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GEOPOLYMERS AND GEOPOLYMERIC MATERIALS

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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 deg.C. 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.

INTRODUCTION

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

In 1978, looking for inorganic-polymer technologies, we were 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 150deg.C.

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However, zeolites were synthesized exclusively for use in the catalysis of organic compounds [2][3]. 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 Poly(sialate) type (-Si-O-Al-O-) or of the Poly(sialate-siloxo) type (-Si-O-Al-O-Si-O-) [4].

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 [5]. 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 [6]; GEOPOLYMERE-France: advanced mineral binders for severe environments, temperature stable resins for moulds and forms, GEOPOLYMITE* binders, ceramic-ceramic composites GEOPOLYCERAM* [7][8][9].

This industrial applied mineralogy, called "soft mineralurgy", is also dramatically changing the habits and the environment of ceramic processings.

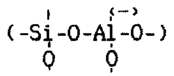
TERMINOLOGY

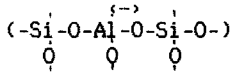
For the chemical designation of geopolymers based on silico-aluminates we suggested poly(sialate). Sialate is an abreviation for silicon-oxo-aluminate. The sialate network consists of SiO_4 and AlO_4 tetrahedra linked alternately by sharing all the oxygens. Positive ions (Na^+, K^+, Li^+, Ca^{++}, Ba^{++}, NH^{3+}, 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:

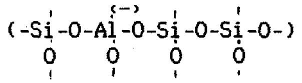
$$M_n(-(SiO_2)_z-AlO_2)_n,\ wH_2O$$

wherein "z" is 1, 2 or 3; M is a monovalent cation such as potassium or sodium, and "n" is a degree of polycondensation [10].

3 types of polysialate have been distinguished:

poly(sialate)

$(-\overset{|}{\underset{O}{Si}}-O-\overset{(-)}{\underset{O}{Al}}-O-)$
PS

poly(sialate-siloxo)

$(-\overset{|}{\underset{O}{Si}}-O-\overset{(-)}{\underset{O}{Al}}-O-\overset{|}{\underset{O}{Si}}-O-)$
PSS

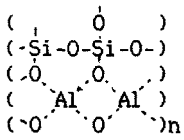
poly(sialate-disiloxo)

$(-\overset{|}{\underset{O}{Si}}-O-\overset{(-)}{\underset{O}{Al}}-O-\overset{|}{\underset{O}{Si}}-O-\overset{|}{\underset{O}{Si}}-O-)$
PSDS

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.

SYNTHESIS AND HARDENING MECHANISM

The geopolymeric materials are "polymers", thus they transform, polycondense and adopt a shape rapidely 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.

