

**30 Years of Successes and Failures
in Geopolymer Applications.
Market Trends and Potential Breakthroughs.**

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Summary:

The presentation included 30 slides describing following geopolymers applications developed since 1972 in France, Europe and USA. The Geopolymer chemistry concept was invented in 1979 with the creation of a non-for profit scientific organization, the Institut de Recherche sur les Géopolymères (Geopolymer Institute).

1. Fire resistant wood panels
2. Insulated panels and walls,
3. Decorative stone artifacts,
4. Foamed (expanded) geopolymers panels for thermal insulation,
5. Low-tech building materials,
6. Energy low ceramic tiles,
7. Refractory items,
8. Thermal shock refractory,
9. Aluminum foundry application,
10. Geopolymer cement and concrete,
11. Fire resistant and fire proof composite for infrastructures repair and strengthening,
12. Fireproof high-tech applications, aircraft interior, automobile,
13. High-tech resin systems.

The applications are based on 30 patents filed and issued in several countries. Several patents are now in the public domain, but others are still valid. The applications show genuine geopolymers products having brilliantly withstood 25 years of use and that are continuously commercialized.

INTRODUCTION

When, 38 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. 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.

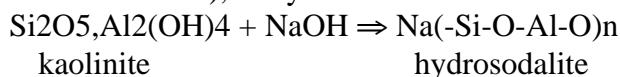
A dramatic photograph showing a firefighter in silhouette, spraying a powerful stream of water onto a multi-story building engulfed in intense orange and yellow flames. The fire appears to be spreading rapidly, with thick smoke billowing from the windows and roof. The scene conveys a sense of emergency and the challenges faced by firefighters in combatting such fires.

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. 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 «géopolymères» geopolymers (mineral polymers resulting from geochemistry or geosynthesis).

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., 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 1969, Besson, Caillère and Hénin at the French Museum of Natural History, Paris, carried out the synthesis of hydrosodalite from various phyllosilicates (kaolinite, montmorillonite, halloysite) at 100°C in concentrated NaOH solution. I developed a technology based on this geosynthesis, which has been disclosed in various patents issued and granted.

Fire-resistant wood-chipboards (1973-1976)

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-Poly(sialate)/quartz nanocomposite), when applying the same thermosetting parameters as for organic resin (see Fig. 1).

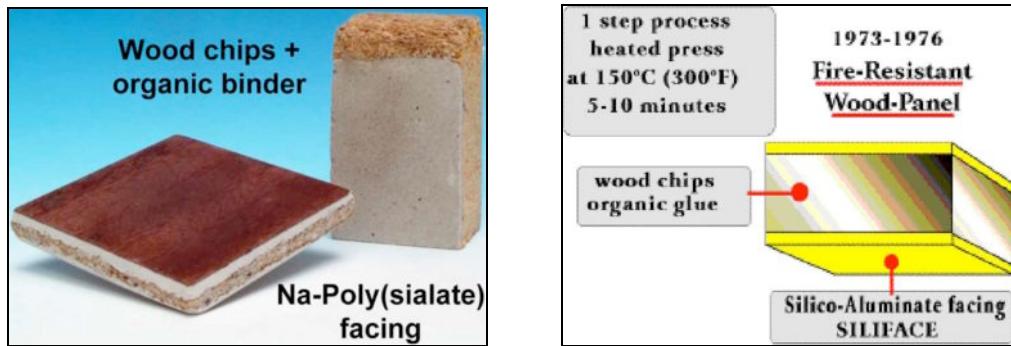


Figure 1!: Manufacture of fire-resistant wood-chipboards faced with geopolymer (Na-Poly(sialate))

