Geopolymer Institute Library

INSTITUT
GÉOPOLYMÈRE

Technical Paper #27 Ferro-sialate
January 2020
https://www.geopolymer.org/category/library/technical-papers/

How to cite this paper:

J. Davidovits and R. Davidovits, (2020), Ferro-sialate geopolymers, *Technical papers # 27, Geopolymer Institute Library*, www.geopolymer.org . DOI:10.13140/RG.2.2.25792.89608/2

Ferro-sialate Geopolymers (-Fe-O-Si-O-Al-O-)

Joseph Davidovits [a*] and Ralph Davidovits [a,b]

[a] *Geopolymer Institute, 02100 Saint-Quentin, France.*

[b] *Matériaux Avancés en Géopolymère, LTI - Université de Picardie Jules Verne, 02100 Saint-Quentin, France.*

* corresponding author: joseph@geopolymer.org (Joseph Davidovits)

ABSTRACT

The implementation in the mass production of geopolymeric cements in the world can no longer be based on coal-fly ashes for different reasons. In addition, Global Warming concerns will inevitably stop the manufacture of this ultimate waste of coal burning, fly ash. Rock-based geopolymer cements are the solution. Yet, it cannot be limited to the geological resources based only on white kaolinitic clays, or on residual eroded granite rocks, low in iron content, as promoted until now. The use of the enormous geological layers that constitute the ferralitic or lateritic rocks and soils is a need. Rock-based geopolymeric binder or cement of the type (Ca,Na,K)-poly (ferro-silico-aluminate) [Fe-O-Si-O-Al-O-] are geopolymeric compounds in which part of the Al atoms is substituted by Fe atoms, with the approximate formula

$$[Ca,Na,K]\bullet[-Fe-O]_x\bullet[-Si-O-(Al-O)_{(1-x)}]\bullet[-Si-O]_y$$

with "x" is a value higher than 0 and lower or equal to 0.5, "y" ranging between 0 and 25. This rock-based geopolymeric binder or cement is the result of the geopolymerization of geological elements rich in iron oxides and ferro-kaolinite, produced by the weathering of acidic rocks such as granite or gneiss, or of basic rocks (mafic) like basalt and gabbro. The manufacturing process of this geopolymeric binder or cement consists in treating the geological elements at a temperature of 600°C to 850°C. During this heat treatment, all iron oxides [goethite $FeO(OH)$ + Fe_3O_4 magnetite] are transformed into hematite Fe_2O_3 and ferro-kaolinite changes into ferro-metakaolin of type Fe-MK-750. Ca-geopolymerization in alkaline milieu involves GGBS. Hardening at room temperature provides compressive strength in the range of 75-90 MPa at 28 days.

Keywords: rock-based geopolymer; iron-rich; ferro-sialate molecule

1. INTRODUCTION

The data presented in this paper are preliminary results collected from various scientific, technological and patent publications. The recent discovery of ancient red geopolymer sandstone monuments in South America (Tiwanaku / Pumapunku, Bolivia) highlights the extraordinary long-term durability of this [Fe-O-Si-O-Al-O-] geopolymer molecule. The ferro-sialate matrix in this artificial red sandstone megaliths withstood at least 1400 years of archaeological burial (Davidovits *et al.*, 2019).

The development and implementation in mass production of geopolymeric cement in the world can no longer be based on coal-fly ashes for different reasons. Fly ashes are all different, from disparate origin, distinct quality, inconsistent composition, nonidentical ages, and available in various quantities. Fly ashes are ultimate wastes, not a standardized material with stable composition. In addition, *Global Warming* concerns will inevitably lead to the decrease of coal burning for the production of electricity and consequently to the exhaustion of this ultimate waste. One single OPC factory in Europe produces 2 Mt/year with invariable quality and steady quantity. Fly ash and mine tailings are exotic in everything, they are unable to provide such constant production needs. Rock-based geopolymer is the solution. Yet, it cannot be limited to the geological resources based only on white kaolinitic clays, or on residual eroded granite rocks, low in iron content, as implemented until now. The use of the enormous geological layers that constitute the ferralitic or lateritic rocks and soils is a need. This can be achieved with the rock-based geopolymer cements of the type (Ca,Na,K)-poly(ferro-sialate) described in this paper. The common characteristic of geopolymeric cements of the prior art is that they contain relatively little amount of iron oxides. This is due to the fact that scientists are wary of the harmful action of some ferrous compounds Fe^{++} which blocks the development of the geopolymeric reaction.

