OBTAINMENT OF CERAMIC TILES BY ALKALINE ACTIVATION

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ABSTRACT

This paper presents a new shaping method for the forming of alkaline inorganic polymer materials, better known as geopolymers. These materials are prepared by alkaline activation and subsequent condensation of aluminosilicate raw materials, which give rise to a polymer gel that provides the end product with high mechanical strength.

At present, ceramic tiles are manufactured at 1100–1200 °C, while geopolymers require a temperature of about 25–150 °C. As a result, the obtainment of ceramic tiles based on the alkaline activation process would decrease the firing stage, thus reducing energy consumption and greenhouse gas (CO_2), as well as sulphur, fluorine, and chlorine emissions.

The raw material used was a reagent material in the alkaline activation process (kaolin). The shaping methods used were a form and extrusion. This latter shaping method is new in the obtainment of alkaline inorganic polymers, since these materials have been studied from the outset by the traditional shaping method used in the cement sector, namely by means of forms.

The results show that the mechanical strength of the material obtained by alkaline activation was of the same order as that of ceramic tiles and was closely related to the nature, microstructure, and chemical composition of the reaction products, as well as to the process variables. In every case, the main reaction product was an alkaline inorganic polymer with cementing properties (N-A-S-H gel), which was largely responsible for the mechanical properties of the material.

1. INTRODUCTION

The ceramics manufacturing process requires an important energy input for the necessary physico-chemical transformations to develop, in order to obtain the end product. The rising price of natural gas, used as fuel in the firing stage, is a serious problem for ceramics manufacturers.

A solution to this problem could be the reduction and/or suppression of the different thermal treatments currently being used, which would reduce manufacturing costs. Hence the interest in investigating alternative synthesis processes, such as the formation of alkaline inorganic polymers, which would enable new materials to be obtained for the same uses as traditional ceramics. The electric and thermal energy saving would also reduce carbon dioxide (CO_2) air emissions, one of the main causes of the greenhouse effect, as well as the emission of other gases such as sulphur, fluorine, and chlorine.

Alkaline activation is a chemical process in which a powdered material of aluminosilicate nature, such as calcined kaolin, is mixed with an alkaline activator to generate a paste that is able to set and harden in a short period of time [1-4]. These materials, known as geopolymers [3] or alkaline inorganic polymers [5,6], constitute a new product family that, among other interesting properties, are able to combine specific qualities of cements with those proper to ceramics, as well as features belonging to the family of zeolites.

The new product is obtained by means of an alternative process to current ones. The process consists of the polymerisation of simple tetrahedral units of aluminium and silicon and comprises two steps:

- Solution of the raw materials in alkaline solutions to form inorganic monomers.
- Polycondensation of the monomers to form polymer oxide structures in three-dimensional networks.

Both steps take place either at ambient temperature or at very low temperature (T < 200 ºC).

Alkaline inorganic polymers have been studied, since they were discovered, by the cement sector. As a result, the only shaping method used for these materials has been the sector's traditional method by means of forms. No studies are available by national or international research groups on alkaline activation using different shaping methods, such as pressing or extrusion. In this work, extrusion has been studied as an alternative shaping method for this type of materials. Moreover, this alternative method could allow materials with enhanced mechanical properties to be obtained, owing to the microstructural improvement that such forming provides [7-8].

2. MATERIALS AND SHAPING METHODS

2.1. MATERIALS

The raw material used was metakaolin. Metakaolin is essentially an anhydrous aluminosilicate deriving from a clay mineral, namely kaolin. Kaolin is a natural raw material obtained by beneficiating raw kaolin or freshly extracted kaolin rock that contains kaolinite as main mineral. The kaolin used was B kaolin supplied by CAO-BAR S.A.

In order to carry out the alkaline activation of the solid material, KOH lentils supplied by PANREAC were used as reagents to prepare the potash solution, in addition to a solution of soluble silicate, supplied by IQE, whose specifications are detailed in Table 1.

