

ORIGINAL ARTICLE



Sulfate consumption during the hydration of Alite and its influence by SCMs

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Abstract

SCMs with a large specific surface area, such as calcined clays or fine limestone powder, can significantly accelerate the occurrence of the aluminate heat flow peak during the early hydration of blended cements. These systems therefore require a higher amount of sulfate. While this effect has been drawn back to the sulfate incorporation into C-S-H, which is formed more rapidly due to the filler effect, it has been recently shown that in systems with high amounts of metakaolin, the sulfate balance is influenced by further mechanisms. This study provides new results on the influence of aluminum-rich and aluminum-free SCMs on the early hydration of alite in presence of calcium sulfate. A synthesized alite was blended with 5 wt% of anhydrite and its hydration was investigated by isothermal calorimetry and in-situ XRD at a w/b ratio of 0.5. It was shown that the formed C-S-H is able to take up the calcium and sulfate ions, indicated by a depletion of the solid anhydrite after approximately 20 hours. This process is significantly accelerated by incorporating 30 wt% of a fine limestone filler. The addition of metakaolin leads to an acceleration of the alite hydration compared to the reference as well, but to a significantly lower extend compared to the limestone. However, this system requires a lower degree of alite reaction to reach sulfate depletion. This indicates that in metakaolin-rich systems, the sulfate demand is influenced by further effects. The results from in-situ-XRD reveal that significant ettringite formation is taking place in the metakaolin-blended system already during the first hours of hydration. Correlations between the degree of alite hydration and the rate of sulfate depletion provide new insights into the mechanisms affecting the sulfate balance and early hydration of blended cements.

Keywords

Alite, Sulfate, C-S-H, SCM, Metakaolin, early hydration, in-situ-XRD, calorimetry

1 Introduction

Calcium sulfate, either present as gypsum, bassanite, anhydrite or a combination of the three, plays a paramount role in cement chemistry. Its use as setting regulator allows the adjustment of a sufficiently long workability of concrete. While its retarding effect on the C₃A hydration (aluminate reaction) has formerly been drawn back to a physical barrier formed by an ettringite layer that hinders diffusion, today most researchers regard surface chemical effects as the dominating mechanism [1, 2]. The effects of calcium sulfate on the aluminate reaction have been extensively investigated since the landmark paper of Lerch [3], however, interaction of sulfate ions with C-S-H only came into focus of research during the past decade [4–7]. Recent investigations have shown that the hydration rate of C₃S is enhanced significantly in the presence of calcium sulfate as well, independent of the availability of aluminum

[8, 9]. In addition, the morphology changes from agglomerated in absence, to needle like C-S-H in presence of sulfate [4, 6]. The C-S-H formed before the aluminate reaction in hydrating cement was observed to take up significant amounts of sulfate [4–6, 10, 11] and thereby influencing the point of depletion of the solid sulfate carrier [7]. This was considered as the main reason for the accelerated aluminate reaction in blended cements, where C-S-H formation is accelerated due to the filler effect, resulting in the adsorption of more sulfate [12]. The incorporation is assumed to be a reversible coupled adsorption mechanism of Ca²⁺ and SO₄²⁻ complexes, which are desorbed after the depletion of the solid sulfate carrier [4, 5, 13]. Mota et al. [4] were only able to measure SO₄ uptake after 7 and 28 days by EDX as the degree of hydration was not high enough at earlier ages, while Berodier et al. [6] proved sulfate uptake after three days. Quennoz and Scrivener [5] demonstrated in model cements that the S/Ca ratio is about twice as high between the silicate and

