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REACTIVITY OF MODIFIED IRON SILICATE SLAG AS SUSTAINABLE ALTERNATIVE BINDER

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ABSTRACT

A possible solution to decrease the CO₂ footprint caused by the cement industry and to enhance the transition to circular economy is to use slags as Supplementary Cementitious Materials (SCM). The study presented here focuses on valorizing and investigating the reactivity and mechanical properties of blended binder systems combining Modified Iron Silicate (MFS) slag and Ordinary Portland Cement (OPC). MFS slag is a fumed by-product synthesized during the production of Copper (Cu) metal. This slag can be used as possible alternative SCM due to its pozzolanic behaviour. To study the replacement level in relation to reactivity and strength development, replacement levels of 15, 30 and 50 wt% of MFS-slag in ordinary portland cement are analyzed. The work can be divided into two categories: 1) assessing the reactivity through thermogravimetric analysis (TGA) and 2) evaluating the compressive strength (as a function of time) of mortar with MFS-slag after 2, 7, 28 and 90 days. TGA at 7, 15, 28 and 90 days allows to determine the reduction of portlandite content which gives an indication on the pozzolanic reactivity. Reactivity of MFS-slag blended systems is also determined relative to inert filler blended systems to discern between the reactive behavior of the MFS-slag and the filler effect.

Keywords: Supplementary cementitious materials, modified iron silicate, ordinary portland cement, thermogravimetric analysis.

INTRODUCTION

As the cement industry is one of the main contributors to the global CO₂ footprint, a possible solution has to be found to decrease CO₂ emissions (Worrell *et al.*, 2001;

Benhelal *et al.*, 2013; US Geological Survey & Orienteering S, 2017). One of these solutions can be to use Supplementary Cementitious Materials (SCM) such as slags. Usage of slags in concrete decreases the need for Portland clinker production and so the industrial CO₂ footprint (Scrivener and Kirkpatrick, 2008). Pyro-metallurgical processes involving oxidation and reduction of Copper (Cu) ore or scrap to synthesize Cu metal also produce slags as by-product (Schlesinger *et al.*, 2011). Cu slag's chemical composition varies depending on the initial Cu source and the processing condition. However, Cu slags are mainly composed of SiO₂, FeO, and CaO, similarly to other natural/artificial pozzolanic materials (Piatak, Parsons and Seal, 2015).

Several types of industrial by-products such as blast furnace slag or fly ash are widely used in the cement industry as SCM (Lothenbach, Scrivener and Hooton, 2011). These by-products are rich in an amorphous phase (typically >90 wt%) containing oxides of Si, Ca, Al and Fe and are latent hydraulic or pozzolanic. When for instance blast furnace slags are added together with ordinary portland cement (OPC) in a mortar or concrete mix, the amorphous phase reacts with the alkaline pore solution (enriched in CH) precipitating hydrates of calcium silicates (C-S-H). These slags can be used as SCM without modification and can satisfy the requirements of demanding construction applications. In terms of literature, a wide range of publications has proven that usage of amorphous materials such as metakolin and blast furnace slags in combination with OPC can enhance the mechanical properties and durability of concrete (Werner *et al.*, 1987; Hooton, 2000; Siddique and Klaus, 2009; Juenger *et al.*, 2011).

Literature has already revealed that Cu slags can be used as a SCM without compromising the mechanical properties of OPC concrete. In the work of Moura *et al.* (Moura, Gonçalves and Lima, 2007), Cu slags were used as SCM and the effect on strength and durability was examined. It was confirmed that replacement of OPC with 20 wt.% Cu slags increased the compressive strength at late ages. Moura *et al.* also stated that use of Cu slag in concrete could improve the durability.

Edwin *et al.* (Edwin, Gruyaert and De Belie, 2017) assessed the reactivity of the Cu slag by incorporating it in a "Reactive Powder Concrete" (RPC) from 0 to 20 wt.%. Findings published showed that the strength of the RPC with 20wt.% Cu slags was better than the reference mixture at 28 days. However, the pozzolanic reactivity determined by the Chapelle test was found to be low. In the work of Edwin *et al.* (Edwin *et al.*, 2016), the reactivity and effect of Cu slag as SCM in ultra-high performance mortar was assessed by isothermal calorimetry, strength activity index, Chapelle test and Frattini test. The final conclusions were that 1) addition of Cu slags slows down the hydration/heat flow of the cement paste and 2) rate of pozzolanic activity of the Cu slag depends on temperature, curing age and particle size. Tixier *et al.* (Tixier, Devaguptapu and Mobasher, 1997) studied the effect of Cu slag on the hydration and mechanical properties of cementitious mixtures. Cu slag was blended with lime to test its pozzolanic behavior. XRD/TGA (X-ray diffraction / thermogravimetric analysis) of

the Cu slag/lime samples indicates a decrease in the available CH content which is an indication of pozzolanic reaction. Mechanical properties of the concrete incorporating SCM showed a significant increase in the compressive strength. This increase in the compressive strength is due to the combination of filler and pozzolanic effect.

