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HYDRATION OF CAC-ALUMINA SYSTEMS IN THE PRESENCE OF DIFFERENT SILICA FUMES

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ABSTRACT

The study is focused on how the hydration of a refractory binder system consisting of commercial white CAC and tabular alumina is changed by the addition of different silica fumes. Four silica fumes, two each of identical quality grade, but obtained from different batches, were selected and characterized by their physical and chemical properties. Then they were added to the system with a SF/CAC ratio of 1 and w/c of 1.4 at 23 °C. Even though no clear differences could be observed between the fumes of the same grade regarding chemical bulk analysis and specific surface area, they exhibited different rheological behavior after paste preparation.

To examine this, the hydration was followed via heat flow calorimetry, in-situ XRD and pore solution analysis. Additionally, hardness development within the first hours of hydration was measured with a Gillmore-needle device (IMETER).

It was found that the mixes with lower viscosity show an additional heat flow event located between the initial heat flow after mixing and the main reaction. This intermediate event is likely correlated to an initial dissolution of CA, which occurs directly after water addition in the mixes without this event. Also, an increased rate of hardness development was observed during the intermediate event. A potential link to the amount of dissolved silicon provided by the silica fumes shown in the pore solution data was examined by adding solutions containing low amounts of sodium silicate to the mixes. By this, the event could be induced in the two systems previously not showing this reaction. Higher concentrated solutions retard the hydration until a critical point, where the main reaction is eventually suppressed for at least 48 h.

INTRODUCTION | BACKGROUND

White, iron-free calcium aluminate cements (CAC) are widely used as binding component in refractory castables, particularly due to their high Al_2O_3 content which contributes to heat resistance. In such systems low porosity is of utmost importance since open porosity increases infiltration e.g. during steel production which accelerates wear and reduces lifetime.

To counteract, fine materials such as silica fume (SF) are added to the matrix. Besides increased mechanical strength, this can also contribute to a reduction of the water demand by filling the pore space and improve flow behavior [1]. SF is a byproduct of the (ferro-)silicon industry and consists of fine, amorphous, SiO_2-rich powder, with spherical primary particles less than 1 µm in diameter. Past studies [2,3] have shown that SF can induce an additional heat flow event between initial period and main reaction. This intermediate event (IE) is correlated to a premature stiffening of the paste which can critically impair the flow of castables. It was observed that the appearance of the IE depends on the SF/CAC ratio in the mix (the higher, the later it begins) and that there may be a correlation to the readily soluble amount of Si initially released by SF upon first contact with mixing water. Therefore, different SFs were investigated regarding their influence on hydration kinetics and hardness development and were additionally mixed with Na_2SiO_3 solutions to evaluate the potential effect.

METHODS

The materials used were a pure white CAC (CA14-S by Almatis), tabular alumina (T60/T64 -45 micron LI by Almatis) and four silica fumes: quality grade “A”, batch “1” and batch “2”, and quality grade “B”, batch “1” and batch “2”. The chemical compositions of these components were analysed via XRF (Table 1). The investigated pastes were composed based on these 3 ratios: SF/CAC = 1, Alumina/CAC = 1.5 and water/CAC = 1.4 or 2.8 (the higher w/c was necessary to extract sufficient solution amounts via centrifugation). The $Na_2SiO_3 \cdot 5H_2O$ was added to the mixing water and the bound water was accounted for to keep the water/CAC constant (Table 2).

Table 1. XRF analysis and specific surface area (SSA) determined by BET of the materials used. Sulfate content was determined via nephelometry.

[wt%]	CAC	Alumina	SF(A1)	SF(A2)	SF(B1)	SF(B2)
CaO	29.2	≤0.1	0.3	0.3	0.3	0.5
Al_2O_3	69.4	99.2	≤0.1	≤0.1	≤0.1	≤0.1
Na_2O	≤0.1	0.2	0.6	0.4	0.6	0.5
K_2O	≤0.1	≤0.1	0.2	0.2	0.6	0.4
MgO	0.2	≤0.1	0.1	0.1	0.3	0.4
Fe_2O_3	0.2	≤0.1	0.1	0.1	0.1	0.1
SiO_2	0.2	≤0.1	97.4	97.5	95.5	95.5
SO_3	-	-	0.2	0.2	0.3	0.4
LOI	0.2	0.3	1.0	1.1	2.3	2.1
SSA [m^2/g]	0.8±0.1	1.5±0.1	26.1±0.2	25.7±0.2	20.4±0.2	20.0±0.2

Every experiment was executed at 23 °C. Heat flow calorimetry was performed for every mix with a TAM air calorimeter. Hardness measurements were executed with an automated Gillmore-needle device (“Imeter” by MSB Breitwieser). For selected SFs quantitative in-situ XRD measurements were performed over the course of 24 h with a D8 ADVANCE diffractometer by BRUKER-AXS. Pore solutions were extracted

via centrifugation, filtered with a 0.2 µm syringe filter and measured by ICP-MS.

Table 2. Composition of pastes. SF(X) is calculated to 100 g, $Na_2SiO_3 \cdot 5H_2O$ is added on top. Nomenclature: e.g. SF(A1)+0.1NaSi = To the mix containing SF(A1) 0.1 %bwoc (by weight of cement) $Na_2SiO_3 \cdot 5H_2O$ was added.