1.1 Controversial role of iron in geopolymerization.

In other scientific publications, the role of iron oxide goethite, FeO(OH), also seems dubious. The oxides of the types Fe_2O_3 hematite and Fe_3O_4 magnetite would seem more favorable. But, for geopolymeric cements manufactured with coal-power plants fly ashes, the experts do not recommend the use of fly-ashes rich in Fe_2O_3 hematite and Fe_3O_4 magnetite would be even harmful.

Although red kaolinitic clays are often recommended as potential raw material for geopolymeric building materials, scientific studies show that the addition of iron oxide hematite to white kaolin, inhibits or at least decreases the mechanical strength of the polycondensed product (Essaidi *et al.*, 2014). However, the study developed in the present paper contradicts this statement. Why ? Because these scientific studies were carried out on well-defined clay products, generally pure white kaolin or kaolinitic clays, to which iron oxide was added. On the opposite, the method described below involves the use of rocks, weathered rocks, not clays. Indeed, even with quantities of hematite as high as 40 % by weight, the compressive strength remains high, of the order of 70 to 90 MPa, at 28 days and room temperature hardening.

This mistrust of the scientists in the field with respect to high iron oxides contents increases when they notice that the presence of too large a quantity of iron atoms prevents the use of certain analytical techniques, which are essential for the comprehension of the geopolymeric molecular structures in the compounds. For example, the use of Nuclear Magnetic Resonance Spectroscopy NMR is impossible. The analytical methods used to determine the structure of the geopolymeric binder produced in the present study are Mössbauer spectroscopy and X-rays diffraction.

X-rays diffraction analysis shows that, after hardening, the geopolymeric binder or cement is made up of an amorphous matrix containing crystalline particles of iron oxide Fe_2O_3 hematite. The other iron oxides (goethite and magnetite) disappeared. The X-rays diffraction spectrum also contains other crystalline minerals, inert fillers, present naturally in the geological rocks, such as quartz, rutile, anatase, pyroxene, olivine, feldspar, muscovite, biotite, to only quote the most usual. When one compares the X-rays diffraction spectra of the geological starting raw materials with those of the geopolymeric cements obtained, one indeed notices that these crystalline minerals do not seem to have reacted with the reactional medium of the Ca-geopolymeric type. On the other hand, the aluminosilicate minerals (kaolinite, ferro-kaolinite, halloysite, montmorillonite, vermiculite) present in the X-rays diffraction spectrum of the raw materials, are absent in the X-rays diffraction spectrum of the hardened geopolymeric cement. The amorphous halo assigned to the geopolymer matrix is located at 27-29° 2θ for Cu(Kα). It is similar and in conformity with that of other geopolymeric cements of the prior art (Davidovits, 1991) .

Kenneth MacKenzie and his team (Lemougna et al., 2013) also stated that iron is not necessarily deleterious to geopolymer formation, as has sometimes been suggested. Geopolymers with very good compressive strength were formed, especially with fine volcanic ash. Their study with Mössbauer spectroscopy demonstrates that the iron Fe^{3+} is included in the geopolymer structure. A simplistic chemical charge-balancing consideration would require it to be located in the tetrahedral sites, i.e. part of the structural network. This could explain the high development of strength. For the authors, this indicates that the behavior of iron Fe^{3+} during geopolymerization relies on its chemical and mineralogical state in the starting materials. In other words, Fe^{3+} is the equivalent of Al^{3+} in the alumino-silicate network, yielding a ferro-silico-aluminate sequence (-Fe-O-Si-O-Al-O-), i.e, ferro-sialate.

1.2 Substitution of Al^{3+} with Fe^{3+}: ferro-kaolinite and ferro-metakaolinite.

Several scientific studies discuss the substitution of the atom Al by Fe in geological materials. Malden e*t al.* (1967) showed this remarkable behavior also in red kaolinitic clays as early as 1967 in their paper titled: "*Substitution by iron in kaolinite*". But subsequent research also explained that this substitution occurs only when the Fe atom is the trivalent Fe^{3+}. This substitution can reach 25% of the Al atoms. It is, however, impossible to separate the substituted kaolinite from that not-substituted. This explains why we designate the mixture of substituted kaolinite + not-substituted kaolinite by the generic term "*ferro-kaolinite*". The molecular sequence $\equiv$Si-O-Al$(OH)_2$ of kaolinite is transformed into the molecular sequence $\equiv$Si-O-Fe$(OH)_2$. Figure 1 displays the chemical structure of ferro-kaolinite.

