MILESTONE in Geopolymer Chemistry and Material Sciences:

Full Paper of the communication presented at
IUPAC Symposium on Long-Term Properties of
Polymers and Polymeric Materials, Stockholm 1976, Topic III.

PROGRAMME OF THE IUPAC SYMPOSIUM ON
LONG-TERM PROPERTIES OF POLYMERS AND
POLYMERIC MATERIALS
Stockholm, August 30 - September 1, 1976

ORGANIZED BY
THE DEPARTMENT OF POLYMER TECHNOLOGY
THE ROYAL INSTITUTE OF TECHNOLOGY
STOCKHOLM SWEDEN

WEDNESDAY, SEPTEMBER 1

TOPIC III, NEW POLYMERS OF HIGH STABILITY

14.30 - SOLIDPHASE SYNTHESIS OF A MINERAL BLOCKPOLYMER
BY LOW TEMPERATURE POLYCONDENSATION OF
ALUMINO SILICATE POLYMERS
by J. Davidovits (Cordi S.A.,
Saint-Quentin, France)
Solid-Phase Synthesis of a Mineral Blockpolymer by Low Temperature Polycondensation of Alumino-Silicate Polymers: Na-poly(sialate) or Na-PS and Characteristics.

Joseph DAVIDOVITS
CORDI SA, 20 rue de la Fère, 02100 SAINT-QUENTIN (France)

1. INTRODUCTION

The work exposed here comes from an attempt to transfer our knowledge of organic polymers and the technologies associated with it to the yet unknown, or hardly known field of the synthesis and transformation of inorganic polymers, in order to develop new materials and new industrial processes. It is a matter of fact that inorganic materials like glass, ceramics, bricks, concrete, and most natural rocks by far outclass organic polymers with respect to their resistance to high temperature. This study provides an answer to the following question: Could we take mineral materials such as clay, kaolinite, that is to say aluminosilicate polymers, and transform them using the extreme low-temperature polymerisation technology of organic polymers? The answer is: yes, we can. The resulting products have similar characteristics to natural rock-forming minerals, such as zeolites, feldspathoids and feldspars. These different minerals are usually called silicates or aluminosilicates in the same way as kaolinite, clays, micas, mullite, andalusite, spinel, etc. that is in brief all the minerals whose empirical formula contains Si, Al, O, and any other elements such as H, Na, K, Ca, Mg, etc. For the development of our knowledge and for a better understanding of the mechanism of this new synthesis of inorganic polymers, we felt we had to introduce a more precise terminology.

1.1 Terminology

In this contribution to the IUPAC Symposium on Long-Term Properties of Polymers and Polymeric Materials, we propose the following terminology, based on the amphoteric character of aluminium oxide Al₂O₃. We restrict the meaning of the term "aluminosilicates" or more precisely said "aluminum-oxo-silicates" to aluminium salts of silicic acid, stable at a pH lower than 7.5. Al³⁺ is in 6-fold coordination with O and OH. All clay are indeed aluminium-oxosilicates, or hydroxy-aluminium-oxo-silicates. See for example the kaolinite macromolecule:

On the other hand, Me-silico-aluminates, where Me is a metallic cation, like Na, K, Ca, etc, are salts of the aluminium hydroxide side groups branched to a silicic acid backbone that is to say, of a silico-alumino acid. Here, Al³⁺ is in 4-fold coordination with O and OH as in aluminate ions Al(OH)³⁻.
Me-sialates or polysialates (Si-O-Al-O)n are chain and ring polymers with Si⁴⁺ and Al³⁺ in 4-fold coordination with oxygen, and may be considered as the result of the polycondensation of a still hypothetical monomer, the ortho-sialate ion [(OH)₃-Si-O-Al(OH)₃]. Sialate is an abbreviated form for silico-oxo-aluminate. The sialate network consists of SiO₄ and AlO₄ tetrahedrons linked alternatively by sharing all the oxygens. The cations Na⁺, K⁺, Ca⁺⁺, Mg⁺⁺, Ba⁺⁺, NH₄⁺, H₃O⁺ must be present in the framework cavities, see Figure 1a, to balance the negative charge of Al in 4-fold coordination. We now complete this nomenclature with following frameworks:
- Sialate link is the bridge Si-O-Al between two polysialate chains:
  \[
  \text{Si} - \text{O} - \text{Al} - \text{O} - \text{Si} - \text{O} - \text{Al} - \text{O}
  \]
- Mono-sialate-siloxo (-Si-O-Al-O-Si-O-) may be considered as the condensation result of ortho-sialate ion with ortho-silicic acid Si(OH)₄. Its isomorph (-Si-O-Si-O-Al-O-) is a siloxo-sialate ion.
- Sialate-disiloxo (-Si-O-Al-O-Si-O-Si-O) and its 4 isomorphs, 1 linear (disiloxo-sialate), 2 branched and 1 cycle.
- Examples of cycles (rings)
  \[
  \text{cyclo(disialate)} \quad \text{cyclo(trisialate)} \quad \text{cyclo(disiloxo-sialate)}
  \]
A mineralogist can easily check that crankshaft chains in feldspars may be described as poly(cyclodisialate) chains in anorthite CaAl₂Si₂O₈ and as poly(cyclodisiloxosialate) chains in albite NaAlSi₃O₈.