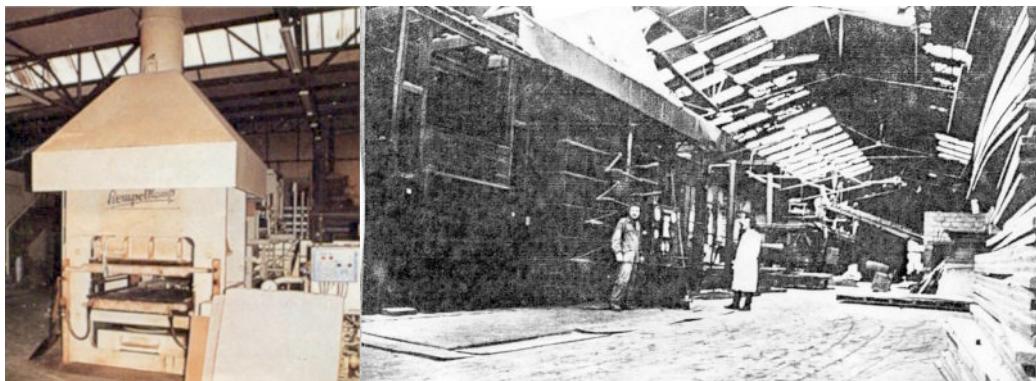


Figure 2!: Pilot and industrial equipments!: heated press

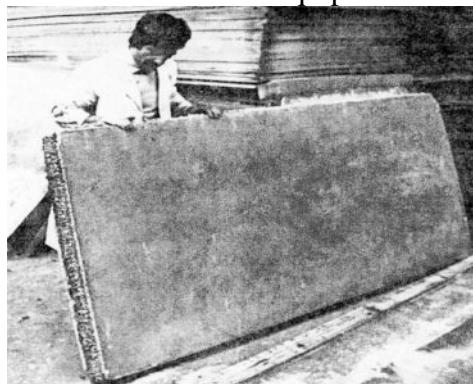


Figure 3!: Geopolymer-chipboard

The thermosetting parameters applied on the industrial equipments (Fig. 2) were:

- temperature: 130°C to 200°C
- applied hydraulic pressure: higher than the saturated vapor pressure of water, for the selected temperature, i.e. 1 to 3 MPa.

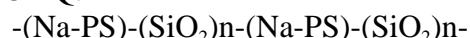
The setting time is relatively short. In the absence of any previous device, i.e. when degassing is not working, the polycondensation into hydrosodalite occurs very rapidly in a time as short as 15-20 seconds per millimeter thickness, at 180°C and 40kg/cm² hydraulic pressure. Yet, due to

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 fire-resistant chipboard panels were developed in 1972-1976 (Fig. 3). The Industry Partners were the French companies A.G.S. and Saint-Gobain and the client was the French Government, for the building of high schools and universities. A decision to build a pilot plant was made but then in 1976 there has been a change in building policy and a Political decision to stop the implementation. The project was abandoned.

Ceramic applications (1977-1978)

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 micelles. One obtains the sequenced poly(sialate) (Na-PS) nanocomposite called SILIFACE Q:



By replacing quartz with synthetic cordierite, $(\text{Si}_5\text{AlO}_{18})\text{Al}_3\text{Mg}_2$, 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%	Stearite	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%		



Figure 4!: Electrical fuses made with geopolymers SILIFACE COR 70

This unique geopolymers was tested for the manufacture of electrical fuses for the French company LEGRAND in 1977-1978 (Fig. 4). The mechanical properties, thermal properties, molding at 120 deg.C, post-treatment at 450 deg.C, were excellent. Yet, water absorption (0.3%) was not good enough, and the project abandoned.

Low Temperature Geopolymeric Setting of ceramic, L.T.G.S. (1977-1982)

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.5).

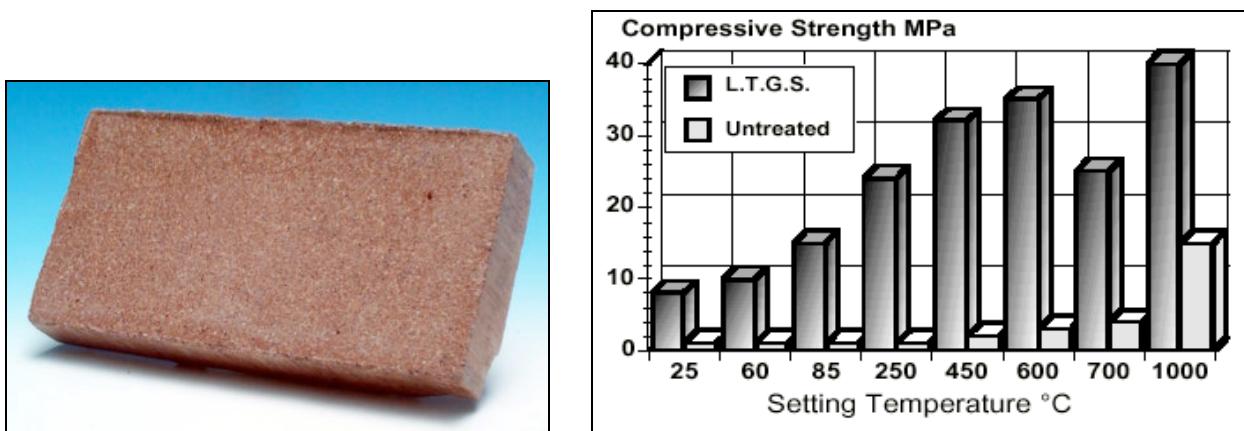


Figure 5: Brick made with L.T.G.S. on kaolinitic soils. Mechanical compressive strength in Mpa for untreated and geopolymersed kaolinitic earth (with 3% by weight equivalent Na₂O). Setting temperature ranges between 20°C and 1000°C.

