GEOPOLYMERS: INORGANIC POLYMERIC NEW MATERIALS

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Summary

Spectacular technological progress has been made in the last few years through the development of new materials such as 'geopolymers', and new techniques, such as 'sol-gel'. New state-of-the-art materials designed with the help of geopolymerisation reactions are opening up new applications and procedures and transforming ideas that have been taken for granted in inorganic chemistry. High temperature techniques are no longer necessary to obtain materials which are ceramic-like in their structures and properties. These materials can polycondense just like organic polymers, at temperatures lower than 100°C. Geopolymerization involves the chemical reaction of alumino-silicate oxides (Al^{3+} in IV-fold coordination) with alkali polysilicates yielding polymeric Si-O-Al bonds; the amorphous to semi-crystalline three dimensional silico-aluminate structures are of the Poly(sialate) type (-Si-O-Al-O-), the Poly(sialate-siloxo) type (-Si-O-Al-O-Si-O-), the Poly(sialate-disiloxo) type (-Si-O-Al-O-Si-O-Si-O-).

This new generation of materials, whether used pure, with fillers or reinforced, is already finding applications in all fields of industry. Some examples:
  - *pure: for storing toxic chemical or radioactive waste, etc.*
  - *filled: for the manufacture of special concretes, molds for molding thermoplastics, etc.*
  - *reinforced: for the manufacture of molds, tooling, in aluminum alloy foundries and metallurgy, etc.*

These applications are to be found in the automobile and aerospace industries, non-ferrous foundries and metallurgy, civil engineering, plastics industries, etc.

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1. Introduction

Thermal behaviour investigations of organic and inorganic materials played a major role in my scientific career. Thirty years ago, when I introduced DTA as a new tool for understanding the structural behaviour of polyurethanes and oligo-urethanes, I had to build my own equipment. The bibliography of my Dr. rer. nat Thesis contained only two references dealing with the differential thermal analysis of organic polymers [1]. Today, state-of-the-art materials characterization is routinely carried out using thermal analysis. 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 the private research company CORDI SA 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 [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]. Study of the literature and of the patent data-banks demonstrates that, before 1978, the idea of using this mineral chemistry for the development of a new family of mineral binders and mineral polymers, had been totally neglected.

The amorphous to semi-cristalline three dimensional silico-aluminate structures were christened «geopolymers» of the types [5]:

    Poly(sialate)   (-Si-O-Al-O-),
    Poly(sialate-siloxo)   (-Si-O-Al-O-Si-O-),
    Poly(sialate-disiloxo)   (-Si-O-Al-O-Si-O-Si-O-) .

Apart from Applied Archaeological Sciences (research carried out at Barry University, Miami, Florida), the aim of our R. & D. long term program was not academic [6]. This explains why very little scientific literature is available on the subject of geopolymers. The majority of references disclosing this application of mineralogy belongs to the patent-literature. The applications of this new family of mineral binders have been tested in pilot plants, in the E.E.C. and in the USA. A good many have reached the industrial stage. LONE STAR INDUSTRIES (USA): new class of special cements and blended cements: PYRAMENT* cements; HÜLS TROISDORF AG (Germany): building products and industrial uses, TROLIT* binders [7]; GEOPOLYMERE Sarl (France): advanced mineral binders for severe environments, temperature stable resins for moulds and forms, GEOPOLYMITE* binders, ceramic-ceramic composites GEOPOLYCERAM* [8][9][10].

2. Terminology

For the chemical designation of geopolymers based on silico-aluminates, poly(sialate) was suggested. Sialate is an abreviation 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:

$$Mn\{-(SiO_2)z\text{-}AlO_2\}n, wH_2O$$

wherein M is a cation such as potassium, sodium or calcium, and «n» is a degree of polycondensation; «z» is 1, 2, 3 [11]. 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-cristalline. Some related frameworks are displayed in Fig.1.
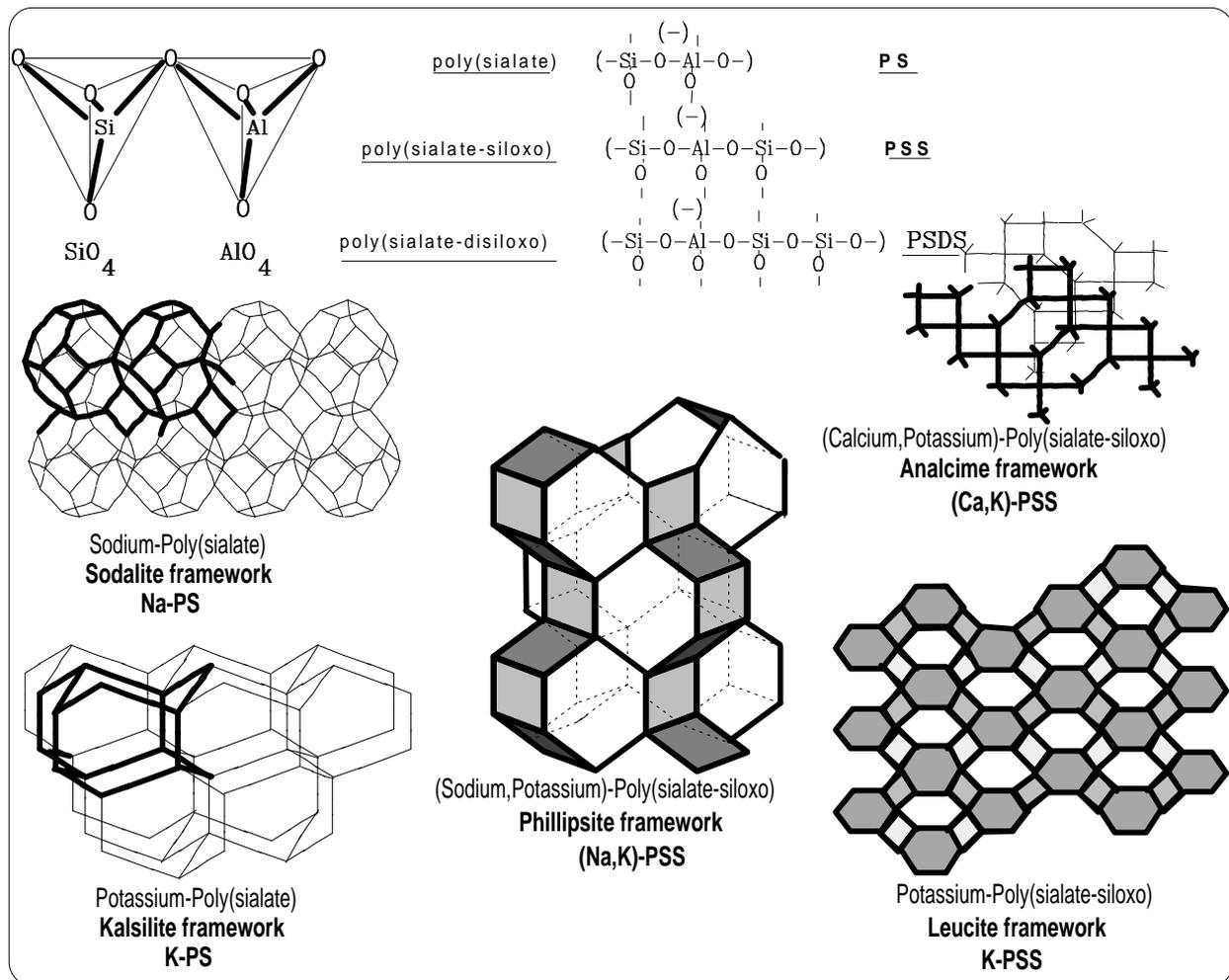
**Figure 1: Computer molecular graphics of polymeric Mn-(-Si-O-Al-O-)n poly(sialate)
and Mn-(-Si-O-Al-O-Si-O-n poly(sialate-siloxo), and related frameworks.**

Geopolymeric compounds involved in materials developed for industrial applications are either crystalline or non-crystalline (amorphous or glassy structure). Crystalline Poly(sialate) Mn-(-Si-O-Al-O-)n and Poly(sialate-siloxo) Mn-(Si-O-Al-O-Si-O-)n result from hydrothermal setting conditions, whereas hardening at ambient temperature induces amorphous or glassy structures.

