

EFFECT OF COOLING WATER CHEMISTRY ON HYDRATION OF GRANULATED BLAST FURNACE SLAG

Romain TRAUCHESSEC¹, Lyès CHAOUCHE¹, Cécile DILIBERTO¹, Patrice REEB², André LECOMTE¹, Samyr EL-BEDOUI³, Klaus-Jürgen ARLT²

¹ Institut Jean Lamour, UMR/CNRS 7198, Université de Lorraine, Équipe matériaux pour le génie civil, IUTNB, CS 90137, 54600 Villers-les-Nancy, France

² Aktien-Gesellschaft der Dillinger Hüttenwerke, Werkstraße 1, 66763 Dillingen/Saar, Germany

³ Cerema, Direction Territoriale Est, Laboratoire Régional de Nancy, 71 rue de la Grande Haie, 54510 Tomblaine, France

romain.trauchessec@univ-lorraine.fr, lyes.chaouche7@etu.univ-lorraine.fr, cecile.diliberto@univ-lorraine.fr, patrice.reeb@dillinger.biz, samyr.el-bedoui@cerema.fr, andre.lecomte@univ-lorraine.fr, klaus.arlt@dillinger.biz

Introduction

Granulated blast furnace slag (GBFS) can be used without grinding and addition as binder of granular mixtures employed for road construction. GBFS reactivity depends on the slag composition and activation as well as the amorphous structure which is generated by quenching with water (granulation process)¹. GBFS contains a part of this industrial water used in closed circuit. This study evaluates the effect of the cooling water composition on granulated slag hydration.

Materials and Methods

Chemical composition of the cooling water from two blast furnaces (BF1 and BF2) of the same factory has been analysed regularly during two weeks. Concentrations were measured by Inductively Coupled Plasma (ICP) (for chlorine, Ionic Chromatography (IC) was used). Four representative samples were selected. Between the two blast furnaces, concentrations have similar orders of magnitude (Table 1). However, in cooling water from BF1, magnesium (Mg) and calcium (Ca) concentrations are 1.9 and 1.6 higher. On the contrary, in water from BF2, sulphur (S), sodium (Na) and potassium (K) concentrations are respectively 1.6, 1.9 and 1.6 higher. These differences could modify GBFS hydration although the GBFS produced have similar chemical and physical properties (Table 2).

This paper compares the chemical composition of the cooling water with the composition of the interstitial solution obtained after hydration of 100 g of GBFS in distilled water during 1, 14 and 28 days (Water/Slag weight ratio = 0.3). Slag water content ($\approx 7\%$) was taken into account. After hydration, water is filtered and analysed by ICP and IC after dilution and addition of nitric acid. GBFS hydration was stopped by isopropanol and diethyl ether and drying at 40°C. Samples were sieved at 100 μm for electronic microscope and X-ray diffraction analysis.

Table 1: Chemical composition of the cooling water (mmol/L)

Sample		Ca	Mg	Fe	Si	Na	K	Al	Cl	S
BF1	A	25.1	4.0	0.000	0.8	14.6	31.7	<0.001	61.2	23.9
	B	24.2	3.8	0.002	0.8	12.3	27.1	<0.001	55.7	25.4
	Average	24.7	3.9	0.001	0.8	13.5	29.4	<0.001	58.4	24.7
BF2	C	10.9	2.2	0.001	0.7	25.1	62.4	<0.001	54.9	32.6
	D	19.6	1.8	0.001	0.8	18.2	49.1	0.001	45.8	46.8
	Average	15.2	2.0	0.001	0.7	21.7	55.7	0.001	50.4	39.7

Table 2: GBFS chemical and physical properties

Sample		Water content (%)	ρ (g/cm ³)	Alpha*	<80 μ m (%)	X-ray fluorescence (%)				
						CaO	Al ₂ O ₃	SiO ₂	MgO	S
BF1	A	6.66	2.91	23	1.75	41.1	11.3	38.1	6.8	0.9
	B	6.72	2.91	19	1.51	42.2	11.4	37.3	6.8	0.9
BF2	C	7.27	2.91	17	1.04	41.2	11.6	38.1	6.6	0.9
	D	7.52	2.91	17	2.35	41.1	12.4	37.7	6.3	1.2

* Alpha coefficient (α) = Blaine surface (cm²/g) x friability (%) / 1000 (NF EN 13286-44).

Results and Interpretations

Chemical composition of interstitial solution

For the different selected samples, concentrations change between 1, 14 and 28 days but the concentrations stay similar (order of magnitude). For example, Ca, K and S concentrations during the first month of hydration are presented in Table 3.

Table 3: Ca, K and S concentration at 1, 14 and 28 days (mmol/L)

		Ca				K				S			
Sample		1d	14d	28d	Average	1d	14d	28d	Average	1d	14d	28d	Average
BF1	A	5.0	5.7	7.0	6.1	7.6	7.3	10.7	9.2	1.5	2.6	2.6	2.9
	B	6.1	6.1	6.9		8.4	9.0	12.3		3.3	4.3	3.4	
BF2	C	2.4	5.0	4.5	3.8	15.6	17.9	19.9	18.4	1.8	9.0	3.5	5.8
	D	3.3	2.4	4.9		15.2	24.3	17.2		8.2	9.2	3.1	

Table 4 compares the composition of the interstitial solution after 14 days. In average, Mg, Fe, Si, Al and Cl concentrations are relatively close but with GBFS from BF2 there is more S, Na and K in solution. On the contrary, for GBFS from BF1, Ca concentration tends to be higher. These differences are also observed for the cooling water (Table 1). Similar observations can be done with the data obtained after 1 day or 28 days (Table 3).