L.T.G.S. may dramatically enhance and modernize the traditional ceramic industry. Once geopolymersed 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. 6).

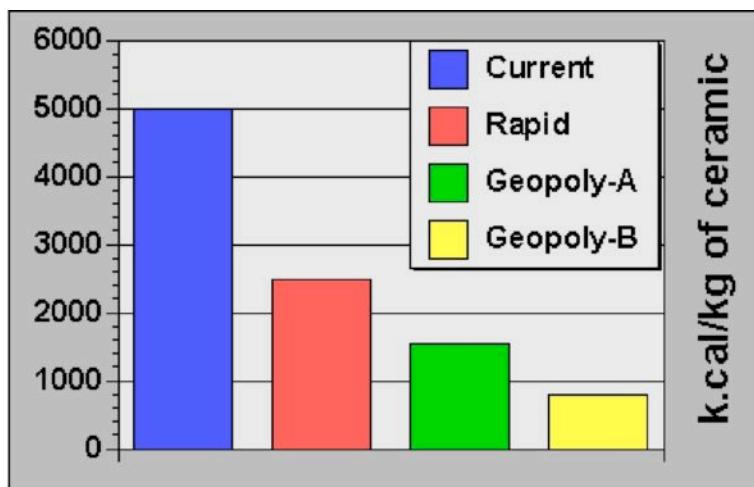


Figure 6: Fabrication of ceramic tile; energy consumption in kcal/kg of tile for current, rapid and geopolymersed methods (Geopoly- A, B) and firing at 1000°C-1200°C.

MAM-MADE ROCK GEOSYNTHESIS The Geopolymer Terminology

We showed that naturally occurring aluminosilicates, such as kaolinite, are transformed at low-temperature, in an astonishingly short time, into tridimensional tecto-aluminosilicates. The thermosetting 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 aluminum ion (6-fold or 4-fold coordination) to induce crystallographical and chemical changes in a silica backbone.

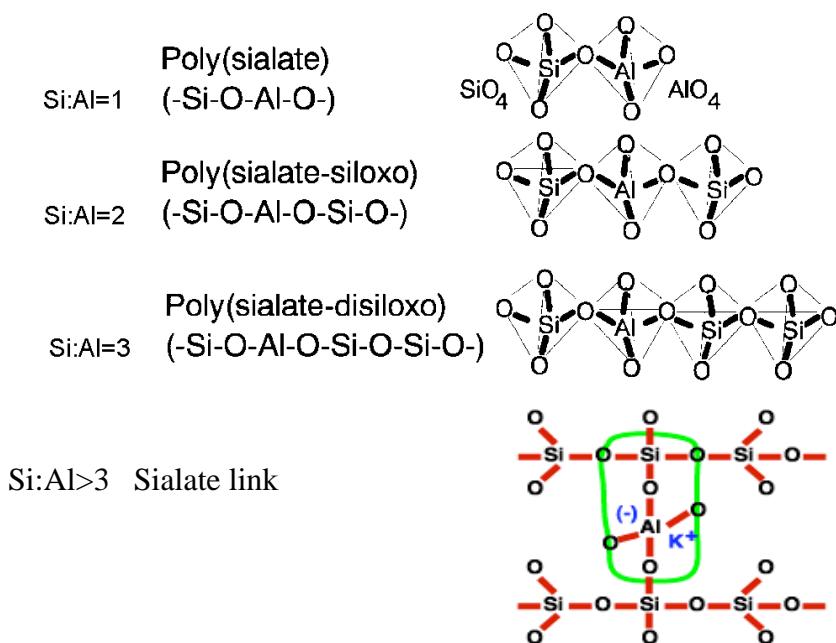
This basic innovation, the low-temperature transformation from kaolinite into hydrosodalite, demonstrated the tremendous latent potential of this new mineral reaction. This potential was neglected by the mainstream ceramics industry, by virtue of the infamous NIH principle (not invented here). It also 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.

