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Synthesis and properties of new materials produced by alkaline activation of glass cullet and red mud

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ABSTRACT

This study presents data regarding the synthesis of binding materials through the alkaline activation of waste glass (bottle glass cullet) with NaOH solution. As addition was used red mud, a residue resulted in bauxite processing, due to its high alkalinity and aluminum content. This paper presents the influence of processing parameters (composition of solid component, curing time and temperature) on the compressive strength and hydrolytic stability of this type of alkali activated cements. The effect of red mud addition on the hardening processes, reaction products and material's microstructure was studied by X-ray diffraction (XRD), scanning electron microscopy (SEM) and thermal analysis (TG & DTA). The main reaction products are sodium silicate or/and sodium silicate aluminates hydrates with amorphous to crystalline morphologies. The amount of reaction products increases with the increase of the initial curing time at 60°C and consequently it was achieved an increase of the compressive strength values. As a negative side effect the hydrolytic stability of these materials is affected by the increase of the initial curing time at 60°C. Despite the fact that addition of aluminum to sodium silicate hydrates improve their hydrolytic stability, the expected positive influence of red mud addition to the studied binding systems was not observed. This can be due to the low amount of supplementary aluminum brought in the activator solution by the red mud as well as the high amount of iron phases present also in this waste.

1. Introduction

Inorganic polymers also known as geopolymers or alkali activated cements are environmentally friendly materials that can be produced starting from a wide range of industrial wastes (Alex et al., 2013; Baščarević et al., 2013; Bădănoiu and Voicu, 2011; Cyr et al., 2012; Davidovits, 2008; Komljenović et al., 2010; Kumar and Kumar, 2013; Moncea et al., 2013; Provis et al., 2012; Shi et al., 2011). Usually, the two precursors used for alkali activated cements synthesis are: i) a solid component (cementitious materials) and ii) alkaline activators (caustic alkalis or alkaline salts). The processes that take place in these binding systems are alkali mediated dissolution and precipitation reaction in aqueous medium (Shi et al., 2011). The reaction products are amorphous to crystalline alkali aluminate silicates, with a structure in which $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedrons are linked in a 3-D structure charge balanced by the alkali cations (Davidovits, 2008; Shi et al., 2011).

Cyr et al. (2012) reported the preparation of geopolymers by the alkaline activation of cullet soda-glass with sodium or potassium hydroxide solutions and curing at 40–60°C. Due to the high value of Si/Al ratio (around 20), these materials need long curing time (minimum 7 days) at high temperatures (40–60°C) to achieve good mechanical performances (50 MPa). A second important drawback of these materials is their low durability when conserved in water.

Red mud is a waste generated in Bayer process during the treatment of bauxite with caustic soda for alumina extraction (Grafe et al., 2009). This slurry is, in general, strongly alkaline (pH range from 9.7 to 12.8; Grafe et al., 2009) and contains a wide range of minerals classified in two groups: i) mineral phases present in the original bauxite, unchanged by the Bayer process and ii) new phases formed during the bauxite digestion stage (Atasoy, 2005). This slurry can contain Al as alkaline anion $Al(OH)_4^-$/$Al(OH)_3$ (aq.) or in solid phases such as aluminum hydroxides (bohemite, gibbsite, diaspore), sodium aluminate silicates (sodalite, cancrinite and others) and calcium aluminate hydrates (Grafe et al., 2009). Due to its high alkalinity and aluminum content, red mud can be used as addition to waste glass in order to decrease the Si/Al ratio. Therefore one of the objectives of this study was to synthesize binding materials starting from waste glass and red mud mixtures by alkaline activation with NaOH solution. To our best knowledge, no information is presently available in literature regarding the geopolymer synthesis by alkaline activation of waste glass and red mud mixture.

No information was found regarding the influence of red mud on the hardening processes and reaction products formed in binding systems

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based on cullet glass waste. For this reason the second objective of this study was to evaluate the effect of red mud addition on the hardening processes, reaction products, microstructure and main properties (mechanical strength and hydrolytic stability) of glass cullet-based alkali activated cements.

2. Materials and methods

2.1. Materials

Waste glass (cullet) from a glass bottles production plant was used as solid component for alkali activated cements synthesis. Glass cullet was milled in a ball mill for 10 h.

Red mud sludge received from alumina plant was dewatered by filtration and dried. The dried red mud (R) was disaggregated in a ball mill for 5 min.

For the preparation of alkali activated binders the following solid components were used:

- green glass powder (G), with Si to Al ratio of 22.12;
- mixtures of glass powder and red mud; two substitution levels of green glass powder with red mud were used — 10% (GR10) corresponding to Si/Al ratio of 9.65 and 25% (GR25) corresponding to Si/Al ratio of 4.65.

The activator solution was NaOH 5 M aqueous solution.

With the formulations based on the above presented solid components, two types of specimens were prepared:

- pastes with liquid to solid ratio of 0.3;
- mortars with binder to sand ratio of 0.5 and different values of liquid to solid (G or G + R) ratios.

