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PROPERTIES OF GEOPOLYMER CEMENTS

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ABSTRACT

Geopolymer cement, high-alkali (K-Ca)-Poly(sialate-siloxo) cement, results from an inorganic polycondensation reaction, a so-called geopolymerisation yielding three dimensional zeolitic frameworks. High-tech Geopolymer K-Poly(sialate-siloxo) binders, whether used pure, with fillers or reinforced, are already finding applications in all fields of industry. These applications are to be found in the automobile and aeronautic industries, non-ferrous foundries and metallurgy, civil engineering, plastics industries, etc. Geopolymer cement hardens rapidly at room temperature and provides compressive strengths in the range of 20 MPa, after only 4 hours at 20°C, when tested in accordance with the standards applied to hydraulic binder mortars. The final 28-day compression strength is in the range of 70-100 MPa. The behaviour of geopolymeric cements is similar to that of zeolites and feldspathoids; they immobilize hazardous materials within the geopolymeric matrix, and act as a binder to convert semi-solid wastes into adhesive solids. Their unique properties which include high early strength, low shrinkage, freeze-thaw resistance, sulphate resistance and corrosion resistance, make them ideal for long term containment in surface disposal facilities. These high-alkali cements do not generate any Alkali-Aggregate-Reaction. Preliminary study involving ^{27}Al and ^{29}Si MASNMR spectroscopy and the proposed structural model, reveal that geopolymeric cements are the synthetic analogues of natural tecto-alumino-silicates.

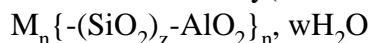
INTRODUCTION

In the aftermath of various catastrophic fires in France in 1970/73, it seemed useful to carry out research into new heat-resistant materials in the form of non-flammable and non-combustible «plastic materials». The geopolymers are the result of this research. My work and the developments carried out in the laboratories of our private research company since 1972, are on the creation of materials designed initially for state-of-the-art technology, and now for the whole industry, with spin-off in other fields such as the arts and archaeometry [1-2].

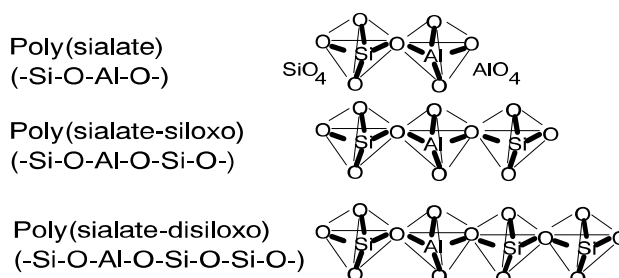
In 1978, looking for inorganic-polymer technologies, I was struck by the similar hydrothermal conditions which were controlling the synthesis of organic phenolic plastics on one hand, and of mineral feldspathoids and zeolites on the other hand. Both syntheses require high pH values, concentrated alkali, atmospheric pressure, and thermoset at temperatures below 150°C. However, zeolites were synthesized exclusively for use in the catalysis of organic compounds [3][4]. Since 1983, in USA, I had been involved in the development of new cementitious concepts involving geopolymeric chemistry. In recent years, new alkali activated inorganic cementitious compositions were commercially introduced into the US market by the American cement manufacturer Lone Star Industries, Inc. - under the brand name Pyrament® blended cements - which resulted from the development carried out on inorganic alumino-silicate polymers or Geopolymers [5,6]. It was only in 1986 that I became aware of the research carried out by Glukhovski & al. on the alkali-activation of granulated slag and on alkaline-soil cements[7]. A preliminary study undertaken in 1985 by the US Corps of Engineers, Vicksburg, described the potential applications of alkali-activated alumino-silicate cements [geopolymeric cements] in military operations [8]. The study based on tests carried out with geopolymeric concretes and data published in the East European literature [9,10] on alkali-activated blastfurnace slags, stressed the unique characteristics of geopolymer cements and alkaline soil-cements in terms of high early strength, high ultimate strength and adaptability in formulation and placement.

Apart from Applied Archaeological Sciences (research carried out at Barry University, Miami, Florida, in 1983-1990), the aim of our R. & D. long term program was not academic [11]. This explains why little scientific literature is available on the subject of geopolymers. The majority of references disclosing this application of mineralogy belongs to the patent-literature. This new generation of materials, whether used pure, with fillers or reinforced, is applied in all fields of industry. These applications are to be found in the automobile and aerospace industries, non-ferrous foundries and metallurgy, civil engineering, plastics industries, etc.

For the chemical designation of geopolymers based on silico-aluminates, poly(sialate) was suggested. Sialate is an abbreviation for silicon-oxo-aluminate. The sialate network consists of SiO_4 and AlO_4 tetrahedra linked alternately by sharing all the oxygens. Positive ions (Na^+ , K^+ , Li^+ , Ca^{++} , Ba^{++} , NH_4^+ , H_3O^+) must be present in the framework cavities to balance the negative charge of Al^{3+} in IV-fold coordination. Poly(sialates) have this empirical formula:



wherein M is a cation such as potassium, sodium or calcium, and «n» is a degree of polycondensation; «z» is 1, 2, 3 [12]. Poly(sialates) are chain and ring polymers with Si^{4+} and Al^{3+} in IV-fold coordination with oxygen and range from amorphous to semi-crystalline. Some related frameworks are displayed in Fig.1. The amorphous to semi-crystalline three dimensional silico-aluminate structures were christened «geopolymers» of the types:



Crystalline Poly(sialate) $\text{M}_n(-\text{Si-O-Al-O-})_n$ and Poly(sialate-siloxo) $\text{M}_n(-\text{Si-O-Al-O-Si-O-})_n$

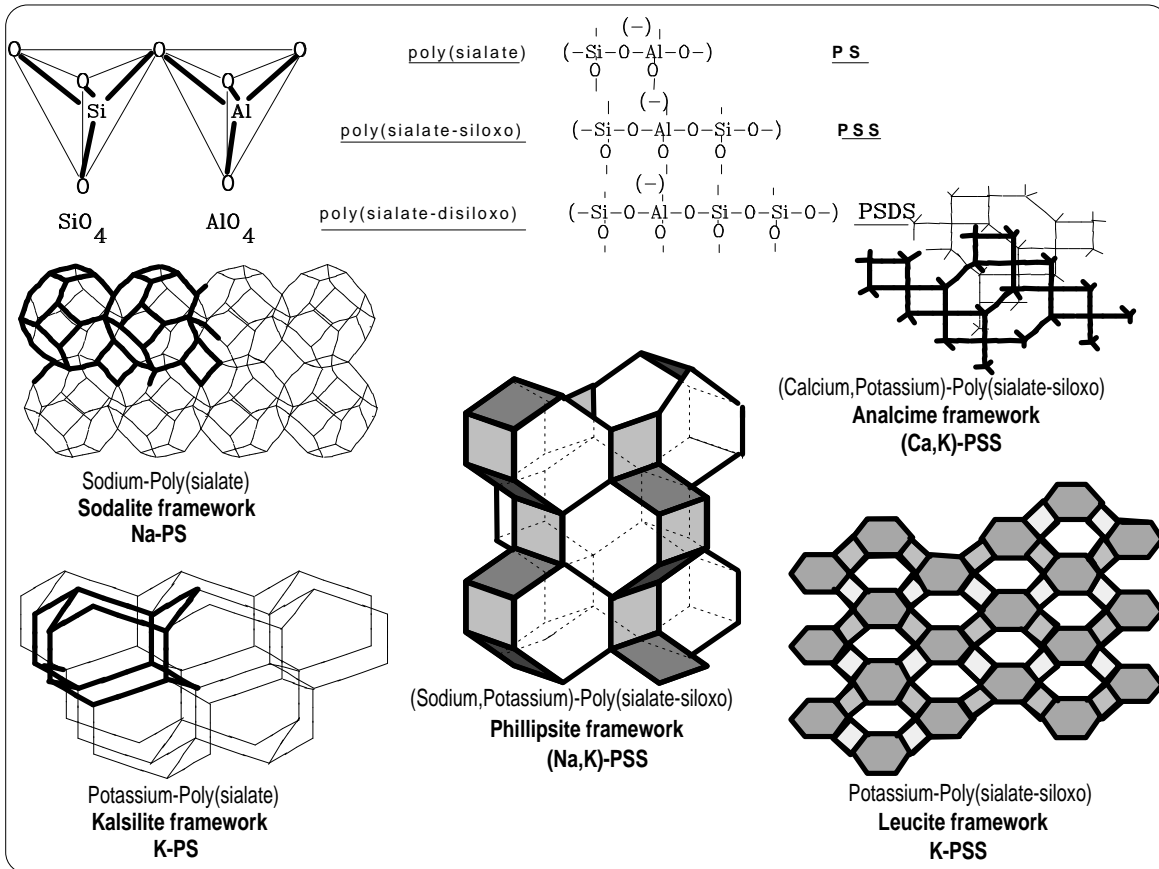


Fig. 1: Computer molecular graphics of polymeric M_n - $(\text{Si-O-Al-O})_n$ poly(sialate) and M_n - $(\text{Si-O-Al-O-Si-O})_n$ poly(sialate-siloxo), and related frameworks.

