

5. Geopolymeric Cross-Linking (LTGS) and Building materials

Claude Bouterin and Joseph Davidovits

Edited version of the paper: "Utilisation des terres latéritiques dans les techniques de géopolymérisation", published in: Actualité de la Construction de Terre in France, Plan Construction, Ministère du Logement, Paris, 1982.

Summary:

After a concise presentation of the chemical principles governing the LTGS geopolymeric cross-linking with the main mineralogical components of soils, earths and clays, the authors present their experiments for a rational use of lateritic materials. Several tests were carried out with African soils of various origins but the standardization of the processes was made by using a material extracted in Provence, France.

The geopolymerisation techniques make it possible to obtain building materials meeting all the architectural needs:

- water stable bricks, hardened at room temperature.
- ceramic bricks with maximum heating from 85°C to 450°C (solar and simple wood fire)
- cement and hydraulic mortar from laterites.
- wall and floor coatings
- roof

5.1 Introduction

The preceding conference, held by Mr Hubert Penicaud on the hygrothermic characteristics of earth materials, constitutes an excellent introduction to my presentation dedicated to the geopolymerisation techniques. Indeed the climatic comfort quality of the earth material is acknowledged.

But Mr. Penicaud emphasized that the degree of comfort was related to the kinetics of water migration through the material. Thus, although the earth material is able to absorb a great quantity of moisture, desorption is carried out relatively slowly. Theoretically, the material ensuring maximum climatic comfort must be able to quickly absorb moisture and to desorb it also quickly, ideally by following the day and night cycles. The geopolymerisation techniques allow the earth material to fulfil this function.

The LTGS geopolymeric cross-linking is an application of the fundamental research carried out these last 20 years in mineralogy and geology.

We know that nature is constituted of 3 distinct reigns: the animal reign, the vegetable reign, and the mineral reign. For 150 years, the aim of chemical science was the understanding and replication of various materials characterizing the animal and vegetable reign. This biochemical research leads to the creation of plastics, synthetic fibres, biochemistry, and modern medicine.

But it is only since 1970 that chemical, mineralogical, and geological sciences allowed the development of materials being able to replicate the mineral reign.

One can now manufacture in laboratory almost all types of mineralogical materials, but the most spectacular results are obtained with geopolymers of the aluminosilicate or polysialate type. Thus, we obtain mineral structures equivalent to many natural components like feldspathoids, zeolites, and amphiboles. We know that the manufacture of these minerals is easy, it is done at

low temperature i.e. under simple normal climatic conditions, or when necessary at relatively moderate temperatures ranging between 45° and 100°C.

Let us return now to the subject of this conference: the use of earth materials. We know that earth consists of argillaceous materials and that these argillaceous materials are the result of the climatic erosion of rocks such as granites. In other words, natural erosion, degradation due to the climate, transforms the feldspathic rocks into sedimentary minerals such as clays.

New research in mineralogy and geology showed the various kinetics of reaction which made it possible to reverse the mineralogical timescale, i.e. to transform the argillaceous sediment into a rock, in other words to make the reverse of what had been made by nature. The low temperature geopolymeric setting (L.T.G.S.) uses these reactional principles.

LTGS transforms any argillaceous material into a group of mineral products, which have the characteristics of rocks, i.e. insensitivity to water, resistance to temperature, hardness, etc.

The following elements were established with an argillaceous material containing approximately 50% of clay of the kaolinite type, which is slightly different from the simple earth materials, generally employed in adobe, pisé, rammed earth, or stabilized soils which, sometimes, contain only 10 to 15% of argillaceous material. It is obvious that according to the quantities of argillaceous materials present or not in the soil, it will be necessary to adapt the formulae. For example, with a soil containing 25% or less argillaceous material, the quantities of reagents will have to be decreased by approximately 50%.

5.2 Stabilization of lateritic soils

The soils that are generally designated under the very vague term of laterite are rich in Iron and Aluminium sesquioxides such as goethite, hematite, gibbsite, and boemite.

The argillaceous matrix is generally based on hydrated aluminosilicates of the $\text{SiO}_2/\text{Al}_2\text{O}_3=2$ (type kaolinitic) type or $\text{SiO}_2/\text{Al}_2\text{O}_3=4$ (type montmorionitic) or more. In the areas of this planet where we meet these soils, it is rather difficult to manufacture bricks by the traditional process of firing at high temperature around 900° to 1100°C.

