

CHANGE OF PROPERTIES AND HYDRATION KINETICS OF CA AND CA₂ BY PROLONGED MILLING

Florian Hueller¹, Dominique Ectors¹, Juergen Neubauer¹, Stefan Kuiper², Friedlinde Goetz-Neunhoeffler¹
¹University of Erlangen-Nuernberg, Erlangen, Germany, ²Almatis B.V., Botlek-Rotterdam, Netherlands

ABSTRACT

High alumina refractory cements usually contain CA (CaAl₂O₄) as main hydraulic phase besides the more refractory but less reactive CA₂ (CaAl₄O₇). In this study the influence of prolonged milling on the microstructural properties and hydration kinetics of lab synthesized CA and CA₂ was investigated. The amount of X-Ray amorphous phase was determined by powder X-Ray diffraction (XRD). The specific surface area was determined using the BET method. Both, CA and CA₂, showed an increase in the BET surface area and in the amount of X-Ray amorphous phase although CA₂ turned out to be more susceptible to milling compared to CA.

Highly time resolved in-situ XRD and in-situ ¹H Time Domain Nuclear Magnetic Resonance spectroscopy (TD-NMR) were applied for studying the dissolution of CA or CA₂ as well as the precipitation of hydrate phases. The corresponding hydration kinetics were investigated by heat flow calorimetry. The hydration kinetics of CA did not significantly change in dependence on the milling time although the hydration reaction of finer CA started later in comparison with coarser CA. A clear acceleration and intensification of the hydration with increasing milling time, however, was observed for CA₂. Additionally, a separated heat flow event occurred only in intensively milled CA₂ samples which can be attributed to the hydration of X-Ray amorphous CA₂.

INTRODUCTION

The influence of particle fineness on the hydration behaviour of cement phases with the intention to improve the hydraulic properties was subject of some studies in the past. Klaus et al. [1] were able to increase the hydration degree of CA (the amount of reacted CA after a certain time – to be more precise) by using finer samples. With increasing fineness, however, the start of the CA main hydration period was shifted to later times which is somewhat surprising. A very reactive CA₂ with a BET surface area of 4 m²/g can be obtained by a special preparation method developed by Song et al. [2]. This method called hydration-burning-method is based on multiple calcination, hydration and sintering of a mixture according to the composition of CA₂. Banawalikar et al. [3] also observed a clear acceleration of the setting and higher strength with increasing specific surface area of CA₂.

An opposite effect can be reached by thermal treatment of CA₂. Moehmel et al. [4] performed a thermal treatment of CA and CA₂ and mixtures of them at 750 °C for 2h. The already low hydraulic potential of CA₂ was lowered in such a degree that it behaved almost inertly after the tempering. The authors were not able to explain this observation but assumed a recovery of lattice defects in CA₂ during thermal treatment to be the cause for the decreased hydraulic activity. Gessner et al. [5] confirmed the effect of a decreased CA₂ reactivity after thermal treatment at 500 °C for 24 h. The heat flow of the thermally treated sample was significantly lower in comparison with the untreated sample and a sharp peak which occurred in the untreated sample prior to the main hydration disappeared after the tempering.

A pronounced heat flow peak prior to the CA₂ main reaction was also observed by Goetz-Neunhoeffler et al. [6]. According to them the typical CA₂ hydration is starting immediately after water addition, although with a very low hydration rate. The heat flow event prior to the broad CA₂ main hydration period was suggested

to result from an impurity of CA in the sample which is below the detection limit for XRD. Dissolution of CA₂ during the period of the sharp heat flow peak was not detected by means of in-situ XRD which finally led to a discrepancy between the calculated heat flow from XRD data and the measured heat flow by calorimetry.