1.2 Poly(cyclotrisialate) and zeolites.

Among the sialate and sialate-siloxo containing salts and/or water in their cavities and pores, an exceptional importance has been given since 1945 to zeolites as adsorbents, catalysts and molecular sieves, and different methods of synthesis (3-5) of zeolitic molecular sieves have been developed, generally based on the reaction of the system SiO₂,Al₂O₃,Na₂O, H₂O in solution, with crystallisation temperature (6-7) in the 50-150°C range. The structures of natural and synthetic zeolites have been classified (8) with their subunits, which are typical arrays of (Si,Al)O₄ tetrahedras: rings, double rings, cages (a, b, g, e,) and so on. We shall focus on the β-cage or sodalite cage, Figure 1,b. In our terminology the β-cage corresponds to the tetra(cyclotrisialate) or as well to the
tri(cyclotetrasilicate intrasiloxane), or again to the di(cyclohexasilicate, 3-10, 4-9 intrasiloxane) or more simply to poly(sialate). Depending upon the conditions of synthesis different types of arrangement of this β-cage may be obtained. The most compact one is cubic, and is represented by the natural mineral sodalite Si₈Al₈O₂₄Na₆Cl whose synthetic equivalent Si₈Al₈O₂₄Na₆OH₄xH₂O is called "Hydrosodalite" (9) or HS. In our terminology, Hydrosodalite corresponds to the Napoly(cyclotrisilicate) or Na-PCTS, with the typical cyclo(tetrasilicate-intrasiloxane) sequence, or Na-PS, Na-poly(sialate), Figure 1c and 1d.

1.3 Synthesis in solution

Generally, the synthesis in solution at a pH greater than 11.0 proceeds by polycondensation of the monomers Si(OH)₄ and Al(OH)₄ with Al in 4-fold coordination (10, 11).

Equation 1:

Silica-gel and alumina-gel condense through an intermediate silicoalumina-gel, since the ortho-sialate monomer has not been yet isolated.

1.4 Synthesis with kaolinite

In fact some natural aluminosilicate polymers may be considered as sources of sialate ions. For example the planar aluminosilicate polymer kaolinite (see Figure 3) reacts with NaOH in solution at 100°C-150°C, and polycondenses into various poly(sialates):

Equation 2:

In 1945 a group at the National Bureau of Standards (12) examined processes for the extraction of alumina from clays and high-silica bauxites. In one step of the process, silica was removed from the sodium aluminate solution by precipitation of a sodalite-type compound. Most of their products produced in this way corresponded in chemical analysis and X-ray powder pattern to Hydrosodalite or Na-poly(cyclotrisilicate) (Na-PCTS) or Na-poly(sialate) Na-PS. In 1949, Borchert and Kiedel (13) obtained Hydrosodalite by heating in a concentrated NaOH solution at 100°C. In 1963, Howell (14) did not employ natural kaolinite to synthetize a β-cage-type zeolite but dehydroxylated kaolinite, to avoid the formation of Hydrosodalite. Then Caillère and Hénin (15) restudied the synthesis of Hydrosodalite (Na-PCTS) from natural aluminosilicate such as kaolinite, montmorillonite, halloysite, in concentrated NaOH solution at 100°C. In 1963, Howell (14) did not employ natural kaolinite to synthetize a β-cage-type zeolite but dehydroxylated kaolinite, to avoid the formation of Hydrosodalite. Then Caillère and Hénin (15) restudied the synthesis of Hydrosodalite (Na-PCTS) from natural aluminosilicate such as kaolinite, montmorillonite, halloysite, in concentrated NaOH solution at 100°C. Berg, Demidenko & al. (16) proposed to bind ceramic products with Hydrosodalite prepared from kaolinite (17) and this industrial application was confirmed by Latapie. In fact, Olsen (18) filed 40 years ago the first patent describing this low-temperature curing technique for ceramic bodies with NaOH.

