

# OPTIMISATION OF HYDRAULIC PROPERTIES OF A C<sub>4</sub>AF, C<sub>3</sub>A-RICH METALLURGICAL RESIDUE

**Ahmet DOK, Lubica KRISKOVA, Remus Ion IACOBESCU, Yiannis PONTIKES**

KU Leuven, Department of Materials Engineering, 3001 Leuven, Belgium

*ahmet.dok@kuleuven.be, lubica.kriskova@kuleuven.be,  
iacobescu.remus@hotmail.com, yiannis.pontikes@kuleuven.be*

## Introduction

Minimising waste production, consumption of natural resources, and CO<sub>2</sub> emissions are frequent topics addressed globally.<sup>1</sup> Production of Ordinary Portland Cements (OPC) is strongly connected to the last two mentioned issues, whilst production of metals in pyrometallurgical processes is connected to a large amount of slag production, which is often landfilled, and therefore contributes to the waste accumulation. It is indeed the reduction in the consumption of the natural resources and the minimisation of the waste production that are the main driving forces behind the development of alternative binders from metallurgical residues.

Several industrial residues, such as blast furnace slag and fly ashes, are already used in the production of blended cements.<sup>2,3</sup> Other residues have been reported as being successfully converted into binders with similar or better properties than OPC.<sup>4-8</sup> The aim of this work was to further extend the family of alternative binders by adapting the chemical and mineralogical composition of a Ca-Si-rich metallurgical residue (MR) from sponge iron production, and creating a hydraulic binder similar to OPC. For this purpose, the MR was mixed with 30 wt% of CaCO<sub>3</sub> and heat treated in a sinter pan. The hydraulic activity of the resulting material was controlled by addition of gypsum, plasticiser and accelerator, aiming to improve both the workability as well as the mechanical strength of pastes.

## Materials and methods

The chemical composition of the as-received MR was assessed by means of X-ray fluorescence spectrometry (XRF, Philips PW 2400). Carbon was measured separately, by thermogravimetric analysis (TGA, STA 409 PC Luxx®, Netzsch), and calculated from the weight loss in the temperature region of 550 – 750°C. To convert the MR into a hydraulic binder rich in C<sub>3</sub>S, the Bogue equations were used as estimation tool. It was found that adding CaO (in form of CaCO<sub>3</sub>) in 30 wt% will be sufficient to produce an OPC replica. Prior sintering of the two components, MR and CaCO<sub>3</sub> were blended together and pelletised in a pelletising dish in the presence of 17 wt% water.

Afterwards, the pellets were dried at 70°C until constant weight and sieved to selected size range (2 – 6.3 mm). Then, pellets of about 40 kg were placed in the sinter pan and covered with about 1 cm layer of coke dust, to be ignited by a gas burner. The sintering reaction was controlled by air suction pressure ( $\Delta p$ ), which was varied between 0.015 - 0.035 bar. This variation was done to assure a fast cooling of the sintered layers of material and to minimise the decomposition of  $C_3S$  into  $C_2S$  and lime. The chemical composition of the resulting (treated) MR was assessed by using the equipment listed above. The mineralogical composition was analysed by powder quantitative X-Ray diffraction analysis (PXRD, Bruker 2D PHASER). XRD patterns were collected in the  $2\theta$  range of 10 – 70° with step size of 0.02°, step time of 0.6 s, and  $Cu_{K\alpha}$  radiation of 30 kV and 10 mA. 10 wt% of ZnO was added as internal standard. The treated MR was milled to a Blaine fineness  $\pm 4000 \text{ cm}^2/\text{g}$ , using an attritor mill (Wiener 1S). Different paste samples were produced, varying the amount of gypsum (5, 10 and 15 wt%), plasticiser - Viscocrete® (0, 0.3 and 0.5 wt%) and accelerator - triisopropanolamine (TIPA, 0, 0.5 and 1.0 wt%). Compressive strength was measured on paste samples at 7 and 28 days of hydration, by means of 250 kN load cell (Instron 5985) using the loading rate of 2 mm/min.