aluminate peak (18 h) than that after 72 h. Similar observations were made by Gallucci et al. [14] during the hydration of a CEM I. Data obtained by Jansen et al. [15] resulting from a complete mass balance approach proved that all sulfate precipitated as ettringite after sulfate depletion. Matschei et al. [16] measured a relatively low sulfate binding capacity of below 0.15 mmol SO_4^{2-} per g of dried C-S-H and pointed out the condition of the sulfate in the C-S-H (in other words the binding mechanism) is unclear, as most data stems from electron beam analysis. As cements become more complex due to the increasing and versatile use of supplementary cementitious materials (SCMs), possible interaction of sulfate ions with the SCMs need to be considered as well. This applies in particular for calcined clays, which can strongly interact with ions from the pore solution due to their high specific surface area (SSA) and negative surface charge [17, 18]. It is indicated, that adsorption of calcium and sulfate ions can occur directly onto the SCM's surface, leading to an even increased acceleration, a higher sulfate demand and a sharper sulfate depletion peak, compared to pure filler effect [19–21]. Furthermore, a pronounced ettringite formation could be observed in clinker free model systems containing metakaolin [21]. In the light of an increasing use of blended cements, especially with calcined clay and limestone (LC^3), the understanding of the interaction of sulfate ions from the pore solution and the SCMs and C-S-H needs to be improved. The objective of this study is to further clarify the impact of possible hosts for sulfate during the dissolution of the solid sulfate carrier in blended cement. In addition, a possible retarding effect on the alite hydration due to an early depletion of the sulfate carrier should be elaborated. These issues are tackled using a reduced cementitious model system consisting of monoclinic alite blended with anhydrite and different types of SCMs, which is investigated during early hydration by isothermal calorimetry and in-situ-XRD.

2 Materials and Methods

Monoclinic alite was synthesized by sintering CaCO_3 , SiO_2 , MgO and Al_2O_3 in the stoichiometric balanced ratio to achieve a chemical composition of 71.7 wt% CaO , 25.9 wt% SiO_2 , 1.8 wt% MgO and 0.6 wt% Al_2O_3 . Magnesium and aluminum were added to obtain the M3 polymorph. The homogenized powders were calcined for 16 h at 1000 °C and sintered several times for 5–6 h at 1400 °C in a laboratory muffle furnace with intermediate grinding and homogenization. The final product was ground to the required fineness in an agate tool. Phase purity was checked by powder XRD. Anhydrite (C\$) was retrieved by dehydration of gypsum for 16 h at 380 °C. XRD analysis revealed a composition of 87.4 wt% Anhydrite II, 8.9 wt% Bassanite and 3.7 wt% Anhydrite III. Three different SCMs were chosen for investigation: a metakaolin (MK) with a purity of 93 wt% [21], a limestone (LS) containing 100 wt% calcite [19] and ground granulated blast furnace slag (BFS) with an amorphous content of 96.5 wt%, designated as S1 in [22]. The chemical composition as well as the physical parameters are given in Table 1. The hydration of the systems was investigated using pastes with a water-to-binder ration of 0.5. The mix design is provided in table 2. The heat flow was measured during the first 36 hours of hydration in a TAM Air isothermal calorimeter at 25 °C. Data was processed and evaluated as described in [19].

Phase development was monitored by in-situ-XRD measurements in a PANalytical Empyrean diffractometer equipped with a cooling stage to adjust the sample temperatures to 25 °C as well. The sample was covered with a 12 μm Kapton film to prevent drying and carbonization. Time dependent quantitative phase analysis was carried out as described in [20], using Profex-BGMN [23].

Table 1 Chemical composition and specific surface area (SSA) measured by BET of the investigated materials

	Alite	MK	LS	BFS
SiO_2	25.9	5	-	35.7
Al_2O_3	0.6	3.5	-	11.9
Fe_2O_3	-	3.5	-	0.8
CaO	71.7	3.5	55.5	41.4
MgO	1.8	7	0.4	7.5
SO_3	-	7	-	1.4
Na_2O	-	-	-	0.3
K_2O	-	-	-	0.3
TiO_2	-	-	-	0.5
LOI	-	-	44.1	< 0.1
SSA [m^2/g]	0.6	14.1	5.2	1.2