Terminology

In 1979, I created and applied the term «geopolymer».

For the chemical designation of geopolymers based on silico-aluminates, poly(sialate) was suggested. Sialate is an abbreviation for silicon-oxo-aluminate. 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:



Geopolymeric Binders (1979-1995)

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.(Fig. 7).

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., Randel & al., at the licensed German Company Dynamit Nobel (later Hüls Troisdorf AG, now sublicense 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 (Fig. 8), mechanical engineering, molding, stamping, foundry work, metal casting, etc.. and it even includes archaeological research.



Figure 7!: decorative items made of (K)-Poly(sialate-siloxo) geopolymers.

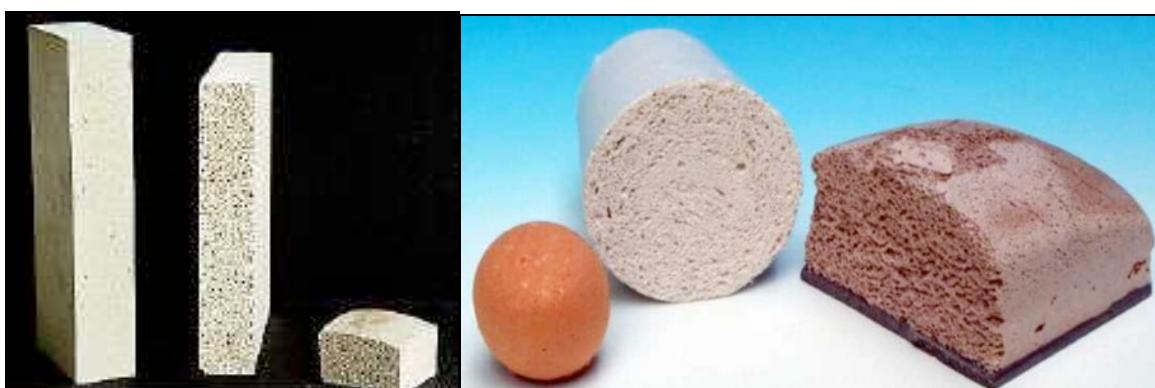


Figure 8!: foamed geopolymers (Na,K)-Poly(sialate-siloxo) resin.

Since 1986, the French aeronautic company **Dassault Aviation** has used geopolymers mold and tooling in the development of the Rafale fighter plane (Fig. 9)



Figure 9!: the French fighter plane Rafale. Courtesy: *Dassault Aviation*

In addition, we made for **Northrop Aviation** a geopolymers composite tooling prototype (self-heated carbon/SiC/Geopolymite composite) used in the fabrication of carbon/APC2 composite designed for a new US Airforce bomber. More than a hundred tooling and items has been delivered for aeronautic applications (**Airbus**) and SPF Aluminum processing.

The Invention of Geopolymer High-Strength Cement (1983)

(K-Ca) (Si-O-Al-O-Si-O-) Poly(sialate-siloxo) cement

In early 1983, Chairman, Mr. James Stewart, and Mr. W. Kirkpatrick, of Lone Star Industries Inc. (then America's leading cement manufacturer), were traveling 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.» Shell Oil supplied the chemical expertise in organic polymers for QUAZITE, while Lone Star supplied the mineral aggregates. 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.

It was discovered that the addition of ground blast furnace slag, which is a latent hydraulic cementitious product, to the poly(sialate) type of geopolymers, 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. Geopolymer cements are acid-resistant cementitious materials with zeolitic properties, developed for the long-term containment of hazardous and toxic wastes (US Patents 4,859,367; 5,349,118). Geopolymerization involves the chemical reaction of alumino-silicate oxides (Al³⁺ in IV-V fold coordination), with alkali and calcium polysilicates, yielding polymeric Si-O-Al bonds, for instance:



Tailored aluminosilicate geopolymeric cement comprises following major compounds, namely:

- specific alumino-silicates of the kaolinitic clay species, calcined at 750°C;
- alkali-disilicates $(Na_2,K_2)(H_2SiO_4)_2$
- calcium disilicates $Ca(H_2SiO_4)_2$ produced by the alkali-reaction with blast furnace slag

Unlike conventional Portland cement, geopolymeric cements do not rely on lime and are not dissolved by acidic solutions. 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 (Fig. 10). The final 28-day compressive strength is in the range of 70-100 MPa.