Since 1972, we have developed a technology based on the synthesis of Na-PS from natural aluminosilicate polymers with the tri-dimensional cross-linking performed in the
solid state, and with reaction times, which would allow industrial applications, involving designed thermosetting technology and casting-mould technique.

2. EXPERIMENTAL

2.1 Solid state synthesis
The techniques used for the solid state synthesis of Na-PS blockpolymers are described by Davidovits & al. (19-21) in various patents filed for the applications of the so-called "Siliface Process". Naturel aluminosilicates in power form are mixed with powdered NaOH in the proportion of 1 mole or less of NaOH for 0,5 mole Al₂O₃. This mixture is moistened to a water content of 6-15% of the initial powdered mixture or 1 g water for 1-1.5 g NaOH. The resulting granules are ground up and the semi-dry powder is placed in a cold mould and pressed under 150 kg/cm². The resulting crude plates are placed under a heated press equipped with pervious systems enabling water evaporation during the thermosetting phase.

2.2 Thermosetting-parameters:

- temperature: 130°C to 200°C
- pressure: higher than the saturated vapour pressure (svp) of water, i.e. 10 to 30 kg/cm²
- time: one minute per millimetre thickness.

Characterization and identification of the synthetized products called SILIFACE were done using X-ray powder diffraction, differential thermal analysis (DTA) and thermogravimetry (TGA). These identifications were carried out in the Laboratoire de Minéralogie du Muséum d'Histoire Naturelle de Paris (Prof. S. Caillère).

3. RESULTS
Na-PS synthesis from kaolinite corresponds to equation 2. The water given off is relatively important so that when pure kaolinite is used, the method is not appropriate for the manufacture of technical products. Nevertheless, the synthesis of pure Na-PS (Na-PCTS) is possible but this is outside the scope of this paper, as our main objective is to manufacture moulded products. We shall just examine here the cases when kaolinite is mixed with silicate additives, mainly quartz, and aluminosilicates, spinel and mullite, obtained by firing kaolinitic clays between 1000°C and 1400°C. The poly(sialate)-blockpolymers are called Siliface Q, Siliface NF and Siliface MU.

3.1 System Kaolinite/Quartz (SiO₂). Siliface Q
A mixture of 100g kaolinite, 100g fine ground quartz,12g NaOH and 16g H₂O is premoulded (cold densification) and thermoset at 150°C under 15kg/cm² for 7 minutes. The X-ray diffraction values of this Siliface Q are summarized in Table 1 together with comparative values of quartz (SiO₂) and Hydrosodalite. Siliface Q is really a mixture of Na-PS and quartz (SiO₂). Some d-values of Na-PS in Siliface Q are overlapped by those of quartz, for instance the 4.44 A corresponding to the (200) plane and the 2.37 A corresponding to the (321) plane of the cubic Hydrosodalite. Na-PS is synthetized in a very short time: 7 minutes for 7 millimetre thick plate. In fact experiments show that Na-PS synthesis from kaolinite is astonishingly rapid and violent, and may occur in 20-30 seconds at 180°C and 40 kg/cm² pressure, when water evaporation is hindered.
3.1.1 Thermal-behaviour-
Transformation of Siliface Q into a glass occurs in the 800-1200°C range, depending on the Na-PCTS/SiO₂ ratio. This glass may crystallise into albite feldspar. Siliface Q is nevertheless only usable at low temperature say 500°C, because of the sudden expansion of Quartz around 573°C.

3.2 System Kaolinite/Spinel/Mullite. Siliface NF, Siliface MU

When heated in air, kaolinite undergoes several transformations. After the endothermic dehydroxylation at 550°C, it converts at 925°C into a defect aluminium-silicon spinel Si₃Al₄O₁₂. Then, at 1050°C, the spinel phase converts into Mullite Si₂Al₆O₁₃ and Silica SiO₂. The industrial products called chamottes and grogs constitute a mixture of silica/spinel/Mullite. In the kaolinite /quartz system the replacement of quartz by chamotte or grog-material leads to a blockpolymer called Siliface NF whose structure is more complex than Siliface Q. The X-ray diagrams are relatively confused, due to the presence of an amorphous phase. Nevertheless, we suspect that the polysialates obtained crystallise in both cubic Na-PS and in another network. With crystallised pure Mullite one obtains Siliface MU, in which however the kaolinite quantity has been reduced to 10% or less.

