TECHNICAL PAPER

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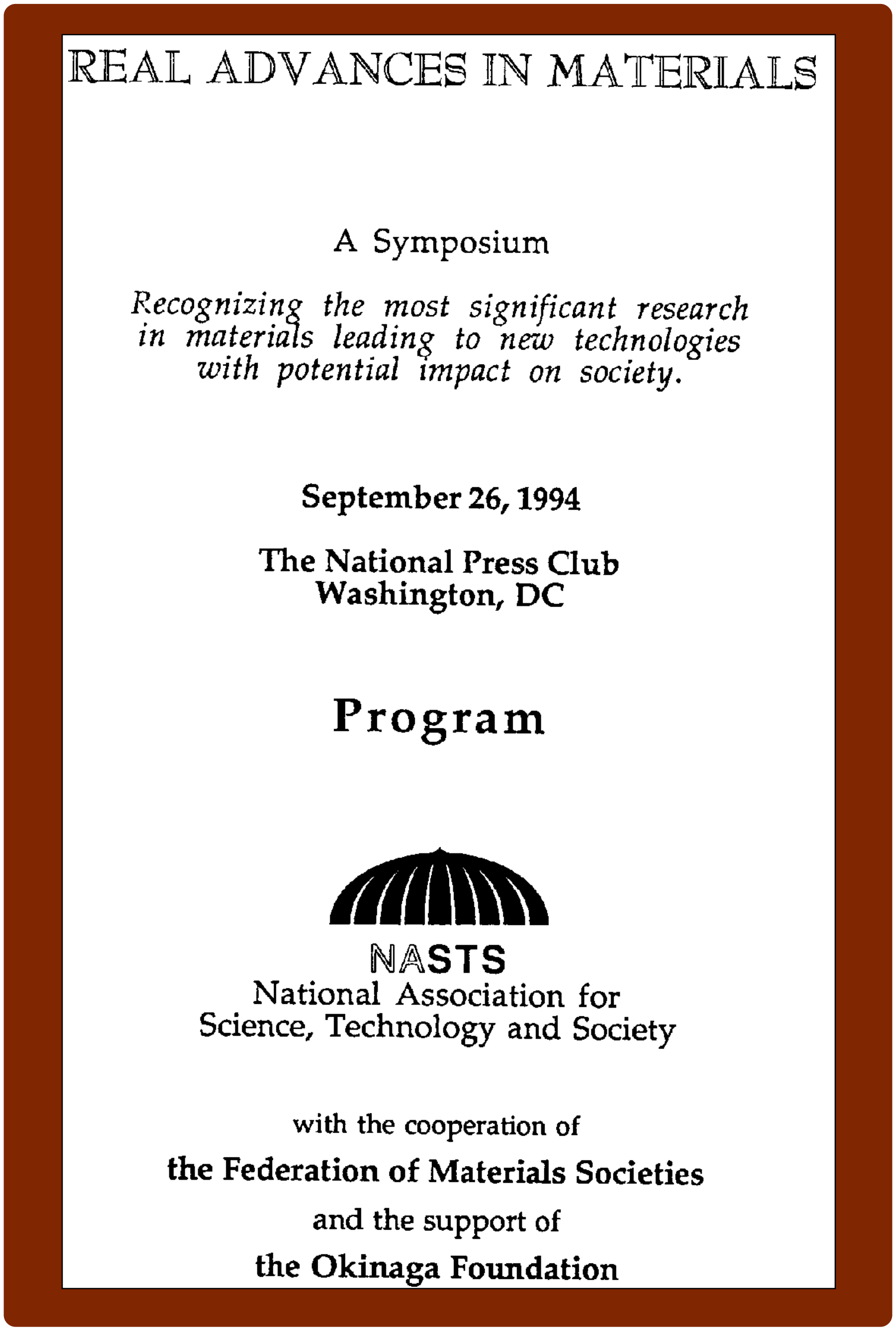

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GEOPOLYMERS: Man-Made Rock Geosynthesis and the Resulting Development of Very Early High Strength Cement

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The NASTS award for the "Development of Very Early High Strength Cement" went to Joseph Davidovits and James Sawyer, the latter now retired from Lone Star Industries Inc., Houston.

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carbon dioxide emission
global warming.

When, 30 years ago, I received the 1964 annual award from the French Textile Chemical Society (ACIT) for works performed on linear organic polymers, I did not imagine that the major part of my scientific career would be conducted outside of the field of organic chemistry [1]. Until 1972, I had been involved in researches dealing with organic binders for foundries, synthetic textile fibers, natural and synthetic leather, collagen, and organic membranes [2-3]. In the aftermath of various catastrophic fires in France between 1970-73, which involved common organic plastic, research on nonflammable and noncombustible plastic materials became my objective. I founded a private research company in 1972, which is today called CORDI-GÉOPOLYMÈRE. In my pursuit to develop new inorganic polymer materials, I was struck by the fact that simple hydrothermal conditions govern the synthesis of some organic plastics and also heat-resistant mineral feldspathoids and zeolites [4]. The scientific and patent literature indicated that, the geochemistry that yields the synthesis of zeolites and molecular sieves had not been investigated for producing mineral binders and mineral polymers. I proceeded to develop amorphous to semi-crystalline three-dimensional silico-aluminate materials, which I call «geopolymers» (mineral polymers resulting from geochemistry or geosynthesis) [5].

1970: catastrophic fires involving plastics

Question: are organic polymers heat resistant?

Answer: No, Nature states that only minerals provide fire and heat resistance.

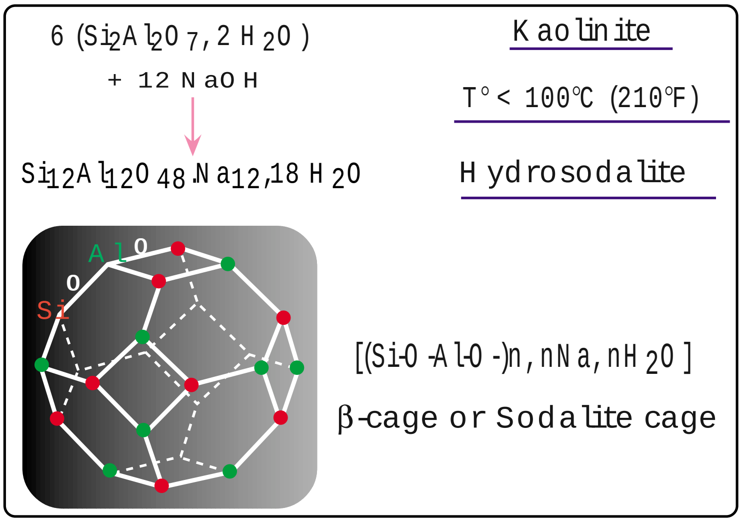
Research target: inorganic polymers

INTRODUCTION

The quest for low-temperature reactive minerals

In 1972, the ceramicist team J.P. Latapie and M. 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. I learned that the industrial applications of this kaolinite reaction with alkali began in the ceramic industry with Olsen in 1934 and was, later on, reinvented in 1970 by the Russian team Berg & al. [6], but without any successful industrial implementation.

The aluminosilicate kaolinite reacts with NaOH at 100°C-150°C and polycondenses into hydrated sodalite (a tectoaluminosilicate), or hydrosodalite.



In 1945, Flint & al. [7] 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 compound. Barrer & al. and Borchert & al [8] prepared hydrosodalite by reacting kaolinite in a concentrated NaOH solution, at 100°C. Howell [9] obtained a Zeolite A type, using calcined kaolin instead of kaolinite, preventing the formation of hydrosodalite. In 1969, Besson, Caillère and Hénin [10] carried out the synthesis of hydrosodalite from various phyllosilicates (kaolinite, montmorillonite, halloysite) at 100°C in concentrated NaOH solution.

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» [11-13].

To a natural kaolinite/quartz blend (50/50 weight ratio) one adds and mixes solid NaOH in the proportion of 2 moles or less of NaOH for 1 mole Al_2O_3 of the contained kaolinite, and water (1-1,5g water for 1 g NaOH). The resulting granules are cold-pressed at 15MPa into a green-body which is then hot-pressed (thermosetting process) in a mold equipped with a porous layer for water evaporation.

The thermosetting parameters are:

- temperature: 130°C to 200°C
- applied hydraulic pressure: higher than the saturated vapour pressure of water, for the selected temperature, i.e. 10 to 30 bars.
- time: one minute per millimetre 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 40kg/cm2 hydraulic pressure. Yet, due to the high internal pressure of water and the danger of explosion, it is recommended to wait until the item has cooled down to room temperature, before opening the mold. The press must be equipped with safety devices.

