymers

A very wide range of phosphate geopolymers may be synthesized by acid-base reaction between an inorganic oxide (preferably that of divalent and trivalent metals) and an acid phosphate. The reaction product is generally a poly(hydrophosphate) or an anhydrous poly(phosphate) that consolidates into a ceramic. The following are the most common examples (Wagh and Yeong, 2003; Wagh, 2004)

$$\begin{gathered} 2CaO + Ca(H_2PO_4)_2 + H_2O \Rightarrow \\ CaO + 2CaHPO_4{\cdot}H_2O \Rightarrow Ca_3(PO_4)_2 + 2H_2O \end{gathered} \qquad \textbf{(1)}$$

$$MgO + KH_2PO_4 + 5\ H_2O \Rightarrow MgKPO_4{\cdot}6H_2O \qquad \textbf{(2)}$$

These reactions occur at room temperature. By controlling the rate of reaction, ceramics can be formed. With trivalent oxides, similar ceramics can be formed at a slightly elevated temperature. A good example is berlinite ($AlPO_4$), which is formed by the reaction between alumina and phosphoric acid:

$$Al_2O_3 + 2H_3PO_4 \Rightarrow 2AlPO_4 + 3H_2O \qquad \textbf{(3)}$$

It was also demonstrated that phosphate geopolymers of trivalent oxides such as Fe_2O_3 and Mn_2O_3 might be produced by reduction of the oxide and then acid-base reaction of the reduced oxide with phosphoric acid. The reaction may be described by the following equation:

$$X_2O_3 + X + 3H_3PO_4 + nH_2O \Rightarrow 3XHPO_4{\cdot}(n{+}3)H_2O \qquad \textbf{(4)}$$

where X is Fe or Mn.

1.4.2 High-molecular phosphate-based geopolymers: cristobalitic $AlPO_4$

Berlinite ($AlPO_4$) is the only known mineral to be isostructural with quartz. Isostructural means that they have the same structure although the two minerals have rather different chemistries. Quartz, SiO_2, would seem to be very different from berlinite, $AlPO_4$. But if the formula of quartz is written as $SiSiO_4$ instead of $2(SiO_2)$ then the similarity is obvious. The reason that berlinite is able to have the same structure as quartz is because the aluminum and phosphorus ions are of similar size to silicon ions with following bond lengths Si-O 1.63 Å, P-O 1.63 Å, Al-O 1.73 Å. Thus the same structure can be achieved since the aluminums and phosphorus can completely replace the silicons without alteration of the quartz structure. The cristobalite form of aluminum phosphate may be obtained by heating the normal berlinite form of aluminum phosphate at an elevated temperature which is preferably in excess of 1000°C.

The synthesis of cristobalitic (high-molecular) $AlPO_4$ geopolymers follows two different routes. The first process includes sol-gel chemistry whereas the second system involves the reaction between phosphoric acid and metakaolinite MK-750 (see in Chapter 14).

1.5 Organo-mineral geopolymers

1.5.1 Silicone

The similarity of the siloxane (Si-O-Si) structure in organo-silicones to the chains, rings, and networks of silicon and oxygen found in silica and the silicate minerals, for example in quartz, has been pointed out many times. Almennigen *et al.* (1963) reported the correspondence in a study of disiloxane H_6Si_2O. As observed by Noll (1968) it is possible to pass from the polymeric silicate to the polymeric covalent molecules of an organosiloxane by replacing the bridging oxide ions of the silicate anions with methyl groups. The structures that result from this replacement closely resemble the silicate and aluminosilicate molecules: monomers, dimers, trimers, etc., rings, chains, sheets and frameworks of corner-sharing silicate $[SiO_4]$ groups.

Chapter 2 and Chapter 15 focus on silicone poly(organo-siloxane). When the organic radical is methylene the structures of the oligomeric poly-methyl-siloxanes are identical with those of poly(siloxonate) (Si-O-Si-O) and poly(sialate) (Si-O-Al-O-Si) geopolymers.

1.5.2 Hybrid organo-mineral geopolymers

This new class of compounds was first obtained by incorporating the geopolymer into the organic polymer structure, adapting the chemical composition of the components. For example a bi-functional epoxy resin, Diglycidyl Ether of Bisphenol A (DGEBA), was mixed with 20 wt% of MK-750 based geopolymer slurry, with a curing agent in an aqueous medium. The resulting hybrid material has excellent mechanical properties and improved fire resistance.