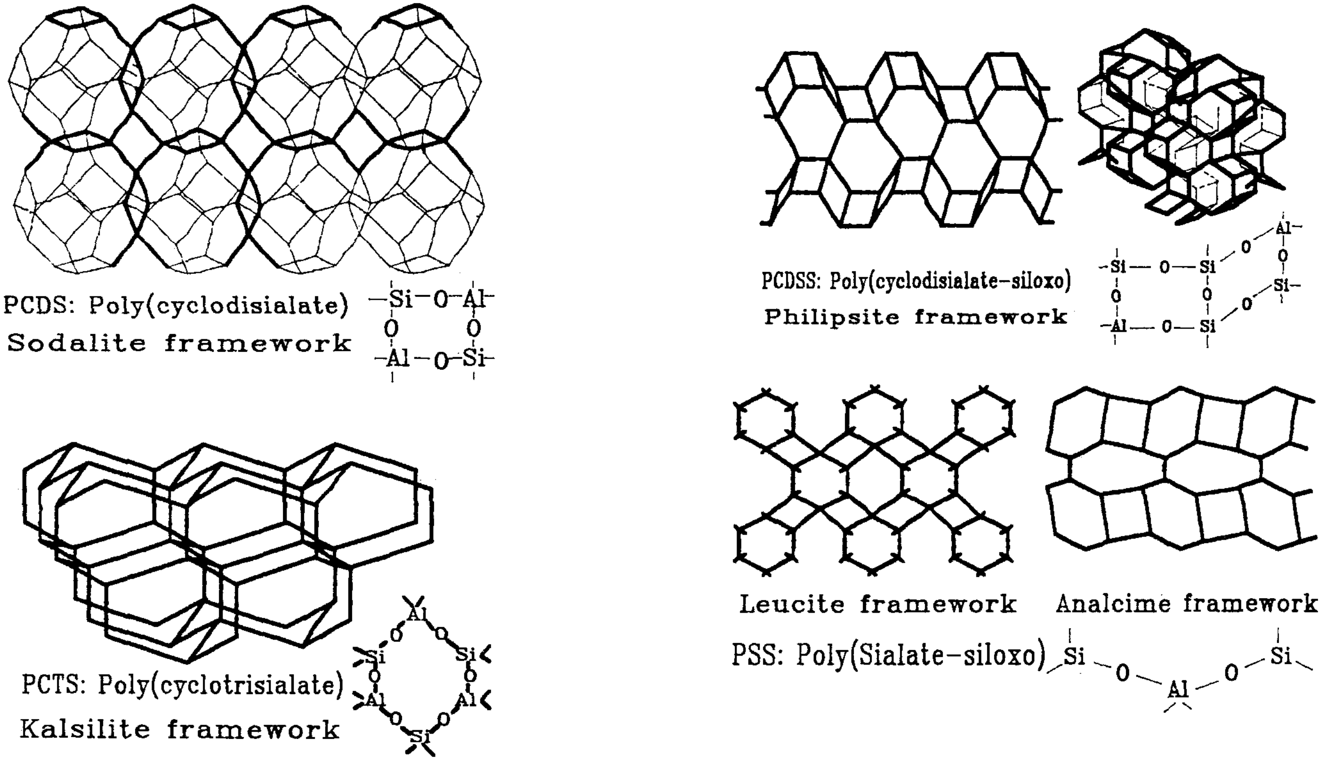
One hardening mechanism among others involves the chemical reaction of alumino-silicate oxides (Al^{3+} in IV-fold coordination) with alkali polysilicates yielding polymeric Si-O-Al bonds. In order to outline the IV fold coordination of Al we usely write $(Si_2O_5,Al_2O_2)_n$ for these particular alumino-silicate oxides instead of $(2SiO_2,Al_2O_3)$.

$(Si_2O_5,Al_2O_2)_n$ =


The fabrication of $(Si_2O_5,Al_2O_2)_n$ is carried out (a) by calcining alumino-silicate hydroxides $(Si_2O_4,AL_2(OH)_4)$, or (b) by condensation of SiO and Al_2O vapors:

(a) $2(Si_2O_4,Al_2(OH)_4) + O_2 \text{ ------}\rightarrow 2(Si_2O_5,Al_2O_2)_n + 4H_2O$

(b) $4SiO \text{ (vapor) } + 2Al_2O \text{ (vapor) } + 4O_2 \text{ ----}\rightarrow (Si_2O_5,Al_2O_2)n$
with also production of:
$2SiO + O_2$---- $2SiO_2$ (Condensed Silica Fume)
$Al_2O + O_2$---- Al_2O_3 (corrundum)



PCDS: Poly(cyclodisialate)
Sodalite framework

PCDSS: Poly(cyclodisialate-siloxo)
Philipsite framework

PCTS: Poly(cyclotrisialate)
Kalsilite framework

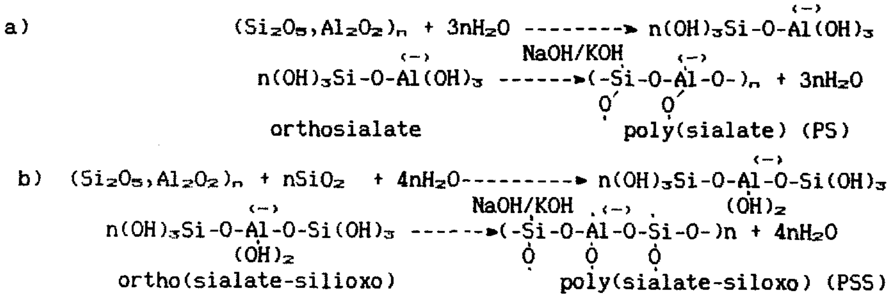
Leucite framework

Analcime framework

PSS: Poly(Sialate-siloxo)

