

KU LEUVEN

Proceedings of the
THIRD INTERNATIONAL

SLAG VALORISATION SYMPOSIUM

THE TRANSITION TO SUSTAINABLE MATERIALS MANAGEMENT

19-20 March 2013
Leuven, Belgium

Editors Annelies Malfliet, Peter Tom Jones, Koen Binnemans, Özlem Cizer, Jan Fransaer, Pengcheng Yan, Yiannis Pontikes, Muxing Guo, Bart Blanpain



ALKALI ACTIVATION OF γ -DICALCIUM SILICATE AND MERWINITE

Lubica KRISKOVA¹, Yiannis PONTIKES¹, Özlem CIZER², Koen VAN BALEN², Peter Tom JONES¹, Bart BLANPAIN¹

¹ Department of Metallurgy and Materials Engineering, KU Leuven, 3001 Heverlee, Belgium

² Department of Civil Engineering, KU Leuven, 3001 Heverlee, Belgium

*lubica.kahalova@mtm.kuleuven.be, yiannis.pontikes@mtm.kuleuven.be,
ozlem.cizer@bwk.kuleuven.be, koenraad.vanbalen@bwk.kuleuven.be,
peter.jones@mtm.kuleuven.be, bart.blanpain@mtm.kuleuven.be*

Abstract

The aim of this work is to study the hydraulic properties of γ - dicalcium silicate (C_2S) and merwinite after alkali activation. These mineral phases have mildly hydraulic properties, which creates an obstacle in the valorisation of stainless steel slag as a hydraulic binder. To stimulate their hydraulic reactivity synthetic γ - C_2S and merwinite, prepared by sintering at 1450°C and 1500°C respectively, were subjected to alkali activation using NaOH solution at 8 wt% Na_2O . This resulted in a significant improvement of their hydraulic reactivity with the formation of C-S-H, $Ca(OH)_2$ and $Mg(OH)_2$ as the main hydration products which developed compressive strength during hydration.

Introduction

Approximately 10 Mt of stainless steel slag is generated worldwide annually. Stainless steel slags are typically used as aggregates and fertilisers¹. However, a higher value application such as a hydraulic binder has been proposed to be a promising route². Merwinite and γ - C_2S , being the main mineral phases of stainless steel slags, are considered to be only mildly hydraulic^{3,4}. Despite their slow hydration kinetics in water, the reactivity of these phases could be enhanced through the action of strong alkalis that stimulate the dissolution of crystalline phases and result in the formation of binding phases⁵. The aim of this work is thus to apply alkali activation by means of a NaOH solution to these mineral phases and to study the effect on their hydraulic activity.

Materials and Methods

Merwinite and γ - C_2S were produced using chemical grade oxides and carbonates that were mixed for 12 h in an ethanol suspension using 10 mm zirconia milling balls, and sintered at designed temperatures (1450°C for γ - C_2S and 1500°C for merwinite) at a rate of 5°C/min for 20 h. Subsequently, the sintered materials were cooled down to room temperature at a rate of 1°C/min and milled in a ball mill (Retsch PM4) for 1 h at 200 rpm using 500 g milling balls. The particle size distribution was determined by laser scattering

(MasterSizer Micro Plus, Malvern) and phase composition was determined by X-Ray diffraction analysis (XRD, D500 Siemens). Patterns were collected in the 2θ range of $10 - 70^\circ$ with step size of 0.02° , step time of 4 s, and $\text{CuK}\alpha$ radiation of 40 kV voltage and current of 40 mA.

Hydraulic properties were studied by means of isothermal calorimetry (TAM Air Device, TA Instruments). Pastes were prepared by mixing of powder with water or alkali solution keeping the liquid to binder mass ratio equal to 1. To monitor the hydration reactions, paste samples were stored in plastic containers for 3, 7 and 28 days. After the designated time, pastes were crushed into powder and dried in a vacuum freeze dryer (Alpha 1-2 LD, Martin Christ) at 0.035 mbar for 2.5 h.

