



Proceedings of the
Fourth International

Slag Valorisation Symposium Zero Waste

15-17 April 2015
Leuven, Belgium

Editors Annelies Malfliet and Yiannis Pontikes

KU LEUVEN

CO-UTILIZATION OF SLAGS WITH CONSTRUCTION WASTES OR RED MUD FOR GEOPOLYMER PRODUCTION

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Introduction

Geopolymers are cementitious materials formed by alkali activation of Al-Si sources at relatively low temperatures. Their properties such as high early strength depend strongly on the properties of the raw materials used.¹ The potential of various industrial wastes such as slag, fly ash and red mud, for the production of geopolymers has been investigated during the last 20 years. The synthesis of geopolymers using construction and demolition wastes (CDW), still remains a challenge and a limited number of studies have been carried out so far.^{2,3}

Methodology

The materials used in the present study are: i) electric arc furnace slag from the “LARCO S.A” ferronickel plant, ii) CDW (tiles, bricks and concrete) and iii) red mud from “Aluminium of Greece”. All materials were dried and pulverized using a FRITSCH-BICO pulveriser (slag: < 120 µm and d_{50} 12 µm, tiles: < 140 µm and d_{50} 14 µm, bricks: < 140 µm and d_{50} 6.6 µm, concrete: < 190 µm and d_{50} 10 µm, red mud: < 76 µm and d_{50} 4 µm). The chemical composition of the raw materials, in the form of oxides, is presented in Table 1.

The activating solution consists of NaOH or KOH anhydrous pellets (ACS–ISO for analysis), distilled water and sodium silicate solution (Na_2O = 7.5-8.5 wt.%, SiO_2 = 25.5-28.5 wt.%, Merck). Raw materials were mixed with the activating solution (8-10 M NaOH or KOH) as described elsewhere.⁴ The specimens produced were heated at 80 °C in a laboratory oven (ON-02G) for 7 days and then subjected to compressive strength testing using an MTS 1600 load frame. X-ray diffraction (XRD) analysis of the final products was performed by a Bruker D8 Advance diffractometer and FTIR analysis on KBr pellets using a Perkin–Elmer Spectrum 1000 spectrometer.

Table 1: Chemical composition (wt.%) of raw materials

Material	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	CaO	Na ₂ O	K ₂ O	MgO	TiO ₂	LOI	SUM
Slag (S)	43.83	36.74	9.32	3.73	-	-	2.76	-	-	96.4*
Concrete (C)	0.75	5.81	1.49	65.42	0.57	1.26	4.21	0.03	21.59	101.1
Bricks (B)	6.00	57.79	14.95	8.79	1.03	2.80	4.75	0.85	1.89	98.9
Tiles (T)	5.39	70.54	9.80	8.78	-	1.37	4.46	0.77	-	101.1
Red mud (R)	41.65	9.28	15.83	10.53	2.26	0.21	-	4.73	16.77	101.3

LOI: Loss on ignition after heating the material at 1050 °C for 4 h, *Cr₂O₃: 2.82 wt.%

Results and discussion

Figure 1 shows the compressive strength of the produced geopolymers as a function of the molarity of the activating solution and the percentage of the raw materials used. For reasons of clarity control-geopolymers are presented only for 10 M NaOH. It is shown that slag-CDW geopolymers prepared with 10 M NaOH acquired higher compressive strength, reaching almost 80 MPa, compared to those synthesized with 8 M NaOH, for which the compressive strength remains almost constant and does not exceed 55 MPa; this value is ~30 % lower than the one acquired by the control slag geopolymer. Higher NaOH concentration enhances the dissolution of raw materials, initiating thus geopolymeric reactions and increasing final strength.