The new developments are focusing on improving the mechanical and physical properties of the geopolymer itself. However, both organic and geopolymer phases are physically incompatible. Obtaining a homogeneous mixture without phase separation requires a new approach (see in Chapter 15).

1.5.3 Humic-acid based: kerogen geopolymer

T.K. Yen and his team, working on the transformation of geomolecules through geochemical processes during diagenesis, (Kim *et al.*, 2004, 2006) have drawn attention to the concept of geopolymer in association with kerogen and petroleum. Kerogen-geopolymer is the most stable material and the final alternating product in the Earth. Some geopolymeric materials can last for a long time due to their unique geopolymeric structure, so-called three-dimensional crosslink. Geopolymers can be classified into two major groups: pure inorganic geopolymers and organic containing geopolymers, synthetic analogue of naturally occurring macromolecules (Kim *et al.*, 2004, 2006). The small content of organics is a key parameter governing the strength and durability of material in a large volume of inorganics. Organic compounds can be incorporated into refractory macromolecules such as lignin and melanodin or humic materials (Henrichs 1992). Humic materials represent an inorganic-organic structure.

Diagenesis of organic matter leads from biopolymers synthesized by organisms through "humin" to Kerogen, a geopolymer, by partial destruction and rearrangement of the main organic building blocks (Figure 1.4). Kerogen is considered to be the major starting material for most oil and gas generation as sediments are subjected to

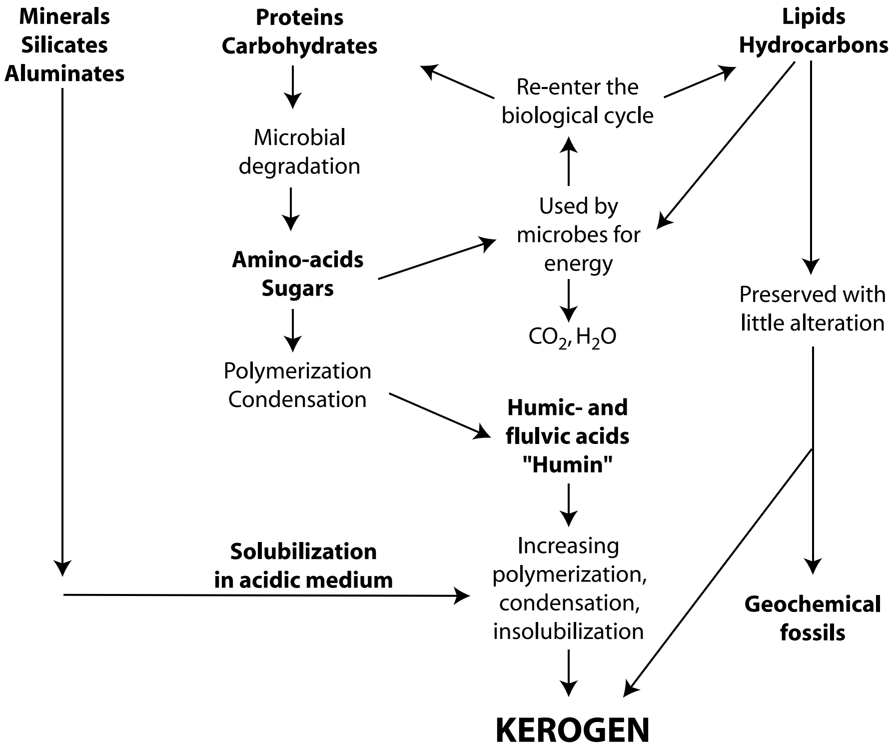

Figure 1.4: Evolution of organic matter to kerogen-geopolymer

geothermal heating in the subsurface. It is the most abundant form of organic carbon on Earth, about 1000 times more abundant than coal, which forms primarily from terrigenous remains of higher plants. Kerogen is a geopolymer that contains a high content of organics. Kerogen geopolymers generally occur in numerous forms: some have more organics and less inorganics, while others have the opposite. It is, however, evident that both inorganics and organics are required in a mix at a certain ratio, which will result in a geopolymeric structure. This geopolymeric structure exhibits a similar organization to human bone and teeth, typical inorganic-organic composites that show extreme durability and mechanical strength. The mechanism of geomacromolecule formation involves the crosslink reaction between the inorganic and organic materials.

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