In this paper, reactivity and mechanical properties of paste/mortar made with a binder consisting of processed Cu slag, more correctly designated as “Modified Ferro silicate (MFS) slags”, as SCM along with OPC were studied. These MFS slags are similar Cu slags as investigated by Edwin et al (Edwin *et al.*, 2016), however an additional fuming process of this slag was carried out to turn it from a by-product into a mineral. In order to enhance the transition towards sustainability, the goal is to use these clean pozzolanic MFS slags as SCM in combination with OPC. Reactivity and hydration products of the SCM paste were analyzed using TGA. Mortar with MFS slags with replacement levels of 15, 30 and 50 wt% of MFS-slag in OPC were prepared to evaluate the compressive strength.

EXPERIMENTAL PROCEDURE

Patented Modified Ferro Silicate (MFS) slag (WO 2016156394 A1) is used as the raw material along with reference materials such as OPC (CEM I 52.5 N) and inert filler (quartz flour type M10). Chemical and mineralogical characterization of the raw materials were performed through X-ray fluorescence (XRF) and XRD. Specific surface area and particle size distribution of the raw materials were assessed by the Blaine method according to EN 196-6 and laser diffraction analysis respectively. Binders were prepared containing replacement levels of 15, 30 and 50 wt% of MFS-slag in OPC (specimens indicated with letter M), along with controls containing the same replacement percentages of inert filler (specimens indicated with letter R), and an OPC reference (Table 1). The water/solid ratio was kept constant at 0.5 for all pastes. Reactivity of the binders in the hydrated pastes was assessed after 7, 15, 28 and 90 days through TGA. Hydration of the pastes at their respective ages was stopped by placing the crushed paste in isopropanol for 4 h and filtering using a 2.7 μm pore size filter. Dry filtered pastes were stored in a vacuum chamber to avoid further hydration. TGA was performed to quantitatively evaluate the presence of CH, by means of a TA instrument SDT2960 (TG-DSC). The experiment was carried out in an Aluminium (Al) crucible, with a heating rate of 10 $^{\circ}\text{C}/\text{min}$ in a N_2 atmosphere. Thermal analysis software (Proteus analysis software was used to measure the quantitative presence of CH in all pastes. Single measurements were performed for a series and no repetitions were carried out. Compressive strength was assessed on OPC, 15M, 30M and 50M mortars (at time of preparation of this paper the test results on the 15R, 30R and 50R specimens were not yet fully available), prepared as per EN 196-1 and cured at 20 ± 1 $^{\circ}\text{C}$ and 95 % relative humidity for 24 h. Later the mortars were demolded and stored in a curing chamber at 20 ± 1 $^{\circ}\text{C}$ and 95 % relative humidity until the compressive strength were performed.

Table 1. Binder composition in wt.%

Mortar/Paste	OPC	MFS	M10
OPC	100	0	0
15M	85	15	0
30M	70	30	0
50M	50	50	0
15R	85	0	15
30R	70	0	30
50R	50	0	50

RESULTS AND DISCUSSION

Characterization of Starting Materials

Tables 2 and 3 provide the chemical and mineralogical composition of the MFS slag. MFS slags mainly possess oxides of Fe^{2+} or Fe^{3+} , Si and Al. Mineralogical analysis through X-ray diffraction shows more than 90 wt% of MFS slag as amorphous phases with presence of minor content crystalline phases such as spinel and metallic iron.

Table 2. Chemical composition of the MFS slags

Oxides	FeO/Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	CaO	Others
wt.%	40.9	32.3	11.0	3.9	11.9

Table 3. Mineralogy of the MFS slag

Phases	Wt%
Amorphous	92.7 ± 0.8
Spinel	6.7 ± 0.6
Iron	0.7 ± 0.2

Table 4 provides the specific surface area and particle size distribution of the starting materials. MFS slags were milled in an attritor grinding process for a specific time to achieve a similar particle size distribution and specific surface area as the OPC. Also, the inert filler material was selected to have similar characteristics.