PLATE 1: the various geopolymeric frameworks

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:



a) $(Si_2O_5,Al_2O_2)_n + 3nH_2O \longrightarrow n(OH)_3Si\text{-}O\text{-}\overset{(-)}{Al}(OH)_3$

$n(OH)_3Si\text{-}O\text{-}\overset{(-)}{Al}(OH)_3 \xrightarrow{NaOH/KOH} (\text{-}\underset{O}{Si}\text{-}O\text{-}\underset{O}{\overset{(-)}{Al}}\text{-}O\text{-})_n + 3nH_2O$

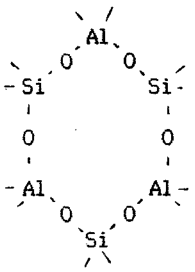
orthosialate poly(sialate) (PS)

b) $(Si_2O_5,Al_2O_2)_n + nSiO_2 + 4nH_2O \longrightarrow n(OH)_3Si\text{-}O\text{-}\underset{(OH)_2}{\overset{(-)}{Al}}\text{-}O\text{-}Si(OH)_3$

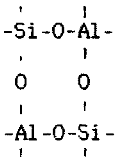
$n(OH)_3Si\text{-}O\text{-}\underset{(OH)_2}{\overset{(-)}{Al}}\text{-}O\text{-}Si(OH)_3 \xrightarrow{NaOH/KOH} (\text{-}\underset{O}{Si}\text{-}O\text{-}\underset{O}{\overset{(-)}{Al}}\text{-}O\text{-}\underset{O}{Si}\text{-}O\text{-})n + 4nH_2O$

ortho(sialate-silioxo) poly(sialate-siloxo) (PSS)

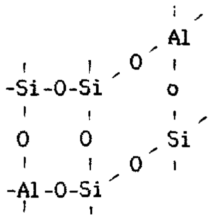
At the moment, only the sodium-poly(sialate), (Na)-PS, the potassium-poly(sialate), (K)-PS, the (sodium, potassium)-poly(sialate-siloxo), (Na, K)-PSS, the potassium-poly(sialate-siloxo), (K)-PSS, are used in geopolymeric materials. It has been assumed that the syntheses are carried out through oligomers (dimer, trimer) which provide the actual unit structures of the three dimensional macromolecular edifice (Plate 1).



(K+)-trisialate



(Na+)-disialate



(Na+,K+)-di(sialate-siloxo)

EXAMPLES OF APPLICATIONS:

a/ 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 1 to 3% 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.1) [11].

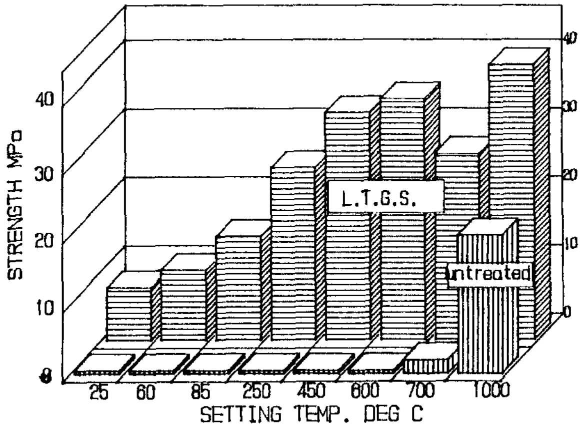


Figure 1: L.T.G.S. on kaolinitic soils. Mechanical compressive strength in Mpa for untreated and geopolymerised kaolinitic earth (with 3% by weight equivalent Na_2O). Setting temperature range between 20°C and 1000°C.