Solids content (%)	Density (g/cm³)	SiO_2/K_2O (by weight)	SiO_2/K_2O (molar)
52.0	1.64	0.64	1.0

Table 1. Potassium silicate (waterglass) specifications

2.2. SHAPING METHODS

2.2.1. Forms

First, test pieces were prepared by the cement sector's traditional method, i.e. by filling *DELRIN* moulds of 80x20x7 mm (Figure 1), on a flat surface (such forming can be performed directly after mixing). After the curing process, the test pieces were demoulded. This shaping method is known as the form system.

Figure 1. Mould used in the form system

2.2.2. Extrusion

Extrusion was performed in a laboratory extruder (Figure 2) with a freshly mixed plastic mass after different rest times. The mass was left to stand for this time so that it would have the same consistency as that of a clay mixed with water and ready for extrusion. Consistency was measured with a penetrometer (using a cylinder with a 1.5 cm diameter).

a) b) c)

Figure 2. Laboratory extruder. a) Description of extruder parts (1: piston; 2: vacuum system; 3: extrusion chamber; 4: die); b) Obtainment of the material; c) Detail of the material exiting the die

3. RESULTS AND DISCUSSION

3.1. STARTING MATERIAL

The kaolin was chemically characterised by X-ray fluorescence (XRF). The results are presented in Table 2.

Oxide	% (by weight)
SiO_2	49.6
Al_2O_3	36.3
Fe_2O_3	0.42
CaO	0.12
MgO	0.10
Na_2O	0.02
K_2O	0.75
TiO_2	0.15
P_2O_5	0.06
Loss on ignition (1000 ºC)	12.5

Table 2. Chemical analysis of the kaolin used

With a view to obtaining an amorphous raw material, it was necessary to calcine the kaolin in order to obtain metakaolin. This step influences the reaction characteristics of metakaolin and different factors, such as the calcination process (kiln used, kiln atmosphere, etc.) and the temperature at which this is carried out, need to be taken into account.

In order to determine the calcination temperature, the reactivity in alkaline solutions was studied. The quantity of Si and Al monomers, measured by ICP-OES, as a function of kaolin calcination temperature after 3 hours' contact with a NaOH solution at 10% by weight (150 mg calcined kaolin, 150 ml NaOH solution, and test temperature of 60 ºC), is shown in Figure 3. The solubility was influenced by the type and content of the predominant mineral in the starting material. The maximum activity was in a temperature range of 650–850 °C.

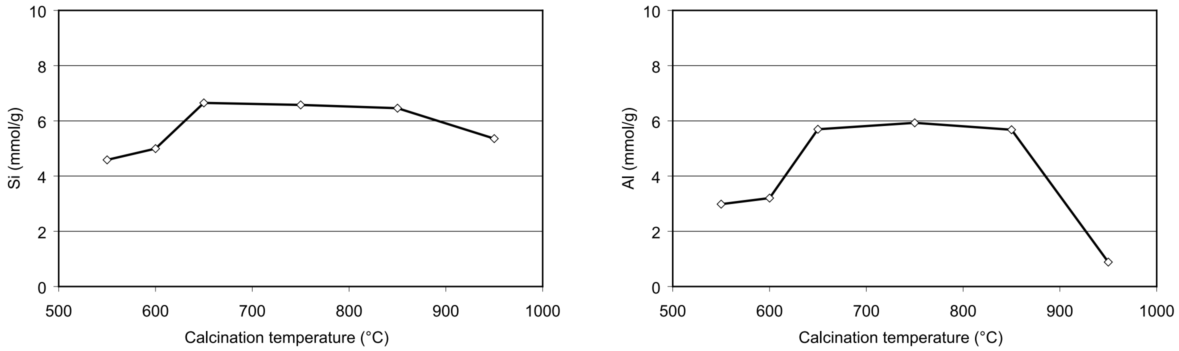

Figure 3. Quantity of Si monomers (left) and Al monomers (right) that reacted after 3 hours' contact with a NaOH solution

In this study, the kaolin was calcined in an electric laboratory kiln and the following thermal cycle was used:

- From 25 to 750 ºC at a heating rate of 3.3 ºC/min.
- 30 minutes at 750ºC.
- Fast cooling (*quenching*).