Table 4. Particle size distribution and Blaine surface of the starting materials

Starting materials	Particle size			Specific surface area (cm ² /g)
	d ₁₀ (μm)	d ₅₀ (μm)	d ₉₀ (μm)	
OPC	1.316	8.912	30.192	4300 ±235
MFS	2.928	12.087	45.514	3800 ±250
M10	3.704	10.963	40.276	4000 ±225

Reactivity Assessment Through Thermogravimetric Analysis

Mass as a function of temperature as well as its derivative (rate in mass change) of the hydrated pastes after 90 days is shown in Figure 1. cement is usually composed of mineralogical phases such as C_3S , C_2S , C_3A and C_4AF which reacts with H_2O to produce hydration product. The important hydration reaction product of the cement paste are C-S-H and CH (Sha, O'Neill and Guo, 1999). Wide range of authors have already studied and described in detail the thermal decomposition of the hydrated cement paste. Major decomposition of the hydrated pastes takes place between 30 to 105°C, 110 to 170°C, 180 to 300°C, 450 to 550°C and 700 to 900°C.

- 1) The first region between the temperature range 30 to 105 °C is mainly due to the dehydration of evaporable water (Alarcon-Ruiz *et al.*, 2005).
- 2) The region in the temperature range between 110 to 170°C is due to the decomposition of C_2S , AFt , SO_4^{2-} -AFm, CO_3^{2-} -AFm (as per cement notation) (Zhou and Glasser, 2001; Alonso and Fernandez, 2004).
- 3) The loss of bound water from the dehydration reactions from C-S-H takes places in the temperature range of 180 to 300°C (Nonnet, Lequeux and Boch, 1999; Zhou and Glasser, 2001; Alarcon-Ruiz *et al.*, 2005; Pane and Hansen, 2005).
- 4) Mass loss in the temperature region between 450 to 550 °C corresponds to the dehydration of CH (Zhang and Ye, 2012; Deboucha *et al.*, 2017).
- 5) The final decomposition occurs due to the decarbonation of carbonate phases in the temperature range between 700 to 900 °C (Grattan-Bellew, 1996; Deboucha *et al.*, 2017).

$$CH(\%) = m_{loss\ 450-550\ ^\circ C} * \frac{MW_{CH}}{MW_{H_2O}} \quad 1$$

The percentage of CH can be calculated by the formula 1 where the parameter $m_{loss\ 450-550\ ^\circ C}$ is included for considering the dehydration of CH and the mass conversion factor of H_2O to CH can be calculated by the ratio of molecular weight (MW) of CH and H_2O (Chen *et al.*, 2007). To be more accurate, for each specific paste, the 450-550 °C boundaries were slightly adjusted given the exact location of the CH region in Figure 1. However, the mass loss due to CH decomposition generally lays between 450 and 550°C which was determined by tangent method.

Figure 2 shows the presence of CH in the hydrated SCM paste at the different ages of 7, 15, 28 and 90 days with comparison to the reference of paste made from inert filler and OPC. It can be clearly seen that all SCM pastes synthesized with the MFS slag show presence of less CH compared to the paste made from inert filler and OPC, especially at 28 and 90 days. This indicates that CH formed as the reaction product during OPC hydration is dissolved in the pore solution and consumed by the MFS slag through pozzolanic reaction.

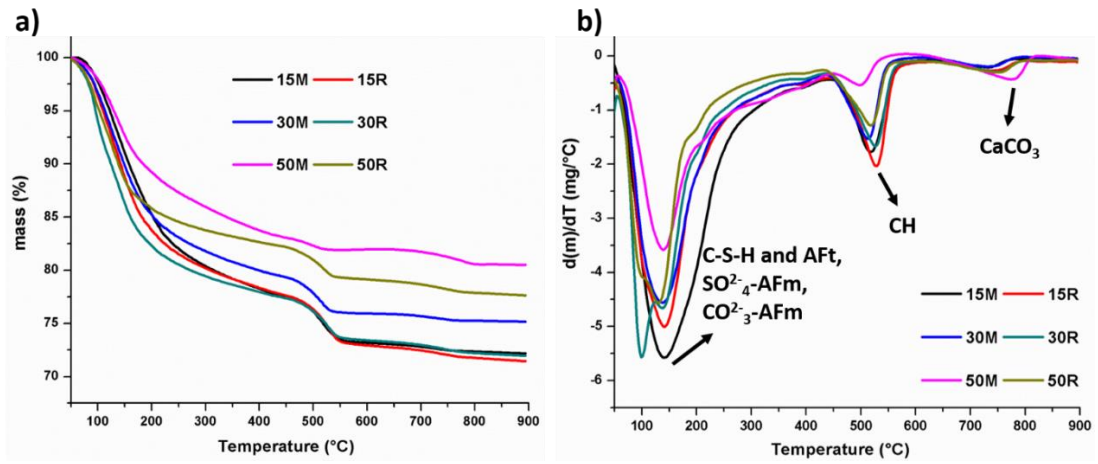


Figure 1. TGA curve of the powdered paste after 90 days: a) mass loss (%) vs temperature (°C), and b) rate of change of mass (mg/°C) vs temperature (°C)

