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# Composition and technological properties of geopolymers based on metakaolin and red mud

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ABSTRACT

New geopolymer formulations were designed by sodium silicate/NaOH activation of metakaolin, iron oxide and red mud mixtures. The effects of source materials on the microstructure and mechanical properties were studied. Each formulation induces different degree of geopolymerization reaction as reflected by the phase composition where the amorphous phase is predominant. These vestiges are related to silica provided by sodium silicate more reactive in the geopolymerization than the silica of metakaolin. Moreover, the variation in strength between the geopolymers is attributed to the same factors, with higher porosity and nonreacted phases found in the red mud based geopolymer matrix. In function of curing time, the mechanical strength increased from day 1 to 28 for the samples with a low amount of red mud. In these two cases, longer curing time improves the geopolymerization state resulting in higher compressive load. The metakaolin and metakaolin/red mud products exhibited comparable water absorption and density.



## 1. Introduction

In the Bayer process for alumina production, 5 tons of bauxite are washed and treated to produce 2 tons of aluminum metal [1]. The world annual production of 21 million ton of aluminum generates 82 million ton of sludge. This extraction residue, highly alkaline (pH = 10) and known as red mud, is produced in huge amounts, evacuated and disposed in huge landfills [2,3]. Red mud could cause serious environmental problems: (i) contamination of surface and underground water resources with NaOH and metallic oxide-bearing impurities [4]; (ii) direct contact with fauna and flora; (iii) evaporation that could originate highly alkaline rainfalls [5]; (iv) visual impact on extensive areas. Some accidents, the most recent one in Ajka (Hungary, 2010) [6,7], provoked irrecoverable damages to the environment.

Many recent studies and semi-industrial trials were directed to the incorporation of the red mud in construction materials; traditional ceramics [8,9], clinker [10,11], mortar and concrete [10,12], cements [13], light weight aggregates [14], etc. The present work is aimed at assessing red mud as raw material for new geopolymer-like compounds that could be used for construction or restoration purposes [15–17].

For several considerations, the geopolymers appears to be a potential alternative to the classic hydraulic binders. Nevertheless, their chemical composition is very different from that of cements or lime. Cements owe their mechanical properties to the formation of the hydrated calcium silicates (C–S–H) while the exothermic reaction of geopolymerisation generates a structure closer to zeolites or aluminosilicate gels [18]. This alkaline aluminosilicate material, generally amorphous is mainly produced from metakaolin (source of Si and Al) reacting with hydroxides or alkaline silicate solutions [19,20]. The geopolymerization mechanism involves Si and Al dissolution from the starting materials generates to make available polysialate units (e.g., sialate [–Si–O–Al–O], sialate siloxo[–Si–O–Al–O–Si–O] or sialate disiloxo [–Si–O–Al–O–Si–O], depending on the Si/Al ratio) cross-linked [AlO4]– and [SiO4] tetrahedral units, with charge balance ensured by Na+ or K+ ions [21].

Moreover, geopolymers have the advantage to be possibly formulated from a wide range of aluminosilicate minerals, as from industrial wastes (e.g. coal fly ash, metallurgical sludge) [19,22,23]. This diversity in material sources places it as interesting solution for red mud incorporation.

Because of its high iron content, this geopolymeric cement products are red in color and look like quality fired clay bricks. There are evidences that iron is incorporated in the geopolymeric framework in both octahedral (in substitution of $Al^{3+}$) and tetrahedral coordination [24,25]. It seems that the molecular structure be composed by a

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Ferro-sialate geopolymeric sequence [–Fe–O–Si–O–Al–O–] were Fe atoms are found in tetrahedral coordination [26–28]. This red mud that can be recycled in generation of geopolymers and insure a good storage method to this tricky waste, is also an alumina-silica bearing material combining aluminum hydroxides (hydrargillite, boehmite, diaspore and at lower rates as corundum), free silica (crystalline and principally amorphous) and various aluminosilicates [26,29]. Moreover, the highly alkaline nature of red mud presents high expectations about its role as activator [27].

## 2. Experimental details

Geopolymers were designed by using metakaolin 1200S (MK) (AGS Mineraux, France) as source of alumino-silicate and red mud, whose chemical composition is reported in Table 1. In water medium, alkaline activators NaOH (ACS AR Analytical Reagent Grade Pellets) and hydrated sodium silicate (Merck, Germany; 8.5 wt.% $Na_2O$, 28.5 wt.% $SiO_2$, 63 wt.% $H_2O$) were used to dissolve aluminosilicate and avoid residual sodium [30]. The target was the following molar oxide ratios: $SiO_2/Al_2O_3 = 1$, $Na_2O/Al_2O_3 = 1$ [19,31]. The water content for all the samples was kept the same with a molar ratio of $H_2O/Na_2O = 17$. The following compositions were prepared: a geopolymer with metakaolin (named GMK) and others where metakaolin was substituted by 1/4, 1/6, 1/8, 1/10 and 1/12 of red mud (named GR4, GR6, GR8, GR10 and GR12, respectively). In addition, 1/12 of $Fe_2O_3$ (Sigma–Aldrich, as reference) was introduced to compare the activation power of red mud (sample GFE).

The mixing of the blends was carried out by Heidolph ST-1 Laboratory stirrer at two different speeds; 100 rpm for 2 min and 200 rpm for 4 min, to insure their homogeneity and avoid bubbles and agglomeration into the sample. The pastes were immediately poured into 20 × 20 × 20 mm cubic molds and placed in oven at 50 °C for 24 h and after left at room temperature for 1 day. Curing was carried out by keeping the geopolymer cubic specimens in distilled water from 1 to 28 days. While standard tests usually perform curing under controlled relative humidity in environmental chamber [32], we need extreme conditions (sample immersed in water) to be sure that geopolymers are fully stable and dissolution does not affect the final properties [33,34].