3.2.1. Thermal-behaviour
Though conversion of Na-PS to carnegieite may begin in the 800-900°C range, the low silica compositions (Siliface MU) are still usable in the 1200°C-1300°C range. The interesting dilatometrical behaviour of Siliface Q, NF, MU and others will be explained at greater length in a later paper.

3.3. System Kaolinite/cordierite. Siliface COR

The filler is here essentially Cordierite Si₅Al₄Mg₂O₁₈. Cordierite melts at 1460°C. Such ceramic filler was selected for its low thermal expansion.

3.4 Yielding of the conversion Kaolinite/ Na-PS

Thermogravimetry allows the determination of the Na-PCTS/Na-PS synthetized during the SILIFACE Process. The DTA-and TGA-graphs for two Siliface Q, Kaolinite, and Quartz are plotted in Figure 2. Untransformed kaolinite can be qualitatively recognized in the DTA by an endothermic peak between 500°C and 600°C, and on the TGA by a sudden loss of weight between 400°C and 600°C (these temperatures depending on the heating rate). The DP (400-600°C) allows the quantitative evaluation of untransformed kaolinite and consequently the Na-PS produced, since the DP (400-600°C) value for pure kaolinite is 13% (fig.2). Synthetic Hydrosodalite corresponds either to Na₄OH,Si₃Al₃O₁₂nH₂O (sodium-rich Hydrosodalite) or Na₃Si₃Al₃O₁₂nH₂O (sodium-just Hydrosodalite). The NaOH content of the initial compounds (samples nr.1 and nr.2, Table 2) gives the theoretical values for Hydrosodalite, whereas the Na-PCTS/Na-PS calculated from the untransformed Kaolinite is shown as sodium-rich PCTS and sodium-just PCTS in Table 2.

The comparison of the values for sodium-rich PCTS/sodium-rich Hydrosodalite, and sodium-just PCTS/sodium-just Hydrosodalite gives surprising yielding varying for the sample nr.1 from 2.1 to 2.7 and for the sample nr.2 from 1.3 to 1.7 .
3.5 Physical characteristics

3.5.1. Density, porosity
The values are for Siliface Q. For the others Na-PS-blockpolymers the corresponding values can be deduced immediately.

True density of Na-PCTS/Na-PS 2.1 to 2.3 kg/dm$^3$
Initial components: Quartz 2.65
kaolinite 2.4 to 2.68
Interstitial NaOH solution 1.2 to 1.5

A simple computation for a sample prepared with 40g kaolinite, 60g quartz, 8g NaOH, 10g H$_2$O, leads to a minimum open porosity of 15%. Measured porosities by water absorption are higher (from 15% to 40%) and depend essentially upon the applied pressure used during the pre-moulding operation (cold-densification) and the thermosetting. The volume of the water given off rated as liquid, is twice the volume of the minimum open porosity. All the properties of PCTS/Na-PS-blockpolymers depend greatly upon their porosity.

3.5.2. Practical characteristics
The main physical characteristics of Siliface Q for technical use are:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>True density (kg/dm$^3$)</td>
<td>2.4 to 2.6</td>
</tr>
<tr>
<td>Bulk density (25% apparent porosity)</td>
<td>1.9</td>
</tr>
<tr>
<td>Apparent porosity</td>
<td>15% to 40%</td>
</tr>
<tr>
<td>Moulding shrinkage</td>
<td>0.2% to 0.4%</td>
</tr>
<tr>
<td>Mohs hardness</td>
<td>4 to 6</td>
</tr>
<tr>
<td>Dynamic Young's modulus X10$^9$ N/m$^2$</td>
<td>15 to 40</td>
</tr>
<tr>
<td>Flexural strength, daN/cm$^2$</td>
<td>60 to 250</td>
</tr>
<tr>
<td>When moistened, loss in flexural strength</td>
<td>40%</td>
</tr>
<tr>
<td>Specific heat capacity, cal/g°C</td>
<td>0.2</td>
</tr>
<tr>
<td>Weight loss on firing</td>
<td>4% to 9%</td>
</tr>
</tbody>
</table>

