# VALORIZATION OF ALUMINA RED MUD FOR PRODUCTION OF GEOPOLYMERIC BRICKS AND TILES

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## Abstract

The production of red mud in almost 1 to 1 mass ratio in relation to metallurgical alumina renders its valorization a first-priority issue for any alumina plant. The huge amount of red mud produced annually all over the world renders necessary the development of several valorization alternatives so that each alumina plant to have the ability to choose among them the ones that are more proper taking into account geographical and economic parameters.   The use of red mud as a filler in production of geopolymeric massive bricks and tiles seems to be a technically feasible valorization alternative. The red mud/metakaolin and the red mud/slag geopolymeric systems proved to be effective and the materials produced have promising mechanical, satisfactory physical and excellent thermophysical properties.

## Introduction

The metallurgical processing of bauxites and laterites in Greece results in the production of very large quantities o f solid wastes, namely red mud [1] (RM) and ferronickel slag [2] (FeNiSG), which have to be disposed on specially designed sites following the Greek and the EU legislation  in force. On the other hand taking into account the EU policy which encourages the re-use of industrial solid wastes/by-products, it is more than obvious that the disposal of wastes is no longer the preferred management option from a sustainability point of view. Towards this direction, extended research has been performed during the last decades focusing at the development of viable technologies for the utilization of solid wastes as secondary raw materials in certain production processes. Among these technologies, geopolymerization gains increasing attention as it achieves to turn a numerous solid aluminosilicate wastes into materials with added value.

Geopolymerization technology [3] can transform several aluminosilicate materials into useful products called geopolymers or inorganic polymers. Geopolymerization involves a heterogeneous chemical reaction between solid aluminosilicate materials and alkali metal silicate solutions at highly alkaline conditions and mild temperatures yielding amorphous to semi-crystalline polymeric structures, which consist mainly of Si–O–Al and Si–O–Si bonds. Inorganic polymers possess excellent physical, chemical, thermal and mechanical properties [4] and therefore are viewed as attractive alternatives for certain industrial applications mainly in the area of construction and building materials [4]. RM and FeNiSG due to their aluminosilicate nature have the potential to be used as source materials for the geopolymerization process. The utilization of RM and slags for the development of geopolymeric construction materials has been and continues to be subject of several research studies [1,5,6,7].

The present paper investigates the development of geopolymericbricks and tiles utilizing RM as well as FeNiSG as raw materials.

## Introduction

### Raw Materials

The chemical analysis of the solid aluminosilicate raw materials used in this work is shown in Table 1. RM was supplied by the metallurgical plant of Aluminium of Greece SA while the FeNiSG was supplied by the Greek pyrometallurgical plant of the LARCO G.M.M.S.A. The metakaolin (MK) used in this work was purchased by Degussa.

**Table 1 - Chemical analysis of Raw Materials**

| A/A | RM % w/w. | MK %w/w | FeNiSG %w/w |
|---|---|---|---|
| $Fe_2O_3$ | 41,80 | 1,83 | - |
| $Al_2O_3$ | 16,54 | 40,98 | 10,11 |
| CaO | 10,98 | 0,18 | 3,65 |
| $SiO_2$ | 7,57 | 52,66 | 40,29 |
| $TiO_2$ | 9,56 | 1,43 | - |
| $Na_2O$ | 3,28 | 0,56 | - |
| MgO | 0,43 | 0,34 | 5,43 |
| $K_2O$ | - | 1,18 | - |
| FeO | | | 37,69 |
| $Cr_2O_3$ | | | 2,48 |
| LOI | 9,79 | - | - |
| TOTAL | 99,95 | 99,16 | 99,75 |

The RM as well as the FeNiSG can be characterized as rich in iron oxides aluminosilicate materials that contain a substantial amount of alkaline earths (Ca, Mg) oxides. RM is principally crystalline consisting of hematite, goethite, cancrinite, katoite, diaspore, gibbsite and anatase. FeNiSG comprises predominately from an amorphous aluminosilicate phase containing ferrite-spinels  $[(Fe^{2+},Mg)(Fe^{3+},Al,Cr)_2O_4]$  as the only crystalline mineralogical phase. Red mud has a BET specific surface area of $3,02m^2/g$ and a mean particle size (d50) of $0,49\mu m$. FeNiSG has accordingly BET specific surface area $1,59m^2/g$ and d50= $6,59\mu m$. MK is an aluminosilicate material rich in both silicon and aluminum oxides that is produced by dehydroxylation at high temperatures (800–1000$^\circ$C) of the industrial mineral kaolin. MK consists of an amorphous aluminosilicate phase as well as crystalline phases such as quartz and illite. Its mean particle size (d50) is $6,09\mu m$.