The simplest process consists in taking these soils and drying them in open-air. It is the technique of pisé, rammed earth, adobe, and brick dried in the sun, strongly used in a majority of countries in Africa. A more elaborate process consists in mixing these soils with ordinary Portland cement, and to make blocks or bricks with a hydraulic binder. Results are starting to be satisfactory, in terms of mechanical resistance and water stability, when at least 150-250 kg per m^3 of cement, generally 300 kg per m^3 are used.

Others proposed to react the "lateritic" soils with lime $\text{Ca}(\text{OH})_2$, either by using silico-calcareous reaction in autoclave, for example by extrapolating the process describes in the French patent n°1.501.753 and his certificate of addition n°2.092.936, or at 97°C, as described by T. RINGSHOLT and T.C. HANSEN in the journal "Ceramic Bulletin" Vol.57, n°5 (1978), page 150: "Lateritic soil as raw material for Building Blocks".

In the quoted French patents, they use a material containing less than 50% by weight of argillaceous matrix, and they add 30% by weight of lime, i.e. approximately 60% by weight compared to the argillaceous matrix. In the process at 97°C, for a laterite soil containing approximately 30% by weight of kaolinitic clay, one adds 17% by weight of lime, that is to say approximately 60% by weight compared to the argillaceous matrix. The products manufactured in autoclave are of the silico-aluminates CSH type, whereas heating in a heat chamber at 97°C would lead to the formation of a tricalcium aluminate hydrated of the C_3AH_6 type. The compressive strength results varied from 25Mpa for C_3AH_6 , to 90 Mpa for CSH.

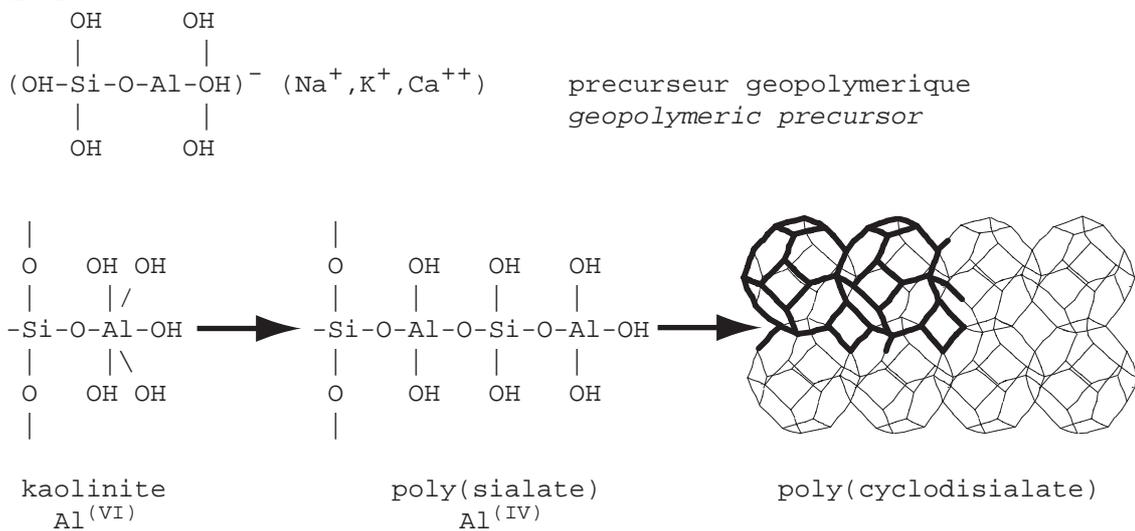
Finally, others use organic binders like asphalt ranging between 10% and 20% by weight of soil.

5.3 Low Temperature Geopolymeric Setting (LTGS)

In the processes described above, the soil material is coated by a binder (lime, cement, asphalt). When the quantities of binder are low (from 5 to 10% by weight for example), the material obtained is a stabilized earth. The mechanical characteristics are weak, but the earth material keeps its bioclimatic properties. On the contrary, when the quantity of binder increases in order to provide good mechanical properties, the bioclimatic characteristic of the material disappears.

The low temperature geopolymeric setting (LTGS) ensures cohesion to the soil material thanks to a completely different principle. There is no addition of binder but catalysts enabling mineralogical components to react between them, to reticulate, to set. It is the argillaceous material itself that manufactures, *in situ*, the binder for agglomeration. It acts like a process comparable to what takes place during ceramic firing at 900°C-1100°C, the difference with LTGS being that the setting can already start at room temperature.