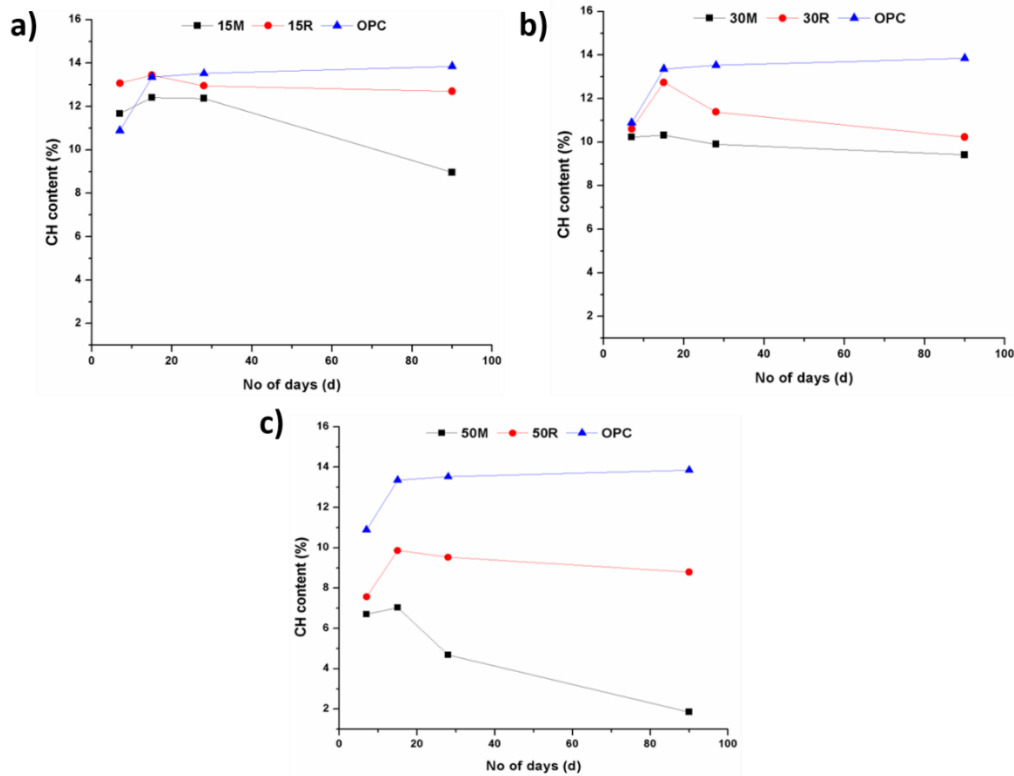


Figure 2. Calculated CH content in wt.% with OPC as reference a) 15M vs 15R, b) 30M vs 30R and c) 50M vs 50R

However, 7 days TGA analysis of MFS slag and inert filler paste showed presence of high CH content compared to the OPC paste which is possibly due to the enhancement of OPC hydration by filler effect, thus producing more CH (Cordeiro *et al.*, 2008). Moreover slight decrease in the trend of CH content between 28 days and 90 days of the inert filler paste especially 30 R and 50 R indicates that quartz filler though assumed inert, consumes a small amount of CH. A similar observation has been made and discussed in the literature (Cyr, Lawrence and Ringot, 2005; Moesgaard *et al.*, 2011; Deschner *et al.*, 2012).

Strength Development of SCM Mortars Synthesized From MFS Slags

Evaluation of the compressive strength was carried out among all MFS mortars, and also compared to 85%, 70% and 50% of the OPC compressive strength as nominal reference values (Figure 4). Note that this comparison is not completely fair, given the difference in underlying hydration mechanism, but allows to observe the trends better. The 2 days strength of the synthesized SCM mortars such as 15 M and 50 M was lower than the respective reference values taking into account the dilution of OPC, whereas the 2 days strength of 30 M was similar to the reference value. This shows that the replacement with MFS slags leads generally into a decrease in the 2 days compressive strength, even surpassing the strength reduction expected from the decrease in OPC content. This might be attributed to the MFS slag delaying the OPC hydration and the MFS slag reaction itself requiring more time.

