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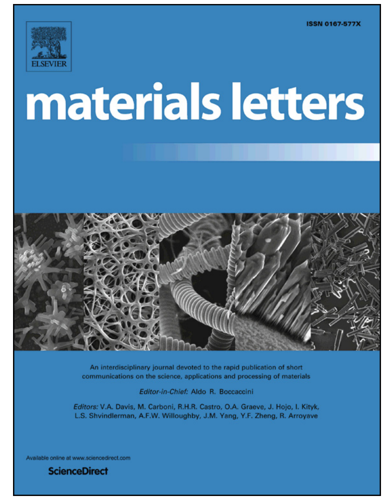

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Novel geopolymers incorporating red mud and waste glass cullet

N. Toniolo[1(*)], A. Rincón[2], Y. S. Avadhut[3], M. Hartmann[3], E. Bernardo[2], A.R. Boccaccini[1(*)]

[1]Institute of Biomaterials, Department of Materials Science and Engineering, University of Erlangen-Nuremberg, Cauerstrasse 6, 91058 Erlangen, Germany

[2]Department of Industrial Engineering, University of Padova, Via Marzolo 9, 35131 Padova, Italy

[3]Erlangen Catalysis Resource Center, University of Erlangen-Nuremberg, Egerlandstraße 3, 91058 Erlangen, Germany

(*) Corresponding author. Email: nicoletta.t.toniolo@fau.de; aldo.boccaccini@ww.uni-erlangen.de

Highlights

- Waste-derived geopolymers synthesized using red mud and waste glass.
- Mechanically competent materials achieved with high incorporation of red mud.
- Formation of a geopolymeric gel confirmed by ^{27}Al MAS NMR and EDX analysis.
- Leaching tests demonstrated complete stabilization of heavy metal ions.

Abstract

Red mud presents significant environmental problems, so that its incorporation in geopolymers could represent an alternative solution to produce valuable products from this residue. Novel geopolymers using red mud as source of alumina and waste glass as silica supplier were developed, using sodium hydroxide as the only ‘non-waste’ material. The formation of a homogeneous polymeric gel, confirmed by solid-state NMR and EDX analysis, promoted the stabilization of possible pollutants. Moreover, the materials exhibit a remarkable compressive strength (up to 45 MPa, for 60 wt% red mud).

Keywords: Geopolymers; red mud; waste glass; MAS-NMR; leaching test.

1. Introduction

Red mud is an inorganic residue generated during the industrial production of alumina by the Bayer process. Red mud is classified as a toxic waste with elevated disposal costs due to the high basicity and leaching potential [1]. An annual world production of 21 million tons of aluminum corresponds to 82 million tons of red mud waste, so that new applications of this industrial residue are urgently needed.

Construction materials such as cements, lightweight aggregates and geopolymers are considered interesting solutions for red mud safe disposal [2]. The term 'geopolymer' identifies an alumino-silicate material with distinctive environmental advantages compared to ordinary Portland cement. The synthesis involves the dissolution of alumino-silicate raw materials in an alkaline medium, followed by condensation and polymerization to achieve a highly stable three-dimensional network structure, where AlO_4 and SiO_4 are linked together sharing oxygen ions. The network has the capability to immobilize possible pollutants when wastes (usually industrial residues) are used as alumino-silicate source [3]. Red mud has been already proposed as raw material in geopolymer production, but always with a supplementary Al source, such as metakaolin [4] or fly ash [5], mainly to enhance the mechanical strength of the products.

The present study aimed to use red mud as the only Al source and to eliminate the use of relatively expensive Na-silicate activating solution. This was supported by the use, as silica source, of soda lime glass (SLG) from urban waste collection. The specific waste glass fraction employed, where plastic and ceramic impurities are concentrated, is currently mostly landfilled [6].

2. Materials and methodology

Red mud (RM) with chemical composition: SiO_2=5.21%, Al_2O_3=15.21%, Fe_2O_3=52.94%, CaO=2.95%, Na_2O=2.40%, K_2O=0.63wt.% (Gardanne, France) and soda lime glass (SLG) (SASIL S.p.a, Biella, Italy) with chemical composition: SiO_2=70.50%, Al_2O_3=3.20%, Fe_2O_3=0.42%, CaO=10.00%, Na_2O=12.00%, K_2O=1.00 wt.%. were dissolved in NaOH solution of desired concentration (4M and 6M) [7]. The SiO_2/Al_2O_3 theoretical molar ratio of the final geopolymers was fixed at 5, 6 and 7, which represents initial mixtures of SLG/RM in wt.% of 40/60, 45/55, 50/50, respectively. The sample designation was established as xSyM, where "x" is associated with the SiO_2/Al_2O_3 molar ratio, "y" refers to the molarity of the activating solution, varying from 4M to 6M. The liquid to solid ratio was fixed at 0.50 for all mixtures. Geopolymer samples were prepared by mechanical mixing waste glass and red mud in a sodium hydroxide solution for 4 hours before being casted in cylindrical polyethylene moulds, cured at 75°C for 10 days.