The kaolin specific surface area, obtained by nitrogen adsorption (BET method), was 9.2 m^2/g, while that of the metakaolin (kaolin calcined at 750 ºC) was 8.9 m^2/g.

Particle size analysis of the kaolin and metakaolin was performed by X-ray absorption (SEDIGRAPH). This technique is based on the particle sedimentation rate, using the Stokes formula, in which the change in mass concentration is monitored when particles fall in a liquid medium. The characteristic diameters obtained of the particle size distribution are detailed in Table 3.

Characteristic diameters	**µm**	
	Kaolin	**Metakaolin**
d(0.9)	7.5	10.5
d(0.5)	1.9	3.5
d(0.1)	0.1	0.7

Table 3. Characteristic diameters of kaolin and metakaolin

3.2. FORMATION PROCESS OF THE ALKALINE INORGANIC POLYMER

Depending on the reactivity of the raw materials and the needs of the technology used to form the end product, it is necessary to identify the most appropriate activator (type and concentration), as well as the addition of any further material (which could be considered a filler).

Using the metakaolin and the activating solution described above, several compositions were designed. The molar ratio of the optimum composition, obtained by taking into account factors such as the workability of the plastic mass, bulk density, and mechanical strength of the end product, etc. is detailed in Table 4.

Molar ratio	
SiO_2/Al_2O_3	3.1
K_2O/SiO_2	0.4
K_2O/Al_2O_3	1.2
H_2O/K_2O	8.9

Table 4. Molar ratio of the optimum composition

The metakaolin was mixed with the activating solution in a laboratory mixer for 10 minutes at a stirring speed of 60 rpm. This yielded a plastic mass that was used to form test pieces, by means of the form system and by extrusion, which were then subjected to a curing stage.

Curing conditions (such as time, temperature, and humidity) play a key role in the microstructural development and properties of the materials obtained by alkaline activation [9]. In this study, the curing process was carried out in a climatic chamber, in which the formed test pieces were placed, in order to have controlled temperature and humidity conditions. The curing conditions [5][6] were as follows:

- Time: 20 hours
- Temperature: 85 ºC
- Relative humidity: 95%

After the curing stage, the samples were subjected to a drying process at ambient temperature and humidity for 24 hours. The tensile bending strength values obtained using the two shaping methods are detailed in Table 5. As may be observed, the mechanical strength values obtained using extrusion were higher than those obtained by the cement sector's traditional shaping method. The extruded test pieces were prepared using three different paste (metakaolin + activating solution) consistencies: < 0.1, 2.8, and 4.5 kg, at a maximum extrusion force of 1600, 3400, and 5600 N, respectively.

Shaping method		Tensile bending strength (MPa)
Form system		3.8 ± 0.7
Extrusion	Consistency: < 0.1 kg	6.1 ± 1.2
	Consistency: 2.8 kg	10.5 ± 0.6
	Consistency: 4.5 kg	11.0 ± 1.1

Table 5. Effect of the shaping method on tensile bending strength

With regard to the drying stage, both time and drying temperature were studied. For that reason, at this point, two different drying conditions were studied (the drying stage takes place after the curing stage):

- The test pieces were maintained at ambient temperature and humidity for 70 days.
- The test pieces were subjected to a drying cycle in a laboratory oven (T ≤ 110 ºC) with a view to enhancing the end properties.

The increase in drying time and the use of a drying cycle, keeping the other process variables constant in both cases, gave rise to increased mechanical strength of the material (Table 6).

Drying	Tensile bending strength (MPa)
24 hours at ambient temperature and humidity	11.0 ± 1.1
70 days at ambient temperature and humidity	14.5 ± 1.2
Drying cycle	16.0 ± 1.0

Table 6. Effect of drying on tensile bending strength

The maximum tensile bending strength attained (16 MPa) exceeded the minimum required for earthenware tile (porosa) (e < 7.5 mm) and was much higher that that required for concrete tiles (Table 7). In view of these results, it would be possible to replace earthenware tiles with a product obtained by alkaline activation.