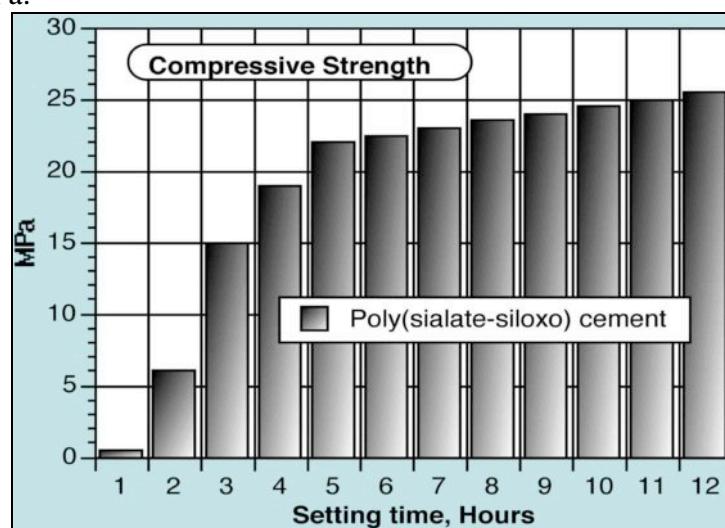


Figure 10!: High-early strength of (K,Ca)-Poly(sialate-siloxo) cement

James Sawyer's team (Richard Heitzmann & colleagues) adapted the geopolymeric cement formulations 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) (Fig. 11). The latter enables pavement to be placed so that heavy traffic can traverse in four hours.



Figure 11!: Use of PYRAMENT in USA as pavement repair material

PYRAMENT® cements, Portland blended cements!:

As early as 1981, I had utilized Portland cement as a room temperature setting admixture for a geopolymers foam compound (French Patent 2,512,806). At Lone Star, Richard Heitzmann and James Sawyer likewise blended Portland cement with geopolymers. Their purpose was to take advantage of the good properties of geopolymers 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 geopolymers 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.

The **Pyrament®** blended-cement is the ideal material for repairing runways made of concrete, industrial pavements, and highway roads. In the case of a runway, a 4-6 hours hardening is enough to allow the landing of an Airbus or a Boeing. The geopolymers cement reaches a compression strength of 20 Mpa after 4 hours, whereas plain concrete gets to this strength after several days. The **Pyrament®** blended cement is recognized in the construction industry for its ability to gain very high early strength quite rapidly. As of fall 1993, PYRAMENT concrete was listed for over 50 industrial facilities in the USA, 57 military installations in the USA, and 7 in other countries, and for nonmilitary airports. In 1994 the US Army Corps of Engineers released a well-documented study on the properties of PYRAMENT Blended Cements based concretes, which are performing better than had ever been expected for high-quality concretes (*Performance of Concretes Proportioned with Pyrament Blended Cement*, by Tony B. Husbands, Philip. G. Malone, Lilian D. Wakeley, US Army Corps of Engineers, Final Report CPAR-SL-94-2, April 1994).

Fireproof Geopolymer Fiber reinforced composites (1987-2000) **Giving Survivors More Time to Escape**



Figure 12!: A Carbon-Epoxy aerospace composite (left) is burning while a Carbon-Géopolymère Composite™ (right) still resists a 1200°C fire.

When a plane crash-lands and catches fire, half the people who survive the impact may not get out in time. That is because the plastics in the cabin -- the seat cushions, carpeting, walls and luggage bins -- are combustible. And when they burn, they give off flammable gases that, in two

minutes, can explode into a fireball. The U.S. Federal Aviation Administration (F.A.A.), wants to give passengers more time to escape. In 1994 the F.A.A. initiated a cooperative research program to develop low-cost, environmentally friendly, fire resistant matrix materials for aircraft composites and cabin interior applications. The GÉOPOLYMÈRE Composite has been selected by F.A.A. as the best candidate for this program (Fig. 13).