The compressive strength was measured by using an Instron 1121 UTS (Danvers, MA) testing machine, operating with a cross-head speed of 0.5 mm/min. 10 cylindrical samples, with diameter of 14mm and height of 20mm, were tested for each batch. Microstructural evaluation was performed by means of scanning electron microscopy (SEM) (LEO 435 VP, Cambridge, UK and Ultra Plus, Zeiss, Jena, Germany), equipped with EDX. Solid-state Magic Angle Spinning (MAS) NMR spectra were recorded on an Agilent DD2 500WB spectrometer equipped with a commercial 3.2 mm triple resonance MAS probe at ^{27}Al resonance frequency of 130.24 MHz.

The heavy metal release was evaluated according to the European Standard for waste toxicity evaluation (EN 12457-2) and analysed using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) (SPECTRO Analytical instruments GmbH, Kleve, Germany).

3. Results and discussion

3.1 Microstructure

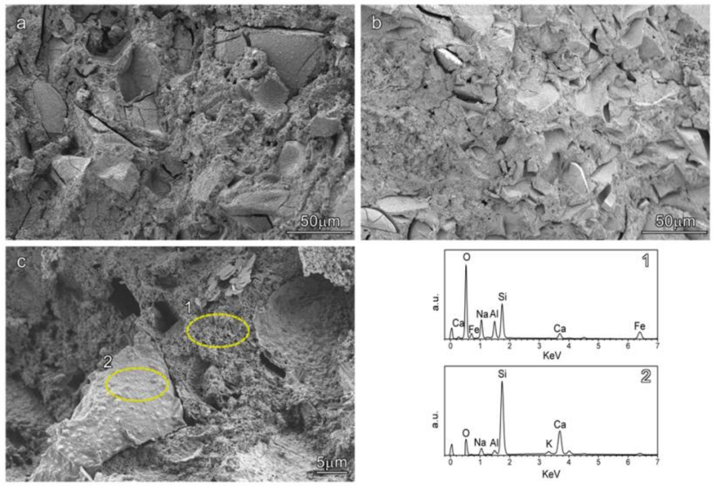

Figure 1. SEM images of 5S4M (a) and 5S6M (b) samples, a higher magnification SEM image of sample 5S6M (c) was used for EDX analysis.

Fig.1 presents high magnification images of samples with SiO_2/Al_2O_3 molar ratio equal to 5, activated with solutions at 4M and 6M. Low alkali activation (Fig.1a) reveals a heterogeneous gel with microcracks and unreacted glass particles embedded in the structure. Meanwhile high molarity activation (Fig. 1b) promoted structural cohesion, as a consequence of an enhanced reaction degree. This observation is further confirmed on the basis of high magnification details of the microstructure (Fig.1c) and EDX analysis on selected points. In fact, spectrum “1”, collected in the amorphous matrix, corresponds to a truly geopolymeric gel, considering the Si/Al and Al/Na molar ratios close to 2 and 1, respectively [8]. The spectrum “2” corresponds to an unreacted glass particle, considering that the EDX signals match with the characteristic elements in the soda-lime glass composition.

3.2 MAS-NMR analysis

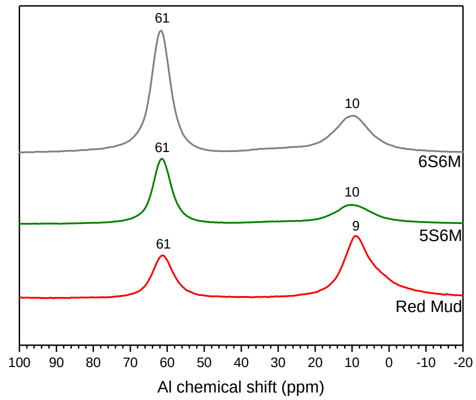

Figure 2. ^{27}Al MAS NMR spectra of raw materials and geopolymers activated with 6M NaOH solution.