The degree of disorder in a geopolymer can be inferred by observations of the way it diffracts X-rays to form a diffraction pattern. 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 are non-crystalline. There structure cannot be investigated from X-ray diffractograms alone. Nuclear Magnetic Resonance (MAS-NMR) spectroscopy provides some insight into the molecular framework [12].

3. Crystalline Poly(sialate) (Si-O-Al-O-)n

With the geopolymeric precursor kaolinite $Si_2O_5,Al_2(OH)_4$, hydrothermal polycondensation at 150°C/5-10MPa with NaOH yields well crystalized sodalite based Na-Poly(sialate) Na-PS $(Si_2O_4,Al_2O_4,2Na),3H_2O$, within 20 seconds of time, according to the schema set forth in Fig.2 [13].
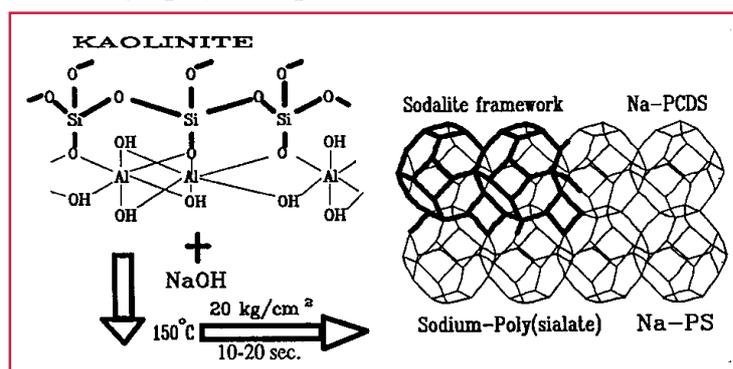
Fig. 2: Hydrothermal polycondensation of Na-Poly(sialate).

The structural unit of Zeolite A is identical

with that of Na-Poly(sialate) and is based on the sodalite cage (Fig.3). The 3-dimensional framework evolves from the polycondensation of the dimer: cyclo-di-sialate (CDS). For Zeolite A the primary condensation unit is the tetramer cyclo-tetra-sialate which is formed in the solution prior to crystallization. The geopolymer K-PS, potassium-poly(sialate) results from the polycondensation with KOH instead of NaOH.
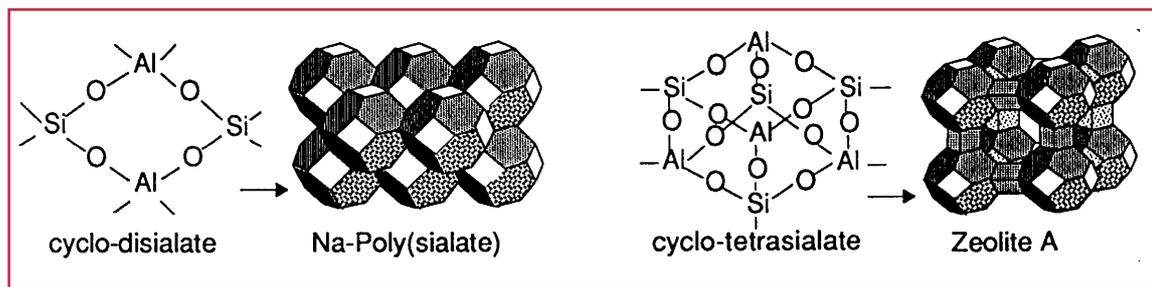
Fig. 3: Structural frameworks of Zeolite A and Na-Poly(sialate)

In 1976, the extremely reactive geopolymeric precursor alumino-silicate oxide (Si_2O_5,Al_2O_2) was used in the manufacture of panels and tiles [14]. Yet the experimental conditions which control the hardening of the ceramic paste, 150°C/15 MPa, do not favour any formation of single crystals, as is generally the case for the preparation of zeolitic species. On the contrary, one obtains a hard microporous ceramic body. X-ray diffraction patterns (Fig.4) suggest a structure comprising a mixture of Na-PS and some Zeolite A, for short-time reaction (10-15 min). With longer reaction time, 45-60 min., only the denser Na-PS is formed.

Fig. 4: X-ray diffractograms for ceramic bodies obtained with alumino-silicate oxide (Si_2O_5,Al_2O_2); increasing reaction time. Typical d-values for Zeolite A are shown only by the 10 min. reaction-time pattern.
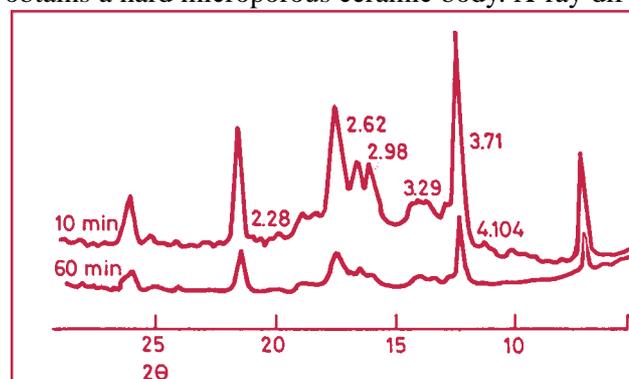
4. Amorphous Poly(sialate-siloxo) (Si-O-Al-O-Si-O)n, (Na,K)-PSS, (Ca,K)-PSS and K-PSS

It is known that the mechanism of formation of crystalline zeolitic species with the ratio Si/Al>2 requires the silico-aluminate gels to be crystallized in a closed hydrothermal system at temperatures varying generally from room temperature to about 175°C. In some cases, higher temperatures to 300°C are used. The pressure is generally the autogenous pressure approximately equivalent to the saturated vapour pressure (svp) of water at the temperature designated. The time required for crystallization varies from a few hours to several days. Aging time at room temperature is 24 hours; crystallization time at 100°C from 50 to 100 hours [4]. For the K_2O-Al_2O_3-SiO_2 system, crystallization temperatures range from 150°C to 230°C. See Fig.5 [15].

Fig. 5: Crystallization temperature ranges for K_2O-Al_2O_3-SiO_2 system adapted from [15].
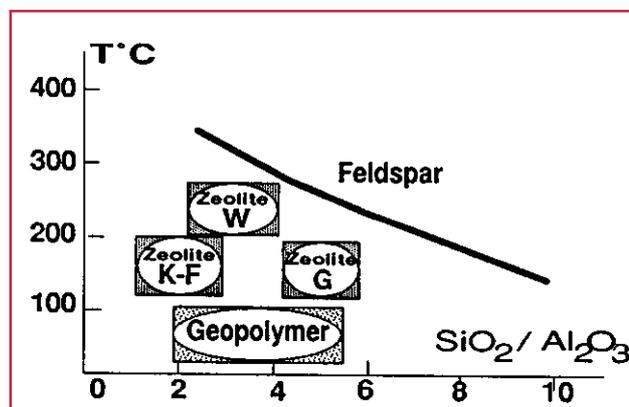
Yet geopolymer binders generally do not implement these hydrothermal conditions. However, in some cases, hydrothermal conditions may be found in the fabrication process of special fibre reinforced composites which requires a relatively higher setting temperature in the 150°-180°C range. One hardening 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 emphasize the IV fold coordination of Al we usually write $(Si_2O_5,Al_2O_2)n$ for these particular alumino-silicate oxides instead of $(2SiO_2,Al_2O_3)$ [16].