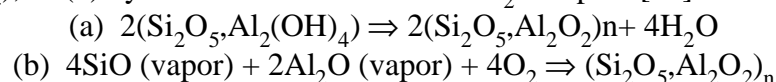
result from hydrothermal setting conditions. Yet geopolymer binders generally do not implement these hydrothermal conditions. Geopolymeric compounds involved in materials developed for industrial applications are non-crystalline (amorphous or glassy structure).

In the non-crystalline state, diffraction of X-rays results in a broad diffuse halo rather than sharp diffraction peaks. Several geopolymeric materials of practical interest like Geopolymer cements are non crystalline. Their structure cannot be investigated from X-ray diffractograms alone. Nuclear Magnetic Resonance (MAS-NMR) spectroscopy provides some insight into the molecular framework [13].

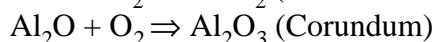
AMORPHOUS POLY(SIALATE-SILOXO) $(-\text{Si-O-Al-O-Si-O}-)$ BINDERS.

One hardening mechanism among others involves the chemical reaction of geopolymeric precursors such as alumino-silicate oxides (Al^{3+} in IV-fold coordination) with alkali polysilicates yielding polymeric Si-O-Al bonds. In order to emphasise the IV fold coordination of Al we usually write $(\text{Si}_2\text{O}_5, \text{Al}_2\text{O}_2)_n$ for these particular alumino-silicate oxides instead of $(2\text{SiO}_2, \text{Al}_2\text{O}_3)_n$.

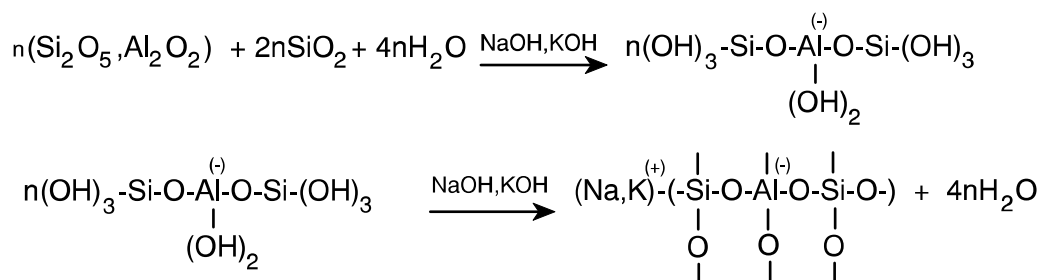
The fabrication of $(\text{Si}_2\text{O}_5, \text{Al}_2\text{O}_2)_n$ is carried out (a) by calcining alumino-silicate hydroxides $(\text{Si}_2\text{O}_4, \text{Al}_2(\text{OH})_4)$, or (b) by condensation of SiO and Al_2O vapors [14]:



with also production of:



Geopolymerisation is exothermic and can be schematised as follows. It may be considered as the result of the polycondensation of still hypothetical monomers, the orthosialate ions:



It has been assumed that the syntheses are carried out through oligomers (dimer, trimer) which provide the actual unit structures of the three dimensional macromolecular edifice.

X-ray diffraction

The (Na,K)-PSS and K-PSS which result from the polycondensation of various alkali-alumino-silicates present in Geopolymite® binders, are actually X-ray amorphous materials which are difficult to characterise. The X-ray diffraction patterns suggest however that (Na,K)-PSS, (Ca,K)-PSS and K-PSS consist of disordered frameworks of short-range order materials with structures similar to those of feldspatic glasses or crystalline zeolites. X-ray diffractograms for various K-PSS and (Na,K)-PSS samples are displayed in Fig.2. They show that the material has a diffuse halo peak at about 3.05-3.30Å (27-29° 2θmax, Cu Kα). Comparison of the values of 2θmax for

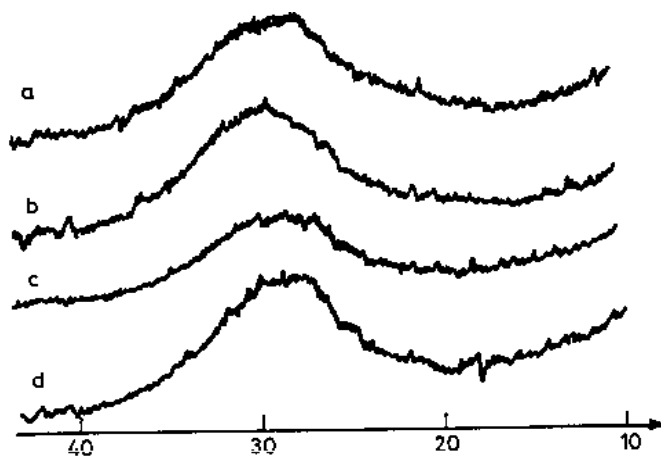


Fig. 2: X-ray diffractograms for (Na,K)-PSS and K-PSS binders.

(Na,K)-PSS and K-(PSS) with the values of the 2θmax diffraction peak for crystalline natural and synthetic framework silico-aluminates shows that (Na,K)-PSS and K-PSS binders are the amorphous equivalent of various tecto-alumino-silicates. The three-dimensional framework assigned to (Na,K)-PSS is Phillipsite and Leucite for the K-PSS geopolymers, respectively. Practical experience suggests that the formation of the Analcime framework necessitates the presence of soluble Ca⁺⁺ ions in complement to Na⁺ or K⁺ ions.

High-resolution Nuclear Magnetic Resonance, MAS-NMR spectroscopy

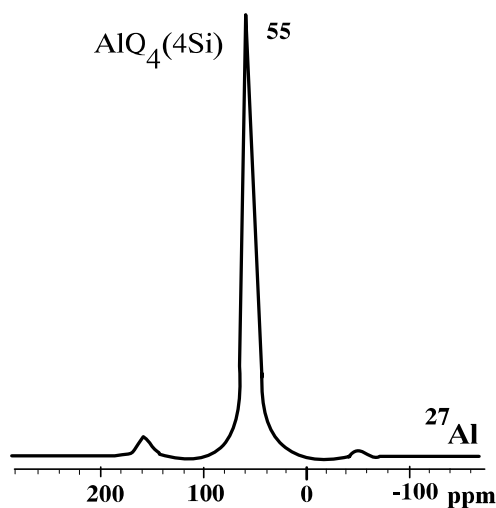
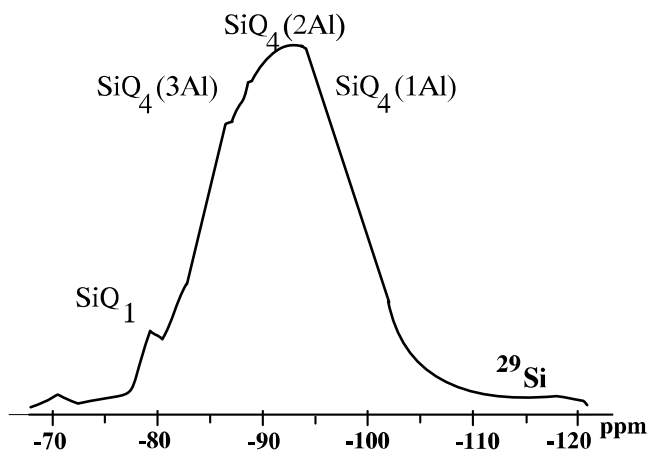
Magic-angle spinning MAS-NMR spectroscopy provides useful structural data for silico-aluminate species (zeolites, clays, ceramics, cements, geopolymers). In particular ²⁹Si and ²⁷Al MAS-NMR studies represent a very powerful tool [15].