Very interesting results were obtained with a natural kaolinite/quartz blend supplied by the French company A.G.S. (Argiles & Minéraux). In this natural blend, the quartz crystals are surrounded with kaolinite micells. One obtains the sequenced poly(sialate) (Na-PS) nanocomposite called SILIFACE Q:

$$\text{-(Na-PS)-(SiO}_2\text{)n-(Na-PS)-(SiO}_2\text{)n-}$$

The same mechanism may occur with other poly(aluminosilicates) yielding various poly(sialate) nanocomposite materials. The Na-PS-quartz nanocomposite results from the interfacial reaction between the poly(sialate) matrix and the quartz crystals. The siloxane link Si-O-Si on the surface of quartz is hydrolysed into silanol Si-OH. These silanols polycondense with the sialates or polysialates of the surrounding kaolinite according to the schema:

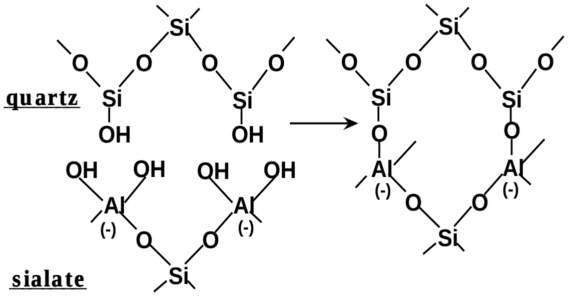


Table 1 gives the X-Ray diffraction patterns typical for the Na-PS-Quartz nanocomposite SILIFACE Q. The X-Ray pattern shows all major d-values characteristic for quartz and hydrosodalite. The d-values typical for kaolinite, namely 7.15, 3.57, 2.33, 2.28, are not found, which suggests that all the kaolinite has been transformed into Na-PS. ,

Table 1: Na-PS-Quartz nanocomposite, SILIFACE Q. X-Ray diffraction patterns for SILIFACE Q, Quartz and Hydrosodalite

SILIFACE Q		Quartz		Hydrosodalite		
d A	I	d A	I	d A	I	hkl
6.25	3			6.28	8	110
4.23	4	4.24	4	4.44	3	200
3.64	5			3.63	10	211
3.35	10	3.35	10			
2.82	3			2.81	6	310
2.57	5			2.56	8	222
2.46	4	2.46	4	2.37	3	321
2.11	3			2.09	8	330
1.82	3	1.82	2	1.81	3	422
1.75	3			1.73	4	501
1.49	3			1.48	3	442

By replacing quartz with synthetic cordierite, $(Si_5AlO_{18})Al_3Mg_2$, melting point 1.460°C, one obtains a nanocomposite called SILIFACE COR70, which has an exceptional temperature stability and very low thermal expansion. The comparative values for ceramics, metals and SILIFACE COR 70 in Table 2, are interesting:

Table 2: Mean linear thermal expansion between 20°C-700°C

Fe	0.96%	Steatite	0.80%
Iridium	0.50%	Mulite	0.40%
Mo	0.45%	Cermet	0.70%
Tn	0.37%	SILIFACE COR 70	0,13%
Silicium nitrid	0.25%		

Applications

Fire-resistant wood-chip board.

The first applications were building products (developed with J.J. Legrand), such as fire-resistant chip-board panels, comprised of a wooden core faced with two SILIFACE Q nanocomposite coatings, in which the entire panel was manufactured in a one-step process (US Patents 3,950,47; 4,028,454). An unusual feature was observed to characterize the manufacturing process: for the first time, the hardening of organic material (wood chips and organic resin) occurred simultaneously with the setting of the mineral silico-aluminate (Na-PS/quartz nanocomposite), when applying the same thermosetting parameters as for organic resin (see Fig. 1).

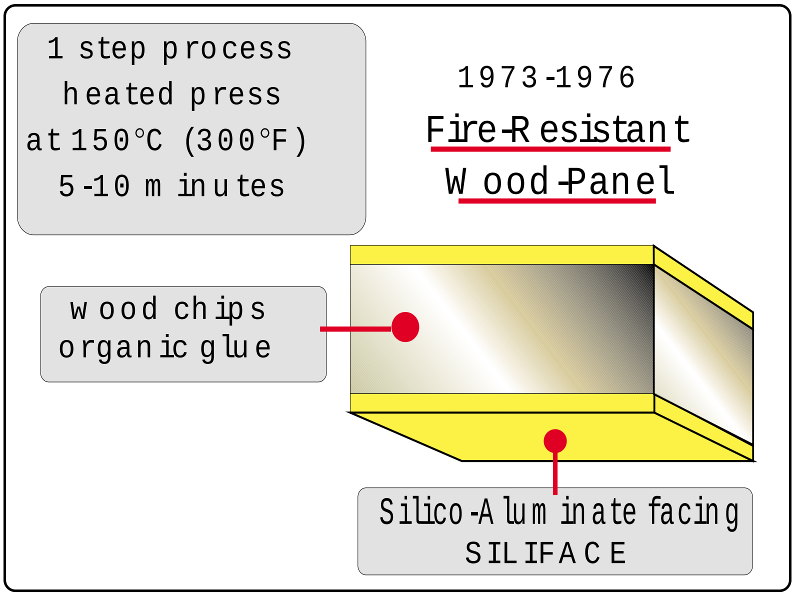


Figure 1: Fire-resitant chip-board with SILIFACE coating

Ceramic type materials: *Low Temperature Geopolymeric Setting of ceramic, L.T.G.S.*

Low Temperature Geopolymeric Setting (L.T.G.S.) takes place at drying temperatures (50°C to 250°C), in alkaline conditions, through an oligosialate precursor (-Si-O-Al-O-) (Na) in concentrations from 2 to 6% by weight of the ceramic paste. 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 (French Patents 2,490,626; 2,528,822) (Fig.2).

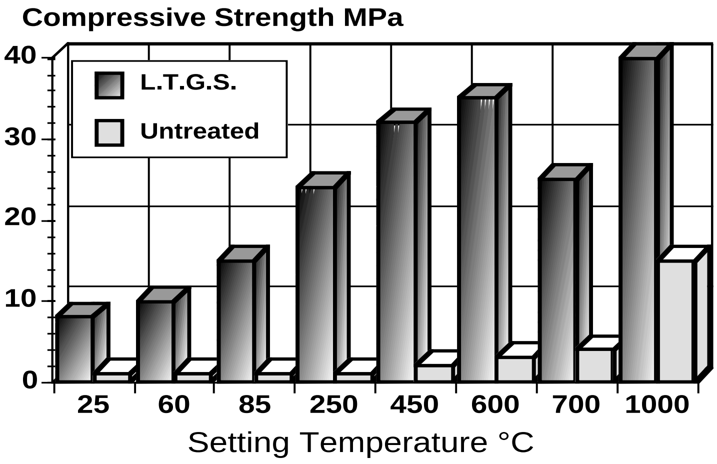
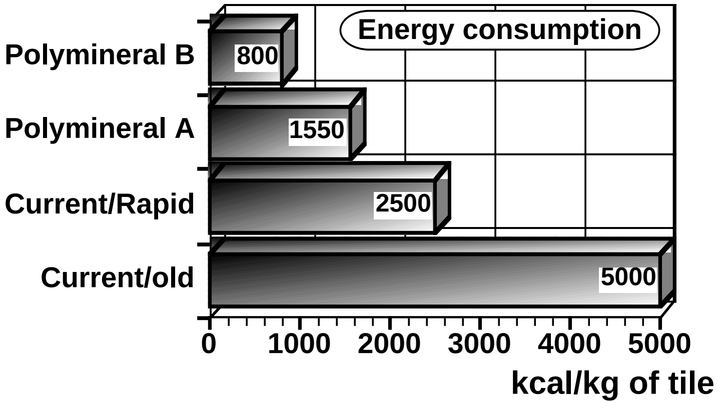


Figure 2: L.T.G.S. on kaolinitic soils. Mechanical compressive strength in Mpa for untreated and geopolymerised kaolinitic earth (with 3% by weight equivalent Na_2O). Setting temperature ranges between 20°C and 1000°C.

L.T.G.S. may dramatically enhance and modernise the traditional ceramic industry. Once geopolymerised into Na-polysialate (Na-PS) or K-polysialate (K-PS), at 125-250°C, ceramic bodies may be ultra rapidly fired at 1000°C-1200°C, to produce high quality ceramics (European Patent 0,101,714) (Fig. 3).

Figure 3: Fabrication of ceramic tile; energy consumption in kcal/kg of tile for current, rapid and geopolymerized methods (Polymineral A, B) and firing at 1000°C-1200°C.



MAM-MADE ROCK GEOSYNTHESIS
THE GEOPOLYMER TERMINOLOGY

We showed that naturally occurring alumino-silicates, such as kaolinite, are transformed at low-temperature, in an astonishingly short time, into tridimensional tecto-aluminosilicates. The thermo-setting method is very similar that used for the polycondensation of organic resins. The process yields nanocomposites that are actually man-made rocks. This geosynthesis is manifest in nature itself in great abundance. At least 55% of the volume of the Earth's crust is composed of siloxo-sialates and sialates, with pure silica or quartz at only 12%. The geosynthesis is based on the ability of the aluminium ion (6-fold or 4-fold coordination) to induce crystallographical and chemical changes in a silica backbone.

This basic innovation, the low-temperature transformation from kaolinite into hydrosodalite, demonstrated the tremendous latent potential of this new mineral reaction. This potential was neglected by the mainstream ceramics industry, by virtue of the infamous NIH principle (not invented here). It also failed to have any impact on other branches of industry because it was classified as an inexpensive clay product and listed under the heading of construction materials. As such, it did not have the «cachet» of developments in the «advanced» or so-called high-tech industries.

To define the importance of this chemistry, in 1976 I established a new terminology that served to properly classify mineral polymers [14-15].

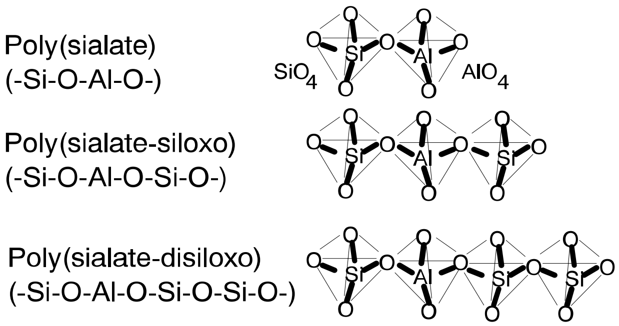
Terminology

In 1978, I created and applied the term «geopolymer» [16].