The fabrication of $(Si_2O_5,Al_2O_2)n$ is carried out (a) by calcining alumino-silicate hydroxides $(Si_2O_5,Al_2(OH)_4)$, or (b) by condensation of SiO and Al_2O vapors:

(a) $2(Si_2O_5,Al_2(OH)_4) \rightarrow 2 (Si_2O_5,Al_2O_2)n + 4H_2O$

(b) $4SiO (vapor) + 2Al_2O (vapor) + 4O_2 \rightarrow (Si_2O_5,Al_2O_2)n$

with also production of:

$2SiO + O_2 \rightarrow 2SiO_2$ (Condensed Silica Fume)

$Al_2O + O_2 \rightarrow Al_2O_3$ (Corundum)
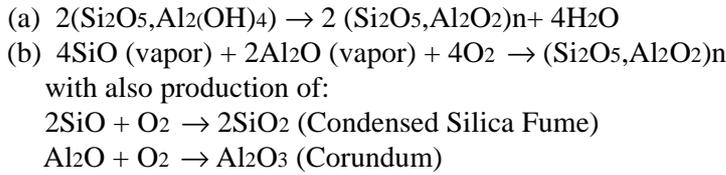
Geopolymerisation is exothermic and can be schematised as follows. It may be considered as the result of the polycondensation of still hypothetical monomers, the orthosialate ions:

$$(Si_2O_5,Al_2O_2)n + nH_2O \xrightarrow{KOH,NaOH} n(OH)_3\text{-}Si\text{-}O\text{-}Al\text{-}(OH)_3^{(-)}$$

$$n(OH)_3\text{-}Si^{(-)}\text{-}O\text{-}Al\text{-}(OH)_3 \xrightarrow{KOH,NaOH} (Na,K)(\ -\underset{\overset{|}{O}}{Si}\text{-}O\text{-}\underset{\overset{|}{O}}{Al}\text{-}O\text{-})n^{(-)} + 3nH_2O$$

$\underline{orthosialate} \qquad\qquad \underline{(Na,K)\text{-}poly(sialate)}$

— —

$$(Si_2O_5,Al_2O_2)n + nSiO_2 + nH_2O \xrightarrow{KOH,NaOH} n(OH)_3\text{-}Si\text{-}O\text{-}\underset{\overset{|}{(OH)_2}}{Al}\text{-}O\text{-}Si\text{-}(OH)_3^{(-)}$$

$$n(OH)_3\text{-}Si^{(-)}\text{-}O\text{-}\underset{\overset{|}{(OH)_2}}{Al}\text{-}O\text{-}Si\text{-}(OH)_3 \xrightarrow{KOH,NaOH} (Na,K)(\text{-}\underset{\overset{|}{O}}{Si}\text{-}O\text{-}\underset{\overset{|}{O}}{Al}^{(-)}\text{-}O\text{-}\underset{\overset{|}{O}}{Si}\text{-}O\text{-})n + nH_2O$$

$\underline{ortho(sialate\text{-}siloxo)} \qquad\qquad \underline{(Na,K)\text{-}poly(sialate\text{-}siloxo)}$
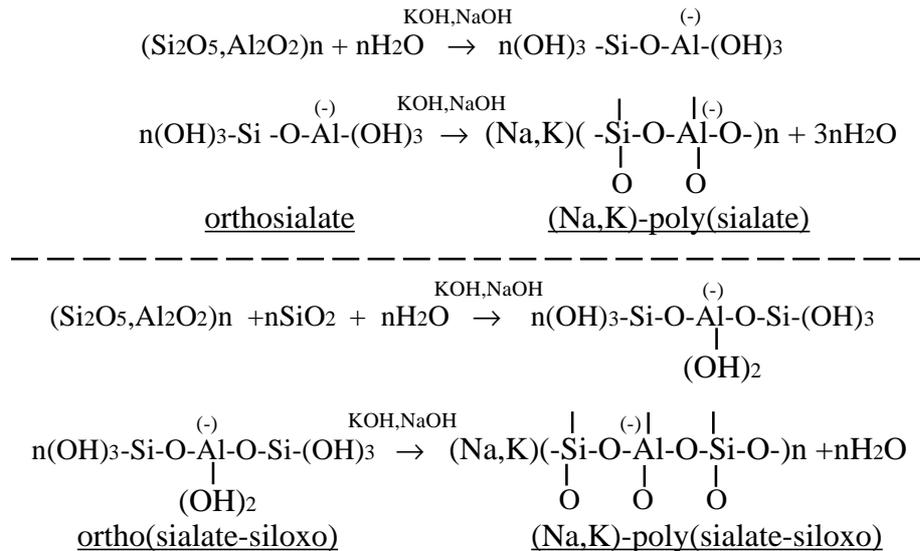
It has been assumed that the syntheses are carried out through oligomers (dimer, trimer) which provide the actual unit structures of the three dimensional macromolecular edifice.

4.1 X-ray diffraction

The (Na,K)-PSS and K-PSS which result from the polycondensation of various alkali-alumino-silicates present in GOPOLYMITE binders, are actually X-ray amorphous materials which are difficult to characterize. 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 described in Tab.1 are displayed in Fig.6 . They reveal that the material has a diffuse halo peak at about 3.05-3.30A(27-29° 2θmax, Cu Kα).
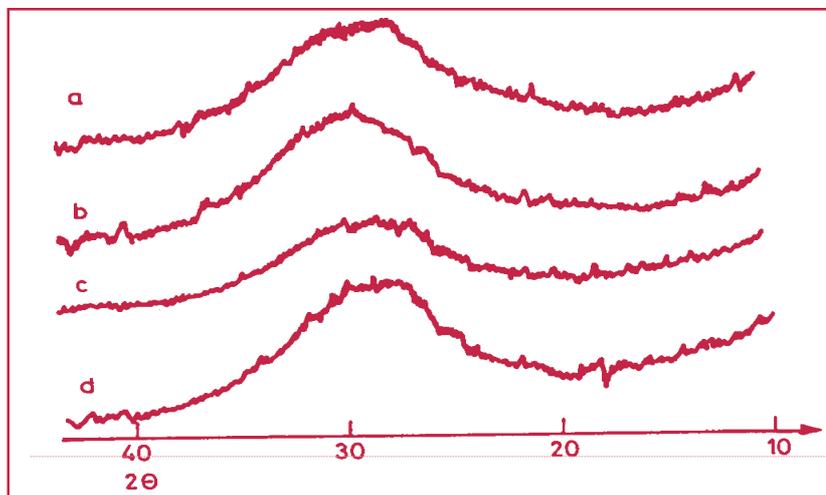
Fig. 6: X-ray diffractograms for (Na,K)-PSS and K-PSS binders of Tab.1.

Table 1: °2θmax for (Na,K)-PSS and K-PSS binders.

	Geopolymer	mole Na$_2$O+K$_2$O/SiO$_2$	mole SiO$_2$/(Al$_2$O$_2$)	Cu(Kα) 2θmax
(a)	(Na,K)-PSS	0.235	4.02	27°
(b)	(Na,K)-PSS	0.386	3.98	29°
(c)	K-PSS	0.296	3.39	27°
(d)	K-PSS	0.366	4.11	28°

Comparison of the values of 2θmax for (Na,K)-PSS and K-(PSS) (Tab.1) with the values of the 2θmax diffraction peak for crystalline natural and synthetic framework silico-aluminates (Tab.2) reveals that (Na,K)-PSS and K-PSS binders are the amorphous equivalent of the major crystalline framework silico-aluminates, except Hydrosodalite and Analcime. Hydrosodalite with its typical sodalite cage, poly(sialate) (Si-O-Al-O-)n network, is not representative of GEOPOLYMITE binders.