²⁷Al MAS-NMR spectroscopy

Earlier investigations [16-18] showed that in aluminate anions, four-coordinated aluminium (with respect to oxygen) resonates at 60-80 ppm, and that in silico-aluminates, four-coordinated aluminium resonates at approximately 50 ± 20 ppm while six-coordinated aluminium resonates at about 0 ± 10 ppm from $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ (Tab.1).

Table 1: Al-coordination in silico-aluminates and ²⁷Al chemical shift:

Name	Formula	Coordination	Chemical shift (ppm)
K-Feldspar	KAlSi_3O_8	4	54
Muscovite	$\text{KAl}_3\text{Si}_3\text{O}_{11} \cdot \text{H}_2\text{O}$	6, 4	-1, 63
Biotite	$\text{K}(\text{Mg}, \text{Fe})_3\text{AlSi}_3\text{O}_{11} \cdot \text{H}_2\text{O}$	4	65
Calcium aluminate	$\text{Ca}_3\text{Al}_4\text{O}_7$	4	71
Sodium aluminate	NaAlO_2	4	76
Phillipsite	$(\text{K}, \text{Ca})\text{AlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$	4	55
K-Poly(sialate-siloxo)	$\text{KAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$	4	55

**Fig. 3: ²⁷Al MAS-NMR spectrum for K-PSS GEOPOLYMITE® binder****Fig. 4: ²⁹Si MAS-NMR spectrum for K-PSS GEOPOLYMITE® binder**

²⁷Al MAS-NMR spectroscopy of all (Na,K)-PSS and K-PSS showed ²⁷Al chemical shifts in the range of 55 ppm from $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ identical to the spectrum displayed in Fig.3, which indicates that the aluminium is of the $\text{AlQ}_4(4\text{Si})$ type and is tetrahedrally coordinated. 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)-PSS and K-PSS are true three-dimensional framework silico-aluminates with polymeric building units. However, ²⁷Al MAS-NMR cannot differentiate between the various frameworks proposed for geopolymeric materials based on poly(sialate) $(\text{Si-O-Al-O})_n$, poly(sialate-siloxo) $(\text{Si-O-Al-O-Si-O})_n$ or poly(sialate-disiloxo) $(\text{Si-O-Al-O-Si-O-Si-O})_n$ polymeric building units. This differentiation can be carried out with ²⁹Si MAS-NMR spectroscopy.

²⁹Si MAS-NMR Spectroscopy

As displayed in Fig.4, K-PSS gives a broad resonance at -94,5 ppm (-92 to -98) associated with a signal at -87 ppm, a small resonance at -81,5 ppm and a small peak at -79 ppm. The later resonance at

-79 ppm is narrow which means that it relates to an ordered environment different from the disordered main part of the matrix. Broad resonances are generally found in zeolitic gels, before crystallization of the zeolites. The resonances found for «disordered» ^{29}Si in K-PSS, namely -81,5 ppm, -87 ppm and -94,5 ppm (-92 to -98 ppm), can be assigned to $\text{SiQ}_4(4\text{Al})$, $\text{SiQ}_4(3\text{Al})$, $\text{SiQ}_4(2\text{Al})$ and $\text{SiQ}_4(1\text{Al})$ respectively. The narrow ^{29}Si shift at -79 ppm is related to nesosilicates (Q_0, Q_1), monomeric or dimeric silicates. Silico-aluminates with an atomic ratio $\text{Si}/\text{Al} > 2$ generally display several ^{29}Si resonances suggesting that the Si and Al tetrahedras are not regularly ordered along the polymeric chains. Tab.2 displays ^{29}Si MAS-NMR data for several natural and synthetic silico-aluminates which clearly show the presence of all $\text{SiQ}(n\text{Al})$ sites within the frameworks. On the other hand, silico-aluminates with atomic ratio $\text{Si}/\text{Al}=1$, only exhibit $\text{Si}(4\text{Al})$ sites.

Table 2: ^{29}Si MAS-NMR spectra of zeolitic species (excerpt from [18])

Zeolite	Formula	Si/Al	^{29}Si chemical shifts (ppm from TMS)				
			Si(4Al)	Si(3Al)	Si(2Al)	Si(1Al)	Si(0Al)
Zeolite A	$\text{NaAlSiO}_4 \cdot \text{H}_2\text{O}$	1.0	-88.9	-	-	-	-
Analcime	$\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$	2.0	-	-92.0	-96.3	-101.3	-108.0
Leucite	KAlSi_2O_6	2.0	-81.0	-85.2	-91.6	-97.4	-101.0
Sodalite	$\text{NaAlSiO}_4 \cdot \text{H}_2\text{O}$	1.0	-84.8	-	-	-	-

The K-PSS ^{29}Si MAS-NMR spectrum suggests that the structural model of K-PSS (Fig. 5) could be assigned to hydrated Leucite, in agreement with the proposed chemical mechanism suggested in earlier studies.

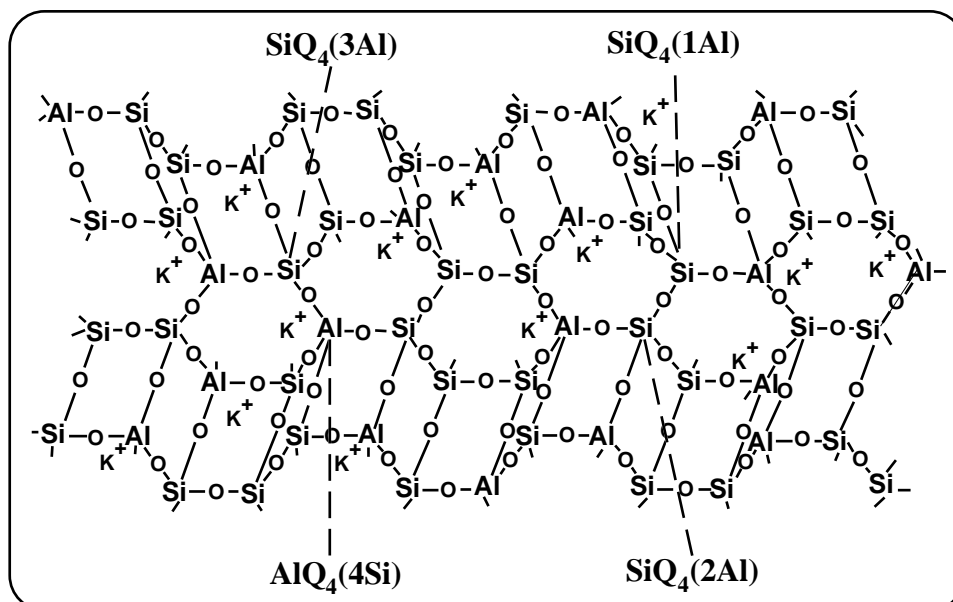


Figure 5: Proposed structural model for K-Poly(sialate-siloxo) Geopolymer.

AMORPHOUS (K-CA) (Si-O-Al-O-Si-O-) POLY(SIALATE-SILOXO) CEMENT.