This property is also observed in ceramics obtained by firing red kaolinitic clays. According to Traore *et al.* (2003) the presence of structural iron in the Al octahedral sites of kaolinite, i.e. the sequence $\equiv$Si-O-Fe$(OH)_2$, increases the reaction kinetics. During firing, the substituted Fe^{3+} favors the chemical reaction of metakaolinite with Ca cations from calcite to produce gehlenite and anorthite. In lateritic rocks, iron-rich clayey soils, (Trolard *et al.*, 1989; Paduani *et al.*, 2009), a considerable number of observations show that the amount of iron Fe^{3+} ranges between 0 and 33 %. Laterites include bauxite, ferricrete, mottle clays, lithomarges and saprolites, and are formed in humid tropical weathering conditions. In most lateritic profiles, kaolinite, goethite, hematite and quartz are the dominant minerals. They result from the weathering of acidic rocks such as sandstone, granite or gneiss, or of basic rocks (mafic) like basalt and gabbro. Because of the high quantity of iron oxides present in the clayey matrix, this "in situ" kaolinite may contain Fe atoms which replace partially Al in the molecular structure.

Like for the traditional manufacturing of metakaolin MK-750, the ferro-kaolinitic raw materials are calcined between 600°C and 850°C. During this heat treatment, the iron oxides goethite FeO(OH) and Fe$_3$O$_4$ magnetite are transformed into Fe$_2$O$_3$ hematite (Castelein *et al.*, 2002), and ferro-kaolinite is transformed into ferro-metakaolin of the type Fe-MK-750. Figure 1 displays the chemical structures of kaolinite, ferro-kaolinite and ferro-metakaolin.

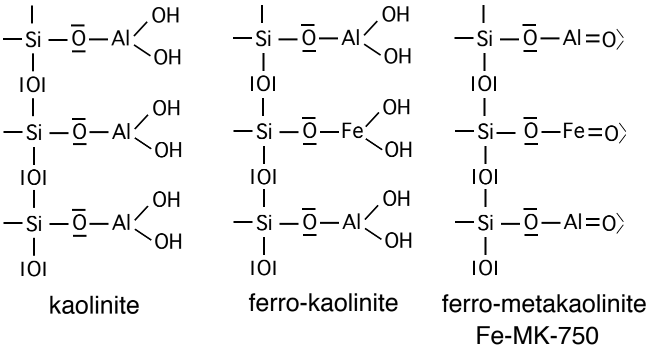

Figure 1: Chemical structures: left, kaolinite; center: ferro-kaolinite; right: ferro-metakaolinite.

2. MATERIALS AND METHODS

2.1 Analytical method: Mössbauer spectroscopy. As already mentioned, the high concentration in Fe atoms prevents the use of the analytical technique based on Nuclear Magnetic Resonance Spectroscopy NMR. The analytical methods applied to determine the structure of the (ferro-sialate) [Fe-O-Si-O-Al-O] geopolymer are Mössbauer spectroscopy and X-rays diffraction. The ^{57}Fe Mössbauer spectroscopy allows to differentiate between Fe atoms combined in oxides [goethite FeO(OH) + Fe$_2$O$_3$ hematite + Fe$_3$O$_4$ magnetite], from those belonging to the molecular structure of geopolymers, i.e. from those involved in the substitution of Al by Fe. The substitution of Al atoms by Fe atoms can be highlighted by the presence of a doublet in the Mössbauer spectrum which is characterized by two parameters, IS (isomer-shift) and QS (quadrupole-Split) for the sextet spectrum S and the broad doublet D (See in Figure 2).

In Figure 3, the Mössbauer spectrum adapted from Gomes *et al.* (2010) indicates that in the geopolymer some Fe^{3+} atoms would be associated with the molecular structure by a replacement of the Al atom with Fe in tetrahedral position, Fe [IV]. A similar sextet spectrum was described earlier by Bowen *et al.* (1995) on aluminous hematite.