Table 2: °2θmax (diffraction peak) for some natural and synthetic framework silico-aluminates.

Mineral (Framework silico-aluminate)		mole Na$_2$O+K$_2$O/SiO$_2$	mole SiO$_2$/(Al$_2$O$_2$)	Cu(Kα) 2θmax
Leucite	K(Si$_2$AlO$_6$)	0,25	4,0	27,24°
Nepheline	(Na,K)(SiAlO$_4$)	0,50	2,0	29,46°
Orthose	K(Si$_3$AlO$_8$)	0,16	6,0	27,70°
Albite	Na(Si$_3$AlO$_8$)	0,16	6,0	27,86°
Analcime	Na(Si$_2$AlO$_6$).H$_2$O	0,25	4,0	26-30°
Phillipsite	(K,Na)(Si$_2$AlO$_6$).H$_2$O	0,25	4,0	27,9°
Hydrosodalite	Na(SiAlO$_4$).H$_2$O	0,50	2,0	24,2°
Zeolite W (K-M)	K(Si$_{1.8}$AlO$_6$).H$_2$O	0,27	3,6	27,42°
Zeolite G (K-G)	K(Si$_{1.95}$AlO$_6$).H$_2$O	0,26-0,37	2,6-4,15	30°
Zeolite Z (K-F)	K(SiAlO$_4$).H$_2$O	0,4	2,3	28,7°

It should be noted that these results comply with the chemical mechanism set forth for poly(sialate-siloxo) (Si-O-Al-O-Si-O-)n species. The three-dimensional framework assigned to (Na,K)-PSS is Phillipsite and Leucite for the K-PSS geopolymers. Practical experience suggests that the formation of the Analcime framework necessitates the presence of soluble Ca^{++} ions in complement to Na$^+$+ or K$^+$ ions. Crystallization within the Analcime framework can also be induced by the addition of fillers which act as crystallization nucleus [16].

4.2 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 [17].

4.2.1. 27Al MAS-NMR spectroscopy

Earlier investigations [18-20] 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 [Al(H$_2$O)$_6$]$^{3+}$ (Tab.3).

Table 3: Al-coordination in silico-aluminates and 27Al chemical shift after De Jong et al.[20]

Name	Formula	Coordination	Chemical shift (ppm)
Anorthoclase	(Na,K)AlSi$_3$O$_8$	4	54
Orthoclase	KAlSi$_3$O$_8$	4	53
Sanidine	KAlSi$_3$O$_8$	4	57
K-Feldspar	KAlSi$_3$O$_8$	4	54
Nephiline	NaAlSiO$_4$	4	52
Calcium aluminate	Ca$_3$Al$_4$O$_7$	4	71
Sodium aluminate	NaAlO$_2$	4	76
Muscovite	KAl$_3$Si$_3$O$_{11}$.H$_2$O	6, 4	-1, 63
Biotite	K(Mg,Fe)$_3$AlSi$_3$O$_{11}$.H$_2$O	4	65

The Loewenstein aluminium avoidance principle states that, whenever two tetrahedra are linked by one oxygen bridge, only one can be occupied by Al and there can hence be no Al-O-Al bridges [21]. In the absence of Al-O-Al linkages the environment of every Al atom is Al(4Si). The Lowenstein rule is obeyed in aluminosilicate anions.

The exclusion of Al-O-Al linkages sets the number of possibilities to five AlQn(nSi) structural units with n=0,1,2,3 and 4. Several resonances were identified in the spectra and the proposed interpretation of the various lines is that, in the series where AlQ denotes the central 4-coordinated Al atom and the corresponding elementary building units, the chemical shift decreases as set forth in Tabl.4. Some typical AlQn(nSi) geopolymeric units are displayed in Fig.7.

27Al MAS-NMR spectroscopy of all (Na,K)-PSS and K-PSS showed 27Al chemical shifts in the range of 55 ppm from $[Al(H_2O)_6]^{3+}$ identical to the spectrum displayed in Fig.8, which indicates that the aluminium is of the AlQ4(4Si) 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.

Table 4: AlQn and corresponding building units with 27Al chemical shift from $[Al(H_2O)_6]^{3+}$.

aluminate	ortho-sialate	cyclo(disialte) cyclo(trisialate) ortho(sialate-siloxo)	di(sialate-siloxo)	poly(sialate-siloxo) poly(sialate)
AlQ0	AlQ1(1Si)	AlQ2(2Si)	AlQ3(3Si)	AlQ4(4Si)
79,5	74,3	69,5	64,2	55
ppm from $[Al(H_2O)_6]^{3+}$.				
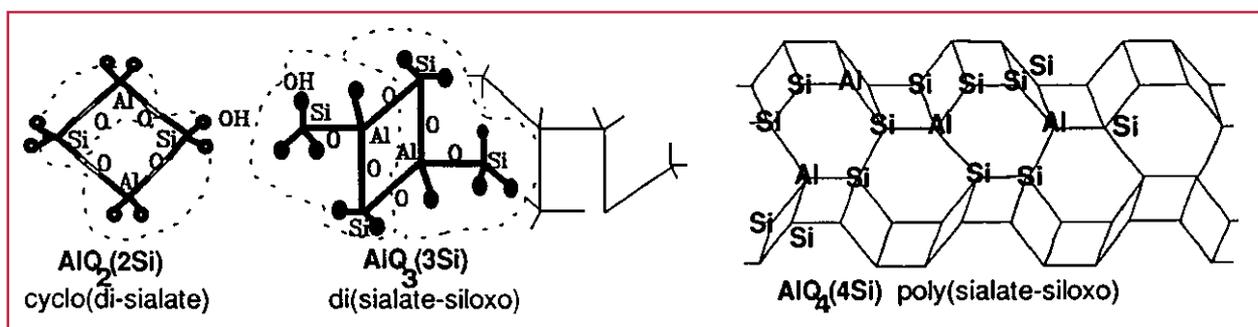
Fig. 7: AlQn(nSi) building units involved in geopolymeric reactions.

However, 27Al MAS-NMR cannot differentiate between the various frameworks proposed for geopolymeric materials based on poly(sialate) (Si-O-Al-O-)n, poly(sialate-siloxo) (Si-O-Al-O-Si-O-)n or poly(sialate-disiloxo) (Si-O-Al-O-Si-O-Si-O-)n polymeric building units. This differentiation can be carried out with 29Si MAS-NMR spectroscopy.

Fig. 8: 27Al MAS-NMR spectra for K-PSS
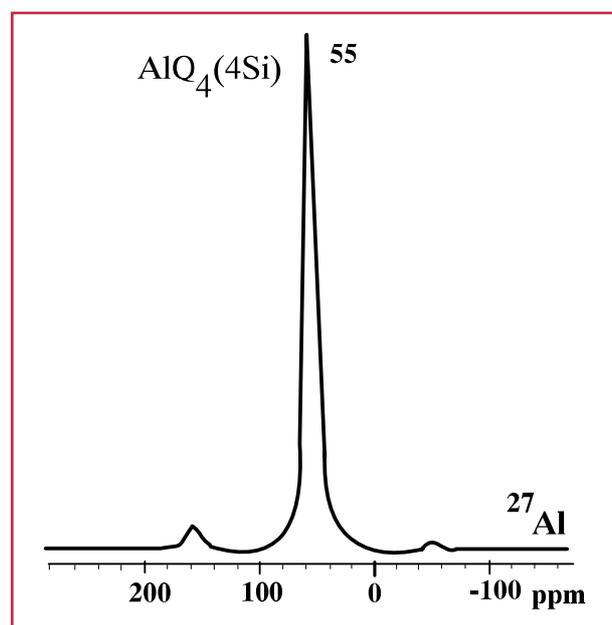
4.2.2 29Si MAS-NMR Spectroscopy

As displayed in Fig.9, K-PSS gives a broad resonance at -94,5 ppm 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.