[g]	CAC	SF	Alumina	$Na_2SiO_3 \cdot 5H_2O$	Deion. H_2O
w/c = 1.4					
SF(X)	20.4082	20.4082	30.6122	-	28.5714
+0.4NaSi	"	"	"	0.0816	28.5368
+0.5NaSi	"	"	"	0.1020	28.5281
+0.6NaSi	"	"	"	0.1224	28.5194
w/c = 2.8					
SF(X)	15.8730	15.8730	23.8095	-	44.4444

KEY FINDINGS | CONCLUSIONS

The heat flow curves and hardness developments of samples with every investigated SF are shown in Figure 1. Independently of quality grade (A or B) pastes display a sharp heat flow peak after a few minutes of hydration (batches A1 and B1) or directly after water addition (batches A2 and B2). This makes paste preparation, especially in SF(B2), extremely hard, which is why SF(A1) and SF(A2) were chosen for further investigations on systems of "good" and "bad" initial rheology.

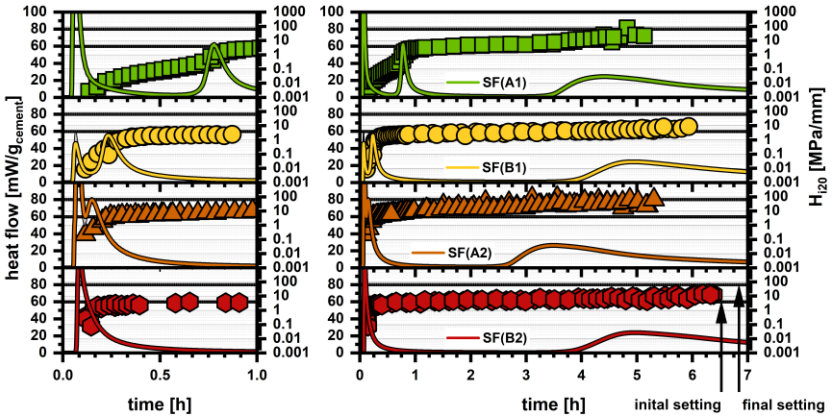

Figure 1. Heat flow curves and hardness development of mixes containing different SFs.

In the left section of Figure 2 the in-situ phase developments of SF(A1) and SF(A2) are shown. Precipitation of the hydrate phases CAH_{10} and C_2AH_x starts with the main reaction, and no crystalline precipitates are detected during the intermediate event. However, in SF(A1) it can be seen, that a small amount of CA is dissolved during the IE. This becomes more obvious in the pore solution data (Figure 2, right section). Before the IE in SF(A1), Ca and Al concentrations as well as pH (around 8-9) are comparatively low. During this period, Si present in solution is consumed until no Si is detectable anymore at the start of the IE. The initial CaO/Al_2O_3 ratio is very high (950/1 at the first measurement point after 5 min) and the dominant aqueous Si species at the given pH of 8.6 is $Si(OH)_4^0$. We therefore suggest

adsorption of $Si(OH)_4^0$ on a metastable Al-rich layer on CA surfaces formed due to incongruent dissolution is causing its stabilization and leading to a retardation of the initial CA dissolution.

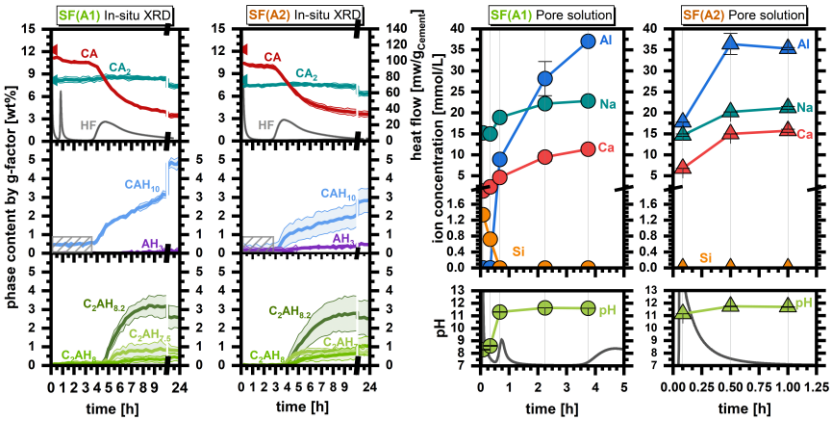

Figure 2. Phase development (left) and pore solution compositions of SF(A1) and SF(A2) (right).

Addition of $Na_2SiO_3 \cdot 5H_2O$ provides dissolved Si and is causing a retardation in the investigated mixes (Figure 3). This underlines the suggested mechanism of readily soluble Si provided by SF potentially being the reason for the observed hydration kinetics. Higher pH of these solutions could lead to different Si species which might explain e.g. the reduced hydration rates. Further investigations are needed to verify this hypothesis.

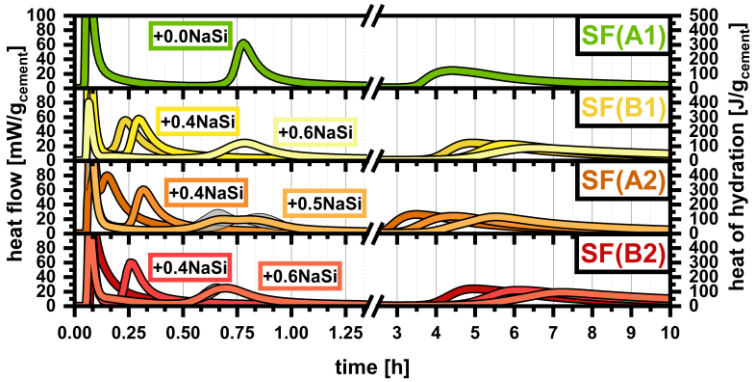

Figure 3. Heat flow curves of pastes containing $Na_2SiO_3 \cdot 5H_2O$.

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