Table 2 Mix Design

Mix	Alite [wt%]	C\$ [wt%]	SCM [wt%]
Alite 5C\$	95	5	-
Alite 30LS	70	-	30
Alite 30MK	70	-	30
Alite 5C\$ 30LS	66.5	3.5	30
Alite 5C\$ 30MK	66.5	3.5	30
Alite 5C\$ 30BFS	66.5	3.5	30
Alite 10C\$ 30LS	63	7	30
Alite 10C\$ 30MK	63	7	30

3 Results and Discussion

3.1 Influence of SCMs on the heat flow curves of alite-C\$ systems

The hydration of alite in presence of 5 wt% C\$ starts after an induction period of approx. 5 h and shows a heat flow maximum at 13 h (Figure 1). All three investigated SCMs induce an acceleration of the alite hydration, but this is not directly coupled to their specific surface area. The LS generates the strongest acceleration and enhancement of the

reaction. The heat flow maximum is accelerated by 6.4 h. The BFS only induces a minor acceleration of the alite reaction of 2.8 h. In the MK-blended system, the alite heat flow peak is accelerated by 4.2 h and enhanced significantly. Beyond that, a clear shoulder appears, which indicates a second reaction taking place.

The stronger impact of LS on the silicate reaction compared to MK, despite of the lower SSA, was already observed in [19] and attributed to the preferred surface of LS regarding C-S-H precipitation on the one hand, and the stronger agglomeration of MK particles, which reduces their filler capacity, on the other. The higher heat flow in the BFS- and MK-blended systems after the main peak indicates a chemical contribution from the SCM, despite a lower DoH of Alite.

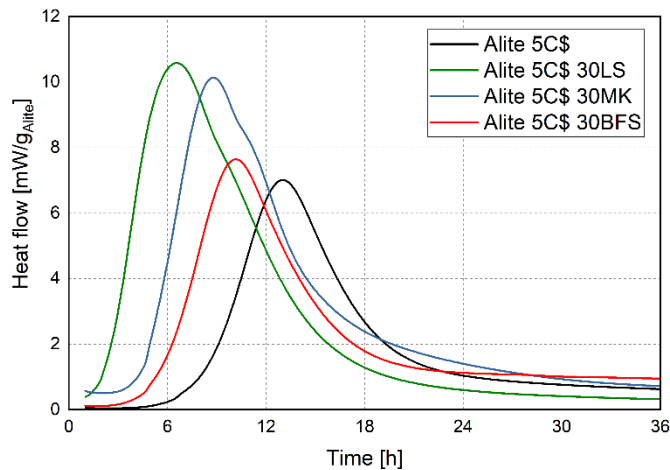


Figure 1 Heat flow curves of the reference system Alite 5C\$ blended with 30 wt% of SCMs during the first 36 hours of hydration

3.2 Influence of alite dissolution and sulfate consumption by the different SCMs

The sulfate consumption during the hydration of Alite 5C\$ proceeds with the dissolution of alite (Figure 2), which indicates the incorporation of Ca^{2+} and SO_4^{2-} into C-S-H, as already described by several authors [4–7, 9, 11]. The anhydrite is depleted after 25 h. At this point, the degree of alite hydration is at 39.7 %, which is equivalent to the formation of 22.3 wt% C-S-H, assuming a composition of $\text{C}_{1.7}\text{SH}_{2.6}$. The formed C-S-H can thus incorporate approx. 13 wt% C\$, which corresponds to a sulfur/calcium ratio of 0.07, being slightly higher than the values given in literature for $\text{C}_3\text{S}/\text{C}_3\text{A}$ systems or blended OPC measured by SEM/EDS (0.04–0.06 [7]). The correlation between the time of depletion of anhydrite and the heat of hydration or degree of alite hydration up to this point reveal the different mechanisms of sulfate consumption in the systems investigated. A higher heat of hydration comes along with a higher degree of alite hydration. In the reference system (Alite 5% C\$), 39.7 wt% of the alite must be dissolved, until anhydrite is depleted. Nearly the same degree of hydration (DoH) is reached in the system with LS (37.3% DoH, 15.4 wt% C-S-H). This indicates that the sulfate adsorption mechanism is nearly unaffected in the presence of limestone, leading to the same sulfur/calcium ratio of 0.07. The major effect causing the accelerated sulfate consumption in this system is the strong acceleration of alite hydration due to the pronounced filler effect of limestone.