Fig. 9: 29Si MAS-NMR spectra for K-PSS (GEOPOLYMITE) (GEOPOLYMITE binder).
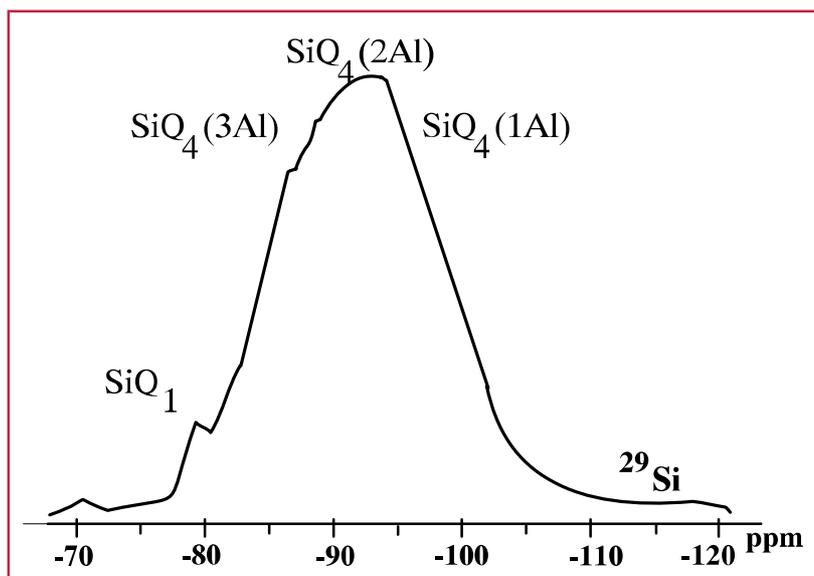
A previous study [21] has shown that the chemical shift of 29Si in an amorphous or highly disordered environment is increased by approximately 5 ppm. The resonances found for «disordered» 29Si in K-PSS, namely -81,5 ppm, -87 ppm and -94,5 ppm, relate to «ordered» 29Si chemical shifts of 86,5 ppm, -92 ppm, -99,5 ppm which can be assigned to Q(4Al), Q(3Al) and Q(2Al) respectively (see Fig.10). The Q(4Al) resonance does not necessarily imply the presence of poly(sialate) (Si-O-Al-O) type species (kaliophilite for example) which could result from the polycondensation of (Si_2O_5, Al_2O_2) without inter-reaction with SiO_2, as suggested above.
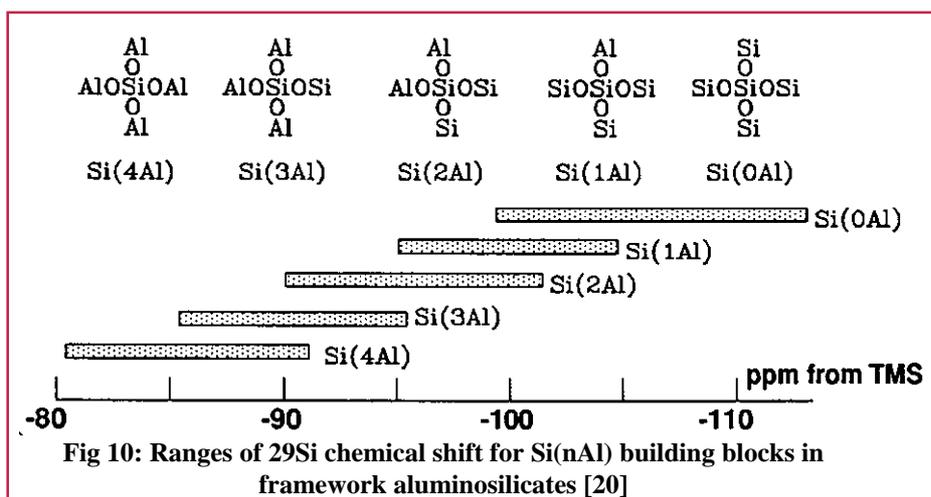
Fig 10: Ranges of 29Si chemical shift for Si(nAl) building blocks in framework aluminosilicates [20]

Indeed, silico-aluminates with an atomic ratio Si/Al >2 generally display several 29Si resonances suggesting that the Si and Al tetrahedras are not regularly ordered along the polymeric chains. Tab.5 displays 29Si MAS-NMR data for several natural and synthetic silico-aluminates which clearly show the presence of all Q(nAl) sites within the frameworks. On the other hand, silico-aluminates with atomic ratio Si/Al=1, only exhibit Si(4Al) sites.

Table 5: 29Si MAS-NMR spectra of zeolitic species (excerpt from [20])

Zeolite	Formula	Si/Al	29Si chemical shifts (ppm from TMS)				
			Si(4Al)	Si(3Al)	Si(2Al)	Si(1Al)	Si(0Al)
Zeolite A	$Na(AlSiO_4).H_2O$	1.0	-88.9	-	-	-	-
Analcime	$Na(AlSi_2O_6).H_2O$	2.0	-	-92.0	-96.3	-101.3	-108.0
Gmelinite	$Na(AlSi_2O_6).H_2O$	2.0	-86.8	-91.7	-97.1	-102.7	-108.0
Leucite	$K(AlSi_2O_6)$	2.0	-81.0	-85.2	-91.6	-97.4	-101.0
Sodalite	$Na(AlSiO_4).H_2O$	1.0	-84.8	-	-	-	-
Mordenite	$Na(AlSi_5O_{12}).H_2O$	5.0	-	-	-100	-105.5	-111.6

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

narrow 29Si shift at -79 ppm is related to nesosilicates (Q0,Q1), monomeric or dimeric silicates. As indicated previously this could be the result of the post-solubilization of solid SiO_2 (silica fume) which became digested during the formation of the secondary K-PSS matrix [22].

5. Physical and thermal properties

The geopolymeric materials are «polymers», thus they transform, polycondense and adopt a shape rapidly at low temperatures (a few hours at 30°C, a few minutes at 85°C and a few seconds with microwaves); but also «geopolymers», thus they are mineral materials which are hard, weather resistant and which withstand high temperature. To sum up: they are used just like thermosetting organic resins, but are stable up to 1000-1200°C. The geopolymer resins (Geopolymite) commercially available in June 1990 are displayed in Table 6. State of the art geopolymer-tooling materials are poly(sialate-disiloxo), M-PSDS, and fluoro-poly(sialate-disiloxo), F,M-PSDS, geopolymers (**) [23]. F,M-PSDS geopolymers, the most promising tooling resins, result from the conjunction of two advanced techniques: geopolymerization and sol-gel technology. F,M-PSDS geopolymers [Patents Pending] comprise a geopolymeric network made of poly(sialate-disiloxo) associated with molecular silicon oxide SiO_2 embedded within the matrix. The trapped molecular SiO_2 yields a low-porosity, highly-packed microstructure, with higher density (see Fig.11). As displayed in Fig.12, Table 7 and Fig.13, physical properties of geopolymers, such as fusion temperature and coefficient of thermal expansion CTE, are a function of the Si/Al ratio.