Geopolymer cements are acid-resistant cementitious materials (trade names PZ-Geopoly® and Geopolycem®), with zeolitic properties, developed in Europe by our group of companies «GEOPOLYMER». Geopolymerization involves the chemical reaction of alumino-silicate oxides (Al^{3+} in IV-V fold coordination), with alkali and calcium polysilicates, yielding polymeric

Si-O-Al bonds, for instance:

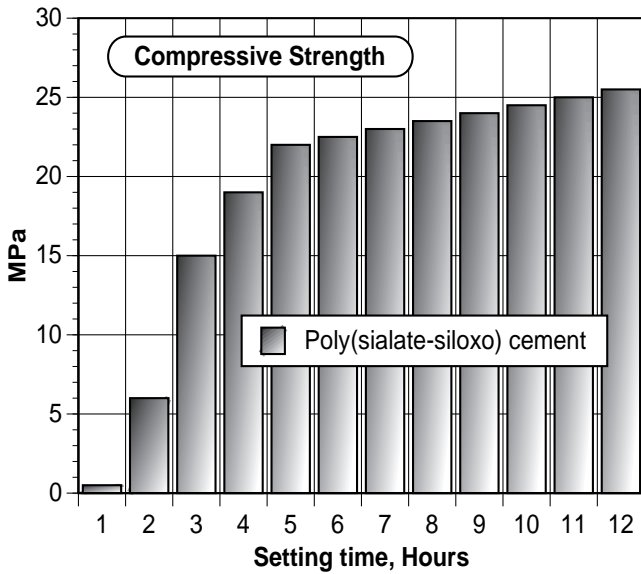
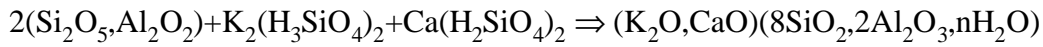


Figure 6: Room temperature setting for concretes made of (K-Ca)-Poly(sialate-siloxo), PZ-Geopoly® cement.

Tailored alumino-silicate geopolymeric PZ-Geopoly® cement [19] comprises major compounds, namely:

- specific alumino-silicates of the kaolinitic clay species, calcined at 750°C;
- alkali-disilicates $(\text{Na}_2, \text{K}_2)(\text{H}_2\text{SiO}_4)_2$
- calcium disilicates $\text{Ca}(\text{H}_2\text{SiO}_4)_2$ produced by the alkali-reaction with blastfurnace slag
- silica fume from ferro-silicon.

This cement hardens rapidly at room temperature and provides compressive strength in the range of 20 MPa, after only 4 hours at 20°C, when tested in accordance with the standards applied to hydraulic binder mortars. The final 28-day compressive strength is in the range of 70-100 MPa, (see Figure 6).

MAS-NMR Spectroscopy

The use of MASNMR Spectroscopy (Magic Angle Spinning Nuclear Magnetic Resonance) for the structural determinations of alkali-activated cements is still in its earliest stages. Nevertheless the technique is a very powerful one. Our preliminary study involving ^{27}Al MASNMR, singular peak at 54 ppm, $\text{AlQ}_4(4\text{Si})$ unit, and ^{29}Si MASNMR, major band at -92 ppm, $\text{SiQ}_4(2\text{Al})$ unit, small band at -78 ppm, SiQ_0 unit, band at -115 ppm related to un-reacted silica-fume

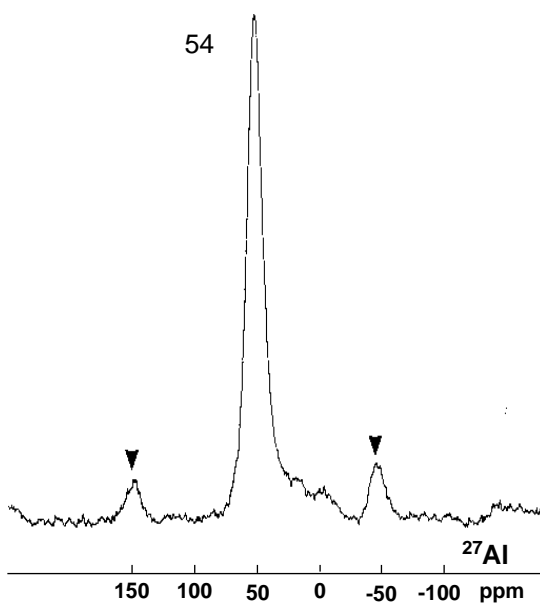


Figure 7: ^{27}Al MASNMR for (K-Ca)-Poly(sialate-siloxo) Geopolymer cement.

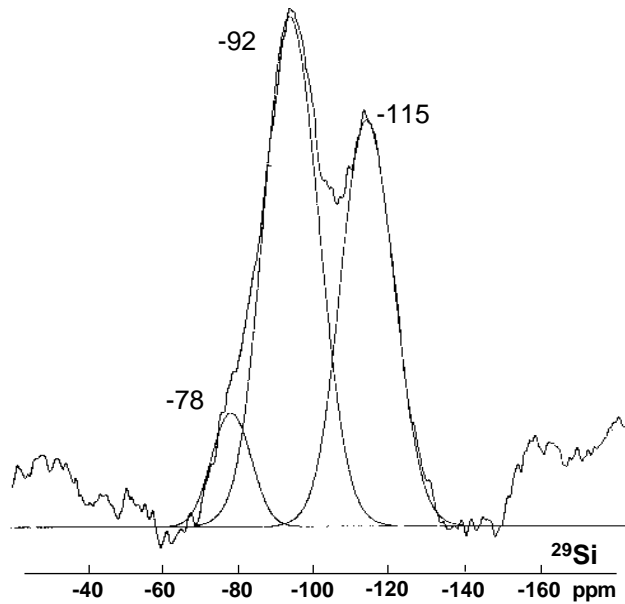


Figure 8: ^{29}Si MASNMR for (K-Ca)-Poly(sialate-siloxo) Geopolymer cement.

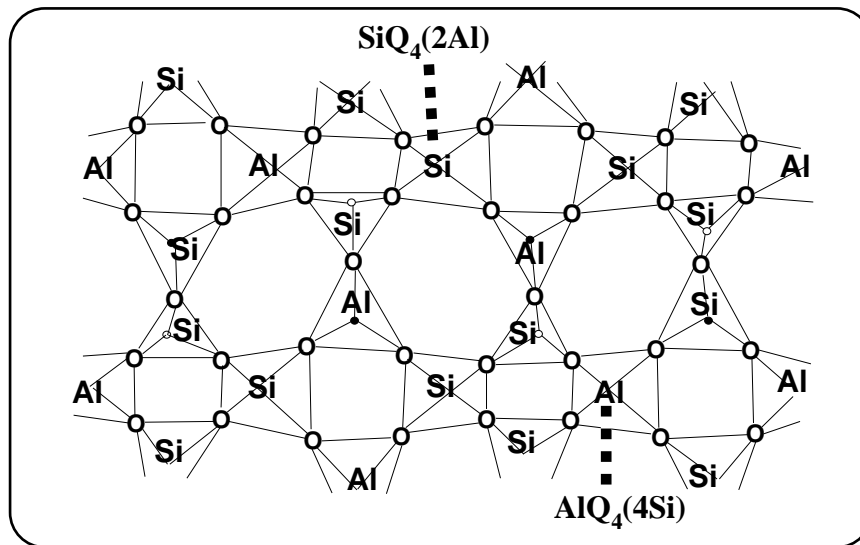


Figure 9: proposed structural model for (K-Ca)-Poly(sialate-siloxo) cement

(SiO_2), (see Fig. 7, 8) and the proposed structural model (Fig. 9) reveal that geopolymeric cements are the synthetic analogues of tecto-alumino-silicates. Tab. 4 compares the chemical make up of some natural tecto-alumino-silicates like Italian pozzolan, Rhineland trass (a pozzolanic material found in Germany) and geopolymer cement PZ-Geopoly®.

Table 4: Oxides and Alkali content, % by weight, in (K-Ca)-Poly(sialate-siloxo) PZ-Geopoly® cement and natural tecto-alumino-silicates (pozzolans).

	PZ-Geopoly	Pozzolan	Rhineland Trass
SiO_2	59.16	54	57
Al_2O_3	17.58	19	20
CaO	11.1	10	6
MgO	2.93	1.5	2
$\text{K}_2\text{O}, \text{Na}_2\text{O}$	9.2	10.6	7

BLENDING PORTLAND/GEOPOLYMER CEMENT

The original concept of the American high early strength cement Pyrament® was to take advantage of the good properties of Geopolymer cement with the low cost manufacture of Portland cement. The Pyrament® cement which was ultimately developed is very close to alkali-activated pozzolanic cement [20]. Pyrament® cement comprises 80% OPC and 20% geopolymeric materials, activated with potassium carbonate and retarded with citric acid.