At 7 days, the observed trend at 2 days, is turned around with higher strengths up to 55 MPa and 40 MPa for respectively 15 M and 30 M. At 28 and 90 days, all synthesized MFS mortars showed high compressive strength compared to their OPC content. Strength development of the SCM mortar synthesized from MFS slags showed slow increase from 2 days to 7 days and high increase in the period from 7 to 90 days compared to the reference value. This kind of strength development is due to the presence of MFS slag itself and linked to the possible mechanism of slow dissolution of amorphous silica in the alkaline pore solution (Barret, Ménétrier and Cottin, 1977) and the formation of strength providing phases such as C-S-H and C-A-S-H which will be further investigated.

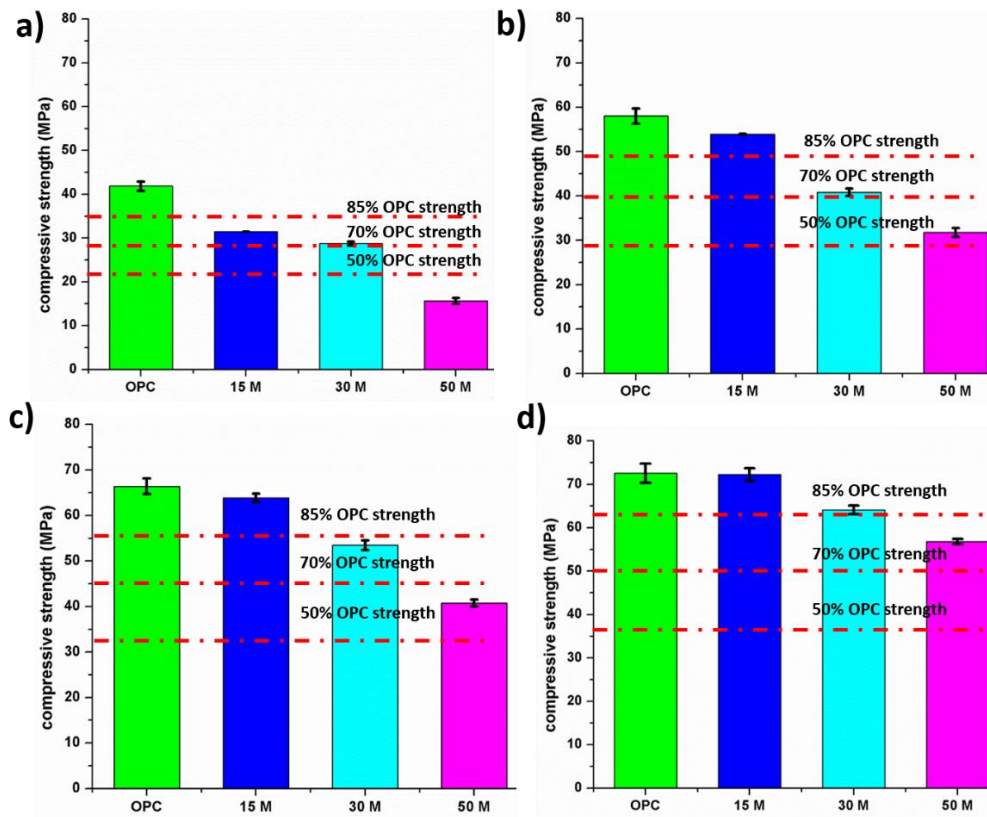


Figure 3. Mean compressive strength of synthesized mortars a) 2 days, b) 7 days and c) 28 days d) 90 days

CONCLUSION

The present work proved that MFS slag can be a promising alternative pozzolanic material. MFS slag, used as a substitute for OPC, contributes to the mechanical properties at later ages (starting to be observed at 7 days and strongly observed at 28 days). Assessment through TGA based on the relative reduction in CH content provided suitable information on the MFS slag reactivity.

In particular the following points can be emphasized

- 1) TGA analysis predicted presence of less CH concentration among all MFS slag binders compared to the inert filler and OPC binder after 28- and 90-days suggesting CH was consumed through pozzolanic reaction.
- 2) Due to the existence of SiO₂ rich amorphous phase in MFS slags, strength development showed an increase above the expected strength considering the reduction in OPC content at the age of 28 days.
- 3) The observed strength increases can possibly be attributed to a combination of pozzolanic reaction and filler effect which is under further investigation.

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