Table 6: Geopolymer resins and applications (**)

Resin	Category	Utilization
GEOPOLYMITE®PS2	*poly(sialate)* **M-PS** $M_n-(Si-O-Al-O-)_n$ Na-PS	thermal insulation fire-resistant board
GEOPOLYMITE 711	*poly(sialate-siloxo)* **M-PSS** $M_n-(Si-O-Al-O-Si-O-)_n$ K-PSS	refractory for aluminum casting
GEOPOLYMITE 50	(K,Ca)-PSS	high-performance cements, toxic wastes, fire-resistant composites
GEOPOLYMITE 70	K-PSS	fire-resistant composites GEOPOLYCERAM composites
GEOPOLYMITE GP 140	*poly(sialate-disiloxo)* **M-PSDS** $M_n-(Si-O-Al-O-Si-O-Si-O-)_n$ K-PSDS	refractory for aluminum casting, fire-resistant composites, GEOPOLYCERAM composites tooling and structural composites for use-temperature range 650°C-1000°C
GEOPOLYMITE HTF1 GEOPOLYMITE HTF2 GEOPOLYMITE HTF3	fluoro-poly(sialate-disiloxo) (F,K,Na)-PSDS	fire-resistant composites, GEOPOLYCERAM composites, tooling and structural composites for use-temperature range 300°C-650°C

Formulations of castable geopolymer materials vary in degree of thermal expansion. Fig.13 displays a comparison between the coefficient of thermal expansion CTE for traditional materials and for geopolymers (K-PSS, K-PSDS, F,M-PSDS types). CTE values measured for geopolymers are those of commercially available Geopolymite resins, without any additional filler. CTE values are a function of the Si/Al ratio as disclosed in Table 7. In the case of F,M-PSDS formulations, CTE values increase with the amount of molecular silicon oxide SiO_2 packed inside the geopolymeric tri-dimensional network.
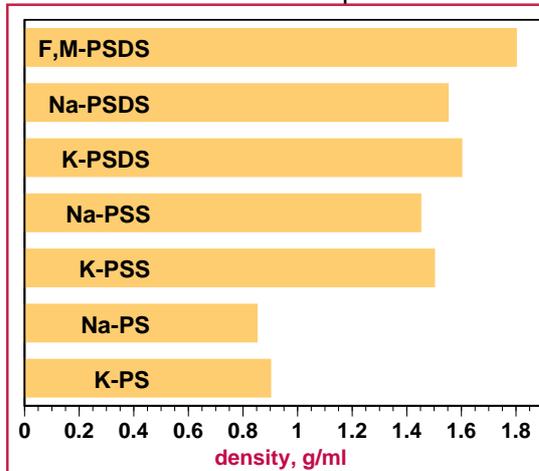
Fig. 11: Density of geopolymers (pure matrix, without filler) (**).
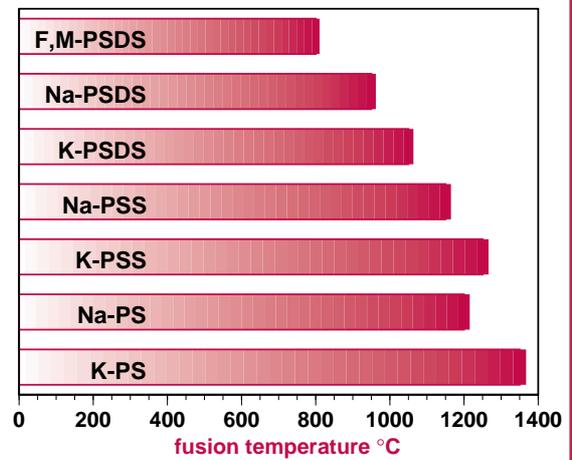
Fig. 12: Fusion temperature of geopolymers (pure matrix) (**)

Fig. 13: Coefficient of thermal expansion for geopolymers and tooling materials.

TABLE 7: Coefficient of thermal expansion (CTE) for geopolymers (**).

	Si/Al	CTE $.10^{-6}/°C$
K-PSS	2	4
K-PSDS	3	6
F,M-PSDS 1	3.5	10
F,M-PSDS 2	5	15
F,M-PSDS 3	20	25
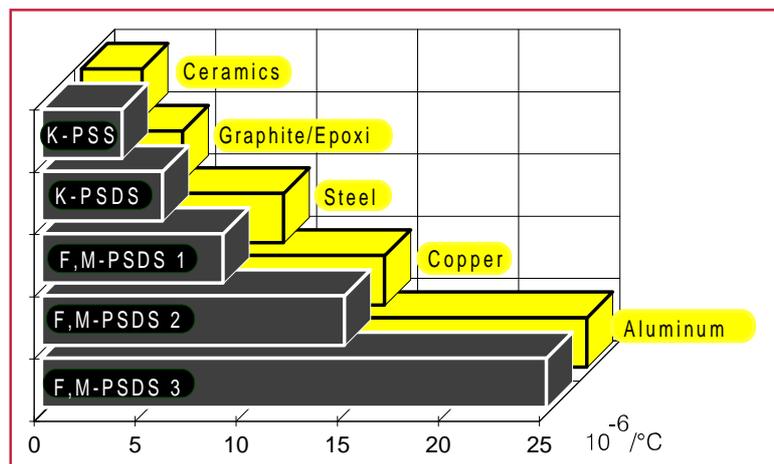
Geopolymite resins are designed to match the CTE of steel, enabling them to be used with steel inserts or frames, or have a CTE matched to that of other metal, carbon-fiber/epoxy parts, or any organic resins.

6. Examples of applications:

6.1 Ceramic type materials: Low Temperature Geopolymeric Setting of ceramic.

Low Temperature Geopolymeric Setting (L.T.G.S.) takes place in alkaline conditions through an oligosialate precursor (-Si-O-Al-O-) (Na) in concentrations from 2 to 6% by weight of the ceramic paste. At drying temperatures (50°C to 250°C) the kaolinite in clays is transformed by LTGS into a three dimensional compound of the poly(sialate) Na-PS sodalite type, stable to water and possessing high mechanical strength (Fig.14) [24].

Fig. 14: L.T.G.S. on kaolinitic soils. Mechanical compressive strength in Mpa for untreated and geopolymerised kaolinitic earth (with 3% by weight equivalent Na2O). Setting temperature range between 20°C and 1000°C.
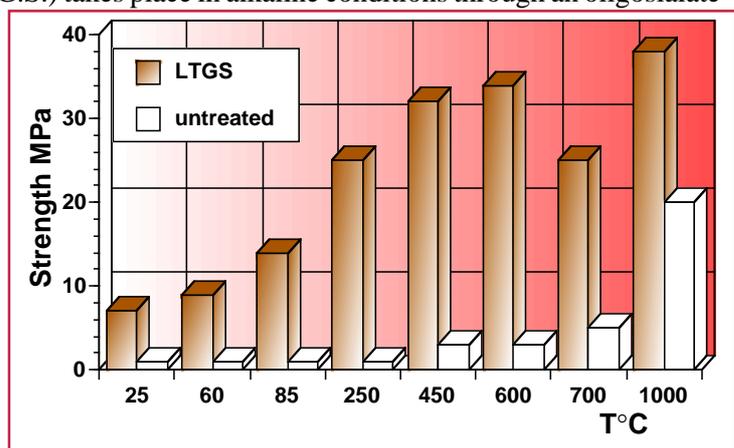
L.T.G.S. may dramatically enhance and modernise the traditional ceramic industry. Once geopolymerised into PCDS (Na-poly(cyclodisialate) or PCTS (K-poly(cyclotrisialate), at 125-250°C, ceramic bodies may be ultra rapidly fired at 1000°C-1200°C, to produce high quality ceramics (Fig. 15)