This mechanism has been well described in [12]. In contrast, the system with MK and 5 wt% C\$ only requires a DoH of 27.4% to deplete the solid anhydrite, verifying that further mechanisms accelerate sulfate consumption. This is in line with previous investigation in blended OPC systems, where sulfate depletion was reached at a lower degree of alite hydration in metakaolin-rich systems [19]. However, while in the real cementitious systems, a higher metakaolin content did not induce a higher ettringite content at the point of sulfate depletion, the alite systems with MK and C\$ investigated here form ettringite right after mixing. It is quite remarkable that this reaction starts before the acceleration period, where the first portlandite precipitates. This proves that the initially dissolved calcium and the rather moderate alkalinity are sufficient to dissolve aluminum from the MK and form up to 2 wt% of ettringite. This value stagnates until alite dissolution starts after 5 h and provides portlandite as reaction partner, which indicates a lack of calcium in pore solution during the first hours. These results are in line with studies of a clinker-free MK system [21], where sufficient portlandite as a reaction partner leads to continuous ettringite formation. The ettringite content at the point of sulfate depletion (10.0 h) in the system Alite 5% C\$ MK is approx. 3.0 wt% (considering a slight overestimation of ettringite), which corresponds to 1.0 wt% C\$. The remaining 1.4 wt% of dissolved sulfate can be explained by adsorption on the C-S-H surfaces, considering the sulfur/calcium ratio derived from the reference system. In comparison to OPC systems, where early ettringite formation can be fully explained by the initially dissolved C_3A , the adsorption of sulfate on the MK surfaces seems to play a minor role. The absence of initial C_3A dissolution could also indicate a lack of calcium availability, which might affect the adsorption behaviour on the negatively charged surfaces of the MK particles as well as the ettringite formation. The fact that there is no significant additional ettringite formation in MK-rich blended OPC systems [19, 24], despite the potential of MK of contributing significantly to ettringite formation before acceleration period and sulfate depletion as shown here, needs further exploration.

The incorporation of 30 wt% BFS to the Alite-5C\$ system only results in a minor change compared to the reference system. The course of the alite quantification differs mainly in an earlier onset when using BFS. This is due to the higher SSA of the BFS compared to alite. After 36 hours, the DoH of the alite is higher compared to the reference but significantly lower compared to the other blended systems. The formation of ettringite starts only after about 12 hours due to the lower reactivity compared to MK. At this time, the main reaction of the alite already subsides (Figure 1), so that no interaction with the alite hydration can be detected. The fact that ettringite continues to precipitate after sulfate depletion in the MK- and BFS-blended systems confirms that sulfate gets desorbed from the C-S-H afterwards and is available for ettringite formation [12].