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. Polysialates have this empirical formula:

$$M_n\{-(SiO_2)_z-AlO_2\}_n,\ wH_2O$$

wherein M is a cation such as potassium, sodium or calcium, and «n» is a degree of polycondensation; «z» is 1, 2, 3. Polysialates are chain and ring polymers with Si^{4+} and Al^{3+} in IV-fold coordination with oxygen and range from amorphous to semi-crystalline. The amorphous to



semi-crystalline three dimensional silico-aluminate structures were christened «geopolymers» of the types:

Crystalline Polysialate M_n-(-Si-O-Al-O-)$_n$ and Poly(sialate-siloxo) M_n-(Si-O-Al-O-Si-O-)$_n$ 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. There structure cannot be investigated from X-ray diffractograms alone. Nuclear Magnetic Resonance (MAS-NMR) spectroscopy provides some insight into the molecular framework.

GEOPOLYMERIC BINDERS

The new terminology was the key to the successful development of new materials. For the user, geopolymers are polymers and, therefore, by analogy with the organic polymers derived from oil, they are transformed, undergo polycondensation, and set rapidly at low temperature, within few minutes. But they are, in addition, GEO-polymers, i.e. inorganic, hard, stable at temperature up to 1250°C and non-inflammable. This gave a tremendous boost to creativity and innovation. Liquid binders,which are the inorganic countertype of organic resins, were developed by the Geopolymere group (with Michel Davidovics and Nicolas Davidovits), GEOPOLYMITE® binders (US Patents 4,349,386; 4,472,199; 4,888,311; 5,342,595; 5,352,427) and by Neuschäffer & al. [17], Randel & al.[18], at the licenced German Company Dynamit Nobel (later Hüls Troisdorf AG, now sublicenced to Willig GmbH, binders TROLIT® and WILLIT®). The field of application developed since 1979 includes aeronautical engineering, the nuclear sector, the reproduction of «objets d'art», thermal insulation of buildings, furnace insulation, mechanical engineering, moulding, stamping, foundry work, metal casting, etc.. and it even includes archaeological research [19-21].

Amorphous Poly(sialate-Siloxo) (-Si-O-Al-O-Si-O-) binders.

This geosynthesis involves the chemical reaction of geopolymeric precursors such as aluminosilicate 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 $(Si_2O_5,Al_2O_2)_n$ for these particular aluminosilicate oxides instead of $(2SiO_2,Al_2O_3)$.

The fabrication of $(Si_2O_5,Al_2O_2)_n$ is carried out

(a) by calcining aluminosilicate hydroxides $(Si_2O_4,Al_2(OH)_4)$,

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

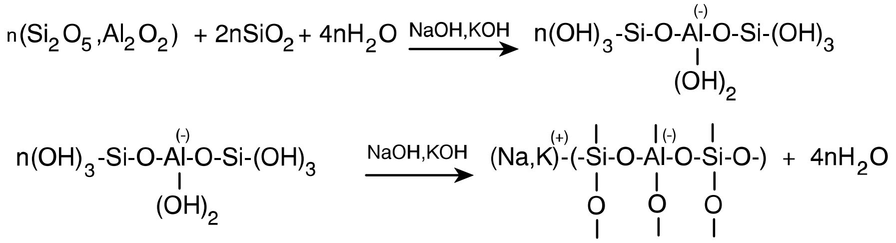
or (b) by condensation of SiO and Al_2O vapors:

$$4SiO\ (vapor) + 2Al_2O\ (vapor) + 4O_2 \Rightarrow (Si_2O_5,Al_2O_2)_n \qquad (b)$$

with also production of:

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

$Al_2O + O_2 \Rightarrow Al_2O_3$ (Corundum)



$$n(Si_2O_5,Al_2O_2) + 2nSiO_2 + 4nH_2O \xrightarrow{NaOH,KOH} n(OH)_3\text{-Si-O-}\underset{(OH)_2}{\overset{(-)}{Al}}\text{-O-Si-}(OH)_3$$

$$n(OH)_3\text{-Si-O-}\underset{(OH)_2}{\overset{(-)}{Al}}\text{-O-Si-}(OH)_3 \xrightarrow{NaOH,KOH} (Na,K)^{(+)}\text{-(-}\underset{\underset{|}{O}}{\overset{|}{Si}}\text{-O-}\underset{\underset{|}{O}}{\overset{|\,(-)}{Al}}\text{-O-}\underset{\underset{|}{O}}{\overset{|}{Si}}\text{-O-)} + 4nH_2O$$

Geopolymerization is exothermic and can be schematized 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)-Poly(sialate-siloxo) (Na,K)-PSS and K-Poly(sialate-siloxo) K-PSS, which result from the polycondensation of various alkali-alumino-silicates present in Geopolymite® and Trolit® 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 feldspathic glasses or crystalline zeolites. X-ray diffractograms for various K-PSS and (Na,K)-PSS samples are displayed in Fig.4. They show that the material has a diffuse halo peak at about 3.05-3.30A(27-29° 2θmax, Cu Kα). Comparison of the values of 2θmax for (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

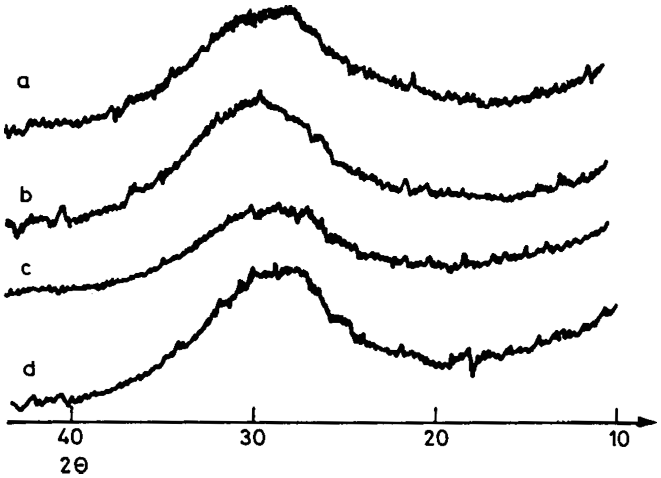


Figure 4 :X-Ray diffractograms for (Na,K)-PSS (a,b) and K-PSS binders (c,d)

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 ^{29}Si and ^{27}Al MAS-NMR studies represent a very powerful tool [22].

^{27}Al MAS-NMR spectroscopy

Earlier investigations [23-25] 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 $[Al(H_2O)_6]^{3+}$ (Tab.3).

Table 3: Al-coordination in silico-aluminates and ^{27}Al chemical shift:

Name	Formula	Coordination	Chemical shift (ppm)
K-Feldspar	$KAlSi_3O_8$	4	54
Muscovite	$KAl_3Si_3O_{11}.H_2O$	6, 4	-1, 63
Biotite	$K(Mg,Fe)_3AlSi_3O_{11}.H_20$	4	65
Calcium aluminate	$Ca_3Al_4O_7$	4	71
Sodium aluminate	$NaAlO_2$	4	76
Philipsite	$(K,Ca)AlSi_2O_6.H_2O$	4	55
K-Poly(sialate-siloxo)	$KAlSi_2O_6.H_2O$	4	55

^{27}Al MAS-NMR spectroscopy of all (Na,K)-PSS and K-PSS showed ^{27}Al chemical shifts in the range of 55 ppm from $[Al(H_2O)_6]^{3+}$ identical to the spectrum displayed in Fig.5, which indicates that the aluminium is of the $AlQ_4(4Si)$ 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. However, ^{27}Al 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 ^{29}Si MAS-NMR spectroscopy.

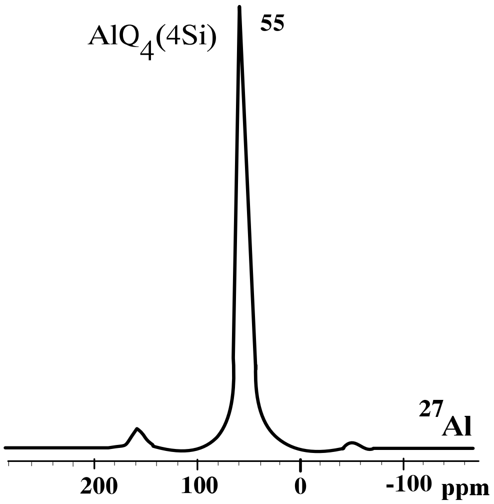


Figure 5: ^{27}Al MAS-NMR spectrum for K-PSS GEOPOLYMITE® binder

^{29}Si MAS-NMR Spectroscopy

As displayed in Fig.6, 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 $SiQ_4(4Al)$, $SiQ_4(3Al)$, $SiQ_4(2Al)$ and $SiQ_4(1Al)$ 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 Si/Al>2 generally display several ^{29}Si resonances suggesting that the Si and Al tetrahedras are not regularly ordered along the polymeric chains.