(zeolithic water, and Hydroxyls OH)

Other interesting data are shown in Table 3 for Siliface Q, NF, MU and COR

3.5.3. Moisture absorption
Samples: Siliface Q (with 65% quartz), 20-25% apparent porosity, 30 days old, stored in air with a relative humidity of 48% at 22°C. The samples are weighed before (W0) and after (W1) drying, then before (W2) and after (W3) a 48 hours stay in an atmosphere of 65% relative humidity:

a) check sample, without drying: (W3-W2)/W2 = +1.43%

b) dried sample, 24h, 110°C immediate reabsorption (W1-W0)/W0 = -1.27%
   (W2-W1)/W1 = +0.25%
   (W3-W2)/W2 = +1.02%

c) dried sample-, 48h, 300°C no immediate reabsorption (W1-W0)/W0 = -2.50%
   (W3-W2)/W2 = +0.39%

3.6 Chemical properties
pH in distilled water, after 5 minutes 10.0
pH at equilibrium, fresh sample 11.0
pH at equilibrium, 1 year old sample 10.5
These pH-values are to be compared with Portland cement (pH=12), and with natural minerals like hornblende and amphibole (pH=10), olivine (pH=10 to 11) (22)

- Resistance to alkalis: excellent
- Resistance to salts: good to excellent
- Resistance to acids: poor for strong acids

4. DISCUSSION

4.1 The transformation mechanism of Kaolinite to Na-PCTS/Na-PS in the solid state

According to the Löwenstein's rule (23) we know that in tridimensional sialate-siloxo frameworks, feldspathoids and zeolites, with Al$^{3+}$ in 4-fold coordination, the Al-O-Al bond cannot exist, only the sequence Si-O-Al-O-Si. In the kaolinite macromolecule (Figure 3), the Si and Al levels (Al$^{3+}$ in 6-fold coordination) are quite distinct. The synthesis of molecular sieves in solution follows a mechanism involving the depolymerisation of the siloxane chain -Si-O-Si- with formation of the monomers Si(OH)$_4$ (see equation 1) and Al(OH)$_4$ with Al$^{3+}$ in 4-fold coordination. These soluble ions in the alkaline medium polycondense in the same way as silica-gel and alumina-gel do, so that the alternation rule is respected.

In our experimental conditions with polycondensation in the solid state, the conversion is so quick, taking only a few seconds, that a quite different mechanism must be considered, i.e. a blockpolycondensation. The scheme proposed (Figure 3) takes into account the initial structure of the kaolinite macromolecule. The following steps occur during the preparation of the samples (incubation time) and the thermosetting in the heated press:

- **Step-one**: in each fundamental kaolinite layer with 6-fold coordination of Al$^{3+}$, formation of the silico-aluminate bi-dimensional network (Al$^{3+}$ in 4-fold coordination), with rupture of the inter-layer hydrogen bonds.
- **Step-two**: depolymerisation of the silico-aluminate network into unstable ortho-sialate monomers and oligomers (Al$^{3+}$ in 4-fold coordination).
- **Step-three**: blockcondensation of the ortho-sialates to linear poly(tetrahydroxy-sialate) chain (Al$^{3+}$ in 4-fold coordination).
- **Step-four**: blockcondensation of 2 or more linear poly(tetrahydroxy-sialate) chains into poly(hydroxy-cyclotrisialate) sheet.
- **Step-five**: interlayer polycondensation into poly(cyclotrisialate), Na-PCTS/Na-PS, with the typical cyclotetrasialate-intrasialoxane sequence (see Figure 1d).