MAS-NMR spectroscopy of fully hydrated Pyrament® blended cements is displayed in Fig. 16 and Fig. 17. ^{27}Al spectrum shows the expected 3 ppm peak of the hydrated Portland phase and the additional 54 ppm peak related to the Geopolymer phase. In the ^{29}Si spectrum, the hydrated Portland phase provides the SiQ_0 and SiQ_1 units typical for CSH, respectively at -76 ppm and -81 ppm, whereas the additional broad band between -85 ppm and -100 ppm characterises SiQ_4 units like those found in tecto-alumino-silicates, i.e. Geopolymer cement.

PROPERTIES OF GEOPOLYMER CEMENTS

Toxic waste management

Zeolitic materials are known for their abilities to adsorb toxic chemical wastes. Geopolymers behave similarly to zeolites and feldspathoids. They immobilise hazardous elemental wastes within the geopolymeric matrix, as well as act as a binder to convert semi-solid waste into an adhesive solid. Hazardous elements present in waste materials mixed with geopolymer compounds are «locked» into the three dimensional framework of the geopolymeric/zeolitic matrix.

Geopolymeric cements designed for waste containment provide early-high strength development which can be enhanced with the adjunction of microwave preheating devices aimed at raising the inside temperature of the waste form up to 30-35°C. Following curing at room temperature yields solid, monolithic, high-strength (100 MPa compressive strength) Geopolymer waste forms. Ambient temperature processing of Geopolymer based waste forms deals essentially with the safe and innocuous disposal of toxic and hazardous wastes and mine tailings. The method involves producing an innocuous material with improved strength and acid resistance.

Many of the contaminated soils contain both inorganic and organic toxic compounds. For wastes with both of these hazards (mixed-wastes), in situ immobilization offers the one-step treatment advantages of speed and economy. According to Dole [21], without any treatment, such hazardous materials require a special landfill with double plastic-and-clay liners and leachate collection systems. These lined hazardous waste landfills are difficult and expensive to install. Also, they require long-term monitoring (30 years) and show high rates of failure in the first decade. On the other hand, geopolymer monoliths are easier to install and are maintenance free. Monitoring becomes inconsequential because the geopolymeric materials conduct no measurable amounts of water (Table.5).

Table 5: Permeability values in cm/s:

sand	10^{-1} to 10^{-3}
clay	10^{-7}
granite	10^{-10}
Fly Ash cement	10^{-6}
Portland cement	10^{-10}
Geopolymer cement	10^{-9}

Also, the binding matrices control the maximum credible concentrations of hazards in the leachates and keep them below known health effect levels. In addition, geopolymer monoliths can hold the hazards below the detection limits of analytical methods.

Immobilization technologies with geopolymeric materials [22-26] have three goals.

The first goal is to seal the hazardous materials into an impermeable monolith. This prevents the direct contact of potential leachates, like ground water and percolating rain. Conventional cheap inorganic binders, soluble silicate based, Portland cement based, fly-ash-lime based, are unsuited for solidification of various industrial wastes, particularly those containing:

- sodium salts of arsenate, borate, phosphate, iodate and sulphides;
- salts of magnesium, tin, zinc, copper, lead.

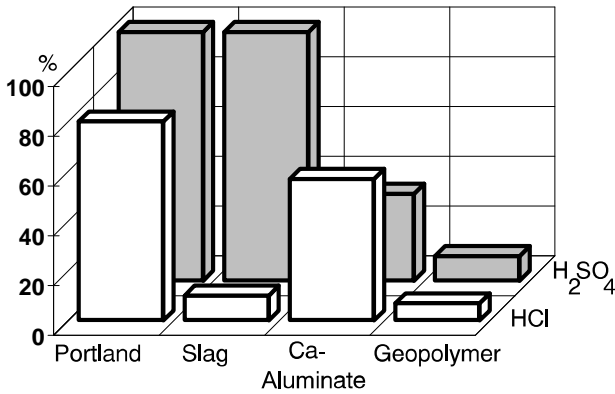


Figure 11: Break up in acidic environment (5% acid solutions) for Portland cement, blended slag/Portland, Ca-aluminate cement and Poly(sialate-siloxo) cement.

Conventional inorganic binders are also unsuited for solidification of end-product residues with high sulphide contents. These mineral and organo-metallic wastes generate sulphuric acid which leaches out heavy metals. Unlike conventional Portland cement, geopolymeric cements do not rely on lime and are not dissolved by acidic solutions (Fig. 11). Portland based cements (plain and slag blended) are destroyed in acidic environment. Calcium aluminate cement is expensive to produce, and does not behave satisfactorily, having 30 to 60% of weight loss (destruction). Geopolymeric cements, Potassium-Poly(sialate-siloxo) type, Geopolymite®, remain stable with a loss in the 5-8 % range.

The second goal is to design a solid matrix that binds the specific hazardous elements. This reduces the mobility of the hazards within the monoliths. A research program on toxic waste stabilisation was funded by CANMET Canada (1988) (Canada Centre for Mineral and Energy Technology) [27]. Fig. 12 and Fig. 13 display examples of the results obtained at Ontario Research Foundation (Canada) on the innocuous solidification and stabilisation of non-metallic and uranium mining tailings. These testing procedures, used in the fundamental research program were conducted in accordance with the Government of Ontario Ministry of Environment regulatory standards (Regulation 309); they represent “worst case” scenarios. Reg. 309 specifies that the solid is pulverized in order to expose a maximum surface area to the acidic solutions, and leached in solutions of acetic acid, 24 hours at constant pH 5, which represents an environment far more harsh than any which will be encountered in natural conditions.

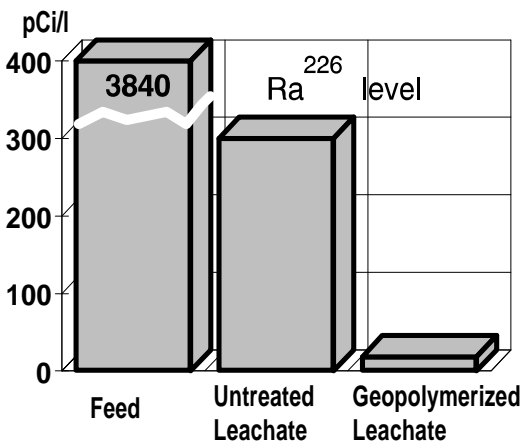


Figure 12: Radium level in uranium waste tailing (acid leaching, constant pH 5, Reg. 309), K-PSS type Geopolymite® binder.

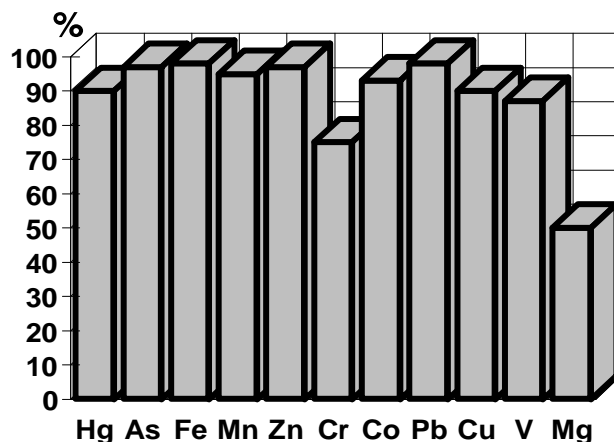


Figure 13: Efficiency of geopolymeric cements, % of trapped heavy metal

The pollutants have become locked into the three dimensional geopolymeric-zeolitic framework.

Acid-resistant geopolymeric containment has been shown to greatly minimize the leaching of iron, cobalt, cadmium, nickel, zinc, lead, arsenic, radium and uranium.