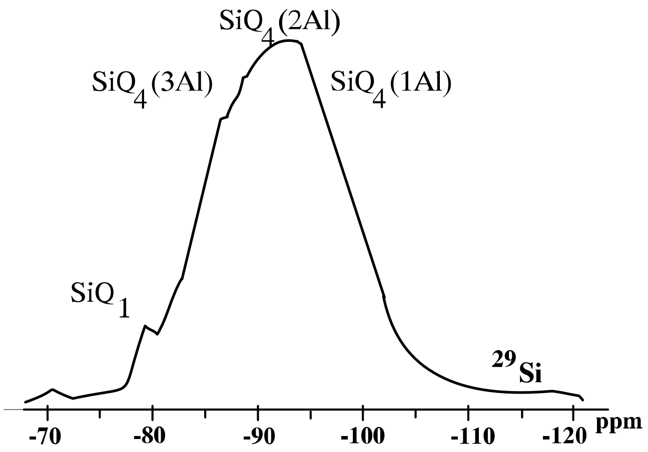


Figure 6: ^{29}Si MAS-NMR spectrum for K-PSS GEOPOLYMITE® binder

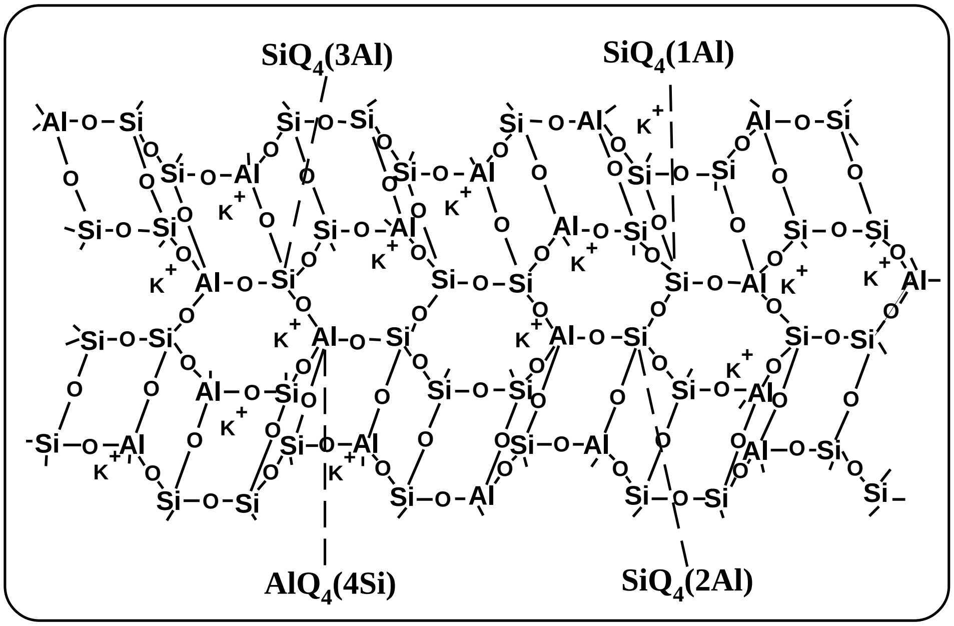


Figure 7: Proposed structural model for K-Poly(sialate-siloxo) Geopolymer.

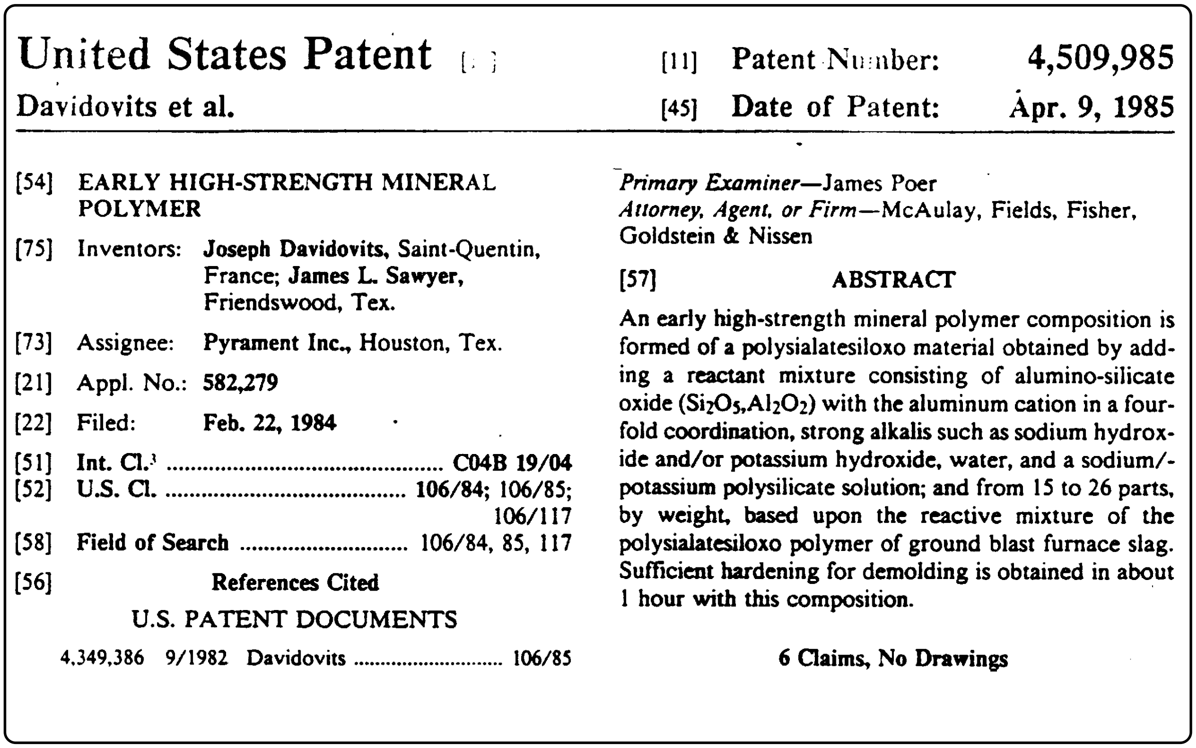
The K-PSS ^{29}Si MAS-NMR spectrum suggests that the structural model of K-PSS (Fig. 7) could be assigned to hydrated Leucite, in agreement with the proposed chemical mechanism suggested in earlier studies.

THE INVENTION OF VERY EARLY HIGH-STRENGTH CEMENT

In early 1983, Chairman, Mr. James Stewart, and Mr. W. Kirkpatrick, of Lone Star Industries Inc. (then America's leading cement manufacturer), were travelling in Europe and learned about my new geopolymeric binders. Lone Star Industries and Shell Oil Company had just announced the formation of the QUAZITE 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. QUAZITE materials were made from mineral aggregates combined with polymers and monomers. In other words, QUAZITE was an «organic polymer concrete.» The chemical expertise in organic polymers for QUAZITE was supplied by Shell Oil, while the mineral aggregates were supplied by Lone Star. By enlisting my 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, we 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. Few months later, Lone Star separated from the Shell Oil deal.

PYRAMENT® cements: geopolymeric cements and Portland blended cements

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/Sawyer 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.



United States Patent [ ]
Davidovits et al.

[11] **Patent Number: 4,509,985**
[45] **Date of Patent: Apr. 9, 1985**

[54] EARLY HIGH-STRENGTH MINERAL POLYMER

[75] Inventors: **Joseph Davidovits**, Saint-Quentin, France; **James L. Sawyer**, Friendswood, Tex.

[73] Assignee: **Pyrament Inc.**, Houston, Tex.

[21] Appl. No.: **582,279**

[22] Filed: **Feb. 22, 1984**

[51] **Int. Cl.³** **C04B 19/04**
[52] **U.S. Cl.** **106/84; 106/85; 106/117**
[58] **Field of Search** 106/84, 85, 117

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Primary Examiner—James Poer
Attorney, Agent, or Firm—McAulay, Fields, Fisher, Goldstein & Nissen

[57] ABSTRACT

An early high-strength mineral polymer composition is formed of a polysialatesiloxo material obtained by adding a reactant mixture consisting of alumino-silicate oxide (Si_2O_5,Al_2O_2) with the aluminum cation in a four-fold coordination, strong alkalis such as sodium hydroxide and/or potassium hydroxide, water, and a sodium/-potassium polysilicate solution; and from 15 to 26 parts, by weight, based upon the reactive mixture of the polysialatesiloxo polymer of ground blast furnace slag. Sufficient hardening for demolding is obtained in about 1 hour with this composition.

6 Claims, No Drawings

Table I of the patent description outlines the state of the art in the strength development of cementitious systems (see Table 4). It gives the compressive strength comparison on 2" cubes for the geopolymer standard mixture (Example I), the early high-strength geopolymer (Example III), cements of Lone Star Industries Type I, Type III, and early high strength Portland cements Super Incor Cement and Reg. Set II Cement.

Table.4: State of the Art 1983, Early High Strength cements, Table I of Davidovits/Sawyer’s patent.