## Results and discussion

The as-received MR consisted mainly of Ca, Si, Fe, Al and C (Table 1). The last was used as fuel during the sintering process. The treated MR contained slightly higher amounts of CaO from the addition of  $CaCO_3$ . No C was detected in the treated MR, indicating its complete consumption. Regarding the mineralogical composition, the treated MR successfully converged into all four cementitious phases present in OPC (*i.e.*  $C_3S$ ,  $C_2S$ ,  $C_3A$ ,  $C_4AF$ ). The high  $C_3A$  and  $C_4AF$  (Table 2) contents have led to optimised gypsum addition, to avoid flash set, as well as the use of other admixtures (*i.e.* Viscocrete® and TIPA).

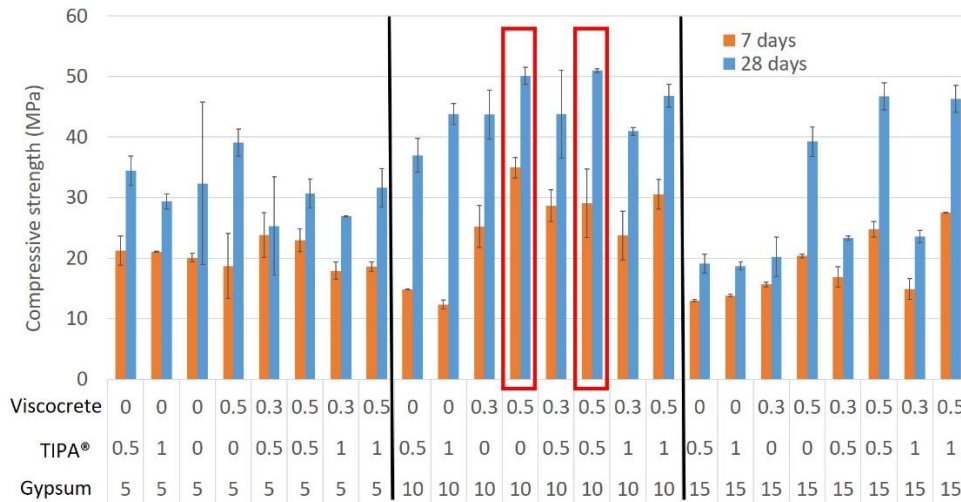
**Table 1:** Chemical composition as determined with XRF (Fe assumed to be all  $Fe^{3+}$ ) and normalised to 100%, in wt%

	CaO	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	TiO <sub>2</sub>	MgO	C
As-received MR	55	14	7	6	2	1	1	14
Treated MR	64	16	9	7	2	1	1	n/a

**Table 2:** Mineralogical composition of the treated MR, in wt%

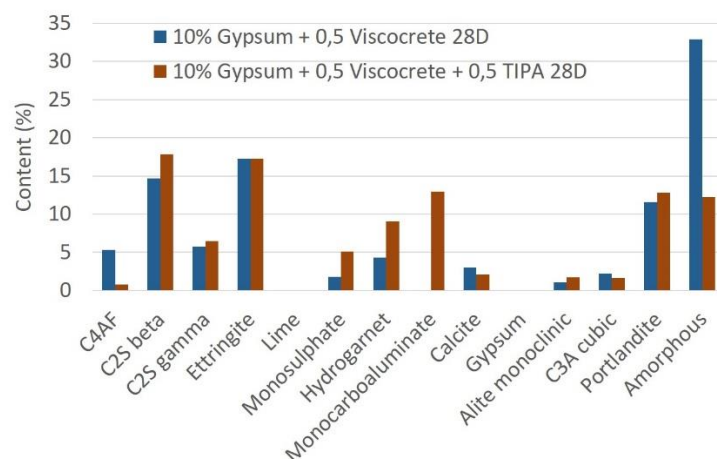
	$\beta - C_2S$	$C_3S$	$C_4AF$	$C_3A$	$\gamma - C_2S$	$Ca(OH)_2$	CaO
Treated MR	37	26	19	8	7	2	< 1

The compressive strength results (Figure 1) revealed that the addition of 10 wt% gypsum is optimal for the treated MR's composition. Smaller or higher additions resulted in lower early-, as well as, late-strength values.