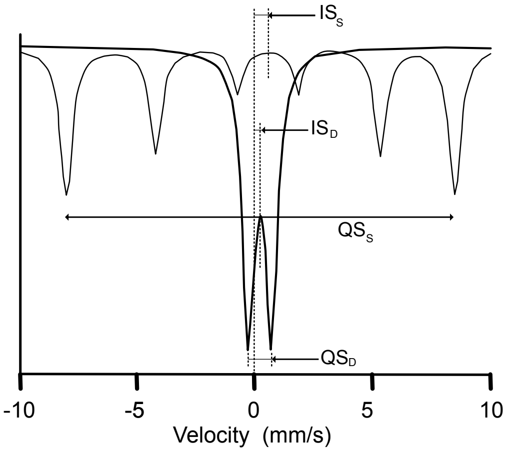

Figure 2: Mössbauer spectroscopy: sextet spectrum Isomer shift IS_S and Quadripol-splitting QS_S; doublet spectrum Isomer shift IS_D and Quadripol-splitting QS_D .

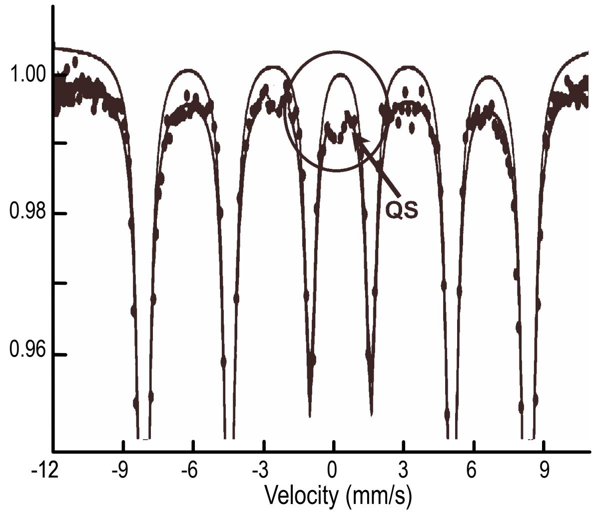

Figure 3: Mössbauer spectroscopy, Quadripol-splitting QS for the sextet spectrum of ferro-sialate geopolymer adapted from Gomes *et al.*, (2010).

The ^{57}Fe Mössbauer spectra allow to follow the transformation of ferro-kaolinite into ferro-metakaolin Fe-MK-750 during calcination. Thus, among the two parameters of the doublet spectrum, IS (isomer-shift) and QS (quadrupole-Split), the value of QS increases very appreciably during calcination; it increases from QS=0,60 mm/s for initial ferro-kaolinite to QS=1,0-1,50 mm/s for Fe-MK-750. Figure 4 displays the values of the doublet according to Murad *et al.*, (1998): isomer-shift IS=0,2mm/s and quadrupole-Split QS= 1,0 to 1,50 mm/s are characteristic of Fe atoms in tetrahedral structural position Fe [IV]. One can deduce that the electronic environment of the Fe atoms changes during calcination. Thus, just like in metakaolin MK-750, where the sequence ≡Si-O-Al(OH)$_2$ leads to the formation of two Al-oxide species, ≡Si-O-Al-O- (aluminum oxide) and ≡Si-O-Al=O (alumoxyle), the sequence ≡Si-O-Fe(OH)$_2$ would become ≡Si-O-Fe-O- (ferro-oxide) and ≡Si-O-Fe=O (ferroxyle) in ferro-metakaolin Fe-MK-750. However, the ^{57}Fe Mössbauer spectrum is delicate to integrate, because it is polluted by the one of hematite, so that it is necessary to subtract the latter in order to visualize the doublet of the ferro-sialate specie.

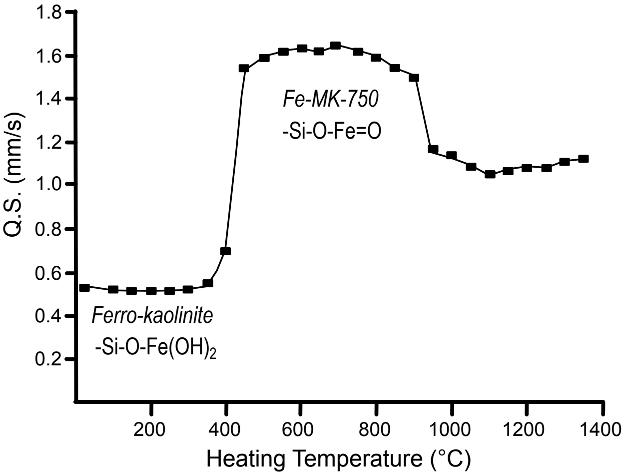

Figure 4: Mössbauer spectroscopy, Quadripol-splitting QS of the doublet: transformation of ferro-kaolinite into Fe-MK-750 above 450°C; adapted from Murad *et al.*, (1998).