The formation of a geopolymeric gel was confirmed also by ^{27}Al MAS NMR analysis (Fig. 2). Red mud shows two small signals at 61 and 9 ppm, attributed to tetrahedral and octahedral coordinated Al [9], respectively. After geopolymerization Al(VI) was mostly converted into Al(IV). The tetrahedral coordination is known to be essential for developing a 'zeolite-like' geopolymeric structure [88].

3.3 Compressive strength test

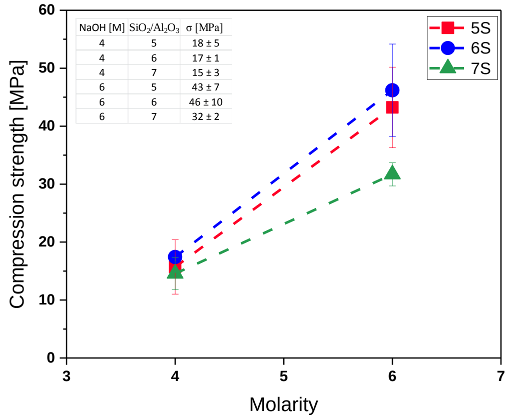

Figure 3. Compressive strength average results as function of NaOH solution molarity and SiO_2/Al_2O_3 molar ratio.

Geopolymers activated with 4M solution showed a compressive strength close to 15 MPa, while using 6M solution the compressive strength exhibited a two-fold increase (up to about 30 MPa), as shown in Fig. 1. Minimum variations are observed changing the SiO_2/Al_2O_3 molar ratio when 4M NaOH solution is used. Whereas using 6M NaOH solution no substantial differences were observed between 5S6M and 6S6M, both featuring a compressive strength close to 45 MPa. A high SiO_2/Al_2O_3 ratio corresponded to an enhanced content of waste glass in the mixture: on one hand, the evolution of compressive strength suggested an upper limit to glass cullet incorporation; on the other hand, the relatively high compressive strength achieved (30-45MPa) is interesting for the significant amount of red mud incorporated [2]. ±

3.4 Leaching test

The potential applications of waste-derived geopolymeric materials require the complete stabilization of the pollutants within the geopolymeric network. Tab. 1 shows that the introduction of red mud in geopolymers generally reduced the leaching of some heavy metals, such as Cr and Mo. The leaching from the developed geopolymers actually exceeded the thresholds for inert materials, according to European Norm EN 12457; however, the leaching was below the limit for non-hazardous materials. The obtained values are analogous to those found in literature even considering the high amount of red mud incorporated [10]. Lower red mud incorporation will probably lead to better leaching results. Moreover a possible alternative could be to use a red mud with lower amount of heavy metals, derived from a preliminary recovery process. In any case the proposed approach has high potential for stabilization of heavy metals; additional tests (for the determination of other elements) as well as specific tests for the assessment of any cytotoxic effect of the developed material [11] will be the subject of further investigations.

Table 1. Leaching results from raw materials and geopolymer samples.

	564M	**5S6M**	**6S4M**	**6S6M**	**7S4M**	**7S6M**	**Red Mud**	**Inert material**	**Non-hazardous material**
Ba	<0.020	<0.020	<0.020	<0.020	<0.020	<0.020	<0.020	2	10
Cd	0.013	0.012	0.01	0.016	0.017	0.016	0.0080	0.004	0.1
Cr	0.0807	0.1026	0.0279	0.0625	0.059	0.037	0.5990	0.05	1
Cu	0.229	0.246	0.201	0.251	0.205	0.298	0.0270	0.2	5
Mo	0.299	0.151	0.188	0.565	0.117	0.113	1.0210	0.05	1
Pb	0.328	0.304	0.093	0.162	0.178	0.187	0.1300	0.05	1
Zn	<0.202	<0.203	<0.203	<0.203	<0.203	<0.203	<0.203	0.4	5

4. Conclusions

We may conclude that:

- Red mud and soda-lime glass cullet are suitable raw materials for geopolymer production.
- Compressive strength values comparable to Portland cement, close to 45 MPa, were achieved for samples produced with 6M solution.
- MAS-NMR and EDX techniques confirmed the formation of geopolimeric gel with Si/Al and Al/Na molar ratios close to 2 and 1, respectively.
- The leaching of heavy metals agreed with values found in literature, despite the relatively high amount of red mud in the formulation.

Acknowledgements

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