MATERIAL AND METHODS

Synthesis and preparation of CA and CA₂

Both CA and CA₂ were synthesized by solid state reaction in platinum crucibles in air in a chamber furnace (temperature accuracy ± 30 °C) starting from ultrapure CaCO₃ and Al₂O₃. The starting materials were homogenized by several short milling steps in a vibratory disc mill (VDM) equipped with agate tool (Retsch, 100 ml). With the purpose to obtain CA₂ samples without any trace of CA the final composition was aimed at 99 wt% CA₂ and 1 wt% CA₆ whereas for CA a mixture with a molar ratio of 1:1 (CaO:Al₂O₃) was prepared. The powdery raw mixtures were calcined for 17 h at 1000 °C for complete emission of CO₂. In the next step the calcined mixtures (each batch 40 g) were homogenized again in the VDM and sintered 2 times at 1400 °C for 4 h in the case of CA and 1 time at 1450 °C for 4 h and a second time at 1500 °C for 5 h in the case of CA₂. After each sintering step the products were finely milled for getting small particles and homogeneous products free from undesired impurities. The final synthesis products were milled to a maximum particle size of ~ 63 µm, checked by powder XRD for purity and subsequently further milled. For generating very fine samples with major amounts of amorphous phase some samples (each 15 g) were milled for 240, 600 and 1200 min in steps of 120 min in a planetary ball mill (PBM) in 125 ml jars together with 175 g Y:ZrO₂ balls (1.25 mm) and 40 ml ethanol. After removing the alcohol and grinding balls the samples were additionally dried for a total time of 5 d at 50 °C in a vacuum drying chamber (2000 Pa) which was flushed with N₂ once every 24 h. All samples are labelled according to their total milling time in minutes. Some of the samples were thermally treated for 17 h at 750 °C in air atmosphere which is indicated by “t.t.” as attachments after the sample labelling.

Determination of the specific surface areas (BET)

The measurements of the specific surface areas were carried out in a Gemini 2360 device (Micromeritics) by N₂ adsorption using the BET method. Prior to the measurements the samples were thermally treated in a He atmosphere (CA₂ at 150 °C and CA at 200 °C) for 3 h in order to clean the surface. A low temperature for surface conditioning was chosen to avoid the recovery of lattice defects. Later investigations, however, revealed that higher surface areas could have been determined after a conditioning procedure at 300 °C for 30 min. The measurements were performed at the boiling point of liquid N₂.

Determination of X-ray amorphous fractions

All samples were prepared by the front loading method for powder XRD analyses using CuKα radiation at a Bruker D8 diffractometer equipped with a LynxEye detector. The generator settings were 40mA/40kV. The obtained diffractograms were evaluated with the

Rietveld method in combination with the G-factor method which is based on an external standard [7,8] which allows the quantification of single crystalline phases besides amorphous phases. All calculated amounts of crystalline CA or CA₂ in the samples were normalized to the amount of crystalline CA or CA₂ in specially fabricated [9] calibration samples which are supposed to contain 100 wt% crystalline material with a very suitable grain size distribution for XRD.

Heat flow calorimetry, in-situ XRD and in-situ ¹H-TD-NMR

For the measurement of the exothermic reaction during the hydration of CA or CA₂ a TAM Air calorimeter equipped with InMixEr tools (mixing device for equilibration, water addition and paste mixing inside the calorimeter [see 10]) and an Erlanger calorimeter (custom made calorimeter based on a water-cooled aluminium block with 3 measurement cells and 1 reference cell placed on Peltier-elements) were used. Prior to the measurements the powder mixtures containing CA or CA₂ in combination with alumina filler (1.5 m²/g, Na₂O < 0.4 wt%) as well as the mixing water were equilibrated for at least 3 h at 23 ± 0.2 °C. The recording of data was always started at the time of water injection. The pastes were stirred for 1 minute.