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. 2)

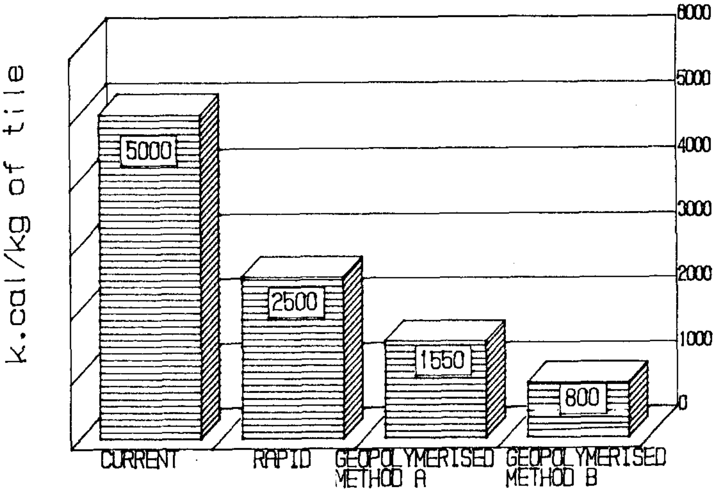


Figure 2: Fabrication of ceramic tile; energy comsumption in kcal/kg of tile for current, rapid and geopolymerised methods and firing at 1000°C-1200°C.

b) TOXIC WASTE MANAGEMENT

Zeolitic materials are known for their abilities to adsorb toxic chemical wastes. Geopolymers behave similarly to zeolites and feldspathoids. They immobilise hazardous elemental wastes within the geopolymeric matrix, as well as act as a binder to convert semi-solid waste into an adhesive solid. Hazardous elements present in waste materials mixed with geopolymer compounds are "locked" into the three dimensional framework of the geopolymeric matrix [12]. (Fig.3 and Fig. 4). Ancient concretes and mortars demonstrate the exceptional durability of zeolitic cements, analagous to synthetic geopolymers discussed here, and are indicative of the erosional resistance which can be expected of modern geopolymeric cements. Al2O3/M2O 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 [13][14].

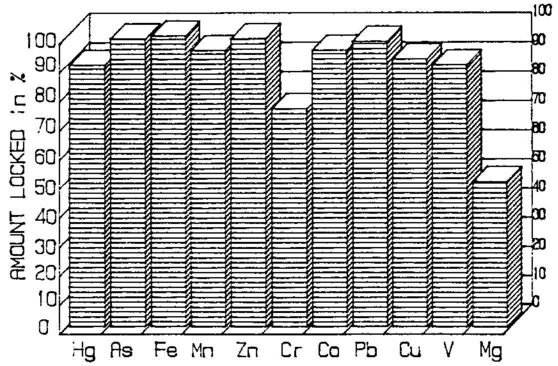


Figure 3: Amount of hazardous elements locked in the geopolymeric matrix.

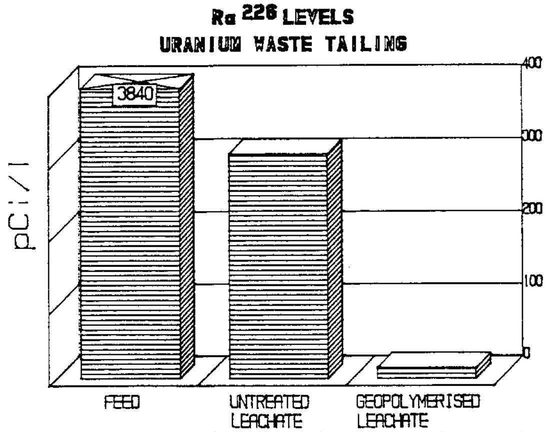


Figure 4: Comparison of geopolymerised and untreated uranium mining tailing. Loss during leaching in pCi/l.

c) 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 [15]. Such products are useful for tooling, for moulding art objets, ceramics, and the like, and as building materials.

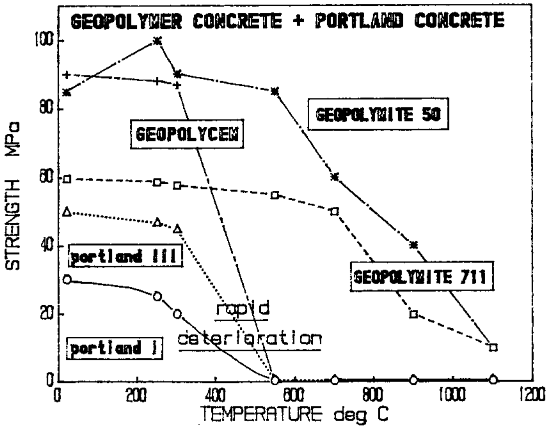


Figure 5: Strength retentions at elevated temperatures for concretes made of Portland Cements (portland I, portland III), blended geopolymer-portland (GEOPOLYCEM), blended geopolymers (GEOPOLYMITE 711, GEOPOLYMITE 50). Hardening at ambient temperature.