TABLE I

COMPRESSIVE STRENGTH COMPARISON, 2" CUBES, PSI

150° F. for 4 hours

	Geopolymer Example I	Geopolymer Example III	Type I (N.O.) Portland Cement	Super Incor Cement	Reg. Set II Cement
as cured 150°F	6730	8350	260	3000	2200
then stored at 73°F					
I day	6400	8770	2130	8150	3600
7 days	7050	8500	4500	8620	4400
28 days	6900	9000	7200	9720	5200

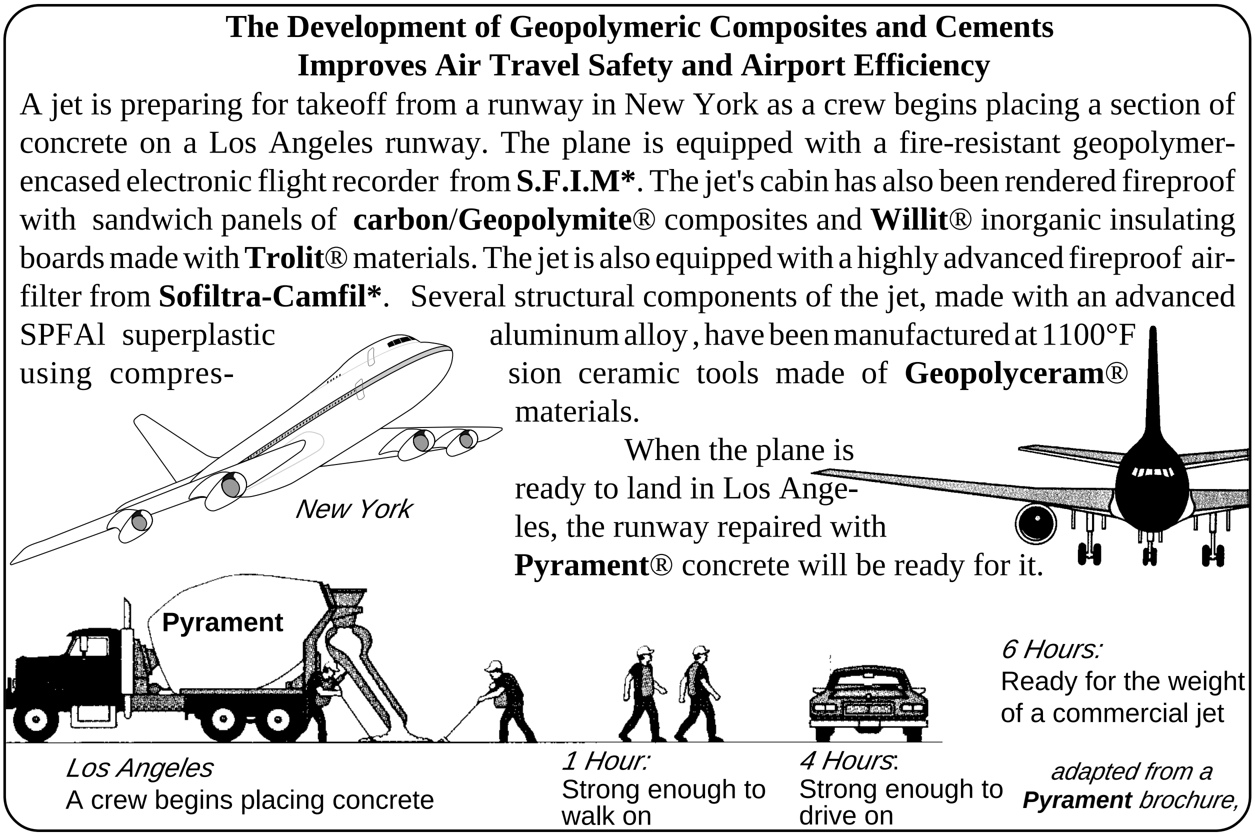
No Heat Curing

	Geopolymer Standard Mixture Example I	Geopolymer Example III	Type I Cement (Miami)	Type III Cement (Greencastle)	Super Incor Cement	Reg. Set II Cement
room temperature						
4 hours	-	3500	-	-	2000	1800
1 day	2000	7920	2000	4500	6600	3800
7 days	4500	8200	5000	6500	8600	4700
28 days	7000	9000	7100	7100	9000	6200

James Sawyer's team (Richard Heitzmann & colleagues) adapted the geopolymeric cement formulations (Geopolymer Example III in TABLE I) for use in the production of precast and prestressed concrete (heat cured PYRAMENT), while also developing ultra-rapid high ultimate strength cement (ambient temperature cured PYRAMENT). The latter enables pavement to be placed so that heavy traffic can traverse in four hours. The PYRAMENT brochures released in 1986 disclosed seven US geopolymeric patents, five acquired from Davidovits and two developed by Lone Star, based on my original geopolymer technology (see Fig. 8).

As early as 1981, I had utilized Portland cement as a room temperature setting admixture for a geopolymer foam compound (French Patent 2,512,806). At Lone Star, 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) is very close to alkali-activated pozzolanic cement (US Patent 4,842,649)[26]. PYRAMENT PBC cement comprises 80% ordinary Portland cement and 20% of geopolymeric raw materials, that is,calcium silicate and alumino-silicates alkali-activated with potassium carbonate and retarded with citric acid. PYRAMENT PBC is recognized in the construction industry for its ability to gain very high early strength quite rapidly.

As of fall 1993, PYRAMENT concrete is listed for over 50 industrial facilities in the USA, 57 military installations in the USA, and 7 in other countries, and for nonmilitary airports. The unprecedented performance of PYRAMENT concrete for the repair of airport runways is illustrated



The Development of Geopolymeric Composites and Cements Improves Air Travel Safety and Airport Efficiency

A jet is preparing for takeoff from a runway in New York as a crew begins placing a section of concrete on a Los Angeles runway. The plane is equipped with a fire-resistant geopolymer-encased electronic flight recorder from **S.F.I.M***. The jet's cabin has also been rendered fireproof with sandwich panels of **carbon/Geopolymite**® composites and **Willit**® inorganic insulating boards made with **Trolit**® materials. The jet is also equipped with a highly advanced fireproof air-filter from **Sofiltra-Camfil***. Several structural components of the jet, made with an advanced SPFAl superplastic aluminum alloy, have been manufactured at 1100°F using compression ceramic tools made of **Geopolyceram**® materials.

When the plane is ready to land in Los Angeles, the runway repaired with **Pyrament**® concrete will be ready for it.

*) S.F.I.M. and Sofiltra-Camfil are French-licensed companies utilizing Geopolymite binders.

Figure 9: example of what a combination of geopolymeric products can offer

in Fig.9. Recently, 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 [27, 28].

In the ^{29}Si MAS-NMR spectrum for fully hydrated Pyrament Blended Cement, 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 weak broad band between -85 ppm and -100 ppm characterises SiQ_4 units like those found in tecto-alumino-silicates, i.e. Geopolymer cement [29]

(K-Ca) (Si-O-Al-O-Si-O-) Poly(sialate-siloxo) cement, PZ-Geopoly®.

Geopolymer cements are acid-resistant cementitious materials (trade names PZ-Geopoly® and Geopolycem®), with zeolitic properties, developed for the long-term containement of hazardous and toxic wastes (US Patents 4,859,367; 5,349,118). 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:

$$2(Si_2O_5,Al_2O_2)+K_2(H_3SiO_4)_2+Ca(H_2SiO_4)_2 \Rightarrow (K_2O,CaO)(8SiO_2,2Al_2O_3,nH_2O)$$

Tailored aluminosilicate geopolymeric PZ-Geopoly® cement comprises following major compounds, namely:

- specific alumino-silicates of the kaolinitic clay species, calcined at 750°C;

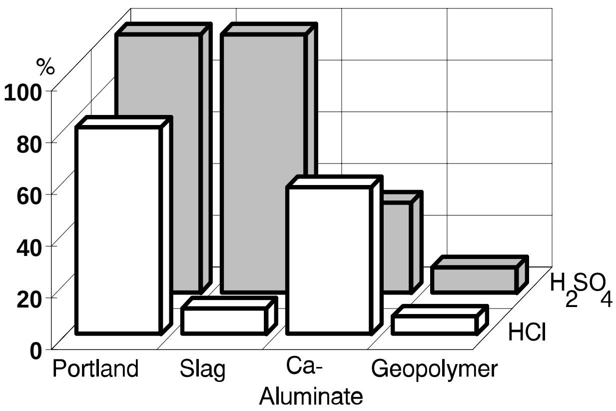


Figure 10: Break up in acidic environment (5% acid solutions) for Portland cement, blended slag/Portland, Ca-aluminate cement and Poly(sialate-siloxo) cement.

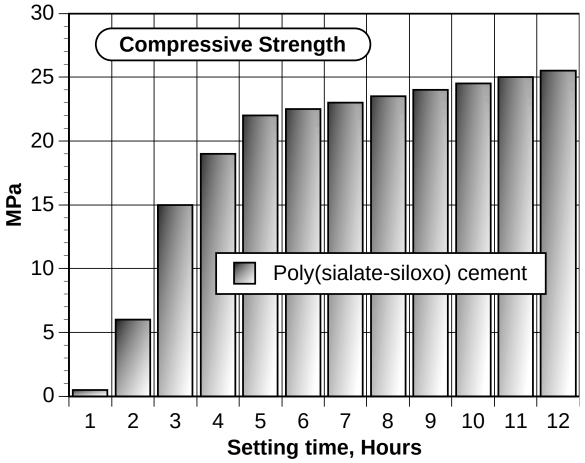


Figure 11: Room temperature setting for concretes made of (K-Ca)-Poly(sialate-siloxo), PZ-Geopoly® cement.

- alkali-disilicates $(Na_2,K_2)(H_2SiO_4)_2$
- calcium disilicates $Ca(H_2SiO_4)_2$ produced by the alkali-reaction with blastfurnace slag
- silica fume from ferro-silicon.

Unlike conventional Portland cement, geopolymeric cements do not rely on lime and are not dissolved by acidic solutions (Fig.10). 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.This acid-resistant 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 Fig.11).