2.2 Materials.

To obtain this new geopolymeric binder or cement one chooses among the weathered geological rocks, those which have a quantity of iron oxides, [goethite FeO(OH) + Fe_2O_3 hematite + Fe_3O_4 magnetite], ranging between 5 % and 40 % by weight of the rock (Davidovits *et al.*, 2010).

The weathering of acidic rocks such as granite or gneiss, or of basic rocks (mafic) like basalt and gabbro, produces kaolinite. However, because of the high quantity of iron oxides, the kaolinite contains Fe atoms which replace partially Al in the molecular structure. After the heat treatment, the geological element contains the geopolymeric precursor Fe-MK-750. It also contains hematite and inert mineral fillers initially present in the weathered acidic rocks, granite and gneiss, or basic (mafic), basalt and gabbro, such as quartz, rutile, anatase, ilmenite, pyroxene, olivine, feldspar, muscovite, biotite.

The weathering of the basic rocks may sometimes generate aluminum hydrates, the quantity of which can be higher than 50 % by weight, such as in bauxite. After thermal treatment at 600-850°C, the aluminum hydrates become very reactive with respect to the reactional medium of the Ca-geopolymeric type. During geopolymerization, each atom of Al must be balanced by one alkaline cation: Na^+, K^+ or one half Ca^{++} cation. High quantities of aluminum hydrates require equivalent high addition of alkaline reagents and this can play a substantial part in the economic assessment of such a process. It is thus preferable to choose a geological layer in which the aluminum hydrates are less concentrated. The quantity in aluminum hydrates [gibbsite $Al(OH)_3$ + boehmite AlO(OH)] should range between 0 % and 20 % by weight.

Example 1: One chooses a residual lateritic rock of the lithomarge type resulting from the weathering of basalt. It contains 12 % quartz, 45 % kaolinite, 30 % hematite, 3 % goethite, 10 % other elements (anatase + ilménite + olivine). One calcines at 750°C for 3 hours, then grinds to an average granulometry of 10-25 microns.

Geopolymeric mixture of Example 1:

- 90 parts calcined lateritic lithomarge;
- 30 parts GGBS ground to 10-25 microns;
- 30 parts K-silicate solution (molar ratio =1,56; H_2O: 55 %);
- 20 parts water.

Example 2: One chooses a residual rock of type saprolite (saprock) resulting from the weathering of basalt. It contains 15 %, plagioclase, 3 % quartz, 10 % pyroxene, 35 kaolinite, 18 % hematite, 3 % goethite, 6 % gibbsite, 5 % montmorillonite, 5 % other elements (anatase + ilménite+ olivine). One calcines at 750°C for 3 hours, then grinds to an average granulometry of 10-25 microns.

Geopolymeric mixture of Example 2:

- 90 parts calcined saprolite;
- 30 parts GGBS ground to 10-25 microns;
- 30 parts K-silicate solution (molar ratio =1,26; H_2O: 53 %);
- 20 parts water.

3. RESULTS AND DISCUSSION

Hardening occurs at room temperature 20°C, in air, in a covered mold to avoid the evaporation of water.

Example 1:

Compressive strength on the paste, without filler.
at 7 days : 30 MPa,
at 28 days : 75 MPa.

The pH of the crushed geopolymeric cement, measured in a water solution at 10 %, is pH=12.20 at 7 days and pH=11.65 at 28 days. The hardened (Ca,K)-poly(ferro-sialate) cement is analyzed by X-rays diffraction. The spectrum shows the characteristic amorphous halo at 28° 2θ for Cu(Kα), with additional lines assigned to hematite, the minerals quartz, anatase + ilménite + olivine. There is no kaolinite and goethite left, after their reaction in the (Ca,K)-geopolymeric reactive mixture.

Example 2:

Compressive strength on the paste, without filler.
at 7 days : 40 MPa,
at 28 days : 90 MPa.

The pH of the crushed geopolymeric cement, measured in a water solution at 10 %, is pH=12.25 at 7 days and pH=11.75 at 28 days. The hardened (Ca,K)-poly(ferro-sialate) cement is analyzed by X-rays diffraction. The spectrum shows the characteristic amorphous halo at 28° 2θ for Cu(Kα), with additional lines assigned to hematite, and the minerals pyroxene, quartz, anatase, ilménite. There is no kaolinite, goethite, gibbsite, montmorillonite left after their reaction.