The third goal is to make a durable monolith that weathers environmental stresses. Using ancient building materials from Rome and earlier civilisations as models, we are able to formulate durable, impermeable monoliths which will endure at least 2,500 to 5,000 years of weathering. In the types of consolidation known in the prior art, the hazardous waste is agglomerated with Portland cement or silicate binders or lime blended fly ashes, and it is assumed that the matrix will not deteriorate. Yet, comparative studies of restorations performed on archaeological buildings dating from the Roman time show that modern Portland cement is strongly affected by aggressive climatic conditions and does not last more than 50 years, whereas Roman mortars are unaffected, even after more than 2000 years. Our studies performed at the Institute for Applied Archaeological Sciences, Barry University, Florida, USA, have demonstrated that the pozzolanic formulation used by the Romans, involved a geopolymeric setting, yielding zeolitic material. Older mortars were studied, such as the lime mortars of Jericho and Tell-Ramad, dating as far as 7000 BC, and which contain up to 40% by weight of analcime zeolite. Ancient concretes and mortars demonstrate the exceptional durability of zeolitic cements, analogous to synthetic geopolymers discussed here, and are indicative of the erosion resistance which can be expected of modern geopolymeric cements.

Acid-resistant geological barriers.

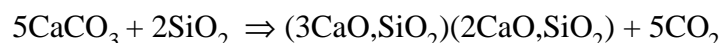
The rapid hardening geopolymeric cement develops compressive strengths higher than 15-20 MPa as early as after 4 hours at 20°C. The final 28-day compression strength is in the range of 70-100 MPa.

The potential applications involve:

- massive concrete panels or grouts,
- fiber reinforced sheets, with high-tech or low-tech fibers and fabrics reinforcements,
- expanded (foam) panels or grouts.

Geopolymeric concretes and the «Green-House» Global-Warming Challenge

Exhaustive discussions on this interesting topic are to be found in the literature [28, 29]. Planned CO₂ related energy taxes are focusing essentially on fuel consumption, not on actual CO₂ emission measured at the chimneys. Ordinary Portland cement results from the calcination of limestone (calcium carbonate) and silica according to the reaction:



The production of 1 tonne of cement directly generates 0.55 tonnes of chemical-CO₂ and requires the combustion of carbon-fuel to yield an additional 0.40 tonnes of CO₂.

To simplify: 1 T of cement = 1 T of CO₂.

Discussions with representatives of the cement industry confirmed that taxation based only on fuel consumption would lead to a cement price increase of 20%, whereas taxation based on actual CO₂ emission would multiply cement price by 1.5 to 2. The 1987 1 billion metric tonnes world production of cement accounted for 1 billion metric tonnes of CO₂, i.e. 5% of the 1987 world CO₂ emission. This was equivalent to the CO₂ generated by the entire Japanese industrial activity. In

developing countries, the increase in cement production has followed an exponential trend since the seventies, contrasting sharply with western countries (USA, EC) where cement production remains constant. Under these conditions, a world-wide freeze of CO₂ emission at the 1990 level as recommended by international institutions, could easily be conceived in western countries but, in contrast, is incompatible with the extremely high cement development needs of less industrialised countries. With the assumption that Europe (EC) and USA will commit themselves to such a freeze, developing countries' cement production will continue to grow and become one of the major sources of CO₂ emission, as shown by Table 6.

Table 6: BaU values for World Cement-CO₂ with 2.5% and 5% yearly increase and «frozen» Europe (EC) total CO₂ emission at 1990 level, million metric tonnes (MT.)

year	1990	2000	2015
Europe (EC) total CO ₂ (freeze)	3500	3500	3500
2.5% World Cement CO ₂ increase	1100	1410	1950
5% World Cement CO ₂ increase	1100	1800	3500

Present cement production growth ranges from 5% (China, Japan) to 16% (Korea, Thailand) and suggests an average growth ratio in favour of the 5% increase scenario. In 25 years from now, world cement CO₂ emissions could equal the 3,500 million tonnes total CO₂ production of Europe (EC), -industry+energy+transportation -, or 18% of present world CO₂ emission. This addresses the need for a drastic change in the cementitious systems involved in the utilization of concrete, through the manufacture of new types of cement which do not rely on the calcination of limestone (and accompanying release of CO₂). The geopolymeric reaction



yields low-CO₂ cementitious materials providing similar or even better properties than current high-CO₂ Portland cement.

Comparison between CaO, Na₂O and K₂O cementitious systems.

The molecular units of any cement are the (SiO₄) and (AlO₄) tetrahedra. From a molecular weight point of view, and for the simplification of the following demonstration, it is useful to assimilate (AlO₄) tetrahedra with (SiO₄). Their molecular weights are respectively 91 and 92, i.e. equivalent. Portland cement is based on the hydration of the calcium silicate yielding a molecular structure based on 3 CaO for 1 (SiO₄), precisely 2.7 CaO (1.7CaO + 1 Ca(OH)₂). Geopolymeric cement of the poly(sialate-siloxo) type, (Na,K)-PSS, comprises a structure based on 1 Na₂O for 6 (SiO₄) equivalent, [one Na⁺ for one (Si-O-Al-O-Si-O-) unit]. Same is the case for potassium-based geopolymeric cement which has a structure based on 1 K₂O for 6 (SiO₄).

Table 7 compares the amount of (SiO₄) produced with one oxide mole CaO, Na₂O, K₂O, and the amount of cement produced with 100g of oxide, respectively. Portland plain means regular ordinary Portland cement. Portland blended 50/50 results from the addition of 50% blastfurnace slag. The oxide CaO refers only to the Portland part. *In the present demonstration, the CaO introduced by slag is not integrated into the calculation. In terms of energy and carbon-dioxide emission, the by-product slag provides a beneficial dilution factor.* Geopolymeric binders and cements are of 3 types. Reference 1 relates to a binder called Geopolymite® 50, successfully tested for the containment of hazardous and radioactive wastes. References 2 and 3 relate to new cements PZ-Geopoly®, also dedicated to environmental purposes, with high-early strength. The calcium cation, which reacts chemically with the other geopolymeric ingredients, originates from

blastfurnace slag. As explained above, it is not integrated in the present calculation.

- Na-PSS 1 refers to Na-(Si-O-Al-O-Si-O-)
 K-PSS 1 refers to K-(Si-O-Al-O-Si-O-)
 Na-PSS 2 refers to the compound (0.6Na,0.2Ca)-(Si-O-Al-O-Si-O-)
 Na-PSS 3 refers to the compound (0.4Na,0.3Ca)-(Si-O-Al-O-Si-O-)
 K-PSS 2 refers to the compound (0.6K,0.2Ca)-(Si-O-Al-O-Si-O-)
 K-PSS 3 refers to the compound (0.4K,0.3Ca)-(Si-O-Al-O-Si-O-)

Table 7: Amount of (SiO₄) produced with one oxide mole CaO, Na₂O, K₂O, and amount of cement produced with 100g of oxide, for Portland-based cements, geopolymeric binders and cements (Geopolymite® 50 and PZ-Geopoly®), respectively.

cement type		oxide	(SiO ₄)	100g oxide yield
Portland cement	plain	CaO	0,3	155g
	blended	CaO	0,6	310g
Geopolymite® binders	Na-PSS 1	Na ₂ O 1	6	990g
	K-PSS 1	K ₂ O 1	6	687g
PZ-Geopoly® cements	Na-PSS 2	Na ₂ O 2	10	1650g
	Na-PSS 3	Na ₂ O 3	15	2475g
	K-PSS 2	K ₂ O 2	10	1145g
	K-PSS 3	K ₂ O 3	15	1717g

Another interesting fact arises on comparing the amount of cements which can be manufactured with an allowance of 100g chemical-CO₂ emission. Under the assumption that the production process for all oxides involves the calcination of carbonates, such as calcium carbonate (limestone) CaCO₃, sodium carbonate (soda) Na₂CO₃, potassium carbonate (potash) K₂CO₃, it becomes interesting to calculate the theoretical yield for 100g chemical-CO₂ emission. This unique comparison, displayed in Fig. 14, highlights the extraordinary potential of the geopolymeric mechanism. In terms of identical carbon-dioxide emission, the geopolymer chemistry enables the manufacture of 5 to 10 times more cement than portland technology, with similar investment and lower energy cost. Introducing geopolymeric cements, not only for environmental uses, but also in construction and civil engineering, would reduce carbon-dioxide emission caused by the cement and concrete industries by 80 to 90%. This perspective would allow an unlimited development in the Third World.