The X-ray diffraction was conducted on a Rigaku Geigerflex D/max – Series instrument (Cu Kα radiation in the 4–80° $2\theta$ range, step of 0.02°), and phase identification by X'Pert HighScore Plus. Moreover, to evaluate the phase content, the powders were characterized by X-ray diffraction (D8 ADVANCE, LynkEye detector-Bruker AXS, Germany) using Cu Ka radiation in the 10–80° $2\theta$ range, scan rate of 0.02° ($2\theta$), and 185 s equivalent per step. The quantitative phase analysis was performed using TOPAS 4.2 – BRUKER software following RIR (Reference Intensity Ratio) and Rietveld refinement techniques. The samples were admixed with 20 wt.% corundum, used as internal standard. Each X-ray powder diffraction pattern consists approximately of 7000 data point and 700 reflections; up to 40 independent variables were refined: phase fractions, zero point, 25–30 coefficients of the shifted Chebyschev function to fit the background, unit cell parameters, profile coefficients (one Gaussian, Gw, and one Lorentzian term, Lx). The agreement indices, as defined in TOPAS, for the final least-squares cycles of all refinements are represented by Rp (%), Rwp (%), GOF. For the refined patterns, they were found in the following ranges: 2.5% < Rp < 4.0%, 3.0% < Rwp < 5.0% and 1% < GOF < 2%. The experimental error is within 5% relative.

**Table 1**
Chemical compositions of metakaolin (MK) and red mud (RM).

| Oxides (wt.%) | MK | RM |
|---|---|---|
| $SiO_2$ | 54.4 | 5.54 |
| $TiO_2$ | 1.55 | 0.23 |
| $Al_2O_3$ | 39.4 | 18.8 |
| $Fe_2O_3$ | 1.75 | 51.8 |
| MgO | 0.14 | – |
| CaO | 0.10 | 3.27 |
| MnO | 0.01 | 0.04 |
| $Na_2O$ | – | 6.84 |
| $K_2O$ | 1.03 | 0.08 |
| $SO_3$ | – | 11.2 |
| L.O.I. | 2.66 | 1.90 |

The X-ray Fluorescence (XRF) was conducted using Philips X'UNIQUE apparatus. The WD-XRF spectrometry was performed on glass beads, obtained from a mixture of 66 wt.% lithium tetraborate and 34 wt.% lithium meta-borate, where 10 wt.% of the sample was dissolved at high temperature. The bead was then analyzed for elemental composition, according to the calibrated procedure. The experimental error is within 1% relative.

The microstructural characterization was carried out by scanning electron microscopy (SEM – Hitachi, SU 70) and energy dispersive X-ray spectrometry (EDS – EDAX with detector Bruker AXS, software: Quantax) operated at 3–30 kV. The particle size distribution was determined using a Laser Coulter LS230.

The compressive strength was measured on a Shimazdu apparatus (Model: AG-X/R Refresh). We determined the open porosity, water absorption and bulk density according to ASTM: C373 on 3 fragments after mechanical test. The leaching test was carried out following the EN 12457-2 standard [35,36] with multiple batches used to determine the leachable proportion of sodium. Geopolymer bodies were crushed and dry ground (all passing the sieve of dry ground 200 μm). The leaching test was performed by placing 5 g of powder in 100 ml of deionized water. The suspension was stirred for 24 h at 10 rpm speed. The leachate concentration was measured (4 repetitions) with flame atomic absorption spectroscopy (GBC Avanta, SIGMA).

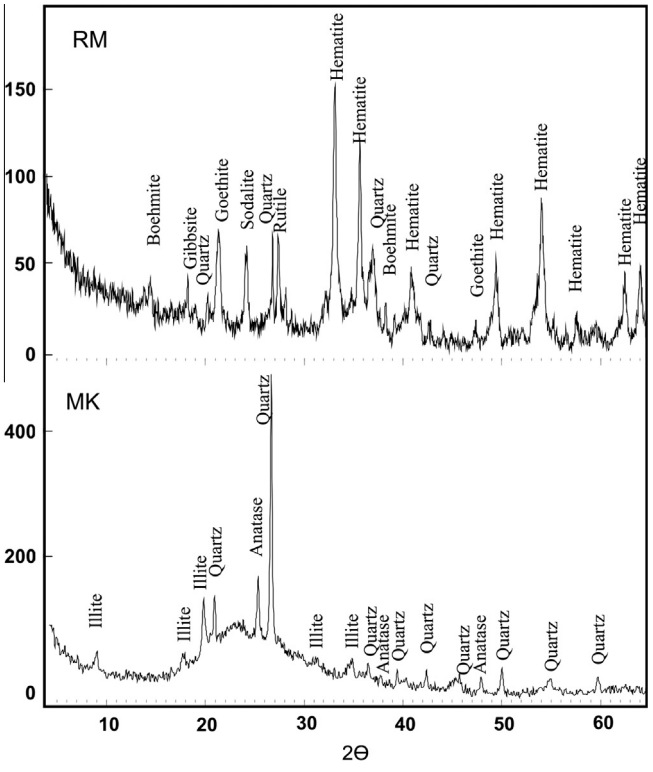


**Fig. 1.** XRD patterns of metakaolin (MK) and red mud (RM).