Aviation applications (1994-2000)

Aircraft cabin materials targeted for GÉOPOLYMÈRE Composite include cargo liners, ceiling, floor panels, partitions and sidewalls, stowage bins, wire insulation, yielding 2500-3000 kg. There is an increase demand for fire-resistant containers

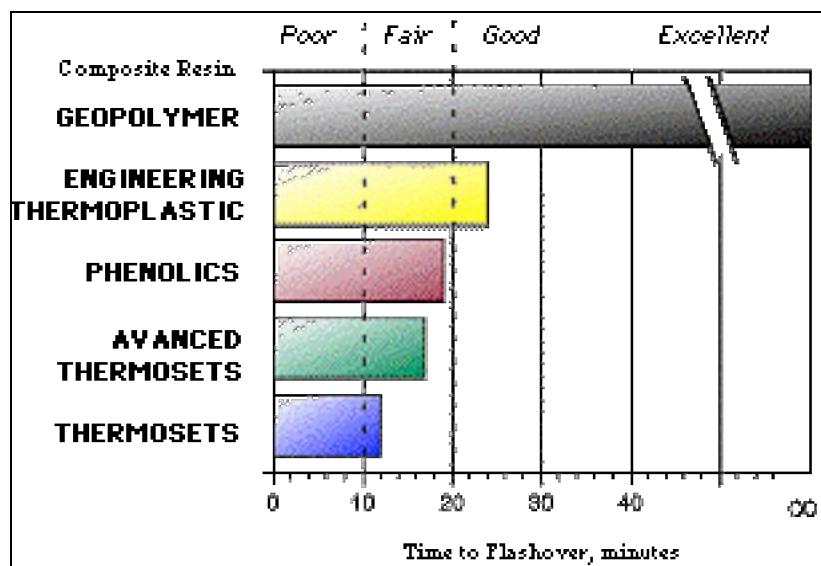


Figure 13!: Time to flashover (minutes) for various organic resins compared to geopolymers resin.

Civil and military ships/submarines

A significant technical issue, which limits composite use on board Naval ships and submarines, is the combustible nature, and hence, the fire, smoke, and toxicity of organic matrix based composite materials. The main conclusion from the extensive fire testing conducted by U.S. NAVY is that unprotected composite systems cannot meet the stringent fire requirements specified for interior spaces. Military vessels must perform their mission even when damaged, and must survive the fire for sufficient period of time to carry out rescue missions. The effects of fires aboard vessels have been demonstrated as a result of collision between ships and ferries during peacetime, and by experiences of the British Navy in the Falkland Islands and the American Navy in the Persian Gulf.

Automotive applications

During the Grand Prix season 1994 and 1995, the Benetton Formula 1 team designed a unique thermal shield made out of GÉOPOLYMÈRE Composite. All the parts were around the exhaust area, with special parts replacing titanium. They brilliantly withstood the severe vibration and heat (over 700 deg. C) seen on a Formula One car. It helped the team to become World Champion of car builders and pilots during these two years. Still today, most Formula 1 teams are using geopolymers composite materials.

In 1999, All American Racers (Dan Gurney's team) has introduced a more sophisticated design on an American C.A.R.T. car (former Indy-Cart) recognizable with its unique design and

distinctive note of the exhaust system going through the molded Carbon Géopolymère Composite body (Eagle 1999) (Fig. 14).



Figure 14!: The Eagle 1999 from All American Racers.

The experience gained on racing cars for exhaust parts could be transferred and applied for the mass production of regular automobile parts (corrosion resistant exhaust pipes and the like) as well as heat shields.

Infrastructure and building applications

F.A.A. is aware that the adoption of the new GÉOPOLYMÈRE Composite materials technology by aircraft and cabin manufacturers requires that it be cost effective to install and use, so it is expected that these new aircraft materials will be broadly applicable in transportation and infrastructure where a high degree of intrinsic fire resistance is needed at low to moderate cost and mass production. To this end the F.A.A. had funded the evaluation program carried out at Rutgers, The State University of New Jersey (the GEO-STRUCTURE program) based on the GÉOPOLYMÈRE technology.

A relatively new and very attractive repair method for concrete, brick and stone structures consists of externally bonding flexible sheets of fiber composites (Fig. 15 and 16). Another application for continuous fiber composites in infrastructure, already well underway in Japan and USA is the wrapping of concrete columns to reinforce new construction and damaged bridges and buildings in earthquake and hurricane prone areas. In this application, particularly for exposed interior building columns, flammability is a serious concern. Fire safety is a concern often voiced by those who are skeptical about the use of composite materials in the infrastructure and building industry.



Figure 15!: Concrete beam (3 meters long) with Geopolymer Carbon composite layers applied on its bottom surface, before testing

In Europe, the market targets on the retrofit of valuable Cultural Heritage buildings where fire safety is the major concern.