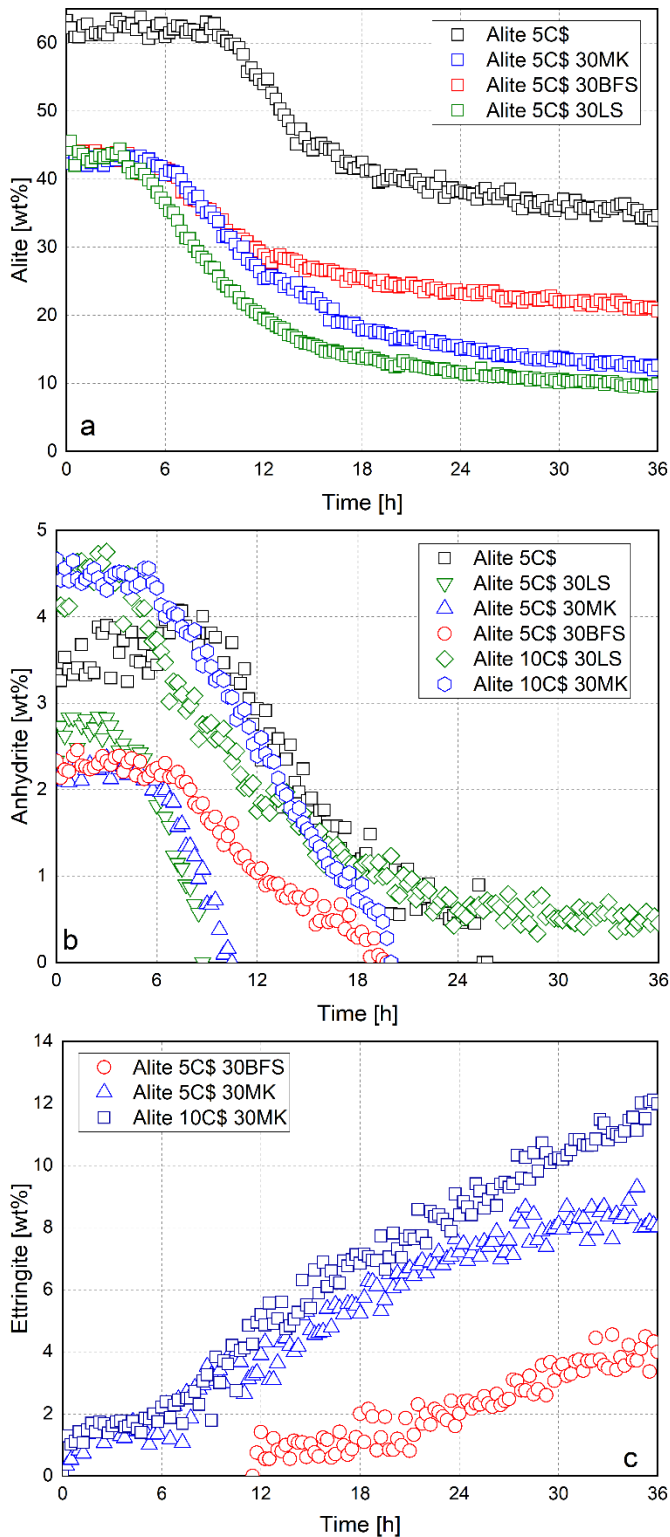


Figure 2 Phase development during the first 36 hours of hydration; a) alite, b) anhydrite and c) ettringite.

Table 2 Evolved heat and degree of Alite hydration until the point of sulfate depletion for the investigated systems

System	Time of sulfate depletion [h]	Heat until sulfate depletion [J/g]	DoH _{alite} at sulfate depletion [%]	DoH _{alite} after 36h [%]
Alite 5C\$	25.0	206	39.7	43.6
Alite 5C\$ 30LS	8.75	187	37.3	77.4
Alite 5C\$ 30MK	10.0	145	27.4	70.8
Alite 5C\$ 30BFS	19.5	213	43.7	51.8
Alite 10C\$ 30MK	20.0	298	48.9	58.6
Alite 10C\$ 30LS	>36.0	349*	-	71.4