Compressive strength was measured on mortars after 3, 7 and 28 days of hydration. The mortar specimens were prepared according to EN 196-1 using CEN standard sand, keeping the sand to binder ratio 3:1. To maintain the flow of mortars in accordance with EN 1015-3, the l/b mass ratio was adjusted to 0.66 for $\gamma\text{-C}_2\text{S}$ and 0.58 for merwinite, respectively. All samples were stored in an air-conditioned room at 20°C and relative humidity higher than 95% and tested for compressive strength using a Schenck-RM100 compression testing machine.

Results and discussion

Heat of hydration

Isothermal calorimetry curves of merwinite and $\gamma\text{-C}_2\text{S}$ mixed with water and NaOH solution are shown in Figure 1.

In case of hydration of $\gamma\text{-C}_2\text{S}$ in water, the cumulative heat release is negligible and equals only about 6 J/g, whereas the heat release of the hydrated merwinite sample is significantly higher, about 36 J/g. Higher heat release of merwinite compared with $\gamma\text{-C}_2\text{S}$ derives probably from the difference in their particle size distribution (d_{50} of $\gamma\text{-C}_2\text{S}$ is 7 μm and that of merwinite is 1.75 μm). Alkali activation (AA) of both phases resulted in a

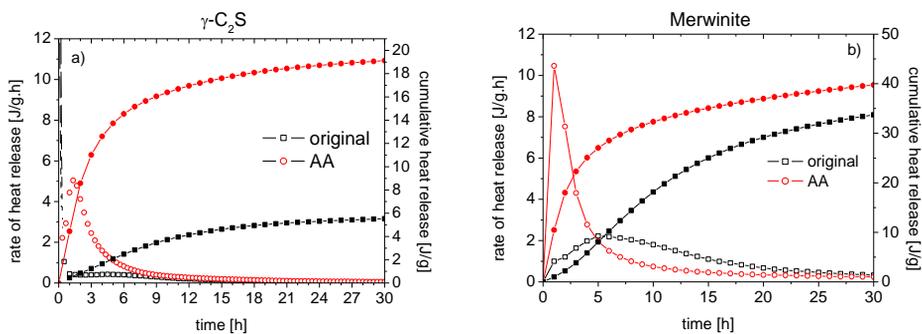


Figure 1: Calorimetry curves of the original and the alkali activated (AA) samples a) $\gamma\text{-C}_2\text{S}$, b) merwinite

significant increase in the heat release which is a strong indication on the enhancement of the hydration reactions. In addition, peak maxima appear much sooner, which indicates an increase in the hydration rate.

Quantitative X-ray diffraction (QXRD) analysis

The synthesised γ -C₂S, contained of 88±4 wt% γ -C₂S and 12±4 wt% β -C₂S. Its alkali activation resulted in a significant increase in the amorphous phase, which reached the value of 21 wt% after 28 days of hydration (Table 1). The amorphous phase could be associated to the formation of calcium silicate hydrate (C-S-H) gel, which is known to be the hydration product of both β and γ -C₂S^{6,7}. This is supported by the formation of portlandite (CH) which precipitates during hydration reaction due to the lower Ca/Si ratio of the C-S-H gel compared to the original C₂S phase. Gaylussite (Na₂CO₃.CaCO₃.5H₂O) and Na₂CO₃ are the other reaction products formed. The amount of gaylussite remained essentially stable or decreased slightly during hydration. The formation of gaylussite was also observed in AA blast furnace slag was attributed to the carbonation of the remaining alkali in the pore solution⁸.