Fig. 15: Fabrication of ceramic tile; energy comsumption in kcal/kg of tile for current, rapid and geopolymerised methods and firing at 1000°C-1200°C.
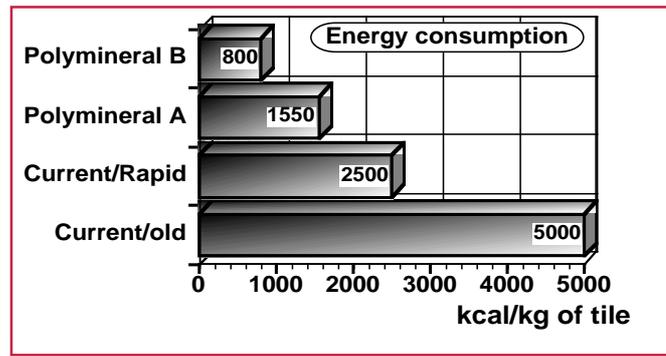
6.2 Toxic waste management

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 acting 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 matrix [25]. (Fig.16 and Fig.17). Ancient concretes and mortars demonstrate the exceptional durability of zeolitic cements, analogous to synthetic geopolymers discussed here, and are indicative of the erosional resistance which can be expected of modern geopolymeric cements. Al_2O_3/M_2O oxide molar ratios (where M is sodium or potassium) in the range of 1.5 to 4.0 are suggested as optimum for long term stability [26][27].

Fig. 16: Amount of hazardous elements locked in the geopolymeric matrix.

Fig. 17: Comparison of geopolymerised and untreated uranium mining tailing. Loss during leaching in pCi/l.
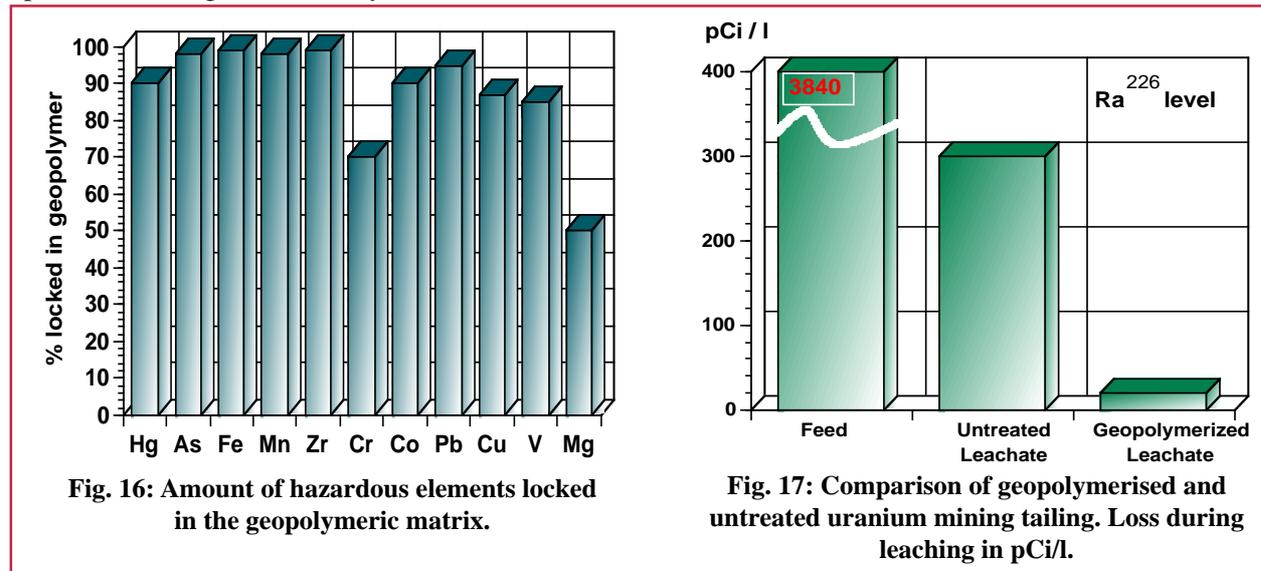
6.3 Geopolymeric binders and concretes.

Geopolymeric binders have been successfully introduced in the industry. They yield synthetic mineral products with such properties as hard surfaces (4-7 on the Mohs Scale), thermal stability, and high surface smoothness and precise mouldability [28]. Such products are useful for tooling, for moulding art objets, ceramics, and the like, and as building materials.

Fig. 18: Strength retentions at elevated temperatures for concretes made of Portland Cements (portland I, portland III), blended geopolymer-portland (PYRAMENT), blended geopolymers (K)-PSS (GEOPOLYMITE 711), (K,Ca)-PSS (GEOPOLYMITE 50). Hardening at ambient temperature.
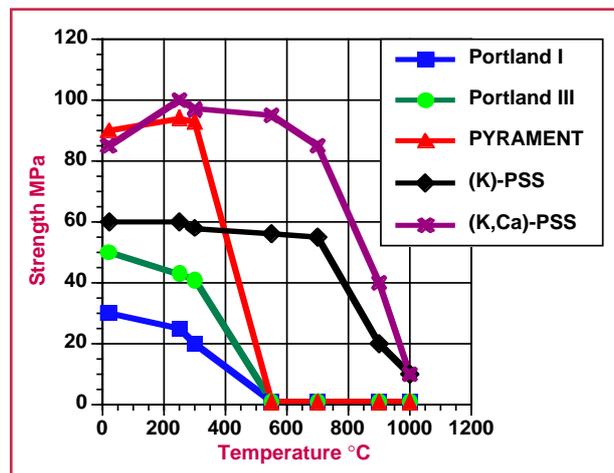
Fig. 19: Room temperature setting for concretes made of geopolymeric cements (GEOPOLYCEM) and portlands cements.
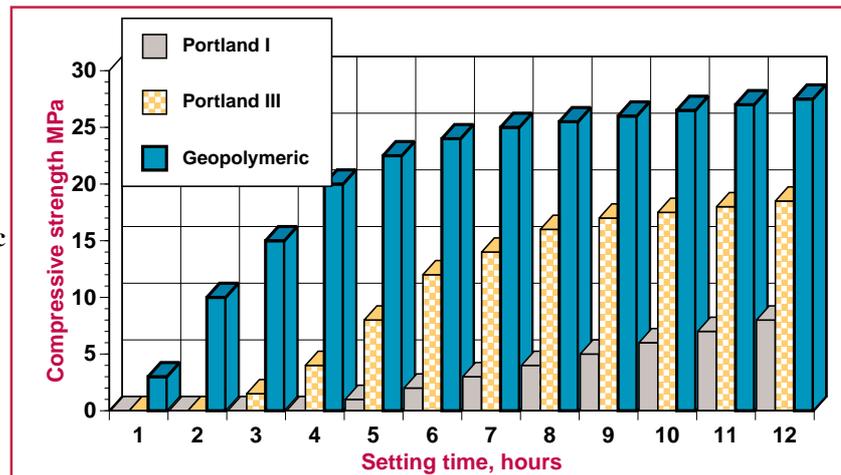
6.4 Geopolymeric concretes and the «Green-House» Global-Warming Challenge

Most of the 67 countries participating at the 3rd Plenary Session of the International Panel on Climate Change (IPCC), Washington, D.C., February 1990, supported a proposal to reduce carbon dioxide emissions 20% by 2000. Sweden has already enacted legislation to freeze its carbon dioxide emissions at 1989 levels. The West German minister for environment said he will propose that West Germany cuts its emissions of carbon dioxide 25% by 2005. [29]. It is expected that CO_2 emissions can be lowered substantially by reducing fossil-fuel use and through new technology and energy conservation.