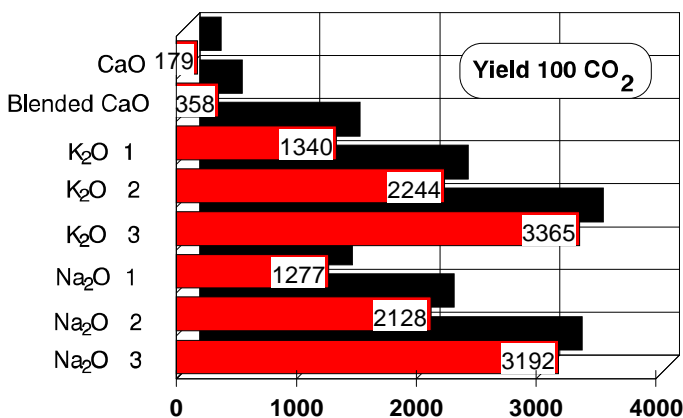


Figure 14: Theoretical yield for cements produced with an allowance of 100g chemical-CO₂ emission, for each oxide CaO, Na₂O, K₂O (see Table 7 for legends).

DISCUSSION: Alkali-Aggregate Reaction and MASNMR Spectroscopy

Alkali-Aggregate-Reaction

The fostering of alkali-based cements means a dramatic change in the research and development presently carried out in Western countries[30]. Alkalis are generally thought of as the cause of deleterious Alkali-Aggregate-Reaction. As a consequence, the tendency has been to avoid any addition of alkali in O.P.C. and commonly to require from the cement manufacturers the supply of low-alkali cements. On the other hand, papers by Mehta [31], Davis & al. [32], Mindess and Young [33] and Roy [34] have shown that the addition of alkaline natural pozzolans (potassium or sodium aluminosilicates) substantially reduces the Alkali-Aggregate-Reaction of high-alkali cements.

Expansion (mm/m)

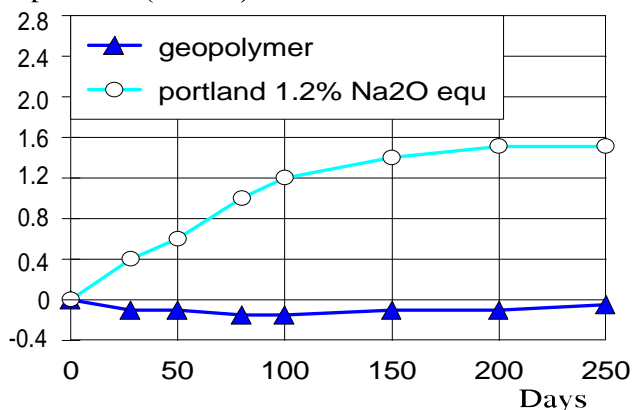


Figure 15: Alkali-Aggregate Reaction; ASTM C227 bar expansion for Poly(sialate-siloxo) Geopolymer cement and ordinary Portland Cement

Sersale and Frigione [35] went further by suppressing the Alkali-Aggregate-Reaction with the addition of zeolites (alkali-aluminosilicates), such as chabazite and phillipsite. Finally, Haekkinen [36], Metso [37], Talling and Brandstetr [38] are claiming that alkali-activated aluminosilicate binders, alkali-activated slags, do not generate any Alkali-Aggregate-reaction. Fig. 15 displays the results of the tests carried out according to ASTM C227 bar expansion on Poly(sialate-siloxo) cement and O.P.C..

Geopolymer cements, even with alkali contents as high as 9.2%, do not generate any dangerous alkali-aggregate reaction.

MASNMR Studies of Alkali-activated Portland Cements and High-alkali Geopolymeric cements.

The action of the alkalis is uncertain and the effects of such factors as concentration gradients, kinetic of nucleation, alkali migration are not fully understood. However, recently some progress has been made through the use of Magic Angle Spinning Nuclear Magnetic Resonance (MASNMR), by collecting data on the structure of alkali-activated calcium-silicates (Portland cement), alkali-activated aluminosilicates (Geopolymer) and alkali-activated Geopolymeric blended cements [19, 39, 40]. In 1982 Lippmaa and his colleagues followed the hydration of tricalcium silicate with ²⁹Si MASNMR [41]. Other papers by Young [42], Hjorth & al. [43], Rodger & al. [44], showed that the kinetics of SiO₄ polymerization which occurs during the hydration of tricalcium silicate follows a series of well-defined steps starting from the monomer (Q₀), followed closely by the formation of dimer (Q₁) and later by a more complex trimer/tetramer (Q₂) and expected finite linear polymeric chain.

Preliminary ²⁷Al MASNMR investigations of the hydration of Portland cement by Hjorth & al. [43] and following paper by Skibsted [45] have shown that it is possible to follow the hydration of the calcium aluminate species, 4-coordinated AlQ₀ into 6-coordinated AlO₆, in spite of the low

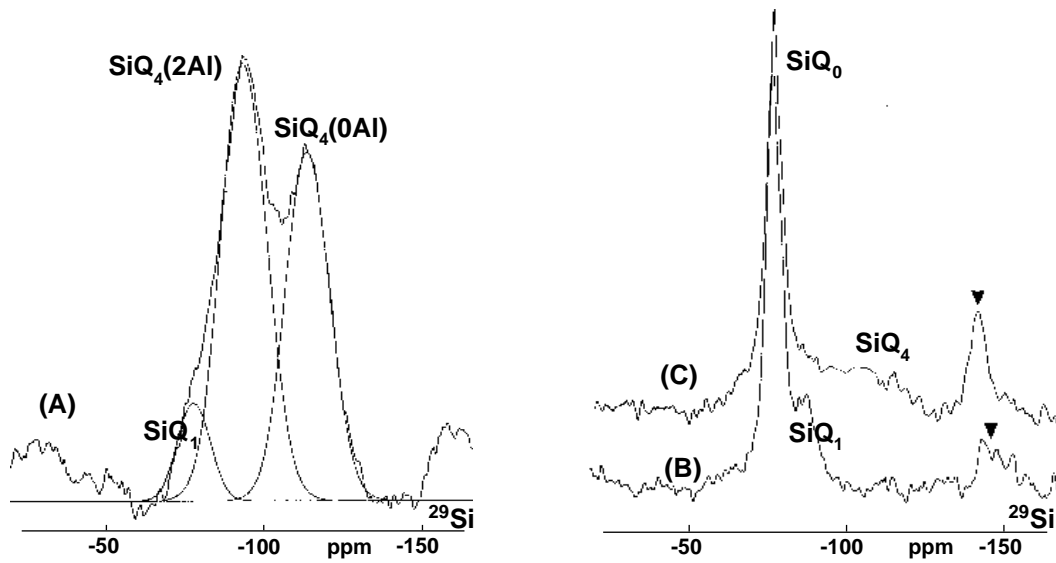
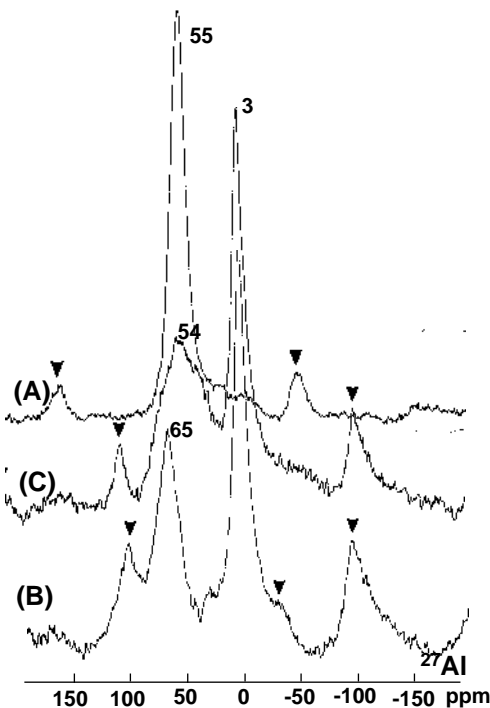


Figure 16: ²⁹Si MASNMR for (K-Ca) Poly(sialate-siloxo) PZ-Geopoly® cement (A), alkali-activated Portland cement (K₂O= 3.5%) (B), Pyrament® cement (K₂O= 3.5%) (C), after hydration and hardening.