4.2 Blockpolymer sequence formation.

In the kaolinite/quartz system (Siliface Q), the quartz crystals are surrounded with kaolinite micelles. The siloxane link –Si-O-Si–O- of the surface of the quartz crystal is hydrolysed into silanol -Si-OH OH-Si- (24). These silanols polycondense with the sialates or polysialates synthetized from the kaolinite:
One obtains the sequenced blockpolymer (Siliface Q)
\[-(Na-PCTS)-(SiO_2)n-(Na-PCTS)-(SiO_2)n\]
The same mechanism may occur in the formation of Siliface NF (written here with pure -Al-
spinel)
\[-(Na-PCTS)-(Si_3Al_4O_{12})_n-(Na-PCTS)-(Si_3Al_4O_{12})_n-\]
and Siliface MU (here with pure Mullite)
\[-(Na-PCTS)-(Si_2Al_6O_{13})_n-(Na-PCTS)-(Si_2Al_6O_{13})_n-\]

4.3 Yielding and mean formula of the Na-PCTS/Na-PS

We have seen in section 3.4 that the yielding is greater than 1 in the range 1.3 to 2.7. One
must admit that cations different from Na are involved in the pol(sialate) network. These
cations can be H$^+$ or more precisely H$_3$O$^+$ and Al$^{3+}$ more or less hydrated. Indeed, at the
thermosetting temperature the partial hydrolysis of the cation induces the replacement of
Na by hydronium H$_3$O$^+$.

So, as the computation on Table 4 shows, a mean formula
\[2Na^+,H_3O^+,(Si_3Al_3O_{12})^{3-},nH_2O\]
is quite admissible for the Na-PS synthetized with the SILIFACE Process. These
conditions differ from those previously practised by their higher temperature, higher
pressure, and higher concentration in Na$^+$ ions in the interface micropores. For
comparison, usual mixture composition for the preparation of a $\beta$-cage type zeolite are
Na$_2$O / SiO$_2 = 0.5$ to 1.5 and H$_2$O / Na$_2$O = 10 to 100. Some authors have sometimes
obtained sodium-poor sodalites or hydrosodalites, and the final composition varies with the
nature of the initial clay mineral and with the reactional conditions (25).

4.4 Lattice defects, framework substitutions

Hitherto, we have admitted as true the ideal formula of kaolinite, with the 2SiO$_2$ / Al$_2$O$_3$
ratio equal to 1. In fact, this ratio may vary between 0.91 and 1.16 for well crystallised
kaolinites, with even wider limits for poorly crystallised ones (26). These vacancies and
substitutions in the kaolinite lattice may induce defects in the PCTS framework. However,
we already know, according to the Lowenstein's exclusion rule, that Si-vacancy gives
either a H$_4$-centered tetrahedra (27,28) or expulsion of one of the Al ion from the sialate
framework into the interstitial solution, or inside a $\beta$-cage, as it is attested in Bancroft
sodalite formula
\[Na_{3.59}Al_{0.12}Cl_{0.96}Si_3Al_3O_{12.0,0.37}H_2O\] (29)
On the other hand, an Al-vacancy gives merely a silixo-sialate sequence Si-O-Si-O-Al-O-.
Most properties of the Na-PS products seem to depend strongly on these lattice defects.
Among them: cation exchange capacity, chemical reactivity and stability, thermal stability,
electrical conductivity, ion mobility, etc. Many further fruitful developments are to be
expected.

5. CONCLUSION

We have shown that aluminosilicate polymers such as kaolinite and its derivatives are transformed under low-temperature and in an astonishingly short time into three-dimensional poly(sialates) Na-PS using techniques very close to the thermosetting methods used in the polycondensation of organic resins. The poly(sialates) Na-PS and their corresponding blockpolymers are man-made rocks. Up to now, they are porous solids and have a zeolithic character. Our opinion is that we have discovered one of the reasons why the research of new inorganic polymers based on the silicon backbone has not been as easy as hoped. All our developments are based on the abilities of aluminium ion (6-fold or 4-fold coordination) to induce crystallographical and chemical changes in a silicic acid backbone. Nature itself exhibits the exceptional importance of this reaction since at least 55% of the volume of the Earth's crust is composed of sialate and sialate-siloxo species, though pure silica or quartz forms only 12%. First applications were for building applications, where fire resistant panels and insulating panels are produced in a one-step process.

An unusual feature characterises these industrial processes: the hardening of organic resins (inner core of the panels) and of inorganic Na-PCTS/Na-PS blockpolymers (facing of the panels) occurs simultaneously under the same thermosetting conditions.

With respect to the present and future development of these man-made rocks, we are convinced that we still have only reached the level of the first organic polymers based on casein, cellulose nitrate, cellulose acetate: we still use natural polymeric minerals for transformation into other mineral polymers. The works made recently upon the low-temperature synthesis of clay minerals pioneered by Caillère and Hénin (31, 32) especially on kaolinite (33, 34) suggest that in the near future it will be possible to perform the synthesis of man-made rocks from monomeric elements, for example from silico-aluminate monomers or oligomers.