Yet CO_2 emissions resulting from chemical reactions will continue to grow with industrial development. This is specifically the case for portland cement manufacturing. Cement (ordinary portland cement) results from the calcination of limestone (calcium carbonate) and silico-aluminous material according to the reaction:

$$5CaCO_3 + 2SiO_2 \Rightarrow (3CaO,SiO_2)(2CaO,SiO_2) + 5CO_2$$

The production of 1 ton of cement generates 0.55 tons of CO_2 and needs the combustion of carbon-fuel into 0.40 tons of CO_2. To simplify: 1 T of cement = 1 T of CO_2.

The 1988 1 billion metric tons world production of cement accounted for 1 billion metric tons of CO_2, i.e. 5% of the 1988 world CO_2 emission. This is equivalent to the CO_2 generated by the entire Japanese activity. Industrial development is strongly associated with the increase of cement and concrete production. Fig. 20 displays the annual world production of cement, and CO_2 until year 2003. A freeze of the production at the 1989 level recommended by Sweden - or the 20% reduction by 2000- means a drastic change in the cementitious systems involved in the utilization of concrete. Concretes should involve less calcium-based cements, the latter being replaced by materials providing similar or better cementitious properties. Geopolymeric concretes, sodium and potassium based-cementitious materials, should provide the answer to this issue.
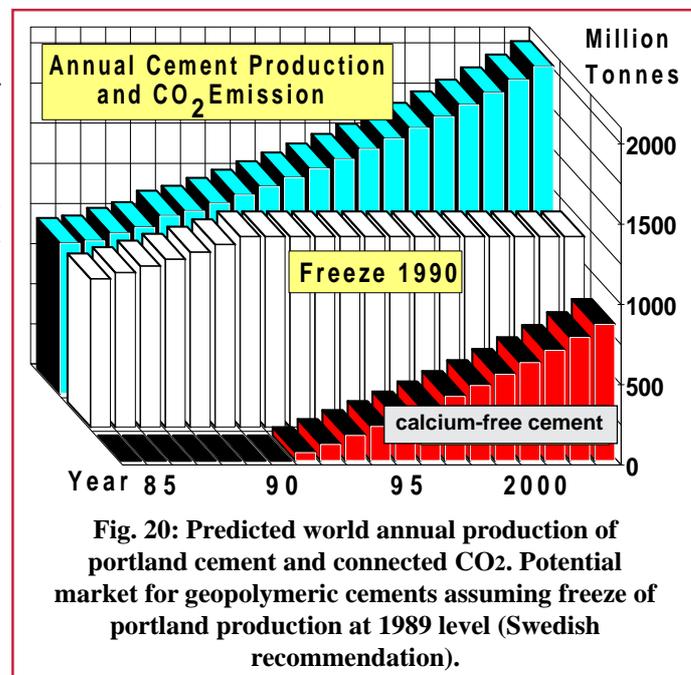
Fig. 20: Predicted world annual production of portland cement and connected CO_2. Potential market for geopolymeric cements assuming freeze of portland production at 1989 level (Swedish recommendation).

6.5 Room temperature ceramic matrix for reinforced fiber-composites

In 1982 we started the development of a geopolymer matrix composite concept [30]. The objective was to fabricate moulding tools and patterns, to replace metal tooling for small production runs in the plastic processing industry and the foundry industry [31].

Setting as our objective the fabrication of high-performance composite-tooling, we started basic research aimed at new geopolymer resins providing very low viscosity and high mechanical strength, and have studied the behaviour of various reinforcing materials currently on the market.

A wide range of alkaline resistant inorganic reinforcements has been combined with geopolymer matrices, in particular SiC fiber, with skills of the reinforced plastics/composites industry, and has yielded the non-burning, non smoking, non-toxic benefits of advanced ceramic/ceramic composite without that industry's high temperature, high energy processing.

Perhaps the fastest growing area is that of geopolymer/composite-tooling, Geopolyceram [32]. The relationship between operating temperature, flexural strength and fiber type, is displayed in Fig.21. E-glass and Carbon fabrics should be used up to 450°C (842°F) with the F,M-PSDS matrix. Higher temperatures require ceramic fibers such as SiC, Nicalon [33] fabrics, or Safil [34] aluminum oxide fibers. In all cases, a use-temperature higher than 700°C (1292°F) implies a M-PSDS matrix.
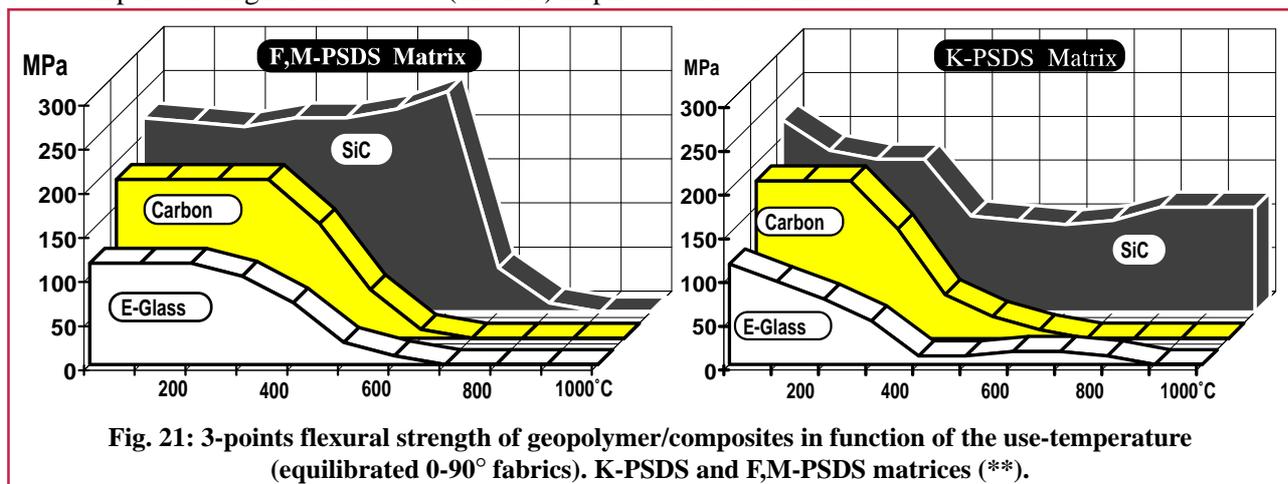
Fig. 21: 3-points flexural strength of geopolymer/composites in function of the use-temperature (equilibrated 0-90° fabrics). K-PSDS and F,M-PSDS matrices (**).

TABLE 8 Comparison between Geopolyceram SiC Fibre/K-PSS Geopolymite composite and SiC Fibre/Ceramic Matrix composites [35]

Composite (fibre/matrix)	Processing temp. °C	Mean Strength MPa
Uncoated SiC/SiC	ca.1400	135
Coated SiC/SiC	ca.1400	170
SiC/Li Alum. Silicate	ca.1400	860
SiC/cordierite	ca.1400	170
SiC/ZrO	ca.1400	180
SiC/mullite	ca.1400	80
SiC/mullite-30%SiC/BN	ca.1500	140
SiC/Vycor Glass	ca.1500	440
SiC/VPS+50% BN	ca.1500	320
SiC/K-PSS Geopolymite	70	380

*) Geopolymite, Geopolycem and Geopolyceram are trademarks of Cordi-Geopolymère SA, France. Pyrament is a trademark of Lone Star Industries Inc., USA. Trolit is a trademark of Hüls Troisdorf AG, Germany.

**) The data concerning K-PSDS and F,M-PSDS geopolymers were added during the final editing of the paper (May 1990), providing updated informations. They were not disclosed at the Conference (see Abstract I 2 PL).

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