Characteristics of K-PS/K-PSS binders and cements.

Polycondensation of K-Poly(sialate) / K-Poly(sialate-siloxo) resins
at ambient temperature or between 20deg.C and 85deg.C
pH of the resin: 14
pH after polycondensation and dehydroxylation

thermal treatment	85deg.C	300deg.C	700deg.C
pH	10.5	9.5	7.5

Shrinkage on dehydroxylation:
at 400deg.C : 0,2% to 1%
at 800deg.C : 0,2% to 2%
Linear expansion (depending on fillers and after shrinkage):
2,1 x10^{-6} to 4,5 x 10^{-6} from 0deg.C to 1000deg.C
Fusion temperature of the pure geopolymer:
1050deg.C to 1250deg.C
Surface hardness:
4 to 7 on the Mohs Scale (7=quartz) (according to fillers)
Surface quality:
faithful reproduction of mould or die surface; precision, fineness, polish, brillance.
E. MODUL: 14.000 to 50.000 MPa (according to fillers)
Chemical stability:
excellent in organic solvent

excellent in alkaline and saline conditions
good in concentrated H_2SO_4 to poor in concentrated HCl.
Density:
approx. 1.4g/cm3 for the Geopolymer;

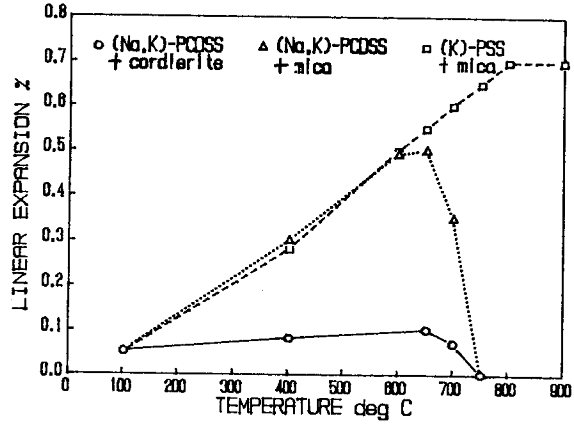


Figure 6: Linear expansion of geopolymers containing ceramic fillers, after heat treatment at 650°C during 2 hours. Thermosetting (geopolymerisation) at 65°C, during 4 hours.

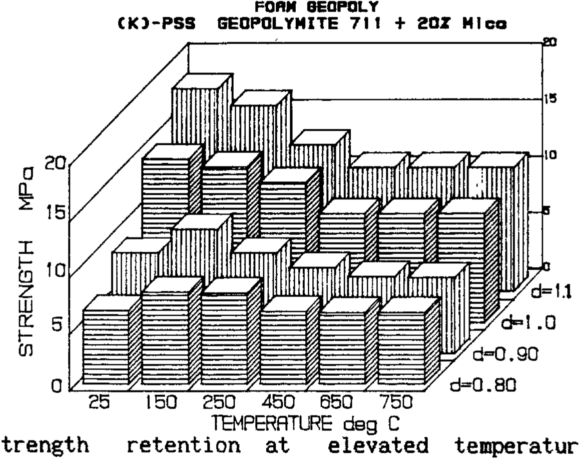


Figure 7: Strength retention at elevated temperatures for foamed geopolymer (light weight) density 0.8, 0.9, 1.0, 1.1; preliminary setting at 65°C.

d) ROOM-TEMPERATURE CERAMIC MATRIX FOR REINFORCED FIBER-COMPOSITES:

A wide range of alkaline resistant inorganic reinforcements have been combined with geopolymer matrices, in particular SiC fiber, with skills of the reinforced plastics/composites industry. SiC Fibre / K-poly(sialate-siloxo) matrix composite shaped and hardened at 70°C for 1h30 develops flexural mean strengths of at least 380 MPa which remains unchanged after firing at 450°C, 700°C and 900°C.

In 1982 we started the development of a geopolymer matrix composite concept [16]. 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 [17].