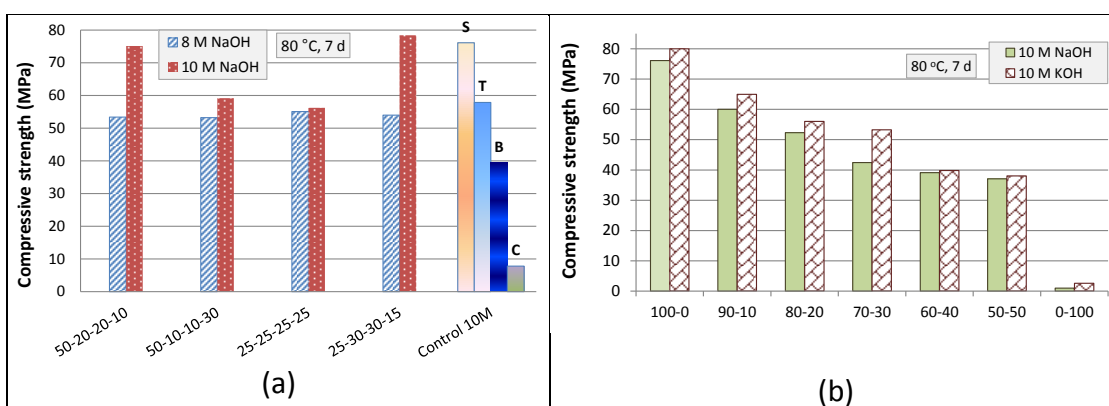


Figure 1: Compressive strength of geopolymers prepared by mixing slag with (a) CDW (eg. 50-20-20-10: % w/w 50 S-20 T-20 B-10 C) and (b) red mud (eg. 90-10: % w/w 90 S-10 R)

The percentage of each CDW component in the initial mixture does not seem to affect the compressive strength of the final specimens produced at 8 M NaOH. In the case of 10 M NaOH when the percentage of concrete in the initial paste is up to 15 % w/w the compressive strength does not seem to be affected compared to the control slag geopolymers. This may be due to the fact that the molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ remains high (8.86 in the mixture 25-30-30-15, 7.33 in the control-geopolymer). When the concrete percentage increases to 25 and 30 % w/w the compressive strength drops to less than 60 MPa. This decrease in the compressive strength may be mainly attributed to the increased CaO concentration in this mixture; the molar ratio of $\text{SiO}_2/(\text{Al}_2\text{O}_3+\text{CaO})$ in the mixtures 50-10-10-30 and 25-30-30-15 is 1.18 and 2.21 respectively, lower than that in the slag-control geopolymer (4.03) (Table 2).

Table 2: Molar ratios of oxides

	S	T	B	C	R	Geopolymer 50-10-10-30	Geopolymer 25-30-30-15	Geopolymer S-R: 50-50
$\text{SiO}_2/\text{Al}_2\text{O}_3$	7.33	12.67	6.84	9.86	1.33	8.26	8.86	3.53
$\text{H}_2\text{O}/(\text{Na}_2\text{O}+\text{K}_2\text{O})$	8.30	9.03	8.32	6.62	8.11	6.96	6.10	6.66
$\text{SiO}_2/(\text{Al}_2\text{O}_3+\text{CaO})$	4.03	4.81	3.30	0.12	0.60	1.18	2.21	1.70
<i>Strength, MPa</i>	<i>76.1</i>	<i>57.8</i>	<i>39.4</i>	<i>7.8</i>	<i>2.5</i>	<i>59.2</i>	<i>78.4</i>	<i>38</i>

S: slag, T: tiles, B: brick, C: concrete, R: red mud, eg. 50-10-10-30: % w/w 50 S-10 T-10 B-30 C

The compressive strength of slag-red mud geopolymers for various mixing ratios, using as alkaline activator NaOH or KOH, is given in Figure 1b. It is seen that the compressive strength decreases gradually with increasing red mud % and reaches around 37 MPa when the slag:red mud ratio is 1:1. The decrease in the compressive strength may be explained by the decreased $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios in the initial mixture when increased red mud percentage are used (3.53 for slag:red mud 1:1). Also, the lower $\text{H}_2\text{O}/(\text{Na}_2\text{O}+\text{K}_2\text{O})$ ratios may indicate that less water is available for geopolymeric reactions. The use of KOH has a slight beneficial effect on the compressive strength of all geopolymers.