One also proceeds to ^{57}Fe Mössbauer analysis. Because of the high quantity of hematite, the first spectrum shows the Sextet 01 which hides the Doublet spectrum. After subtraction of Sextet 01, the Doublet spectrum appears and has the parameters isomer-shift IS=0,2mm/s and quadrupole-Split QS= 1mm/s. These two parameters are characteristic of the Fe atom in tetrahedral structural position Fe [IV] in the molecular structure of the geopolymer.

Structural Fe^{3+} must be already present in the kaolinitic phase of the geological material. After calcination at 600-850°C and alkaline geopolymerization, part of the Fe atoms are in structural tetrahedral Fe[IV] or pentahedral Fe[V] position in the ferro-sialate geopolymer sequence [-Fe-O-Si-O-Al-O]. The quantity of substituted Fe atoms may range between 5 % and 50 % of the total quantity of Fe_2O_3 contained in the geopolymer binder or cement, the remainder, ranging between 50 % and 95 % being combined in the crystalline iron oxide Fe_2O_3 hematite.

If one complies with the writing in use for geopolymers, the geopolymeric compound constituting the (Ca,Na,K)-poly (ferro-sialate) type has the approximate formula:

$$[Ca,Na,K]\bullet[\text{-Fe-O}]_x\bullet[\text{-Si-O-(Al-O)}_{(1-x)}]\bullet[\text{-Si-O}]_y$$

where "x" is a value higher than 0 and lower or equal to 0.5, "y" is a value ranging between 0 and 25.

The (Ca,Na,K)-geopolymeric geopolymerization with regular metakaolin, MK-750, is described in the prior art (Davidovits, 2017). One learns that the MK-750/slag-based geopolymeric cement obtained according to this reaction is a geopolymeric compound made up of a solid solution comprising:

- a) calcium poly(di-sialate),$Ca[\text{-Si-O-Al-O}]_2\bullet nH_2O$ with anorthite like structure;
- b) sodium and/or potassium poly(sialate) [Na,K][-Si-O-Al-O];
- c) sodium and/or potassium poly(sialate-disiloxo) [Na,K] [Si-O-Al-O-Si-O-Si-O];
- d) calcium di(siloxonate) hydrate Ca[Si-O-Si-O],H_2O coined CSH in the jargon of the Portland cement specialists. The formation of this calcium di(siloxonate) hydrate depends on the quantity of blast furnace slag (glass mellilite) present in the geopolymeric medium.

The substitution of Al atoms by Fe in the ferro-sialate molecule changes substantially the composition of this geopolymeric compound. It is believed that this substitution takes place mainly in the sodium and/or potassium poly(sialate) geopolymer and in the sodium and/or potassium poly(sialate-disiloxo) geopolymer. Some quantity of Fe may also be associated with calcium di(siloxonate) hydrate, with replacement of Ca^{++} by Fe^{++}. In the present state of science, it is not possible to say whether the substitution of Al by Fe occurs or does not occur in the poly (di-sialate) of calcium CSH. That is why we do not introduce it here, but we cannot exclude it.

Similarly, the (Ca,Na,K)-poly(ferro-sialate) geopolymeric binder or cement is a geopolymeric compound made up of a solid solution comprising at least two components selected from:

- a) calcium poly(di-sialate),$Ca[\text{-Si-O-Al-O}]_2\bullet nH_2O$ with ananorthite like structure;
- b) sodium and/or potassium poly(ferro-sialate) [Na,K][-Fe-O-Si-O-Al-O];
- c) sodium and/or potassium poly(ferro-sialate-disiloxo) [Na,K][Fe-O-Si-O-Al-O-Si-O-Si-O];

In certain cases, when the amount of Ca reagent is higher than the quantity needed to produce the calcium poly(di-sialate), $Ca[\text{-Si-O-Al-O}]_2\bullet nH_2O$, the solid solution also contains ferro-calcic di(siloxonate), derived from CSH, with Ca substitution by Fe.

4. CONCLUSION

The implementation in the mass production of rock-based geopolymeric cements in the world cannot be limited to the geological resources based only on white kaolinitic clays, or on residual eroded granite rocks, low in iron content, as described in the prior art. The use of the enormous geological layers that constitute the ferralitic or lateritic rocks and soils is a need. This can be achieved with rock-based geopolymeric cements of the type (Ca,Na,K)-poly(ferro-sialate).