The LTGS geopolymeric cross-linking takes place with the help of a geopolymeric precursor:



Kaolinite present in clays is transformed by this oligosialate into a three-dimensional, water stable compound, having a strong mechanical resistance. The oligosialate geopolymeric precursor contains 50% by weight of NaOH, KOH equivalent.

According to the quantity of oligosialate added to the argillaceous material, the geopolymeric cross-linking is more or less complete. For a lateritic earth, we can say that:

- from 0,5% to 2% by weight, the earth is stabilized with a good behaviour against water.
- from 2% to 5%, blocks are water stable, with a compressive strength ranging between 4Mpa and 6Mpa.
- from 5% to 10%, blocks are comparable to fired brick, with resistances ranging between 8Mpa and 60Mpa.

These mechanical characteristics depend on the setting temperature. Each setting temperature yields a very particular finished product.

5.3.1 Geopolymeric setting at room temperature: temperature at most equal to 65°C.

It is used to manufacture blocks or bricks, water stable, of medium mechanical resistance.

The oligosialate reagent is added as a powder, generally accompanied by a mineral additive making it possible to correct the argillaceous nature of the soil, and the mix "soil + reagent" is

crushed in a hammer mill for example. This mixture can be stored for a long period if necessary. Then, it is hydrated in a mixer in order to obtain a semi-plastic paste, the quantity of added water depending exclusively on the nature of each soil. This semi-plastic mixture will mature during at least 24 hours (Fig.5.1).

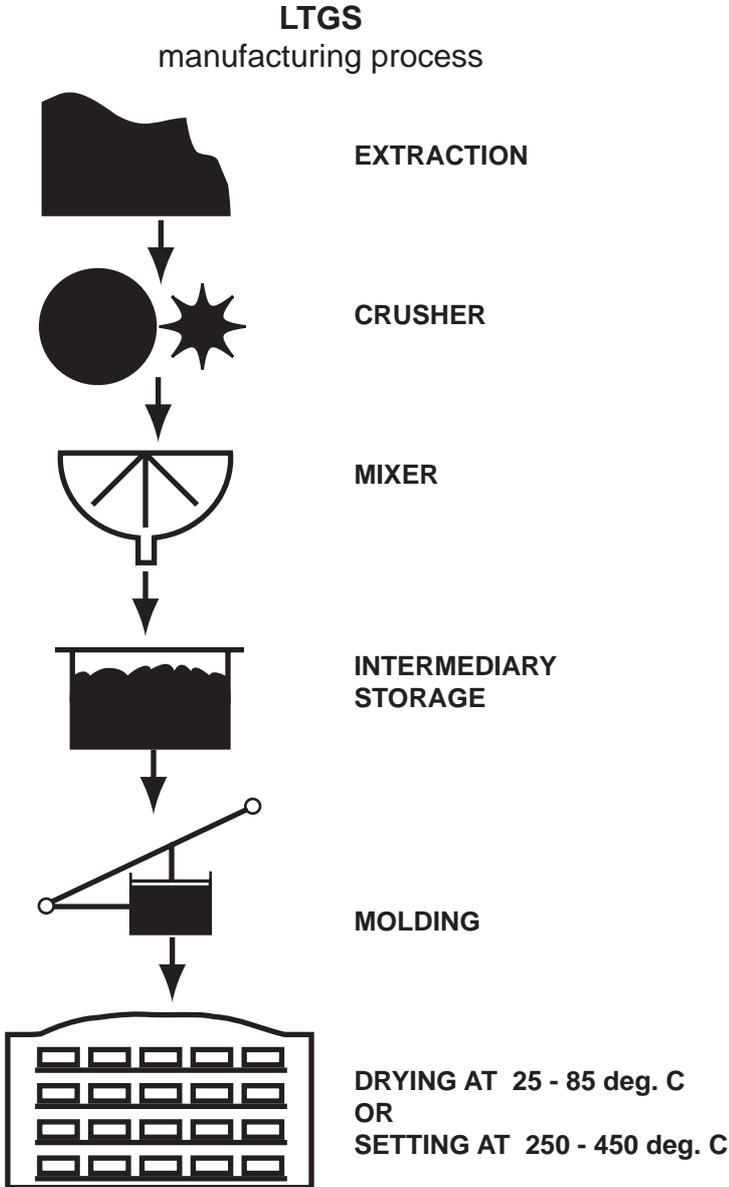


Figure 5.1: Manufacture of LTGS geopolymeric cross-linking bricks

5.3.1.1 Room temperature

We measure the progression of compressive strength with time. In this case, we used 6% of oligosialate reagent of the GEOPOLY ® KNA type (3% NaOH, KOH equivalent), the values obtained are as follows:

at the end of 3 days	4,1 Mpa
at the end of 15 days	7,9 Mpa
at the end of 45 days	7,7 Mpa

5.3.1.2 Temperature equals to 60°-65°C

A brick put in a heated chamber at 60°C, during 3 to 5 hours gives a compressive strength equal

to 7.0 Mpa.

5.3.2 Geopolymeric setting at temperature ranging between 80°C and 450°C:

The materials obtained are equivalent to ceramic bricks. Table 5.1 (Fig.5.2) shows the relation between the GEOPOLY ® KNA reagent in percent and the compressive strength.

Table 5.1: Compressive strength according to the quantity of GEOPOLY KNA ® reagent, its NaOH, KOH equivalent and the temperature of geopolymeric cross-linking LTGS.

% reagent geopolymer	% equivalent NaOH, KOH	Temperature of Geopolymerisation	
		85°C	450°C
2	1	6 Mpa	14 Mpa
4	2	12 Mpa	25 Mpa
6	3	15 Mpa	30 Mpa
8	4	17 Mpa	45 Mpa
10	5	18 Mpa	60 Mpa

The compressive strength, after 4 days of immersion in water, loses approximately 30%, compared to dry value. Thus a 12.6 Mpa dried brick manufactured at 85°C gets after 4 days immersion in water, 8.0 Mpa (P.V. n°134 from CEMEREX, 1982) (Fig.5.3).

The compressive strength for a brick treated at 400°C is 36 Mpa, gets 28 Mpa after 4 days of immersion in water.

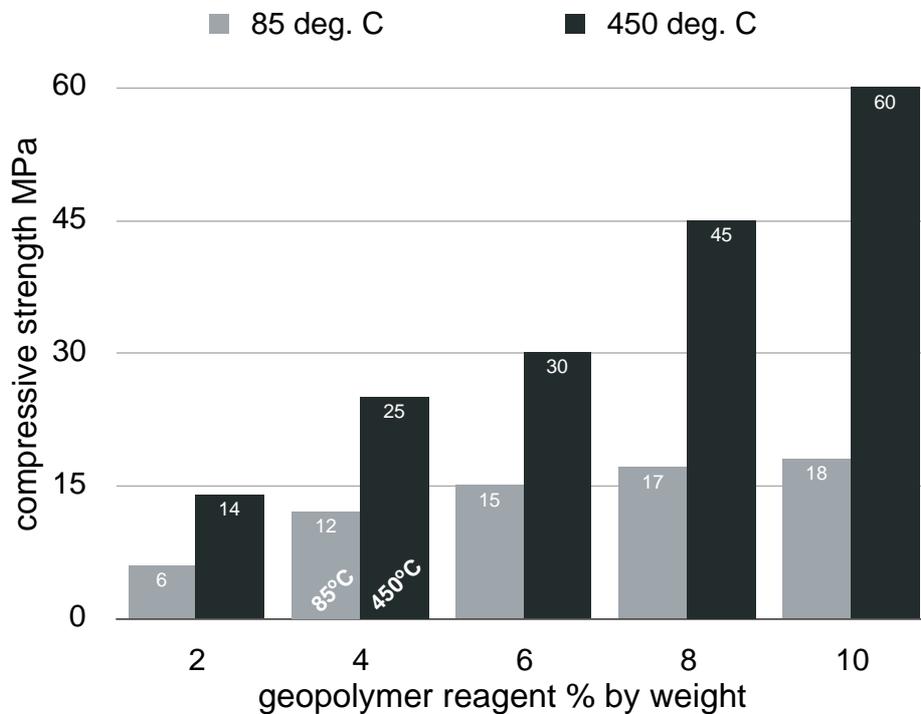


Figure 5.2: Compressive strength for various quantities of GEOPOLY KNA ® reagent and the temperature of LTGS geopolymeric cross-linking.