*)after 36 h, as anhydrite is not depleted before 36 h

3.3 Influence of C\$-content on the hydration rate of blended alite systems

The impact of the C\$-content on the hydration rate was investigated for the LS- and MK-blended system (Figure 3). In absence of C\$, the reaction rate is lower in both systems. This is well known from experiments in pure C₃S systems in presence and absence of C\$ and attributed to a change in the growth mechanism of C-S-H and a higher nucleation density [8]. Apparently, the hydration in the system Alite 30MK seems to be more suppressed compared to Alite 30LS. This can partly be drawn back to the heat flow attributed to the ettringite formation in the 5C\$ system. The broader alite peak is due to the higher aluminum content in the pore solution. This underlines once more the importance of proper sulfation of calcined clay blended cements. However, an additional increase in C\$ content does not further enhance alite hydration. This proves, that presence of sulfate is only important during acceleration period, as in the two 5C\$ systems sulfate is already depleted during the main hydration peak. The results from the systems with 10 wt% C\$ based on the alite content confirm furthermore, that the sulfate content of the C-S-H at sulfate depletion represents the maximum possible value. In the system Alite 10C\$ 30MK, the calculated sulfate/calcium ratio is identical to the system with 5C\$. In the system Alite 10C\$ 30LS there seems to be too little C-S-H to dissolve all of the anhydrite. After 36 h, there are still approx. 0.5 wt% anhydrite present (Figure 2b). Considering the calculated C-S-H content of 26.6 wt% after 36 h leads to a possible incorporation of 13.5 wt% C\$, which is almost similar to the value retrieved after sulfate depletion in the 5C\$ system.

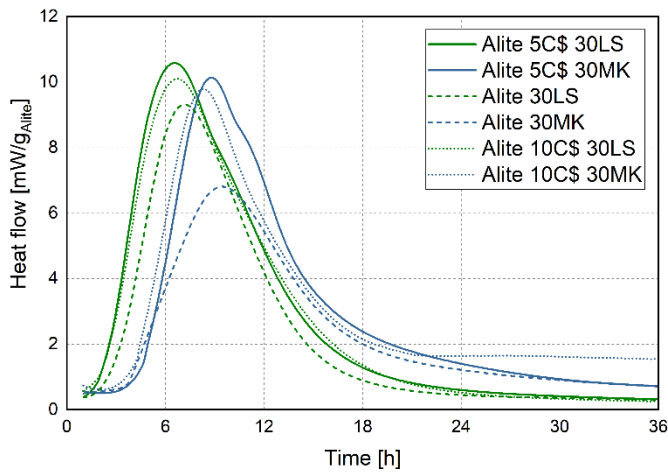


Figure 3 Influence of C\$ content on the course of the heat flow of the systems with MK and LS.

The comparison of the cumulative heat after 36 hours shows hardly any differences between the sulfate-free alite 30LS and 30MK systems (Figure 4). The significantly higher filler effect of the LS during the first hours of alite hydration is compensated for in the MK system up to 36 h. The addition of C\$ in these systems causes an additional acceleration of the alite hydration. While the LS systems show only a slight heat evolution after the main reaction of the Alite has completed, the MK systems continue to exhibit a significant heat evolution. This can be explained by the reactivity of the MK and the resulting continuous ettringite formation. After about 25 h, this yields a higher cumulative heat in the MK compared to the LS systems. A further increase in heat evolution can also be observed for the BFS system due to its reactivity after the alite hydration has subsided.

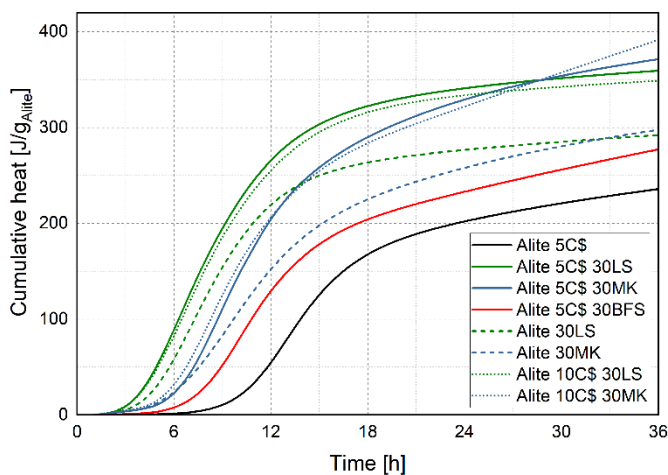


Figure 4 Cumulative heat for all systems investigated during the first 36 hours of hydration.