For two samples (BF1B and BF2C), a higher water slag ratio (W/S) was also used (W/S=1.0 instead of 0.3). When this ratio is multiplied by 3.3, Na, K and Cl

concentrations are reduced by a factor also close to three (Table 5). Ca, Mg, Si, Al and S concentrations are less affected by the W/S ratio due to slag dissolution. This result was confirmed by tests done after 1 day and 28 days of hydration.

Table 4: Chemical composition of the interstitial solution at 14 days (mmol/L)

Sample		Ca	Mg	Fe	Si	Na	K	Al	Cl	S
BF1	A	5.7	0.02	0.001	0.3	3.8	7.3	0.1	12.0	2.6
	B	6.1	0.02	0.001	0.2	5.1	9.0	0.1	13.9	4.3
	Average	5.9	0.02	0.001	0.3	4.4	8.2	0.1	13.0	3.5
BF2	C	5.0	0.02	0.001	0.6	7.7	17.9	0.1	15.0	9.0
	D	2.4	0.03	0.002	0.1	14.3	24.3	0.4	12.0	9.2
	Average	3.7	0.02	0.002	0.4	11.0	21.1	0.2	13.5	9.1

Table 5: Solution composition at 14 days for two Water/Slag ratio (mmol/L)

Sample		Ca	Mg	Fe	Si	Na	K	Al	Cl	S
BF1	W/S=0.3	6.1	0.02	0.001	0.2	5.1	9.0	0.1	13.9	4.3
B	W/S=1.0	7.2	0.01	0.000	0.5	1.5	2.7	0.0	4.4	4.7
BF2	W/S=0.3	5.0	0.02	0.001	0.6	7.7	17.9	0.1	15.0	9.0
C	W/S=1.0	3.8	0.01	0.001	0.7	2.5	6.0	0.1	5.0	3.5

These experiments show that concentrations of Na, K and Cl in solution during GBFS hydration is linked to the composition of the cooling water. This can change the solution ionic strength and modify hydrates stability. However, Na and K concentrations are low: in comparison with slag cement, concentrations (139 and 153 mmol/L respectively) can be 10-30 times higher². These amounts of Na, K and Cl could be simulated by the dissolution of only 0.04% of salt in the slag. These low concentrations can only induce minor differences between GBFS of BF1 and BF2. The slow GBFS dissolution and hydrates formation maintain Ca, S, Si, Al and Mg concentrations relatively constant. In agreement with the literature, thermodynamic calculations (not presented here) reveal that for these concentrations and pH, hydrates as CSH, ettringite and hydrotalcite are stable (saturated or oversaturated) whereas Portlandite and gypsum are undersaturated. The low proportion of sulphur (S²⁻) in the slag (S≈1%, Table 2) is unstable (oxidation SO₄²⁻, SO₃²⁻, etc.) and might be responsible of the slag hydration without activators and ettringite formation³.

Slag hydration

For the four samples, after mixing granulated slag and water, pH is basic but relatively low: between 10.9-11.5 after 1 day and around 11.6 until 28 days. These results are in agreement with the literature^{4, 5}. For comparison, in slag cement or with activators, pH is higher (around 13.0). X-ray diffraction (Figure 1) and electronic microscope analysis of the hydrated GBFS (fraction sieved at 100 μm), indicates the formation of ettringite in GBFS from BF1 and BF2. Calcite is also detected and could be formed by carbonation of unstable hydrates (calcium aluminate).

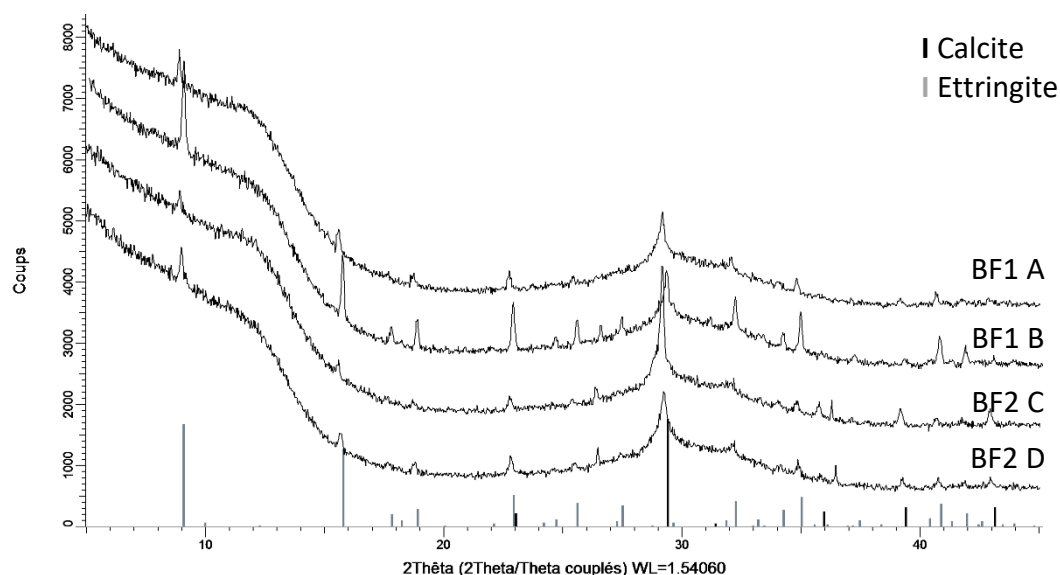


Figure 1: X-ray analysis of the samples after 28 days of hydration

Conclusions

This study shows for samples from two blast furnaces and different water/slag ratio a correlation between the sodium, potassium and chlorine concentrations in the cooling water and the interstitial solution during hydration. The range of concentrations, pH and X-ray analysis indicate a moderate effect of the cooling water on GBFS hydration.

References

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