Standard	Material		Tensile bending strength (MPa)
UNE-EN 14411: 2007	Porosa	e ≥ 7.5 mm	≥ 12
		e < 7.5 mm	≥ 15
UNE-EN 1339: 2006	Concrete tiles		≥ 2.8
			≥ 3.2
			≥ 4.0

Table 7. Minimum tensile bending strength according to the standards

Other properties of the product obtained after alkaline activation were also studied. These are presented in Table 8.

Bulk density	1.4 g/cm^3
Curing shrinkage	< 0.05 %
Porosity	~ 30 %
Mohs Hardness	4-6

Table 8. Properties of the product obtained by extrusion

3.3. DECORATION

Finally, the possibility was considered of decorating the pieces obtained. A literature search was therefore performed of the fluxing compositions that might be used for this type of product. Based on the search results, three different composition systems were tested: '$BaO\text{-}B_2O_3\text{-}SiO_2$', '$ZnO\text{-}B_2O_3\text{-}Na_2O\text{-}SiO_2$', and '$Li_2O\text{-}B_2O_3\text{-}SiO_2$'. With a view to avoiding cracks and achieving good bonding between the substrate and the glaze, the coefficient of expansion of the substrate needed to be very similar to that of glaze. The foregoing compositions were therefore reformulated and a more appropriate frit for the needs of the product was prepared (Tables 9 and 10).

Oxides	% (by weight)
SiO_2	10.4
Al_2O_3	13.4
B_2O_3	46.6
CaO	9.9
BaO	6.9
Li_2O	2.8
PbO	10.0

Table 9. Optimum composition obtained from the system $PbO\text{-}BaO\text{-}CaO\text{-}B_2O_3\text{-}Al_2O_3\text{-}SiO_2$

Raw materials	% (by weight)
Alumina	9.5
Boric acid	58.9
Barium carbonate	6.3
Lithium carbonate	3.3
Lead oxide	7.1
Calcium oxide	0.7
Wollastonite	14.2

Table 10. Mixtures of raw materials for obtaining the compositions indicated in Table 9

The greatest problem posed by using a low-temperature frit that is applied by the wet method is the overlapping of organic matter decomposition with the glaze sealing phase at the same temperature. In order to avoid the presence of organic matter in the glaze composition, a series of actions were undertaken:

- First, the carboxymethyl cellulose (CMC) additive, which is usually added to the glaze composition, was suppressed. Owing to the elimination of CMC from the composition, it was considered convenient to use a vehicle (one of those that are typically used in glass decoration, since they exhibit the singularity of having a high vapour pressure and therefore evaporate at low temperatures) that could partly perform the functions of the CMC. This solution turned out to be inappropriate and the fired glaze continued to display a dark colour.
- It was then thought that the organic matter existing in the kaolin (a raw material that is also added to the frit in preparing the glaze composition) might be having an impact. It was therefore attempted to prepare a suspension solely with frit; however, the result was not satisfactory either.
- Finally, it was decided to replace kaolin with metakaolin (in preparing the glaze composition) in order to provide the composition with a certain plasticity without introducing any organic matter.

Since all the actions undertaken to suppress the dark/greyish colour of the glaze composition, which was applied by the wet method, did not work, dry glaze application was studied. The frit involved was therefore dry milled until a grit of d < 120 μm was obtained. The grit was applied with an applicator rod that was 15 μm thick. The resulting piece (substrate obtained by alkaline activation + dry grit application) was then fired at 600 ºC. The result is shown in Figure 4.

Figure 4. Glaze composition applied by the dry method

4. CONCLUSIONS

Alkaline inorganic polymers or geopolymers constitute a new product family that, among other interesting properties, are able to combine certain specific features of traditional ceramics, which make them particularly interesting with relation to the manufacture of ceramic pieces with similar, though not identical properties to those of traditional ceramics.

A new shaping method (extrusion) was studied in the alkaline activation process of aluminosilicate materials, which yielded higher mechanical strength values than those obtained by the traditional shaping method (using forms).

It was observed that when the pieces were subjected to a drying cycle, this directly and proportionally influenced the mechanical properties of the formed product.