Composite made with alkali-resistant fibres, such as SiC, and Potassium-Poly(sialate-siloxo) K-PSS, called GEOPOLYCERAM* are thermostable up to 1100°C [18].

METHOD:

SiC taffeta 220g (50% by weight)/K-PSS GEOPOLYMITE (50% by weight).
impregnation,
polycondensation at 70°C for 1h30,
cooling,
drying at 70°C.

The room-temperature flexural strength after treatment at 70°C, 300°C, 450°C and 700°C is listed in Table 1. Flexural strength remains practically unaffected by the thermal treatment. Table 2 compares processing temperatures and mean strength of various SiC Fibre/Ceramic Matrix composites with a composite obtained with K-PSS GEOPOLYMITE matrix.

TABLE 1 SiC taffeta 220g/m^2 fabric / K-PSS GEOPOLYMITE
Room-Temperature Flexural Strength after treatment at (Temp.):

	70°C	300°C	450°C	700°C
Flexural strength	190 MPa	180 MPa	180 MPa	150 MPa

E. Modulus: 40-60 GPA

Rupture did not take place at maximum load. Delaminating of the layers was observed. The rupture is internal and due to exceeding of shearing limits.

TABLE 2 Comparison between SiC Fibre/K-PSS GEOPOLYMITE Composite and SiC Fibre/Ceramic Matrix composites [19]

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

Geopolymers are formulated from mineral earth resources. The Geopolymer Matrix Composites are made with skills of the reinforced plastics/composites industry and yield the non-burning, non-smoking, non-toxic benefits of ceramics without that industry's high temperature, high energy processing.

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Zusammenfassung - Durch die Entwicklung von solchen neuen Materialien wie "Geopolymere" und neuen Verfahren wie "Sol-Gel" kam es in den letzten paar Jahren zu einem bedeutenden Fortschritt in der Technologie. Neue, mittels Geopolymerisationsreaktionen dargestellte Avantgarde-Materialien öffnen den Weg zu neuen Anwendungen, Verfahren und zur Umsetzung von Ideen, die in der anorganischen Chemie für selbstverständlich angenommen wurden. Zur Herstellung von in Struktur und Eigenschaften keramikähnlichen Stoffen sind keine Hochtemperaturverfahren mehr notwendig. Diese Materialien können wie organische Polymere bei Temperaturen unter 100°C polykondensieren. Diese neue Generation von Materialien hat - rein, mit Füllern oder faserverstärkt angewendet - ihren Anwendungsbereich auf allen Gebieten der Industrie schon gefunden:

- rein: zur Endlagerung von toxischen, chemischen und radioaktiven Abfallstoffen usw.
- mit Füllern: zur Herstellung von Spezialbetons und Formen zur Gestaltung von Thermoplasten usw.
- faserverstärkt: zur Herstellung von Formen und Werkzeugen für die Giesserei und in der Metallurgie der Aluminiumlegierungen usw.

Diese Anwendungen können in der Automobil-, Luftfahrtindustrie, in der Nichteisenmetallurgie, im Baugewerbe, in der Kunststoffindustrie usw. angetroffen werden.

Резюме - За последние несколько лет достигнут захватывающий технологический прогресс в области разработки таких новых материалов как „геополимеры" и новых методов таких как „золь - гель". Новые материалы, полученные искусственно с помощью реакций геополимеризации, открывают новые области использования методов и идей принятых в неорганической химии. Высокотемпературные методы больше не являются необходимыми для получения материалов, являющихся подобными керамическим как по структуре, так и свойствам. Такие материалы, подобно органическим полимерам, могут вступать в реакции поликонденсации при температуре ниже 100°. Это новое поколение материалов могут

быть использованы как чистыми, так и в смеси с наполнителями и укрепителями, и уже нашли широкое применение во многих областях промышленности и техники. Приведены некоторые примеры их использования: а/ в чистом виде они используются для хранения токсичных химических и радиоактивных отходов и т.п., б/ с наполнителями - для изготовления специальных бетонов, форм для формовочных термопластмасс и т.д. , в/ с армирующими добавками - для производства форм, обрабатывающих резцов, при литье алюминиевых сплавов, в металлургии и т.д. Они находят применение в автомобильной, цветной и металлургической промышленности, в космической технике, в производстве пластмасс и т.д.