Except for the solid raw materials, a strongly alkaline aqueous silicate solution was used as an activating phase for the synthesis of geopolymers. The activating phase was prepared by dissolving anhydrous sodium hydroxide pellets (Merck, 99.5% purity) in de-ionized water and then adding sodium silicate solution (Merck, $Na_2O$ = 8%, $SiO_2$ = 27%, $H_2O$ = 65% and d = 1.346 g/l) to control the initial dissolved silica content in the activating phase.

Experimental Procedure

The geopolymeric specimens were prepared by a multi-stage procedure. Initially, a viscous paste was prepared by mixing mechanically the solid phase, consisting of a mixture of RM/MK or RM/FeNiSG, with the activating phase for 5 minutes until a homogeneous paste was obtained. In the second stage, the paste was molded in plastic cubic molds (50 × 50 × 50mm), which were firmly closed by a plastic cap. The closed molds were cured at 60°C for 6 hours in order to allow the paste to set, then the specimens were left at the ambient temperature for 18 hours to be cooled before be demolded. Then, the demolded specimens were weighed and their curing procedure was continued at different temperatures (40 - 80 °C) and relative humidity 70% for several time periods. At the end, several mechanical, physical and thermophysical properties were measured according to the relevant Greek and international standards.

**Results & Discussion**

Based on the fact that the RM consists from components that are either insoluble or have been precipitated in a high alkaline environment, it can be considered that its solubility in a strongly alkaline aqueous silicate solution, which is normally used as an activating phase in geopolymerization, is very limited. Therefore, the RM was used in this work as filler in a geopolymeric paste formed through alkali activation either of MK or of FeNiSG. Based on a previous work [1] the formulation for the preparation of the geopolymeric specimens in the RM/MK system was the following: the paste solid to liquid ratio was equal to 2,9g/ml. The solids were composed from 85%w/w RM and 15%w/w MK. The aqueous activating phase had a sodium hydroxide concentration of 8M and an initial dissolved silica ($SiO_2$) concentration of 3,5M.

The effect of curing temperature and time on water removal from geopolymeric specimens is shown in Figure1. It is concluded that at every curing temperature the water removal follows a slow procedure tending towards an equilibrium level which is not attained even after 7 days. The amount of entrapped water inside the geopolymeric materials decreases substantially as the curing temperature increases. None the less even at the highest studied temperature of 80°C, around 37%w/w of the initial water in the paste is entrapped in the geopolymeric material.
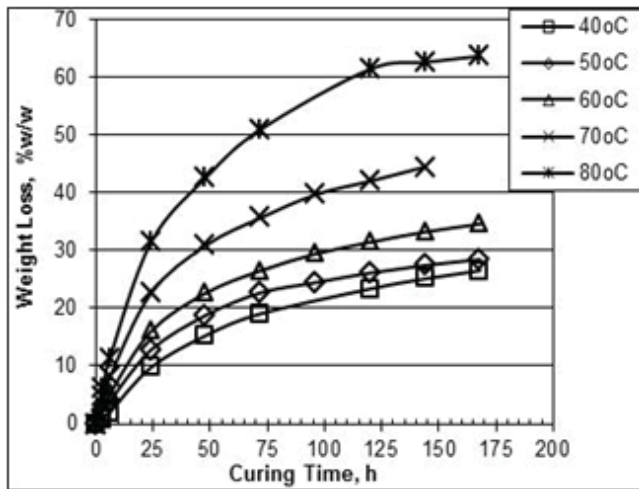
The drying rate of geopolymeric materials as a function of curing temperature and duration is shown in Figure 2. The maximum drying rate at any temperature is achieved during the initial curing period of three hours. Then, it decreases rapidly with the curing duration and becomes practically negligible after a curing duration of 96h. At 40°C the drying rate reaches a plateau in-between 3-24h of curing duration and then decreases following the general trend observed at higher temperatures.
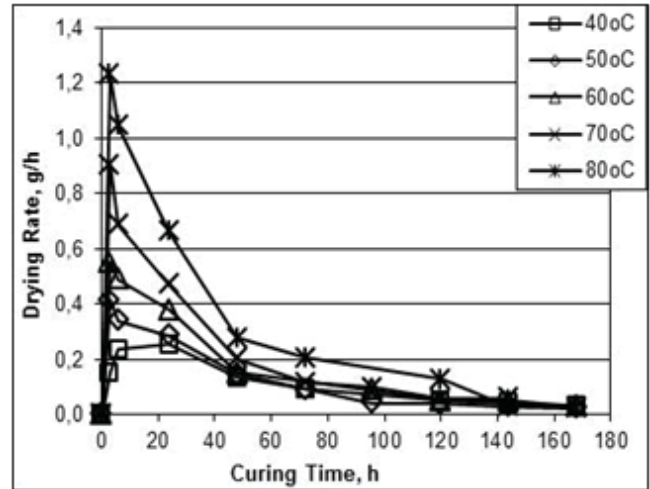