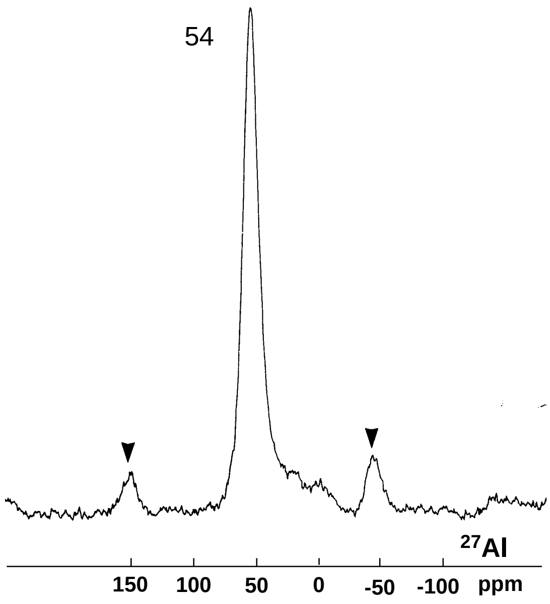


Figure 12: ^{27}Al MASNMR

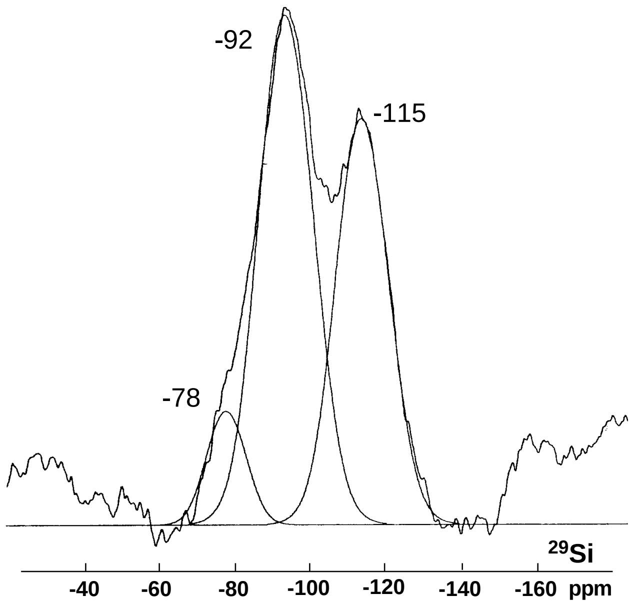


Figure 13: ^{29}Si MASNMR

for (K-Ca)-Poly(sialate-siloxo) Geopolymer cement.

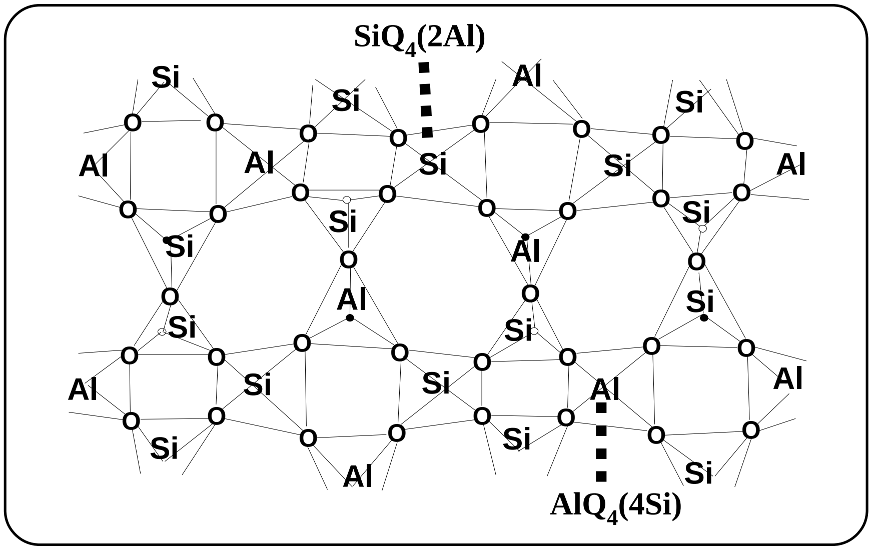


Figure 14: proposed structural model for (K-Ca)-Poly(sialate-siloxo) cement

MAS-NMR Spectroscopy

Our preliminary study involving ^{27}Al MAS-NMR, singular peak at 54 ppm, AlQ_4(4Si) unit, and ^{29}Si MAS-NMR, major band at -92 ppm, SiQ_4(2Al) unit, small band at -78 ppm, SiQ_0 unit, band at -115 ppm related to un-reacted silica-fume (SiO_2), (see Fig. 12, 13) and the proposed structural model (Fig. 14) reveal that geopolymeric cements are the synthetic analogues of tecto-alumino-silicates. Tab. 5 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 5: 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	5.16	54	57
Al_2O_3	17.58	19	20
CaO	11.1	10	6
MgO	2.93	1.5	2
K_2O,Na_2O	9.2	10.6	7

THE DIFFERENCE BETWEEN ALKALI-ACTIVATED CEMENTS AND GEOPOLYMERIC CEMENTS

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

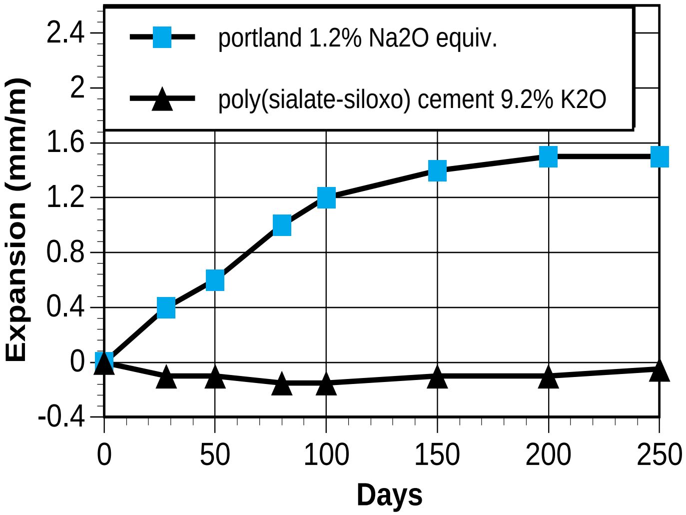


Figure 15: Alkali-Aggregate Reaction; ASTM C227 bar expansion for Poly(sialate-siloxo) cement and ordinary Portland Cement

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 alumino-silicates) substantially reduces the Alkali-Aggregate-Reaction of high-alkali cements. Sersale and Frigione [35] went further by suppressing the Alkali-Aggregate-Reaction with the addition of zeolites (alkali-alumino-silicates), such as chabazite and phillipsite. Finally, Haekkinen [36], Metso [37], Talling and Brandstetr [38] are claiming that alkali-activated alumino-silicate 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 alumino-silicates

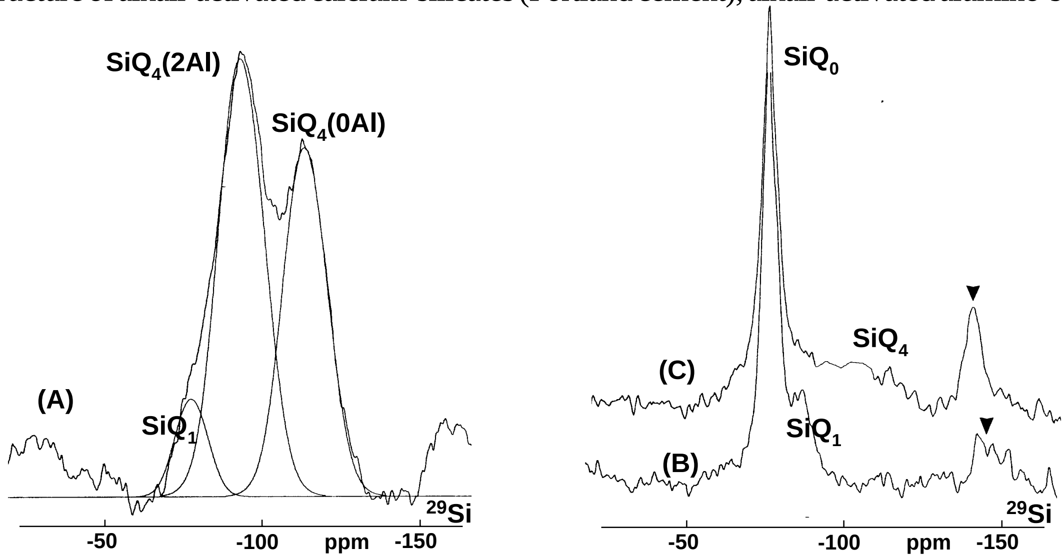


Figure 16: ^{29}Si MASNMR for (K-Ca) Poly(sialate-siloxo) PZ-Geopoly® cement (A), alkali-activated Portland cement (K_2O= 3.5%) (B), Geopolycem® cement (K_2O= 3.5%) (C),

(Geopolymer) and alkali-activated Geopolymeric blended cements [39, 40]. In 1982 Lippmaa and his colleagues followed the hydration of tricalcium silicate with ^{29}Si MASNMR [41]. Other papers by Young [42], Hjorth & al. [43], Rodger & al. [44], showed that the kinetics of SiO_4 polymerization which occurs during the hydration of tricalcium silicate follows a series of well-defined steps starting from the monomer (Q_0), followed closely by the formation of dimer (Q_1) and later by a more complex trimer/tetramer (Q_2) and expected finite linear polymeric chain.