Al content. Alkali-activated O.P.C. has two distinct ²⁷Al chemical shifts, one in the range of 65 ppm, which indicates that the aluminium is tetrahedrally coordinated and is of the AlQ₃(3Si) type, and the second in the range of 0 ppm typical for hydrated 6-coordinated AlO₆ compounds (Fig.



17). Recent published study shows a similar effect in alkali-activated slag [46]. The intensity of the AlQ₃(3Si) resonance at 65 ppm is a function of the alkali concentration which indicates that the alkali cations are less involved in the formation of the AlO₆ hydrate species but rather are taking part in the formation of the Al substituted C-S-H-compounds. The free hydroxyl ions of the AlQ₃(3Si) structural unit could be responsible for the alkali ion concentration found in the pore fluid of concrete and for the deleterious alkali-aggregate reaction. The addition of selected synthetic alumino-silicates [19], essentially those displaying ²⁷Al MASNMR resonance in the range of 20-50 ppm, transformed any AlQ₃(3Si) units into stable AlQ₄(4Si) geopolymeric unit with 55 ppm ²⁷Al resonance.

Figure 17: ²⁷Al MASNMR for (K-Ca) Poly(sialate-siloxo) PZ-Geopoly® cement (A), alkali-activated Portland cement (K₂O= 3.5%) (B), Pyrament® cement (K₂O= 3.5%) (C), after hydration and hardening.

Table 8: Al-coordination, ²⁷Al chemical shift and AlQ_n units, in alkali-activated cements and Poly(sialate-siloxo) cement.

Name	Coordination	Chemical shift (ppm)	AlQ _n
K-PSS Geopolymer	4	55	AlQ ₄ (4Si)
(K,Ca)-Geopolymeric cement	4	55	AlQ ₄ (4Si)
Alkali-activated Portland Cement	6, 4	66, 3	AlQ ₃ (3Si)
Alkali-activated Pyrament cement	6, 4	54, 3	AlQ ₄ (4Si)
Alkali-activated synthetic slag	6,4	65, 3	AlQ ₃ (3Si)

TERMINOLOGY: GEOPOLYMER VS. ALKALI-ACTIVATED ALUMINO-SILICATE

We mentioned above that, because alkalis are generally thought of as the cause of alkali-aggregate-reaction, the present tendency is to avoid any addition of alkali in ordinary Portland cement. According to the terminology generally in use by cement scientists and concrete experts, both cementitious systems discussed above in terms of the relationship between alkali-aggregate-reaction and ^{27}Al MASNMR spectroscopy, should be named «alkali-activated cements» [47]. Yet, the cement which resonates at 55 ppm, $\text{AlQ}_4(4\text{Si})$ building units (Fig.17 and Table 8), does not generate any deleterious alkali-aggregate-reaction (Fig. 15, ASTM C227 bar expansion test), whereas the cement which resonates at 66 ppm, $\text{AlQ}_3(3\text{Si})$ building units, reacts with susceptible silica. In addition, in the first cement category, the SiO_4 tetrahedrons are of the three-dimensional cross-linked framework (Q_4) type, $\text{SiQ}_4(3\text{Al})$ - $\text{SiQ}_4(2\text{Al})$ - $\text{SiQ}_4(1\text{Al})$ (Fig. 16), and are essentially different from the $\text{Si}(\text{Q}_0)$, $\text{Si}(\text{Q}_1)$, monosilicate and disilicate structures of calcium silicate hydrates, which are the main constituents of the second alkali-activated Portland cement category. It becomes obvious that the terminology in use generates confusion and is a severe obstacle for any further beneficial scientific and commercial developments of alkali cementitious systems.

The concept of Geopolymer and Geopolymerization is well accepted in the science and technologies involving advanced materials. Geopolymers result from the polycondensation of polymeric aluminosilicates and alkali-silicates, yielding three-dimensional polymeric frameworks. Cement scientists should admit that cements involving alkali contents of 9.2% and higher, which do not generate any dangerous alkali-aggregate reaction, cannot comply with the existing codes and guidelines and should get a distinct appellation. To call them Geopolymer cements or Geopolymeric cementitious compounds or Poly(sialate) cements, focuses on their unique properties without being confused with regular alkali-activated Portland cements.

CONCLUSION

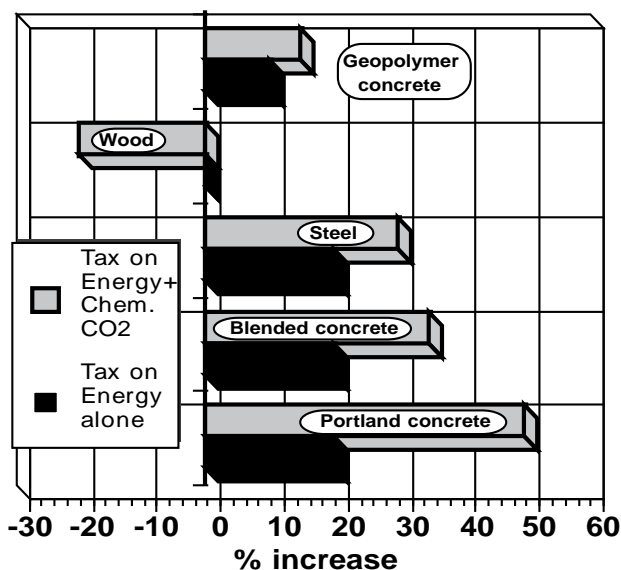


Figure 18: Estimated increase or decrease of production costs for construction materials, due to planned Eco-taxes on Energy alone or on actual CO_2 emissions (Energy+Chem. CO_2).

Eco-taxes, when applied, would have a major impact on the evolution of production costs for construction materials. Fig. 18 displays our estimation for Portland cement based concretes (50% increase in costs), to be compared with other materials such as steel (30% increase), wood (20% decrease) and Geopolymer cement based concretes (15% increase). Wood absorbs carbon-dioxide and it is likely that this material might be subsidised and get reduction in costs as high as 30%.

According to the US Corps of Engineers «..alkali-activated aluminosilicate binders (cements) have the potential to become the best and in many cases the most economical binder for routine construction and may evolve into a

new generation of building materials». Geopolymer cements are manufactured in a different manner than that of Portland cement. It does not require extreme high temperature kilns, with large expenditure of fuel, nor does it require such a large capital investment in plant and equipment. Thermal processing of naturally occurring alkali-silico-aluminates and alumino-silicates (geological resources available on all continents) provides suitable geopolymeric raw-materials. The author is involved in the European programs GEOCISTEM which is presently fostering the industrial development of this geological route, and seeks to manufacture cost-effectively cements for applications dealing primarily with the long term containment of hazardous and toxic wastes. The technology reduces also the energy consumption during cement manufacturing. Introducing these low-CO₂ geopolymeric cements, not only for environmental uses, but also in construction and civil engineering, would reduce CO₂ emission caused by the cement and concrete industries by

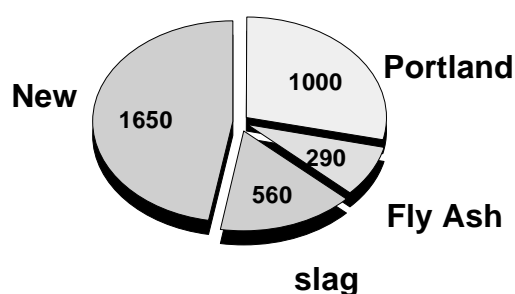


Figure 19: Distribution of BaU world cement market for the year 2015, total 3500 million tonnes, assuming Portland world production frozen at 1990 level.

80%. In year 2015, assuming that world Global Climate treaties might authorise an amount of Portland clinker production in the order of 1000 million tonnes (frozen world production capacities for 1990) to be blended with 290 million tonnes of fly ash and 560 million tonnes of granulated slag, the complementary need for new low-CO₂ cementitious materials, in the range of 1650 million tonnes, would be easily covered by these novel cements and would allow an unlimited development of concrete infra-structures in our Global Economy (Fig. 19) (see further developments on this topic in

references [28-29]).

*) Geopolymite, Geopolycem, PZ-Geopoly are trademarks of Cordi-Geopolymère SA, France. Pyrament is a trademark of Lone Star Industries Inc., USA.

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