It was verified that a low-temperature glaze composition and a dry glazing process were suitable for the decoration of the substrate obtained by alkaline activation.

ACKNOWLEDGEMENTS

This study was funded by the Generalitat Valenciana, through the Valencian Institute of Small and Medium-sized Enterprise – IMPIVA (in the R&D Programme for Technology Institutes), and by the European Fund for Regional Development (EFRD) in the Operational EFRD Programme of the Valencia Region 2007–2013 (project reference: IMIDIC/2009/12-IMIDIC/2010/70-IMDEEA/2011/48).

This project, *Ecofriendly ceramic tile development by geopolymerization* (GeopolyTile), was submitted in the 6th Pilot Call of CORNET II. It is led by *Seramik Araştırma Merkezi* (SAM) from Turkey, with the participation of the Instituto de Tec-

nología Cerámica (ITC-AICE) and the *German Ceramic Society* (DKG). The German Ceramic Society (DKG) is represented by two research centres, namely the *RWTH Institut für Gesteinshüttenkunde* (GHI) of Aachen and the *Professur Bauchemie* of *Bauhaus-Universität Weimar* (BUW).

https://extranet.itc.uji.es/GeopolyTile

REFERENCES

[1] GLUKHOVSKY, V.D. *The soil silicates*. Kiev: Gosstroy, 1959. [Tesis doctoral].

[2] KRIVENKO, P. Alkaline cements: terminology, classification, aspects of durability. En: JUSTNES, H. (ed.). *10th International Congress on the Chemistry of Cement. Proceedings: vol 4. Performance and durability of cementitious materials*. Gothenburg: ICCC, 1997, p. 4iv046-4iv050.

[3] DAVIDOVITS, J. Geopolymer chemistry and properties. En: DAVIDOVITS, J.; ORLINSKI, J. (eds.). *Geopolymers'88: First European Conference on Soft Metallurgy. Volume 1.* Saint-Quentin: Institut Géopolymère, 1988, p. 25-48.

[4] PALOMO, A.; GLASSER, F.P. Chemically-bonded cementitious materials based on metakaolin. *Br. Ceram. Trans. J.,* 91(4), 107-112, 1992.

[5] FERNÁNDEZ-JIMÉNEZ, A.; MONZÓ, M.; VICENT, M.; BARBA, A.; PALOMO, A. Alkaline activation of metakaolin-fly ash mixtures: Obtain of zeoceramics and zeocements. *Microporous Mesoporous Mat.,* 108, 41-49, 2008.

[6] MONZÓ, M.; FERNÁNDEZ-JIMÉNEZ, A.; VICENT, M.; PALOMO, A.; BARBA, A. Activación alcalina de metacaolín. Efecto de la adición de silicato soluble y de la temperatura de curado. *Bol. Soc. Esp. Ceram. Vidr.,* 47(1), 35-43, 2008.

[7] KORC, G.; KARA, A.; KARA, F.; VICENT, M.; MONZÓ, M.; SUZUK, K.G.; TELLE, R.; HOHMANN, M.; SEIFFARTH, T.; KAPS, C. Geopolytile: Développement de carreaux céramiques respectueux de l'environnement par geopolymerisation. *Ind. Céram. Verr.,* 1032/1033, 26-31, 2010.

[8] KORÇ, G.; KARA, K.; KARA, F.; VICENT, M.; MONZÓ, M.; SÜZÜK, K.G.; TELLE, R.; HOHMANN, M.; SEIFFARTH, T.; KAPS, C. Geopolytile: Eco-desarrollo de baldosas cerámicas obtenidas por geopolimerización. En: Qualicer 2010: XI Congreso Mundial de la Calidad del Azulejo y del Pavimento Cerámico. Castellón: Cámara Oficial de Comercio, Industria y Navegación, 2010.

[9] CRIADO, M.; PALOMO, A.; FERNÁNDEZ-JIMÉNEZ, A. Alkali activation of fly ashes. Part 1: Effect of curing conditions on the carbonation of the reaction products. *Fuel,* 84(16), 2048-2054, 2005.