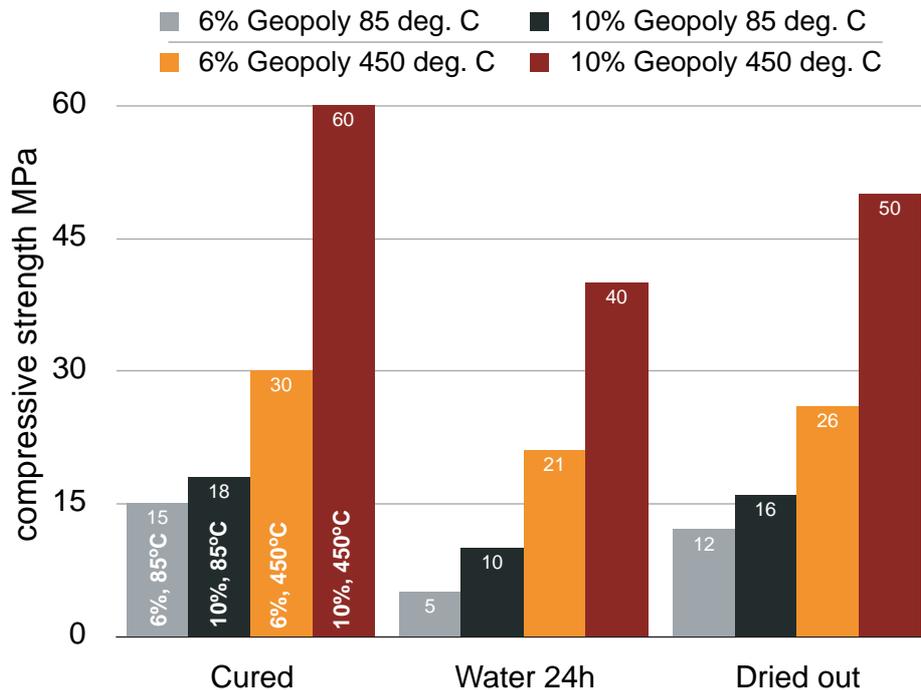


Figure 5.3: Compressive strength for various quantities of GEOPOLY KNA ® reagent, at 85°C and 450°C, after 24 hours of immersion in water, then dried out.

5.4 Quality of comfort:

All materials manufactured with LTGS geopolymeric cross-linking preserve the quality of comfort specific to earth materials. This quality remains and is neither disturbed by the medium temperature treatments (85-450°C), nor by the quantities of added GEOPOLY ® reagent.

This quality of "interior comfort", like the one obtained from pisé or rammed earth, is due to the "air-conditioning" property provided by the physical and chemical characteristics of geopolymers obtained with LTGS. These geopolymers, which constitute the matrix of the brick, have properties known as zeolitic, i.e. the property "to breathe", to be in constant hygrometrical balance with the interior of a house and constitute therefore an excellent insulation material against heat.

Indeed, contrary to the generally propagated idea, the heat insulation of buildings against warm climate does not follow the same rules and laws as the heat insulation against cold climate. It is known that, in hot and dry areas, the traditional earth material is providing a comfort much higher than modern insulating material used in northern industrialized countries. Bricks manufactured by LTGS geopolymeric cross-linking absorb water vapour. At night, they store condensation moisture from the surrounding air. During the day, they release this moisture, either inside, if the relative humidity should be compensated for, or outside. There is evaporation, therefore a drop in the temperature of the material, therefore a cooling of the house, and insulation against heat.

5.5 Building materials made with the concept of geopolymerisation:

The LTGS geopolymeric cross-linking is an innovative use of soil materials. In each country, by changing only certain parameters, all materials needed in building can be manufactured namely:

- pisé, rammed earth water resistant
- adobe, water resistant
- bricks
- beams
- foundations
- coatings
- coating of wall
- floor covering, pavement
- roof

The studies, currently in development, have already shown that it is also easy to conceive the manufacture of some type of mortars and hydraulic binders within the frame of this technology.

The LTGS geopolymeric cross-linking applied to the earth industry was the subject of a French ANVAR contract of assistance to the innovation, between Company CORDI-GEOPOLYMERE SA, 02100 SAINT-QUENTIN, France and the Company GARDIOL, 04200 SISTERON.

GEOPOLY ® is a trademark of Cordi-Géopolymère SA.