Preliminary ^{27}Al 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 AlQ_0 into 6-coordinated AlO_6, in spite of the low Al content. Alkali-activated O.P.C. has two distinct ^{27}Al chemical shifts, one in the range of 65 ppm, which indicates that the aluminium is tetrahedrally coordinated and is of the AlQ_3(3Si) type, and the second in the range of 0 ppm typical for hydrated 6-coordinated AlO_6 compounds (Fig. 17). Recent published study shows a similar effect in alkali-activated slag with the formation of AlQ_2(2Si)[46] (see Table 6) . The intensity of the AlQ_3(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 AlO_6 hydrate species but rather are taking part in the formation of the Al substituted C-S-H-compounds. The free hydroxyl ions of the AlQ_3(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, essentially those displaying ^{27}Al MASNMR resonance in the range of 20-50 ppm, transformed any AlQ_{2-3}(2-3Si) units into stable AlQ_4(4Si) geopolymeric unit with 55 ppm ^{27}Al resonance (GEOPOLYCEM®, US Patent 5,288,321).

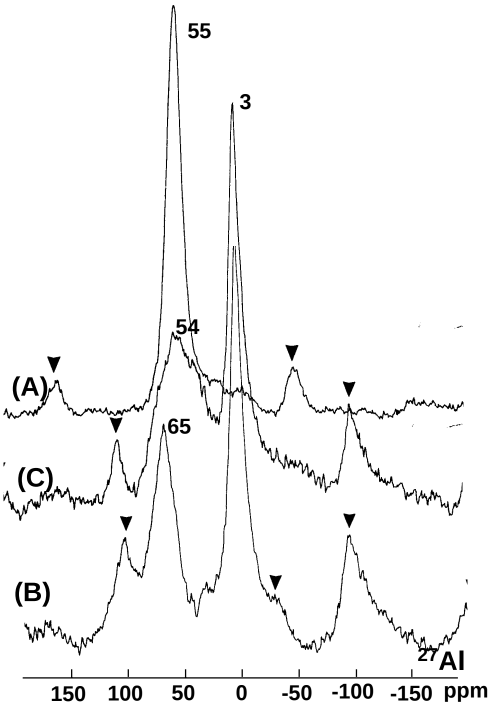


Figure 17: ^{27}Al MASNMR for (K-Ca) Poly(sialate-siloxo) PZ-Geopoly® cement (A), alkali-activated Portland cement (K_2O= 3.5%) (B), Geopolycem® cement (K_2O= 3.5%) (C), after hydration and hardening.

Table 6: Al-coordination, ^{27}Al chemical shift and AlQ_n units, in alkali-activated cements and Poly(sialate-siloxo) cement.

Name	Coordination	Chemical shift (ppm)	AlQn
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 Geopolycem cement	6, 4	54, 3	AlQ_4(4Si)
Alkali-activated synthetic slag	6,4	75-65, 3	AlQ_{2-3}(2-3Si)

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, AlQ_4(4Si) building units (Fig.17 and Table 6), does not generate any deleterious alkali-aggregate-reaction (Fig. 15, ASTM C227 bar expansion test), whereas the cement which resonates at 66 ppm, AlQ_3(3Si) 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, SiQ_4(3Al)-SiQ_4(2Al)-SiQ_4(1Al) (Fig. 16), and are essentially different from the Si(Q_0), Si(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 [48,49]. Geopolymers result from the geosynthesis of polymeric alumino-silicates 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 ,Geopolymeric cementitious compounds,Geocements or Poly(sialate) cements, focuses on their unique properties as opposed to other cementitious compounds..

GLOBAL-WARMING CONCERNS FOSTER NOVEL CEMENT TECHNOLOGIES.

Life would not be possible on the earth without the greenhouse-effect. Through a natural phenomenon, radiation from earth is trapped by the gases in the atmosphere, thus maintaining an average temperature of 15 degrees Celsius. It is the additional greenhouse effect due to human activity that worries scientists. The concentration of “greenhouse responsible gases” has been increasing continuously for the last two decades (Fig. 18): with 55%, carbon dioxide (CO_2) contributes most to greenhouse warming, followed by methane (CH_4) 15%, and the chlorofluorocarbons (CFC) 14%. One of the predictable consequences is that the earth’s temperature will rise. But this global warming will only be gradual up to the end of the next century, due to the inertia of climatic phenomena and the role played by the oceans. The IPCC (Intergovernmental Panel on Climate Change), the international authority on the topic, the work of which was the basis of the Rio de Janeiro Conference (1992), estimates that the rise in temperature should reach 1.9°C to 5.3°C. It is extremely difficult to evaluate the consequences of this global warming. The level of the oceans would rise between 20 and 80 centimetres, leading to the flooding of entire regions by the sea. The southern bank of the Mediterranean would be transformed into a vast desert, whereas Siberia would become the grain house of Europe.

It is expected that carbon dioxide emissions can be lowered 5-10% by reducing fossil-fuel use and through energy conservation and new energy technology. Higher reductions are expected only through major scientific and technological breakthroughs [50]. Although Europe, Japan, and USA, seem to agree on a stricter carbon dioxide emission policy, very few other countries are following suit. Studies performed in the US, China, and the former Soviet Union, suggest that in the year 2030 these countries will alone produce more carbon dioxide than the present total for the planet as a whole. After Germany proposed to cut its emission of carbon dioxide 25% by 2005 [51], the European Communities Commission, seeking to limit carbon dioxide emissions linked to global warming, recommended on September 25, 1991, that member states adopt a new energy and fuel tax. Yet, the tax is based on energy and fuel consumption, not on actual carbon dioxide emission measured at the chimneys. Chemical reactions which produce carbon dioxide -chemical-CO_2 as opposed to the carbon dioxide which results from the combustion of carbon-fuel- are not taken into account, even though chemical-CO_2 emissions could represent, in the near future, 15% to 20% of today's total carbon dioxide emissions. This is particularly the case for cement and iron manufacturing. Very few papers deal with the issue of carbon dioxide produced during Portland cement manufacturing. In 1990, the US Dept. of. Energy. Carbon Dioxide Information Analysis Center, endorsing the validity of chemical-CO_2 emissions, provided data which included carbon dioxide emissions from fossil-fuel burning and cement production [52]. The topic was also discussed at a recent Portland Cement Association Conference with supplementary world statistics and technical data [53,54], and at the 1993 American Ceramic Society Meeting [55]. Portland cement clinker is made from the calcination of limestone (calcium carbonate) and siliceous material according to the reaction:

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

The production of 1 tonne of cement directly generates 0.55 tonnes of chemical-CO_2; the combustion of carbon-fuel yields an additional 0.40 tonnes of carbon dioxide.

To simplify: *1 T of cement = 1 T of carbon dioxide.*

The 1987, 1 billion metric tonnes of world production of cement accounted for 1 billion metric tonnes of carbon dioxide, i.e. 5% of the world carbon dioxide emission. This is equivalent to the carbon dioxide generated by the entire Japanese industrial activity. Recognising the need to save energy and raw materials, the iron, glass and chemical industries are presently involved in programs aimed at increasing the use of recyclable materials. Indirectly, these industries may undertake programs which would contribute to a reduction of chemical CO_2 emissions.

But the greatest difficulties concern the developing countries, which are in urgent need of basic industries. Some suggest that these countries could immediately have access to the most efficient technologies. But this vision is probably much too naive. Obviously, research for new and efficient technologies and energy sources is not on the agenda of developing countries. They are more concerned with the development of an industrial base capable of producing the necessary goods for building construction in order to meet the needs of their population. **In fact, the level of any national economic development is judged by the growth rate of infrastructures which is linked to the cement production.**

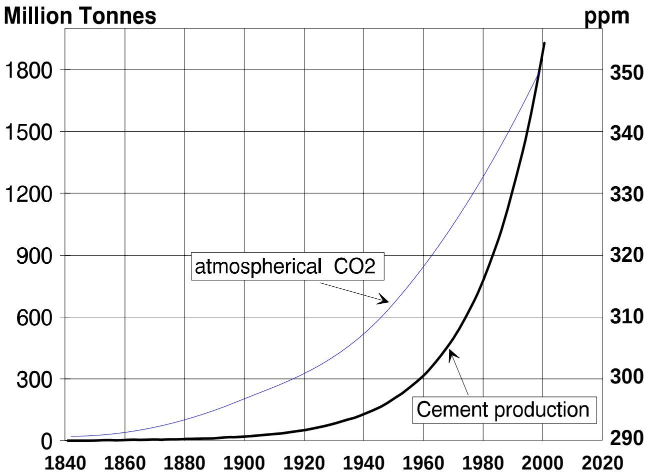


Figure 18:: Atmospheric CO_2 concentration (ppm) and world portland-cement production (million tonnes) for the period 1840-2000. Sources: IPCC and Cembureau

Fig. 18 displays the atmospheric carbon dioxide concentration increase for the time range 1840-2000 and the development of world portland cement production since 1840. Since the 1970s, due to exponential increase in concrete use, cement production has increased at a much higher rate than atmospheric carbon dioxide concentration from all activities, including energy and transportation. As time goes by, it will thus have a greater influence on the trends of CO_2 emissions and the predicted values for future atmospheric carbon dioxide concentration should be corrected accordingly. Predicted values for cement production are those obtained according to a BaU (Business as Usual) scenario, which assumes a continuation of present demographic and industrial trends, without any major technological revolution and other particular restrictive measures. In developing countries, especially China and India, and in the industrialised Pacific region (South Korea, Taiwan) the increase in cement production has followed an exponential trend since the seventies, contrasting sharply with western countries (USA, EC) where cement production has not increased significantly (see Fig.19). The question now is whether this trend will continue. There can be no doubt about the on-going nature of the present evolution, since other developing countries, like Thailand and Mexico, are now being listed as the top 15 cement producers in the world. Under these conditions, a world-wide freeze of carbon dioxide emission from portland cement production at the 1990 level as recommended by the EC, could easily be achieved in industrialised countries but, in contrast, would be incompatible with the development needs of less industrialised countries. Bearing in mind that international actions aimed at reducing carbon dioxide emission must be undertaken, a drastic change in the cement-based systems involved in the making of concrete is necessary. Fig. 20 displays the predicted annual world production of cement with the BaU scenario, and carbon dioxide until year 2003. The freeze requires the search for alternative binders and their production. We discuss this issue in the next chapter. Yet, concretes should utilise less calcium-based cements, the latter being replaced by calcium-free binders (sodium- or potassium-based geopolymer cements) pro-