The mistrust of the workers in the field with respect to high iron oxides contents increases when they notice that the presence of too large a quantity of iron atoms prevents the use of certain analytical techniques, which are essential for the comprehension of the geopolymeric molecular structures in the compounds. For example, the use of Nuclear Magnetic Resonance Spectroscopy NMR is impossible. The analytical methods used to determine the structure of the geopolymeric binder produced in the present study are Mössbauer spectroscopy and X-rays diffraction. ^{57}Fe Mössbauer spectroscopy allows to follow the transformation of ferro-kaolinite into ferro-metakaolin Fe-MK-750 during calcination. It also provides some information on the (ferro-sialate) [-Fe-O-Si-O-Al-O] geopolymer structure. Furthermore, it is remarkable to notice that, like for other geopolymeric systems, its long-term durability is based on ancient technologies.

REFERENCES

Bowen L. H., De Grave E., (1995), Mössbauer spectra in external field of highly substituted aluminous hematites, *J. Magnetism and Magnetic Materials*, 139, 6-10.

Castelein O., Aldon L., Olivier-Fourcade J., Jumas J. C., Bonnet J. P., Blanchart P., (2002), ^{57}Fe Mössbauer study of iron distribution in a kaolin raw material: influence of the temperature and the heating rate, *Journal of the European Ceramic Society* 22, 1767–1773.

Davidovits, J., (1991), Geopolymers: inorganic polymeric new materials, *J. Thermal Analysis* 37, 1633-1656.

Davidovits Joseph, Davidovits Marc, Davidovits Frédéric, Davidovits Ralph, (2010), Ciment Géopolymère de Type Ca-Poly(ferro-sialate) et Procédé d'Obtention, *French Patent* FR 10 0421 (2 966 823).

Davidovits, J.: Geopolymer cement review (2013), Geopolymer Institute *Technical Paper # 21* at <https://

www.geopolymer.org/library/technical-papers/21-geopolymer-cement- review-2013/>.

Davidovits J., (2017), Geopolymers: ceramic-like inorganic polymers, *J. Ceram. Sci. Technol.* , **08** [3] 335-350.

Davidovits J., Huaman L., Davidovits R., (2019), Ancient geopolymer in South American monument. SEM and petrographic evidence, *Material Letters* 235 (2019) 120-124. DOI: doi.org/10.1016/j.matlet.2018.10.033. See also Davidovits J., Huaman L., Davidovits R., (2019), Tiahuanaco monuments (Tiwanaku / Pumapunku) in Bolivia are made of geopolymer artificial stones created 1400 years ago, *Archaeological Paper #K*, Geopolymer Institute Library, www.geopolymer.org. DOI: 10.13140/RG.2.2.31223.16800.

Essaidi N., Samet B., Baklouiti S., Rossignol S., (2014), The role of hematite in aluminosilicate gels based on metakaolin, *Ceramics-Silikaty* 58 (1), 1-11.

Gomes K. C., Lima G. S. T., Torres S. M., De Barros S., Vasconcelos I. F., Barbosa N. P., (2010), Iron distribution in geopolymer with ferromagnetic rich precursor, *Materials Science Forum*, 643, 131-138.

Lemougna P. N., MacKenzie K. J. D., Jameson G. N. L., Rahier H., Chinje Melo U. F., (2013), The role of iron in the formation of inorganic polymers (geopolymers) from volcanic ash: a ^{57}Fe Mössbauer spectroscopy study, *J. Mater. Sci.* 48:5280–5286.

Malden P. J. and Meads R. E., (1967), Substitution by iron in kaolinite, *Nature* 215, 844-846.

Paduani C., Samudio Pérez C. A., Gobbi D., Ardisson J. D., (2009), Mineralogical characterization of iron-rich clayey soils from the middle plateau in the southern region of Brazil, *Applied Clay Science* 42, 559–562 .

Traore K., Kabre T. S.,Blanchart P., (2003), The presence of structural iron in Al octahedral sites of kaolinite increases the reaction kinetics. Gehlenite and anorthite crystallisation from kaolinite and calcite mix, *Ceramics International*, 29 377–383.

Trolard F. and Tardy Y., (1989), A Model of Fe^{3+} kaolinite, Al Fe^{3+} goethite, Al Fe^{3+} hematite equilibria in laterites, *Clay Minerals* 24, 1-21.