Figure 2a shows the XRD patterns of geopolymers synthesized from slag, CDW and red mud. Pirssonite ($\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$), which is a brittle and soluble phase is the only new phase detected in geopolymers T, C, B and G1, as a result of atmospheric carbonation. Unreacted or partially reacted phases, such as quartz, calcite, anorthite, hematite and albite have also been detected in geopolymers.

Figure 2b shows the FTIR spectra of selected geopolymers produced from slag and CDW. FTIR analysis confirms the presence of the major fingerprints of an aluminosilicate geopolymeric matrix (around 1050 cm^{-1}). These bands are attributed to Si–O stretching vibrations of SiO_4 and Si–O–Si or Al–O–Si asymmetric stretching

vibrations. The broader peaks correspond to higher compressive strength for geopolymers. A small peak at 1050 cm^{-1} is detected in concrete geopolymers that acquire the lowest strength as shown in Figure 2b. The other peaks (2500, 1800, 1650, 1450, $450\text{--}800\text{ cm}^{-1}$) are assigned to bound water molecules or CO_3 vibrations.⁴

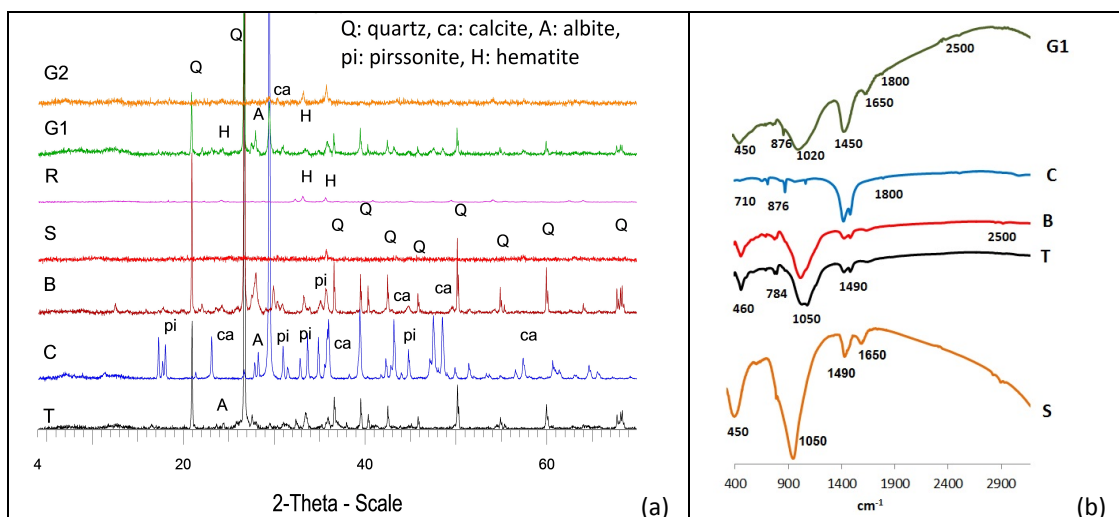


Figure 2: a) XRD patterns of geopolymers synthesized from slag, CDW and red mud and (b) FTIR spectra of selected geopolymers (T: tiles, C: concrete, B: bricks, S: slag, R: red mud, G1: 25-30-30-15 % w/w S-T-B-C, G2: 50-50 % w/w S-R)

Conclusion

Slag can be successfully co-utilized with various by-products/wastes such as CDW and red mud for the production of geopolymers with compressive strength between 37 and 80 MPa using 10 M NaOH or KOH as alkali activator. The presence of the major fingerprints of the aluminosilicate geopolymeric matrix was revealed by XRD and FTIR analysis.

Acknowledgements

The present study has been co-funded by the European Commission (European Regional Development Fund) and by national funds through the Operational Programme “Competitiveness and Entrepreneurship” (OPCE II 2007–2013), National Strategic Reference Framework – Research funded project DURECOBEL 11SYN_8_584 in the framework of the Action COOPERATION 2011.

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