4 Conclusion

The presented results reveal significant differences regarding the influence of sulfate consumption during early hydration of alite between the three investigated SCMs, namely limestone, metakaolin and blast furnace slag and therefore further contribute to the understanding of the sulfate balance of blended cements. The following conclusions can be drawn:

1. The C-S-H precipitated during the hydration of alite-C\$ systems can take up approx. 13 wt% of C\$ which is equivalent to a sulfur/calcium ratio of 0.07.
2. Limestone acts as the strongest filler and therefore accelerates the alite hydration, and thus sulfate uptake by C-S-H the most.
3. Metakaolin reacts significantly faster than blast furnace slag and contributes to ettringite formation right from the beginning of hydration before precipitation of portlandite. This proves that metakaolin-rich calcined clays are potentially able to contribute to hydrate phase formation and thus sulfate consumption before the acceleration period. In the system investigated, this effect makes up 42% with regards to sulfate depletion.
4. The lower degree of alite hydration in the system with metakaolin is in line with results by the authors derived from blended OPC systems. However, in latter systems no contribution of the metakaolin to ettringite formation before sulfate depletion could be evidenced. This fact requires further elaboration in future studies.
5. The positive impact of sulfate on the alite hydration is only present during acceleration period. Afterwards, no significant effect is detectable.

References

- [1] Myers, R. J.; Geng, G.; Li, J. et al. (2017) *Role of Adsorption Phenomena in Cubic Tricalcium Aluminate Dissolution*. *Langmuir* 33(1), pp. 45–55. doi: 10.1021/acs.langmuir.6b03474.s001
- [2] Liu, X.; Feng, P.; Lyu, C. et al. (2020) *The role of sulfate ions in tricalcium aluminate hydration - New insights*. *Cement and Concrete Research* 130, p. 105973. doi: 10.1016/j.cemconres.2020.105973
- [3] Lerch, W. (1946) *The Influence of Gypsum on the Hydration and Properties of Portland Cement Pastes*. *Proceedings of the American Society for Testing and Materials* (46), pp. 1252–1291.
- [4] Mota, B.; Matschei, T.; Scrivener, K. (2015) *The influence of sodium salts and gypsum on alite hydration*. *Cement and Concrete Research* 75, pp. 53–65. doi: 10.1016/j.cemconres.2015.04.015
- [5] Quennoz, A.; Scrivener, K. L. (2013) *Interactions between alite and C3A-gypsum hydrations in model cements*. *Cement and Concrete Research* 44, pp. 46–54. doi: 10.1016/j.cemconres.2012.10.018
- [6] Bédodier, E. M.; Muller, A.C.; Scrivener, K. L. (2020) *Effect of sulfate on C-S-H at early age*. *Cement and Concrete Research* 138, p. 106248. doi: 10.1016/j.cemconres.2020.106248
- [7] Zunino, F.; Scrivener, K. (2020) *Factors influencing the sulfate balance in pure phase C3S/C3A systems*. *Cement and Concrete Research* 133, p. 106085. doi: 10.1016/j.cemconres.2020.106085