**Figure 2. Drying rate of geopolymeric materials as a function of curing temperature and time**

The dimension shrinkage of the geopolymeric materials as a function of curing temperature and duration is shown in Figure 3. It is obvious that the substantial amount of shrinkage takes place during the initial stages of curing procedure where the materials drying rate is relatively high. For example, the material cured at 80°C shows after 48h a shrinkage of 2,57% while the measured shrinkage after the curing period of 7 days is 2,96%. The materials cured at temperatures higher than 60°C undergoes shrinkage in their dimensions of the order of 3-3,2% while the ones cured in-between 40-50°C of the order of 2,2%.
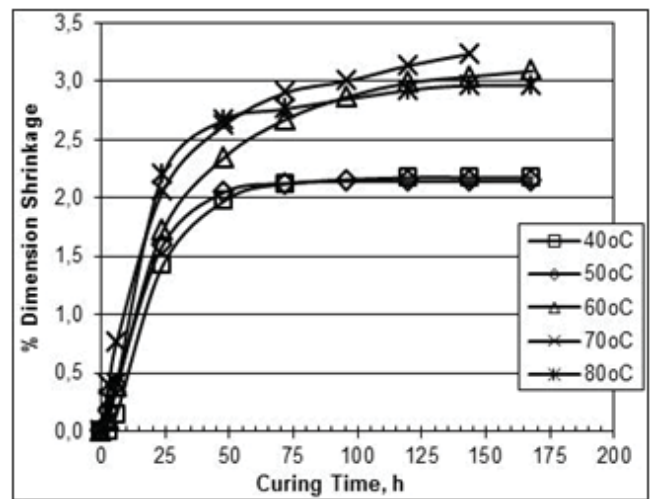


**Figure 3. Shrinkage of geopolymeric materials as a function of curing temperature and time**



**Figure 1. Water removal from geopolymeric materials as a function of curing temperature and time**

The compressive strength of geopolymeric materials after the end of the curing procedure at 168h is shown in Figure 4. The increase of the curing temperature from 40°C to 80°C causes an increase of the compressive strength from 5MPa to 25MPa accordingly. The values of compressive strength for the materials cured at temperatures higher than 60$^{\mathbf{o}}$C render them suitable for application as bricks under severe weathering conditions according to the Greek as well as ASTM international standards for clay bricks.
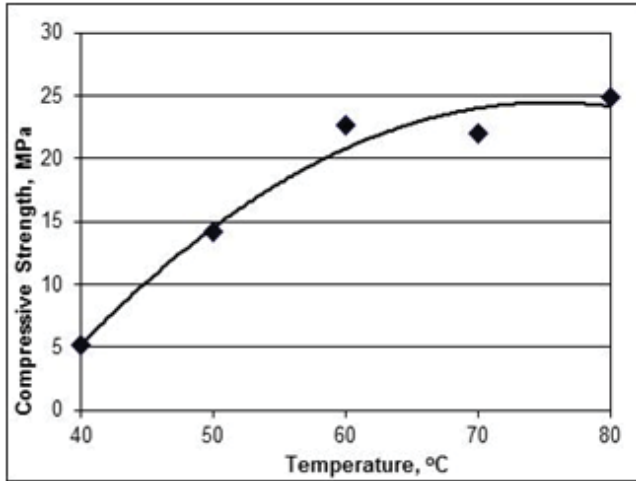


**Figure 4. Compressive strength of geopolymeric materials at 168h as a function of curing temperature**

The specimens cured at 40-50$^{\mathbf{o}}$C start forming cracks after the first 24h of curing which became more intense as the time passed. On the other hand, some cracks were observed on the specimens cured at 60-80$^{\mathbf{o}}$C during the first 3h of their curing process. The cracks were insignificant at 60$^{\mathbf{o}}$C and became gradually significant as the temperature increased. The most important observation was that the surface cracks were self-repaired till the end of the curing procedure at 168h as is seen in Figure 5.This observation shows that under that temperature conditions the geopolymerization process continued inside the materials producing an inorganic polymer that was diffused towards outside and thus filling the initially formed surface cracks.

Taking into account the above results it was concluded that the geopolymers cured at 60$^{\mathbf{o}}$C show very good compressive strength without the formation of surface cracks due to their moderate drying rate that renders the geopolymerization process fully controllable. Therefore, the development of compressive strength at 60$^{\mathbf{o}}$C as a function of curing time was studied in detailed and the results are shown in Figure 6. The material immediately after demolding has very low but not negligible strength (2,5MPa) but as the time pass the strength increases reaching 20MPa at 4 days and around 25MPa after 7 days.

It was therefore concluded that the optimum curing conditions for the RM/MK geopolymers are 60$^{o}$C, 96 hours curing time and 70% relative humidity because a) the drying rate after 96h has practically diminished, b) the dimension shrinkage has practically completed and c) the material has developed almost the 86% of the maximum compressive strength that it can develop.