REFERENCES

3) R.M. BARRER, J. Soc. Chem. Ind. 64 (1945) 130
5) S.C. EASTWOOD, R.D. DREW and F.D. HARTZELL, Oil Gas-J. 60 (1962) 152
11) S.P. ZHDANOV, in (8), p. 20.
12) E.P. FLINT, W.F. CLARKE, E.S. NEWMAN, L. SHARTSIS, D.L. BISHOP and L.S.
11

17) J.P. LATAPIE, private communication 1972
18) N. OLSEN, German Patent 600.327(1934) .
20) J. DAVIDOVITS and J.J. LEGRAND, Belgian Pat. 823.804 (1975)
21) J. DAVIDOVITS and J. LAVAU, Belgian Pat. 841.637 (1976)
22) R.E. STEVENS and M.K. CARRON, Amer. Mineral. 33 (1948) 31
Figure 1:

a) A sialate network with the SiO$_4$ and AlO$_4$ tetrahedra linked alternatively by sharing all of the oxygens. Na$^+$ ions balance the negative electrostatic charge of Al$^{3+}$ in 4-fold coordination with oxygens.

b) The sodalite-cage or $\beta$-cage. Oxygens and Na$^+$ are not represented.

c) $\beta$-cages stacking in the cubic Hydrosodalite or Na-PCTS viewed approximately along [311] axis.

d) Structural formula corresponding to the condensation of the cyclo-trisialate rings, with the cyclotetrasialate-intrasialoxane sequence; the sialate link Si-O-Al-O binds Si$^{4+}$ in position (2) and Al$^{3+}$ in position (7).
Figure 2: Differential Thermoanalysis DTA for kaolinite (1), quartz (4), SILIFACE 1 (2) and 2 (3). Thermogravimetical analysis TGA for kaolinite (1), SILIFACE 1 (2) and 2 (3).

Table 1: Na-PCDS-Quartz blockpolymer, SILIFACE Q. X-Ray diffraction patterns for SILIFACE Q, Quartz and Hydrosodalite (Barrer and White, 1952; Borchert and Keidel, 1949)

<table>
<thead>
<tr>
<th>SILIFACE Q</th>
<th>Quartz</th>
<th>Hydrosodalite (Na-PCDS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d A</td>
<td>l</td>
<td>d A</td>
</tr>
<tr>
<td>6.25</td>
<td>3</td>
<td>4.24</td>
</tr>
<tr>
<td>4.23</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>3.64</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>3.35</td>
<td>10</td>
<td>3.35</td>
</tr>
<tr>
<td>2.82</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>2.57</td>
<td>5</td>
<td>2.46</td>
</tr>
<tr>
<td>2.11</td>
<td>3</td>
<td>1.82</td>
</tr>
<tr>
<td>1.82</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>1.75</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>1.49</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>
Table 2: Na-PCDS-Quartz blockpolymer SILIFACE Q. TGA Determination of the yielding in Na-PCDS synthesized from kaolinite (TGA-dP data). Variation of the quartz/kaolinite/NaOH ratio.

<table>
<thead>
<tr>
<th>SILIFACE Q sample N°</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>reactional mixture, in % by weight</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 quartz</td>
<td>22</td>
<td>40</td>
</tr>
<tr>
<td>3 kaolinite</td>
<td>72</td>
<td>50</td>
</tr>
<tr>
<td>4 NaOH</td>
<td>6,3</td>
<td>10</td>
</tr>
<tr>
<td><strong>SILIFACE Q</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 theoretical Na-PCDS</td>
<td>22</td>
<td>37</td>
</tr>
<tr>
<td>6 TGA-dP between 400-550°C</td>
<td>4,2</td>
<td>1,2</td>
</tr>
<tr>
<td>7 unreacted kaolinite</td>
<td>32</td>
<td>9</td>
</tr>
<tr>
<td>8 converted kaolinite</td>
<td>40</td>
<td>41</td>
</tr>
<tr>
<td>9 synthesized Na-PCDS</td>
<td>47</td>
<td>48</td>
</tr>
<tr>
<td>10 geopolymerisation yielding (ratio line 9/line 5)</td>
<td>210</td>
<td>130</td>
</tr>
</tbody>
</table>

Figure 3: Transformation mechanism of kaolinite to Na-PCTS/Na-PS