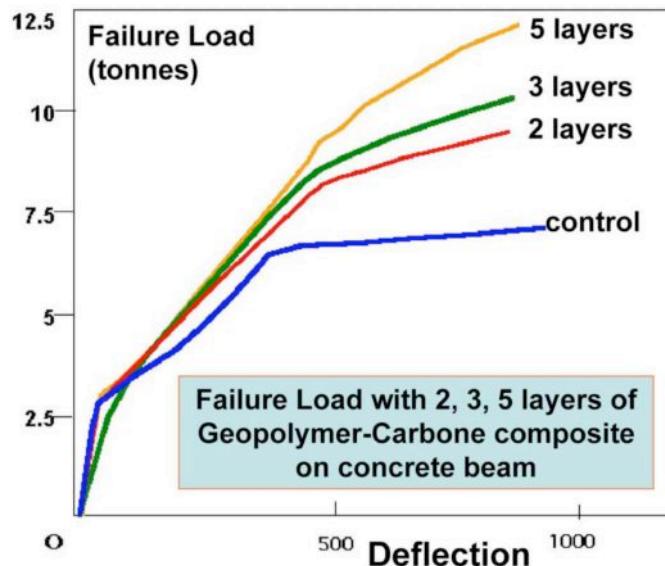


Figure 16!: Load vs Deflection for concrete beams with 0, 2, 3, 5 layers of Geopolymer Carbon composite.

Successful applications!

The following Figure 17 summarizes the successful applications carried out since 1979 with geopolymers of different types.

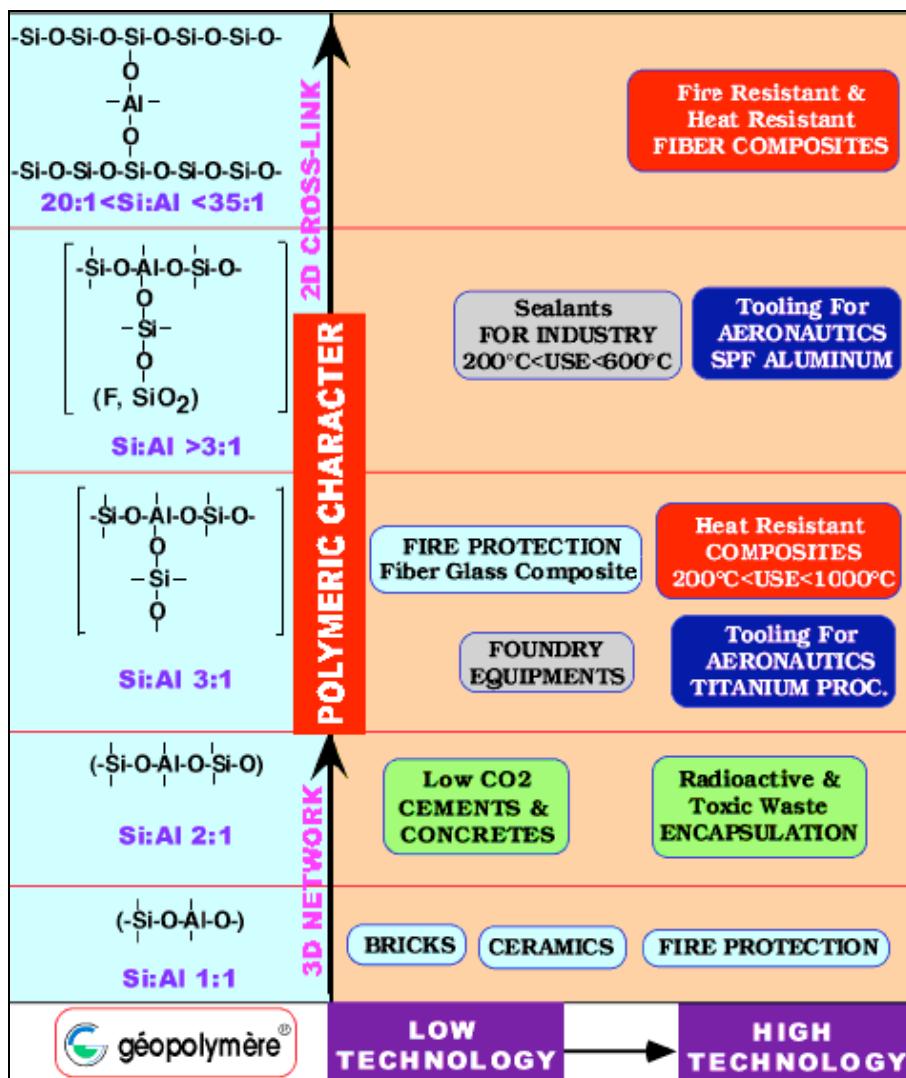


Figure 17!: Geopolymer types involved in successful applications.

