

Reaction kinetics of calcined phyllosilicates in synthetic cement systems

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1. Introduction

The influence of calcined clays on the silicate and the aluminate clinker reaction during early hydration is still a matter of debate. Current literature describes physical effects as a major influence on early hydration [1]. Thereby, the filler effect leads to an acceleration of the silicate clinker reaction and the high surface area of the resulting C-S-H serves to adsorb sulfate from the pore solution and consequently accelerates the aluminate clinker reaction. Nevertheless, further literature shows that calcined clays influence early hydration due to their complex surface properties [2] and confirm a clear chemical reaction in clinker-free systems within the first day [3]. Furthermore, Maier et al. [4] described an acceleration of the aluminate reaction which can take place in the absence of C-S-H. The investigations aim to separate physical and chemical effects on the individual clinker reactions during main hydration and reveal an improved understanding of the mechanism of calcined phyllosilicates during early hydration.

2. Materials and methods

Two test series with a synthetic cement (SyCEM, Blaine $\approx 4000 \text{ m}^2 \text{ g}^{-1}$) consisting of alite (87.5 wt.-%), C₃A (8.5 wt.-%), gypsum (3.25 wt.-%) and basanite (0.75 wt.-%) were investigated by means of calorimetry, in situ X-ray diffraction (in situ XRD) and thermogravimetry (TG) up to 48 h. The first test series was performed with a replacement level of 20 wt.-% of the SyCEM by one of three different, preferably pure calcined phyllosilicates (metakaolin (MK), metakillite (MI) and metamuscovite (MM)). In the second test series, 10 wt.-% of the SyCEM was replaced by limestone powder (LL) in the reference system. The characterization of the calcined phyllosilicates is published in [3,5] and of LL in [6]. The experimental setup and procedure used for calorimetry, in situ XRD and TG are provided in [3].

3. Results and discussion

All systems investigated show an acceleration of the silicate clinker reaction compared to the respective reference system (Fig. 1). No clear correlation can be observed between the total surface area of the systems (numbers in brackets in Fig. 1) and the acceleration of the silicate reaction. This could be due to agglomeration effects of the calcined clay particles as already described by [2]. Despite comparable acceleration of the silicate reaction by the calcined phyllosilicates, there are clear differences in the point in time of the aluminate reaction maxima (numbers in brackets in Tab. 1). While the silicate reaction accelerates most in the MM systems, this is the case for the aluminate reaction in the MK systems. This indicates a chemical contribution of MK or an adsorption of sulfate ions on the MK particles, which affects the point in time of the aluminate reaction. Due to the very low aluminum solubility of MM and MI and lower surface charges [3], the acceleration of the aluminate reaction is reduced. Thus, 2:1 phyllosilicates show significant differences to 1:1 phyllosilicates.

Table 1 provides the heat of hydration up to the onset of the aluminate reaction. Since the systems SyCEM-MK(MI)(MM) and SyCEM-LL-MK(MI)(MM) have the same sulfation (SO₃ content: 1.54 and 1.35 wt.%, respectively), the theory of adsorption of sulfate on C-S-H [1] requires comparable values of the heat of hydration. Thus, the differences shown here indicate further effects besides the filler effect and cannot be ascribed to adsorption on C-S-H alone. Effects like adsorption of ions from the pore solution on the negatively charged surface (zeta potential) of the clay particles [2], the chemical contribution (especially in the case of MK) [3], as well as physical parameters such as water absorption [5,7] must be taken into account.

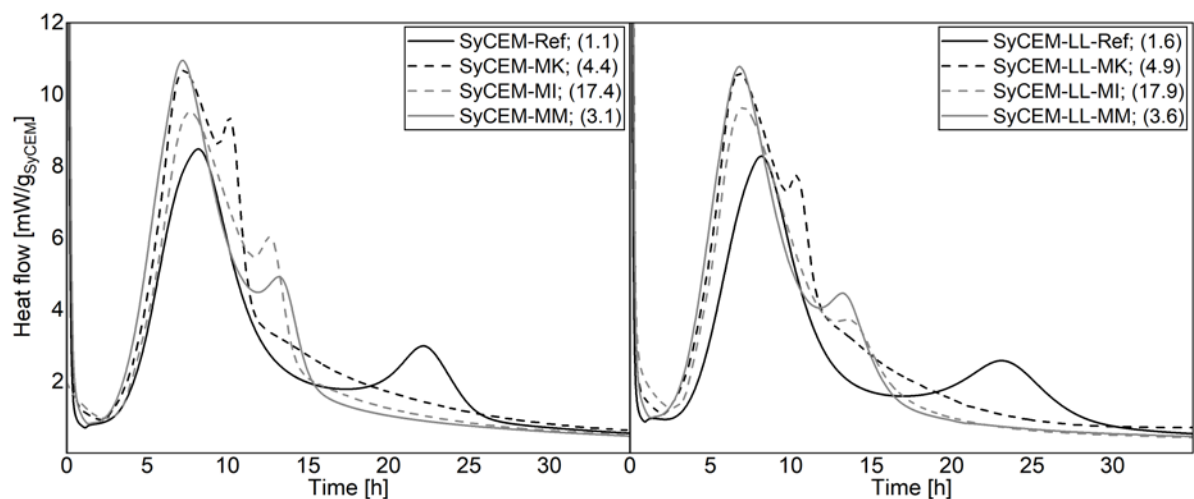


Figure 1 Heat flow up to 35 h of the SyCEM systems without (left) and with LL (right). The number in brackets shows the total surface area [$\text{m}^2 \text{g}^{-1}$] of the corresponding system

Table 1 Hydration heat [J g^{-1}] from the minimum of the dormant period until the onset of aluminate reaction (identification according to [1]) and the point in time at maximum aluminate reaction [h] in brackets

	Ref	MK	MI	MM
SyCEM	136.7 (22.2)	132.4 (10.1)	126.5 (12.6)	145.5 (13.2)
SyCEM-LL	131.1 (23.1)	142.0 (10.3)	128.6 (13.5)	144.5 (13.2)

4. Conclusion

In absence of the possibility to present related interesting in situ XRD and TG results, the statements have to be limited to general considerations. The silicate reaction is comparably accelerated for all calcined phyllosilicate systems. In addition to the adsorption of sulfate onto C-S-H, other factors influence the point in time of the aluminate reaction. Significant deviations occur between calcined 1:1 and 2:1 phyllosilicates due to their different physical and chemical properties.

5. References

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