**Figure 1:** Compressive strength results on samples with various amounts of gypsum (5-15 wt%), TIPA (0 - 0.5 wt%) and Viscocrete® (0 - 0.5 wt%)

The presence of Viscocrete® showed, overall, a positive effect on the compressive strength. Increasing the addition resulted in an increase in compressive strength. However, additions as high as 0.5 wt% resulted in high paste fluidity with risk of particle settling/separation. For future research it is suggested to limit the addition of Viscocrete® to 0.1 wt%. The effect of TIPA was not clear from the compressive strength results (Figure 1); therefore, XRD analysis was performed on selected hydrated samples (with and without TIPA) aiming to elucidate the role of TIPA.



**Figure 2:** Hydration phases formed after 28 days of hydration, in systems with 10 wt% gypsum, 0.5 wt% Viscocrete® and with (0.5 wt%, red) and without (green) TIPA addition

The PQXRD analysis shows that TIPA significantly influenced the formation of hydrated products (Figure 2). Monocarboaluminate predominantly formed in TIPA-rich sample, most probably due to the consumption of  $C_4AF$ . Additionally, monosulphate and hydrogarnet were formed in higher amounts compared to no-TIPA sample. Formation of these phases happened at the expense of C-S-H (resulted in lower amorphous content) despite the fact that  $C_3S$  and  $C_2S$  were about equally consumed. The above indicates, that although the effect of TIPA on strength could be neglected, it affected the formation of hydration phases with an impact, probably, on the long term performance of the product and maybe even durability.

## Conclusions

MR originating from a sponge iron production was successfully converted into a hydraulic binder after adjusting its chemical and mineralogical composition by means of  $CaCO_3$  addition and sintering in a sinter pan. The resulting material (*i.e.* OPC replica) contained all four main hydraulic phases:  $C_3S$ ,  $C_2S$ ,  $C_3A$  and  $C_4AF$ . The relatively high amount of  $C_3A$  and  $C_4AF$  led to an increased requirement of gypsum addition. From the additives selected, Viscocrete® showed to have a positive effect on strength results, however its addition should be limited to 0.1 wt% due to increased risk of particle sedimentation/separation. TIPA significantly influenced the hydration products, with no noticeable impact on compressive strength.

## References

1. R. Kikuchi, "Recycling of municipal solid waste for cement production: pilot-scale test for transforming incineration ash of solid waste into cement clinker", *Resour Conserv Recycl*, **31** (2) 137-147 (2001).
2. Slag Cement Association, "Slag Cement Benefits and Use in Concrete", [www.slagcement.org](http://www.slagcement.org) (accessed:28/11/2018)
3. M. Thomas, "Optimizing the Use of Fly Ash in Concrete", *Portland Cement Association* (2007).
4. Y. Pontikes, L. Kriskova, Ö. Cizer, P. T. Jones, B. Blanpain, "On a new hydraulic binder from stainless steel converter slag", *Adv Cem Res*, **25** (1) 21-31 (2013).
5. J. B. F. Neto, C. Fredericci, J. O. G. Faria, F. F. Chotoli, T. R. Ribeiro, A. Malynowskyj, A. N. L. Silva, V. A. Quarcioni, A. A. Lotto, "Modification of BOF Slag for Cement Manufacturing", in *Proceedings of the 10th International Conference on Molten Slags, Fluxes and Salts*, Edited by R. G. Reddy, P. Chabul, P. Ch. Pistorius, U. Pal. Springer, Washington, US, 2016.
6. J. B. Ferreira Neto, J. O. G. Faria, C. Fredericci, F. F. Chotoli, A. N. L. Silva, B. B. Ferraro, T. R. Ribeiro, A. Malynowskyj, V. A. Quarcioni, A. A. Lotto, "Modification of Molten Steelmaking Slag for Cement Application", *J Sustain Metall*, **2** (1) 13-27 (2016).
7. W. Banda, H. Lagendijk, "Metallothermic production of cement extender from manganese slags", in *Proceedings of the 5th International Slag Valorisation Symposium*, Edited by R. I. Iacobescu and A. Malfliet. KU Leuven Department of Materials Engineering, Leuven, Belgium, 2017.
8. A. Ehrenberg, D. Algermissen, "Electrical arc furnace slag - A potential substitute for Portland cement clinker and granulated blast furnace slag?", in *Proceedings of the 5th International Slag Valorisation Symposium*, Edited by R. I. Iacobescu and A. Malfliet. KU Leuven Department of Materials Engineering, Leuven, Belgium, 2017.