The properties of the RM/MK geopolymeric material under the optimum conditions described above are given in Table 2.

**Table 2 - Properties of RM/MK Geopolymer**

| Property | Results |
|---|---|
| Compressive Strength | 20±2MPa |
| Flexural Strength | 371 N |
| Cold Water Absorption | 0,88 % w/w |
| Water impermeability | Impermeable |
| External fire performance | Class A Roof |
| Reaction to fire | A1 (Incombustible) |
| Durability in Freezing-Thawing | F0 (Slight Exposure) |
| Density | 2166,13 kg/m$^3$ |



**Figure 5. Specimen after curing at 80$^{o}$C for 3 hours (left) and 7 days (right)**
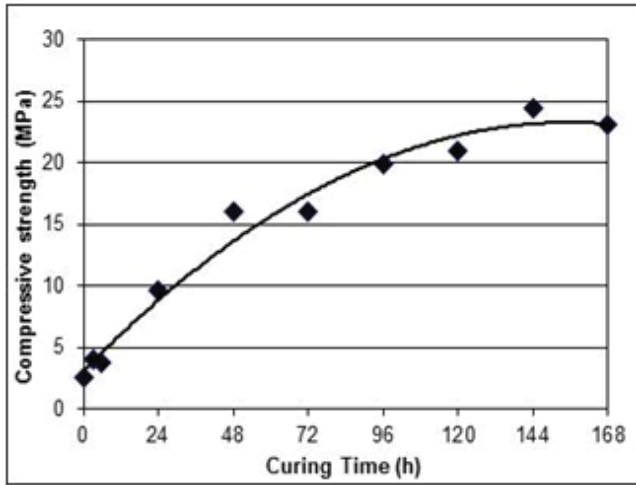
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**Figure 6. Compressive strength of geopolymeric materials at 60ºC as a function of curing time**

The RM/MK Geopolymer as a substitute of clay bricks shows excellent a) compressive strength, b) 24h-cold water absorption and c) reaction to fire that render it a suitable material for application under severe weathering conditions. The main drawback of material is its limited durability in frost which classifies the material in Class F0 according to the Greek standards that renders it appropriate for application under slight frost exposure conditions.

The RM/MK Geopolymer as a substitute of clay roof tiles shows excellent a) 24h-cold water absorption, b) water impermeability,

c) external fire performance and d) reaction to fire that render it able to withstand severe weathering and fire exposure conditions. The two main drawbacks are the very low flexural strength and the very limited durability in frost (only two freezing-thawing cycles) which render the material improper as a substitute of clay roof tiles.

The above results showed that the MK based geopolymeric binder has inappropriate mechanical strength in order to create a RM/MK composite geopolymeric material with notable flexural strength and acceptable durability in frost. Therefore, the development of RM/FeNiSG composite geopolymeric material was studied taking into account that the pure FeNiSG based geopolymers have shown compressive strengths of the order of 120 MPa [5] which is substantially higher to the ones ($\approx$25 MPa) obtained with pure MK based geopolymers [8]. Based on a previous work [5] on FeNiSG based geopolymers, the formulation for the preparation of the RM/FeNiSG geopolymeric specimens was the following: The paste solid to liquid ratio was equal to 4g/ml. The solids were composed from 50% w/w RM. The aqueous activating phase had a sodium hydroxide concentration of 7M and an initial dissolved silica ($SiO_2$) concentration of 4M. The curing was performed at 60ºC and 70% relative humidity in closed molds for a period of only 6 hours. The material had minimal 24h-cold water absorption of 0,57% w/w, flexural strength of 1012N, compressive strength of 45MPa and moderate durability in frost which classifies the material in Class F1 according to the Greek standards while failed to pass the ASTM C 67-03a standard because it withstood 20 freezing-thawing cycles before broken into two pieces as is seen in Figure 7.



[a]     [b]
**Figure 7. Sample (a) before and (b) after 20 freezing-thawing cycles**

The RM/FeNiSG composite geopolymeric material can be applied as a substitute of clay roof tiles in negligible to moderate weathering conditions while has the potential after proper optimization and improvement to withstand under severe weathering conditions.

## Conclusions

The RM/MK Geopolymeric material produced in this work possess excellent compressive strength, cold water absorption and reaction to fire while has limited durability in frost and therefore it can substitute the clay bricks under slight frost exposure conditions. Unfortunately, due to its very low flexural strength

the material renders improper to be applied as a substitute of clay roof tiles.

An improved form of the above material is the RM/FeNiSG geopolymeric material which has substantially better flexural strength and durability in frost that makes this material proper as construction bricks under moderate weathering conditions and as roof tiles under negligible to moderate weathering conditions.

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