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# HYDRAULIC REACTIVITY OF QUENCHED Fe, Si-RICH SLAGS IN THE PRESENCE OF Ca(OH)<sub>2</sub>

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## Abstract

*In this study, two synthetically produced Fe, Si-rich slags, namely S1 and S2 (Fe and Si content 17 wt% and 48 wt% in S1 and 41 wt% and 29 wt% in S2, respectively) were investigated for their hydration reactivity with Ca(OH)<sub>2</sub> in 20 wt% (S1CH and S2CH). The isothermal calorimetry results reveal that both slags show a hydration response in the presence of Ca(OH)<sub>2</sub>. The reaction occurred slowly with time, forming most probably calcium silicate hydrate. Quantitative X-ray diffraction analysis has shown more Ca(OH)<sub>2</sub> consumed at early days in S1CH compared to S2CH due to a higher amorphous content. In sample S2CH, the magnetite did not participate in the hydration reactions.*

## Introduction

The non-ferrous industry incorporates a range of productive activities along various stages including (technospheric) mining, smelting and refining upstream and casting and fabrication of intermediaries further downstream. The composition of slag varies depending on the products and sector, being typically rich in Fe, Si, Al and Ca, varying in content. Elements such as Mg, Ti, Zn, Cu, Cr and Pb can also be found in minor amounts. The (hydraulic) reactivity of these slags can be enhanced via fast cooling, thereby increasing the amount of amorphous (glassy) phase over the crystalline phases<sup>1,2</sup>. Nevertheless, the Fe and Al content in the amorphous phase seems to be critical in achieving desirable hydration products. Earlier work indicated that highly amorphous Fe-Al-rich slag is extremely reactive with CH but develops a prevailing phase of hydrogarnet which induced strength reduction<sup>2</sup>. The objective of the present contribution is, therefore, to investigate the hydration potential of fast cooled slags, rich in Si and Fe, but poor in Al, when mixed with CH.

## Materials and methods

Slags were synthetically produced from analytical grade chemicals in a bottom loading furnace at 1550°C for a 30 min dwell time under an Ar flushing gas stream. A platinum crucible was used. Fast cooling was applied by pouring the molten slag in water. The bulk analysis (Table 1) was performed by XRF (Philips PW 2400 spectrometer). For XRD/QXRD analysis, the slag was milled together with 10 wt% ZnO as an internal standard and 10 ml Hexane as grinding agent. The ground material was dried at room temperature, and then stored in sealed plastic bags. Quantitative (QXRD) analysis was performed using the normalised Rietveld method (Table 2). For hydration tests, each slag (S1, S2) was milled below 80 µm and mixed with 20 wt% calcium hydroxide (CH - 95% purity). The liquid/solid ratio used was 0.5. The heat of hydration was monitored by isothermal conduction calorimetry at 20°C (TAM Air device, TA Instruments). A benchmark sample (without CH) was used for comparison. The produced pastes were poured in plastic capsules, closed tightly, immersed in water, and cured at 20°C. This was done in order to prevent carbonation. After 3 and 28 days of curing, the hydration was stopped by the freeze drying procedure. Samples were analysed by TG/DTG and XRD/QXRD. The former was done in a TA Instruments in N<sub>2</sub>, at a heating rate of 10°C/min, from room temperature until 800°C, whereas for the latter, the aforementioned procedure was used.

## Results and discussion

### Characterisation of slags

The XRF and QXRD analyses of the produced slags (S1 and S2) are presented in Table 1. The chemical composition varies in Fe<sub>2</sub>O<sub>3</sub> from 17.5 wt% in S1 to 41.8 wt% in S2 and in SiO<sub>2</sub> from 48.8 wt% in S1 to 29.5 wt% in S2. No distinction has been made between Fe<sup>+2</sup> and Fe<sup>+3</sup> in the analysis.

**Table 1:** Bulk chemical and quantitative mineralogical analyses of slags, in wt%

Bulk chemical analysis (XRF)										
Compounds	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>	MgO	K <sub>2</sub> O	CuO	TiO <sub>2</sub>	BaO	MnO
S1	48.9	17.5	14.8	11.9	1.9	1.7	1.2	0.9	0.4	0.2
S2	29.7	41.9	12.9	5.9	1.6	0.9	1.1	0.9	1.4	2.7
Mineralogical analysis (QXRD)										
Samples	Magnetite		Quartz		Periclase		Calcite		Amorphous	
S1	0		0.4		0		0		99.6	
S2	26.1		0.6		1.6		0.7		70.9	

Due to the fast cooling applied, the amorphous content is 99.6 wt% in S1 and 70.9 wt% in S2 with magnetite being the main precipitated crystalline phase. Combining the

chemical and mineralogical analyses (Table 1) a difference in the Fe content in the glassy slag phase is expected (17.5 wt% in S1 vs. 15.7 wt% in S2).