The aggregate was siliceous sand and fulfilled the requirements of European and corresponding Romanian norm (SR EN 196–1, 2006).

For mortar specimens preparation the solid component (glass powder or mixtures of glass powder and red mud) was mixed with sand and alkali activator solution; the resulting material was cast in rectangular molds (15 × 15 × 60 mm) and vibrated for 2 min. The specimens were cured in the mold (covered with cling film) at 60°C the first 24 h, then de-molded and cured at 60°C in humid air (R.H. 85%) up to 3 days. The curing time at 60°C was shorter as compared with the one used by Cyr et al. (2012) i.e. 7–56 days. After the thermal treatment the specimens were stored in air (R.H. 65%) at 20 ± 2°C.

2.2. Methods

Chemical composition of soda lime silicate glass was assessed using the analytical procedures stipulated in Romanian Standards 5771/1-11/89 (1989).

The elemental composition of red mud was assessed by X-ray fluorescence spectrometry (S8 Tiger Bruker).

The mineralogical compositions of red mud and alkali activated binders were assessed by X-ray diffraction (XRD) analysis using a Shimadzu XRD 6000 diffractometer. The XRD patterns were obtained using a monochromatic CuKα radiation (λ = 1.5406 Å), range 2θ from 5 to 60°.

The particle size distribution of the glass powder and red mud were assessed with a Malvern Mastersizer 2000 laser particle size analyzer.

SEM analyses were performed on selected mortar specimens coated with Ag, using a Hitachi S2600N microscope.

Compressive strength was assessed, using a Tonitech machine, on mortar specimens (15 × 15 × 60 mm), prepared and cured as presented in Section 2.1. The compressive strength value is the average of at least three strength values assessed on specimens cured in similar conditions.

The durability of studied compositions was assessed by the immersion of mortar specimens, cured in different conditions, in demineralized water (water to solid ratio of 1.3) (Cyr et al., 2012). The immersion solutions were renewed daily, the first 4 days, and then weekly up to 28 days. The solutions pH and conductivity were assessed with a laboratory multiparameter PCD 6500 (pH-meter & conductometer).

Mass variation of mortar specimen immersed in water was calculated with the Formula (2.1):

$$\Delta m = \frac{m_t - m_i}{m_t} \times 100(\%) \quad (2.1)$$

where: m_t = specimen mass after "t" days of water immersions (g) and m_i = specimen mass before immersion in water (g).

Compressive strength (Cs) variation of mortar specimens after 28 days of immersion in water was calculated with the Formula (2.2):

$$\Delta C_S = \frac{C_{Sw} - C_{Sa}}{C_{Sa}} \times 100(\%) \quad (2.2)$$

where: Cs_w = compressive strength of specimens immersed in water for 28 days (MPa) and Cs_a = compressive strength of specimens cured in air for the same time (MPa).

Mass variation and compressive strength values are the average values of at least three individual values assessed on specimens cured in similar conditions.

The thermal analysis were performed with a Shimadzu DTA-TG-50H instrument. The analyses were conducted in air in the temperature range: 20–400°C with a heating rate of 10°C/min.

3. Results and discussions

3.1. Characterization of waste

The components of waste glass, assessed by chemical and analytical procedures stipulated in Romanian Standards 5771/1-11/89 (1989), are: silica (68.26%), alkalis ($Na_2O_{eq} = Na_2O + 0.658K_2O$) 13.88%, calcium oxide (10.21%), aluminum oxide (2.73%), magnesium oxide (2.09%), Fe_2O_3 (2.41%) and small amount of chromium (III) oxide (0.18%).

The density of R powder determined by pycnometric method was 1.69 g/cm^3. The elemental composition of dried red mud (R) is presented in Table 1.

The main mineralogical compounds, assessed by X-ray diffraction of red mud (Fig. 1), are: hematite (Fe_2O_3 — PDF 73-2234), iron titanium oxide (εFe–Ti–O — PDF 09-0317), sodium aluminum silicate ($Na(AlSiO_4)$ — PDF 81-2081), aluminum silicate hydrate ($Si_2Al_2O_5(OH)_4$ — PDF 74-1023), cancrinite ($Na_8(Si_6Al_6O_{24})H_{0.88}(CO_3)_{1.44}(H_2O)_2$ — PDF 77-1145) and calcium aluminum silicate hydrate ($CaAl_2Si_2O_7(OH)_2H_2O$, PDF 77-1994).

Fig. 2 shows the particle size distribution of the red mud (R) and green glass powder (G). As it can be seen, the red mud has a higher fineness as compared with green glass (Fig. 2a); it has also a multimodal size distribution (Fig. 2b) opposite to the continuous distribution of green glass (Fig. 2c); this multimodal distribution is determined by

Table 1
Elemental composition of red mud (R).

Element	Fe	Na	Al	Ti	Si	Ca	Cr	P	S	K	Other elements
Concentration (%)	37.81	25.49	17.39	5.97	5.59	2.64	0.25	0.18	0.17	0.06	4.28