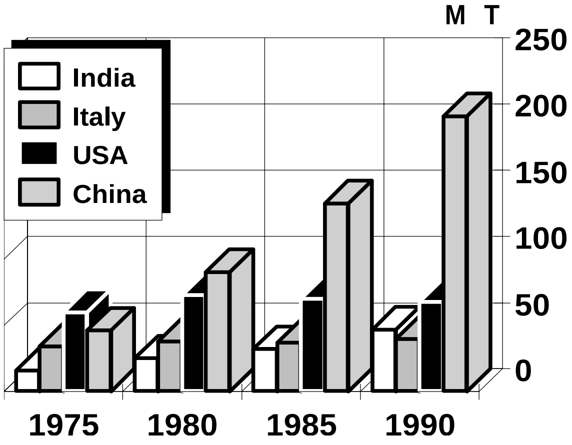


Figure 19 : Annual cement production for China, India, Italy , USA in million tonnes (MT). Source: Cembureau

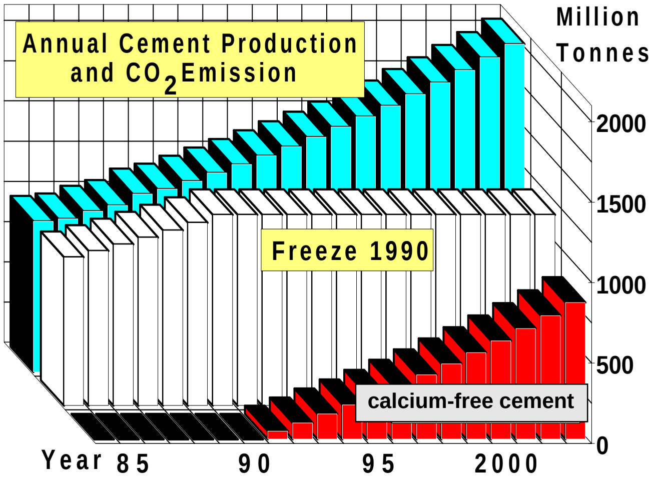


Figure 20:The uper plot shows the predicted world annual production of portland-cement and connected carbon dioxide (BaU). The lower plot shows the potential market for calcium-free cements assuming freeze of portland-cement production at 1990 level; data from [22, 53]

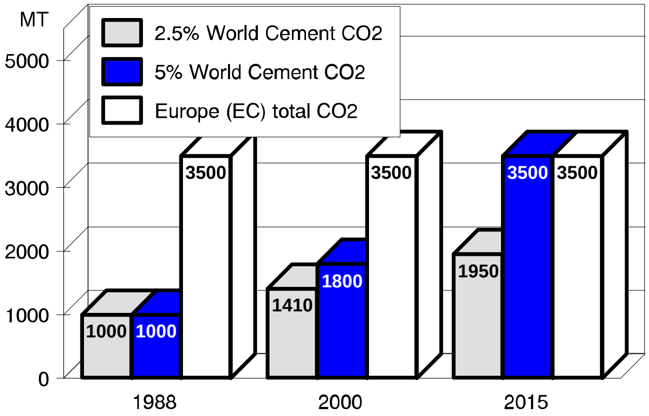


Figure 21: BaU value for World Cement-carbon dioxide with 2.5% and 5% yearly increase and «frozen» Europe (EC) total carbon dioxide emission at 1990 level, million tonnes (MT.).

viding similar or even better cementitious properties.

With the assumption that Europe (EC) and USA will commit themselves to such a freeze, the third world cement production will continue to grow and become the major source of carbon dioxide emission. Fig. 21 illustrates BaU values for World Cement-carbon dioxide, (years 2000, 2015), assuming a 2.5% and 5% yearly increase, respectively, and «frozen» Europe (EC) total carbon dioxide emission at 1990 level. The question could be raised on the probability of having a constant growth in the 5% range. Present annual cement production statistics are suggesting an average growth ratio in favour of the 5% increase scenario. In 25 years from now, world cement carbon dioxide emissions could equal the 3,500 million tonnes total carbon dioxide production (industry+energy+transportation) of Europe (EC) or 65% of present total USA CO_2 emissions. This addresses the need for new technologies to be adapted to the economy of the developing countries.

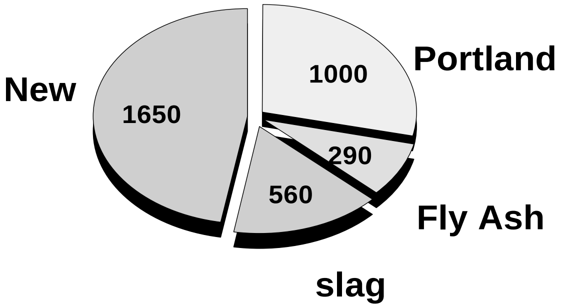
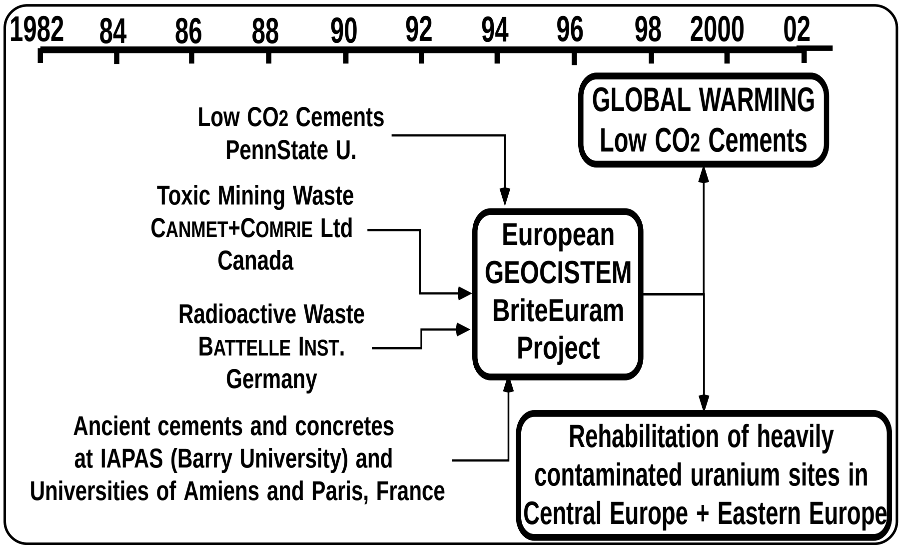


Figure 22: Distribution of BaU world cement market for the year 2015, total 3500 million tonnes.

In terms of the 5% growth scenario set forth for the year 2015, 1000 million tonnes of portland cement might be blended with 400-600 million tonnes of slag and about 300 million tonnes of fly ash or 300 million tonnes natural pozzolan. According to Fig. 21, the BaU world cement prediction for the year 2015 equals 3500 million tonnes. Based on an amount of Portland blended cement production in the order of 1850 million tonnes (1000 Mt. Portland + 560 Mt. slag + 290 Mt. fly ash), the need for new low-CO_2 cementitious materials could be in the range of 1650 million tonnes, as displayed in Fig. 22.

In preparation for the Rio Conference (June 1992), several multinational industry leaders, gathered in the Business Council for Sustainable Development (BCSD) [56], came to the conclusion that industries must imperatively integrate environmental considerations into their research and development strategy. They must manufacture products and equipment goods that are less polluting, do so with cleaner processes and better energy efficiency. This concerns of course mainly high energy-consuming industries such as steel and aluminum. But it also concerns production as a whole, like the concrete industries, where chemical-CO_2 emission reduction efficiency can be improved.



Geopolymer cements are manufactured in a different maner than that of Portland cement. They do not require extreme high temperature kilns, with large expenditure of fuel, nor do they 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) will provide suitable geopolymeric raw-materials. Geosynthesis is the objective of the European multidisciplinary **BriteEuram** industrial research project GEOCISTEM which is presently fostering the industrial development of this geological route. The project seeks to manufacture cost-effectively geopolymeric cements for applications dealing primarily with the long term containment of hazardous and toxic wastes, and for restoring sites highly contaminated with uranium mining waste (WISMUT sites in former East-Germany). The technology reduces also the energy consumption during cement manufacturing. Introducing these low-CO_2 geopolymeric cements, not only for environmental uses, but also in construction and civil engineering, would reduce CO_2 emission caused by the cement and concrete industries by 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 850 millions tonnes of cementitious by-products, the complementary need for new low-CO_2 cementitious materials, in the range of 1650 million tonnes, would be easily covered by these novel cements developed from geosynthesis, and would allow an unlimited development of concrete infra-structures in our Global Economy [57].

*) Geopolymite, Geopolycem, PZ-Geopoly are trademarks of Cordi-Geopolymère SA, France. Pyrament is a trademark of Lone Star Industries Inc., USA. Trolit is a trademenark of Hüls Troisdorf AG, Germany. Willit is a trademenark of Willig GmbH, Germany.

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