Synthesised merwinite consisted of 93 wt% of merwinite (C₃MS₂), 5 wt% of akermanite (C₂MS₂) and 3 wt% of amorphous phase. During hydration of AA sample, the amount of amorphous phase increased while that of the merwinite and akermanite decreased. Besides, crystalline tobermorite was formed and reached the value of 8 wt% after 28 days of hydration. Formation of amorphous phase related to the hydration of merwinite at ambient temperature has been earlier reported⁹, and was attributed to the formation of C-S-H gel. However, no crystalline tobermorite has been reported yet. This finding could be crucial in furthering our understanding of the hydration mechanism of the merwinite phase.

Table 1: QXRD analysis of original and hydrated merwinite and γ -C₂S samples

(wt%)	Merwinite				γ -C ₂ S			
	Original	3d	7d	28d	Original	3d	7d	28d
Merwinite	93	87	72	59				
Akermanite	5	1	<1	<1				
Brucite		<1	1	1				
γ -C ₂ S					88±4	76	71	67
β -C ₂ S					12±4			
Magnesite		<1	<1	<1				
Portlandite		2	3	5		6	6	5
Calcite		2	4	5				
Na ₂ CO ₃						7	8	6
Tobermorite		4	7	8				
Gaylussite						2	2	1
others/amorphous	2	3	13	20		9	13	21

Compressive strength

Alkali activated γ -C₂S and merwinite mortar specimens yielded a mechanical strength development of 9.2 MPa (\pm 1.4) and 3.3 MPa (\pm 0.5) respectively. This clearly shows that both materials are solely capable of developing mechanical strength when alkali activated. Microstructural investigations indicated the generation of a compact microstructure composed of C-S-H phases playing an important role in the mechanical resistance.

Conclusions

Alkali activation increased the hydraulic activity of both materials while a C-S-H gel and other hydration phases were formed. This resulted in a mechanical strength development.

References

1. F. Engstrom, Y. Pontikes, D. Geysen, P. T. Jones, B. Björkman and B. Blanpain, "Review: Hot stage engineering to improve slag valorisation options", *2nd International Slag Valorisation Symposium*, Leuven, Belgium, 231-251 (2011).
2. Y. Pontikes, L. Kriskova, Ö. Cizer, P. T. Jones and B. Blanpain, "On a new hydraulic binder from stainless steel converter slog", *Advances in Cement Research*, **25** (1) 21-31 (2013).
3. S. N. Ghosh, P. B. Rao, A. K. Paul and K. Raina, "Review, The chemistry of dicalcium silicate mineral", *Journal of Materials Science*, **14** 1554-1566 (1979).
4. Q. Wang, P. Yan and J. Feng, "A discussion on improving hydration activity of steel slag by altering its mineral compositions", *Journal of Hazardous Materials*, **186** (2-3) 1070-1075 (2011).
5. C. Shi, P. K. Krivenko and D. Roy, "Alkali-Activated Cements and Concretes", Taylor & Francis, NY, USA, (2006).
6. M. Salman, Ö. Cizer, Y. Pontikes, R. Snellings, D. Geysen, B. Blanpain, L. Vandewalle and K. V. Balen, "Thermo-Alkali Activation of Continuous Casting Stainless Steel Slag", *proceedings of the European Ceramic Society - ECerS XII*, Stockholm, Sweden, (2011).
7. "Lea's Chemistry of Cement and Concrete", Hewlett, P. C. (Ed), (2004).
8. S. A. Bernal, J. L. Provis, D. G. Brice, A. Kilcullen, P. Duxson and J. S. J. van Deventer, "Accelerated carbonation testing of alkali-activated binders significantly underestimates service life: The role of pore solution chemistry", *Cement and Concrete Research*, **42** (10) 1317-1326 (2012).
9. L. Muhmood, S. Vitta and D. Venkateswaran, "Cementitious and pozzolanic behavior of electric arc furnace steel slags", *Cement and Concrete Research*, **39** (2) 102-109 (2009).
10. E. N. Kani, A. Allahverdi and J. L. Provis, "Efflorescence control in geopolymer binders based on natural pozzolan", *Cement and Concrete Composites*, **34** (1) 25-33 (2012).