PATENTS REFERENCES:

The majority of the patents (with very few exception such as the PYRAMENT patents) were first filed in France at the Paris Patent Office (INPI). The list provides the title of the patent translated into English, the publication number, the date of filing and the names of the inventors.

- Process for the fabrication of sintered panels and panels resulting from the application of this process. FR 2.204.999, FR 2.246.382 , 02/11/1972, 09/10/1973, Joseph Davidovits.
- Process for the fabrication of caustic soda NaOH in powder. FR 2.259.056, 29/01/1974!; Joseph Davidovits, Jean-Jacques Legrand
- Process for agglomerating compressible mineral substances under the form of powder, particles or fibres. FR 2.324.427, FR 2.346.121, 11/01/1974, 03/06/1975 , Joseph Davidovits, Jean-Jacques Legrand.
- Process for the fabrication of molded refractory items and products resulting from the process. FR 2.314.158, 09/06/1975 , Joseph Davidovits, Jacques Laveau.
- Fabrication process of light panels for insulation and high compressive strength, and products resulting from the process. FR 2.366.233, 03/06/1975 , Joseph Davidovits, Jean-Jacques Legrand, Jacques Laveau.
- Process for the fabrication of synthetic feldpathoids., FR 2.341.522, 20/02/1976 , CORDI-Géopolymère, Joseph Davidovits, Jacques Laveau, Alfred Emberger.
- Process for the fabrication of ceramics and products resulting from the process. FR 2.358.371, 12/07/1976 , Joseph Davidovits.

Mineral Polymers and methods of making them. FR 2.424.227, FR 2.489.290, 04/09/1979, 03/09/1980, Joseph Davidovits
Synthetic mineral polymer compound of the silicoaluminates family and preparation process. FR 2.489.291, 03/09/1980, Joseph Davidovits.
Process for the fabrication of building materials made with kaolinitic, lateritic, ferrallitic soils and products resulting from the process. FR 2.490.626, 23/09/1980 , Joseph Davidovits
Foamed mineral silico-aluminates products based on K-Poly(sialate) and/or (Na,K)-Poly(sialate-siloxo). FR 2.512.805, 17/09/1981, Joseph Davidovits, Jean-Jacques Legrand
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Method for manufacturing decorated, enamelled ceramics by monfiring, with geopolymer silico-aluminates. FR 2.523.118, 08/03/1982, Joseph Davidovits, Michel Davidovics
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Ceramic-Ceramic composite material and production method. FR 2.604.994, 14/10/1986, Nicolas Davidovits , Michel Davidovics, Joseph Davidovits
Method for eliminating the alkali-aggregate reaction in concretes and cement thereby obtained. FR 2.657.867, 05/02/1990, Joseph Davidovits
Geopolymeric fluoro-alumino-silicate binder and process for obtaining it. FR 2.659.320, 07/03/1990, Joseph Davidovits , Michel Davidovics, Nicolas Davidovits
Fire-proof géopolymeric panels for thermal protection and process for obtaining them. FR 2.659.963, 20/03/1990, Joseph Davidovits , Michel Davidovics, Nicolas Davidovits
Method for obtaining an early high-strength geopolymeric matrice for then impregnation of composite materials and products obtained thereof. FR 2.666.328, 04/09/1990, Joseph Davidovits , Michel Davidovics, Nicolas Davidovits
Process for obtaining a geopolymeric alumino-silicate and products thus obtained. FR 2.671.344, 03/01/1991, Joseph Davidovits , Michel Davidovics, Nicolas Davidovits
Alkaline aluminosilicate geopolymeric matrix for composite materials with fibre reinforcement and method for obtaining same. EP 0. 815.064, 15/03/1995, Joseph Davidovits , Michel Davidovics, Nicolas Davidovits
Method for bonding fiber reinforcement on concrete and steel structures and resultant products. FR 2.756.840, 06/12/1996, Joseph Davidovits

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complete and detailed lists of scientific papers are to be found in following references (all listed in the Library at <www.geopolymer.org>)!

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