A combination of highly time resolved XRD and ¹H-TD-NMR allowed us to correlate events observed by heat flow calorimetry with the dissolution or precipitation of both amorphous and crystalline mineral phases. During the TD-NMR measurements the T2 relaxation times of the protons which are contained in the paste are measured. The relaxation times of protons that are incorporated into crystalline phases are significantly shorter than those of the protons in the mixing water. For a detailed description of the in-situ TD-NMR and in-situ XRD analyses as well as experimental settings the reader is referred to the paper by Hueller et al. [9] and references therein. Both devices (Bruker D8 diffractometer and Bruker minispec mq20 TD-NMR device) were temperature controlled at 23 °C during the whole measurement time. For the XRD measurements the samples were prepared by frontloading and covered with a Kapton film which should avoid water evaporation as well as CO₂ input. The samples for TD-NMR were transferred into narrow glass tubes and covered with Teflon plugs.

RESULTS AND DISCUSSION

Influence of prolonged milling on X-Ray amorphous contents and BET surface areas of CA and CA₂

The BET surface areas as well as the amounts of X-Ray amorphous phase increased with longer milling times. From Tab. 1, however, it can be seen that – in comparison with CA – the destruction of CA₂ proceeds faster as indicated by higher values for X-Ray amorphous contents and BET surface areas after equal milling times. Since the X-Ray amorphous fractions were completely restored by the thermal treatment in each case we assume that the crystals are not fully destroyed but highly strained and defective with coherent scattering domain sizes which are too small to be detected by conventional XRD.

Influence of prolonged milling on CA₂ hydration kinetics

In Figs. 1a and 1b the heat flow curves of four CA₂ samples with increasing fineness are shown as measured by heat flow calorimetry at an Erlanger calorimeter in pastes containing 20 wt% CA₂ and 80 wt% alumina filler at a w/s ratio of 0.275 and 23 °C.

Tab. 1: X-Ray amorphous contents and BET surface areas of the investigated samples.

Sample	X-Ray amorphous content [wt%]	BET surface area [m ² /g]
CA-3	n.d.*	0.27 ± 0.05
CA-6	1.4 ± 0.1	0.47 ± 0.00
CA-21	1.6 ± 0.2	0.70 ± 0.01
CA-70	4.1 ± 0.5	0.83 ± 0.02
CA-106	4.5 ± 1.3	1.47 ± 0.01
CA-600	29.0 ± 0.6	7.65 ± 0.18
CA-1200	39.6 ± 3.5	9.65 ± 0.19
CA ₂ -8	3.5 ± 0.1	0.9 ± 0.05
CA ₂ -20	3.9 ± 0.3	1.1 ± 0.03
CA ₂ -20 t.t.	1.5 ± 0.4	1.0 ± 0.04
CA ₂ -55	6.2 ± 0.0	1.6 ± 0.09
CA ₂ -60	5.4 ± 0.6	1.6 ± 0.09
CA ₂ -60 t.t.	0.8 ± 0.3	1.3 ± 0.02
CA ₂ -240	18.2 ± 1.3	6.2 ± 0.02
CA ₂ -600	26.1 ± 1.0	9.6 ± 0.09
CA ₂ -600 t.t.	0 ± 0.0	7.8 ± 0.09
CA ₂ -1200	49.6 ± 2.8	13.2 ± 0.09