- [8] Zunino, F.; Scrivener, K. (2022) *The influence of sulfate addition on hydration kinetics and C-S-H morphology of C3S and C3S/C3A systems*. Cement and Concrete Research 160, p. 106930. doi: 10.1016/j.cemconres.2022.106930
- [9] Andrade Neto, J. S.; Rodríguez, E. D.; Monteiro, P. J. et al. (2022) *Hydration of C3S and Al-doped C3S in the presence of gypsum*. Cement and Concrete Research 152, p. 106686. doi: 10.1016/j.cemconres.2021.106686
- [10] Nachbaur, L.; Nkinamubanzi, P.-C.; Nonat, A. et al. (1998) *Electrokinetic Properties which Control the Coagulation of Silicate Cement Suspensions during Early Age Hydration*. Journal of colloid and interface science 202(2), pp. 261–268. doi: 10.1006/jcis.1998.5445
- [11] Valentini, L.; Dalconi, M. C.; Favero, M. et al. (2015) *In-Situ XRD Measurement and Quantitative Analysis of Hydrating Cement - Implications for Sulfate Incorporation in C-S-H*. J Am Ceram Soc 98(4), pp. 1259–1264. doi: 10.1111/jace.13401
- [12] Zunino, F.; Scrivener, K. (2019) *The influence of the filler effect on the sulfate requirement of blended cements*. Cement and Concrete Research 126, p. 105918. doi: 10.1016/j.cemconres.2019.105918
- [13] Barbarulo, R. (2003) *Experimental study and modeling of sulfate sorption on calcium silicate hydrates*.
- [14] Gallucci, E.; Mathur, P.; Scrivener, K. (2010) *Microstructural development of early age hydration shells around cement grains*. Cement and Concrete Research 40(1), pp. 4–13. doi: 10.1016/j.cemconres.2009.09.015
- [15] Jansen, D.; Naber, C.; Ectors, D. et al. (2018) *The early hydration of OPC investigated by in-situ XRD, heat flow calorimetry, pore water analysis and 1H NMR - Learning about adsorbed ions from a complete mass balance approach*. Cement and Concrete Research 109, pp. 230–242. doi: 10.1016/j.cemconres.2018.04.017
- [16] Matschei, T.; Skapa, R.; Lothenbach, B. et al. (2007) *The distribution of sulfate in hydrated Portland cement paste*. 12th international congress on the chemistry of cement, p. 14.
- [17] Sposito, R.; Maier, M.; Beuntner, N. et al. (2021) *Evaluation of zeta potential of calcined clays and time-dependent flowability of blended cements with customized polycarboxylate-based superplasticizers*. Construction and Building Materials 308, p. 125061. doi: 10.1016/j.conbuildmat.2021.125061
- [18] Schmid, M.; Plank, J. (2021) *Interaction of individual meta clays with polycarboxylate (PCE) superplasticizers in cement investigated via dispersion, zeta potential and sorption measurements*. Applied Clay Science 207, p. 106092. doi: 10.1016/j.clay.2021.106092
- [19] Maier, M.; Sposito, R.; Beuntner, N. et al. (2022) *Particle characteristics of calcined clays and limestone and their impact on early hydration and sulfate demand of blended cement*. Cement and Concrete Research 154, p. 106736. doi: 10.1016/j.cemconres.2022.106736
- [20] Maier, M.; Scherb, S.; Neißer-Deiters, A.; Beuntner, N.; Thienel, K.-C. (2021) *Hydration of cubic tricalcium aluminate in the presence of calcined clays*
- [21] Scherb, S.; Maier, M.; Beuntner, N. et al. (2021) *Reaction kinetics during early hydration of calcined phyllosilicates in clinker-free model systems*. Cement and Concrete Research 143, p. 106382. doi: 10.1016/j.cemconres.2021.106382
- [22] Li, X.; Snellings, R.; Antoni, M. et al. (2018) *Reactivity tests for supplementary cementitious materials - RILEM TC 267-TRM phase 1*. Mater Struct 51(6), pp. 1–14. doi: 10.1617/s11527-018-1269-x
- [23] Doebelin, N.; Kleeberg, R. Profex: a graphical user interface for the Rietveld refinement program BGMN
- [24] Zunino, F.; Scrivener, K. (2022) *Insights on the role of alumina content and the filler effect on the sulfate requirement of PC and blended cements*. Cement and Concrete Research 160, p. 106929. doi: 10.1016/j.cemconres.2022.106929