### Isothermal calorimetry of slag pastes

The heat of hydration and cumulative heat release are presented in Figure 1. There is clear evidence that both slag samples do not hydrate when mixed with water only, but in the presence of CH a heat release occurs. The reaction can be considered relatively fast during the first few hours most probably due to dissolution from the amorphous phase and the reaction with calcium ions forming a C-S-H type of reaction product, as is presented later on. The reaction is then decelerated slowly following a gradual evolution with time. It is interesting to note that both samples follow the same trend up to 55h, although there is a difference in the amorphous content as well as in the chemistry of the glassy fraction (predominantly silica). Most probably during the early stage, this is dictated by the dissolution kinetics and/or reactivity of the amorphous phase but not by its content.

### Thermo-gravimetric analysis of the hydrated slags

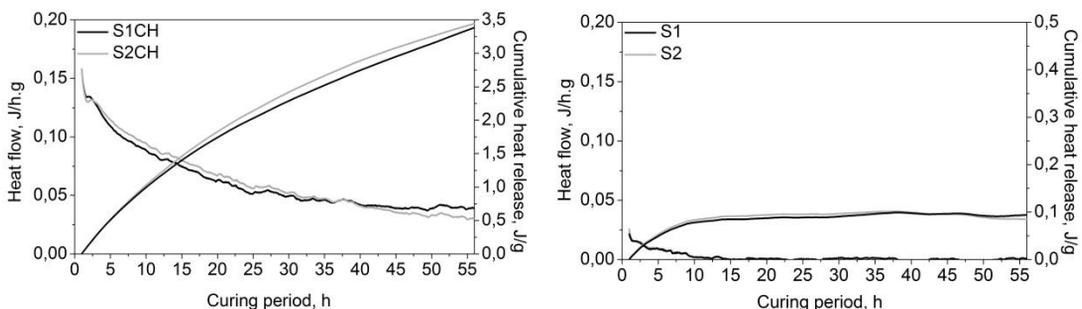
The DTG curves based on TG analysis at different curing ages are shown in Figure 2.

At 100°C the weight loss suggests the dehydration of C-S-H type hydration product, whereas between 400°C to 450°C the weight loss is associated with CH dehydration.

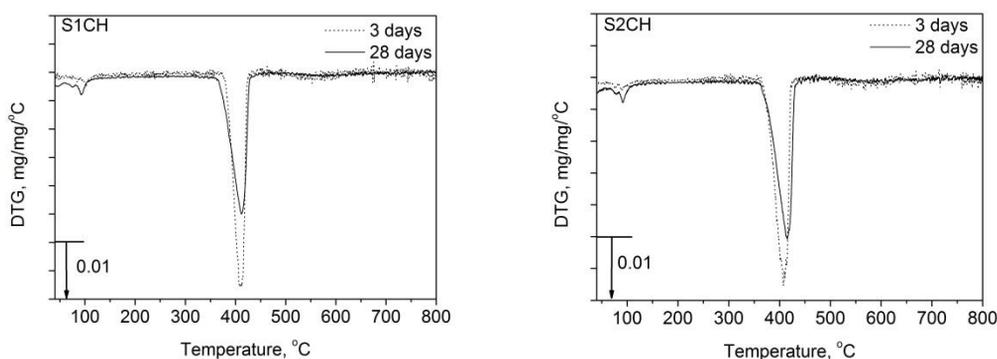
As the curing period increases, the CH peak intensity decreases, as CH is consumed by C-S-H formation. At 3 days and 28 days, CH consumed in S1CH was 23 wt% and 32 wt% whereas in S2CH 22 wt% and 29 wt%, from its total content, respectively.

### Mineralogical analysis of the hydrated slags

The mineralogical composition of samples S1CH and S2CH after different curing periods is presented in Table 2. With increasing curing period, the amount of CH decreases. A certain drop is presented at 3 days, corroborated with the increment in their heat release in Figure 1. At 28 days, a big part of CH was consumed in both samples. Most probably a part was carbonated as revealed by the increment in calcite content. This must have happened eventually during sample preparation for QXRD as this was not



**Figure 1:** Heat flow and cumulative heat release behaviour of slag samples pastes with and without 20 wt% CH (left - with CH, right - without CH)



**Figure 2:** DTG curves of S1CH and S2CH after 3 and 28 days of hydration

seen in DTG curves. Based on the TGA results, most of the CH consumption occurs before day 3. With regards to the amorphous content, there is an increase noticed for both samples, from their starting values (coming from the 80 wt% slag used) of 79 wt% in S1CH and 56 wt% in S2CH, to 82 wt% and 60 wt%, respectively. This is attributed to amorphous C-S-H growth. At later ages of hydration, part of the portlandite presumably undergoes carbonation although the mechanism is not fully clear yet (Table 2).

**Table 2:** Mineralogical variation upon curing period of slag samples with CH, in wt%

Samples	Curing days	Magnetite	Portlandite	Quartz	Calcite	Amorphous
S1CH	3	-	14.7	1.4	1.7	82.2
	28	-	6.5	3	11.8	78.7
S2CH	3	20.6	16.5	0.7	2	60.2
	28	20.6	8	7.1	12.4	51.8

## Conclusion

Both slags reacted with CH and presumably formed a type of amorphous C-S-H. Magnetite did not participate in the reaction. In both slags, most CH had reacted prior to 3 days. The higher silica content slag indicated a slightly higher reaction, with more CH consumed, probably due to a higher silica content in the amorphous phase.

## References

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