* Sample too coarse for XRD

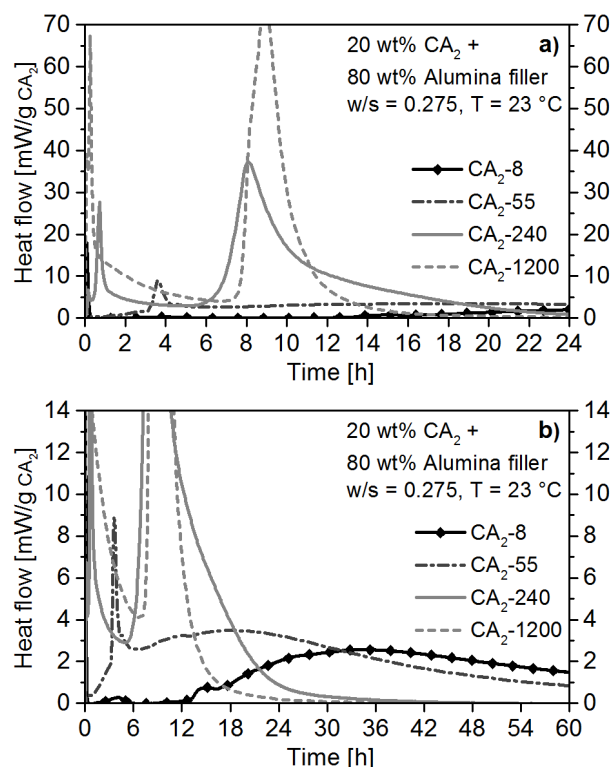


Fig. 1: a) Heat flow curves of CA₂-8, -55, -240 & -1200. b) Detail of the heat flow curves of CA₂-8 & -55 for a better illustration. Data recorded at an Erlanger calorimeter after external stirring.

All values are normalized to 1 g CA₂. In Fig. 1a the heat flows are shown for a hydration period of 24 h with a maximum of 70 mW/g, whereas in Fig. 1b the maximum values of the heat flow and time scales are adjusted in order to highlight the low heat flow curves of CA₂-8 and CA₂-55. The heat flow of CA₂-8 (see Fig. 1b) is very low over the entire period of 72 h. During the induction period the heat flow is temporarily negative. The main hydration period starts 12 h

after water addition and is not finished after 72 h. In our opinion the curve of CA₂-8 represents the hydration kinetics of a moderately milled CA₂ which was often described in literature. Sometimes, however, the main hydration starts immediately or quite soon after water addition with a heat flow feature (referred to as “preliminary heat flow event” in the following) which could not be explained so far [6]. This kind of hydration kinetics is shown by CA₂-55 (see Fig. 1b) or CA₂-60 (see Fig. 2a). It has to be mentioned that a low preliminary heat flow event already occurred in sample CA₂-20. This explains the apparently unpredictable occurrence of the preliminary heat flow event in hydrating CA₂ samples. Depending on the milling device, sample volume, milling time and sintering density of the used CA₂ the degree of mechanical activation varies between differently prepared powders. More intense milling as represented by CA₂-240 leads to a complete separation of the preliminary heat flow event from the main hydration period (see Fig. 1a). Furthermore, the main hydration period is considerably shortened, intensified and completed after 36 h. Sample CA₂-1200 represents an exceptional case with respect to the milling time. The corresponding preliminary heat flow event merges with the initial heat flow after mixing and the main hydration period is completed after 24 h (see Figs. 1a and 1b), which is most remarkable for CA₂.

Influence of thermal treatment on CA₂ hydration kinetics

In [5] and [6] the influence of thermal treatment on the CA₂ hydration was investigated and discussed. We were able to confirm and explain their findings and observed even more pronounced differences between thermally treated and untreated samples (see Figs. 2a and 2b). For our experiments we chose two fundamentally different CA₂ samples one milled for 60 min (Fig. 2a) and another milled for 600 min (Fig. 2b). In both cases the hydraulic activity was considerably lowered although the maximum heat flow of CA₂-600 t.t. was still significantly higher (~ 17 mW/g) in comparison with both CA₂-60 and CA₂-60 t.t. The preliminary heat flow event completely disappeared in both samples and a dormant period could be observed which lasted for 24 h in CA₂-60 t.t. The changes in hydration kinetics correlate well with a reduction of the BET surface areas and the X-Ray amorphous contents (see Tab. 1). A recovery of lattice defects which leads to a lower reactivity as proposed in [5] seems thus very likely to explain this.

In-situ investigations of a hydrating CA₂-60 paste

The sample CA₂-60 was chosen as representative sample for our in-situ experiments (XRD and NMR) because it contains an appropriate amount of X-Ray amorphous CA₂ and because it shows a significant preliminary heat flow event. The amount of CA₂ in the dry mix should be 40 wt% related to the solid material with the purpose to generate proper signals. The initial amount of crystalline CA₂ in the paste was therefore 27.1 wt% after subtraction of the amorphous content and CA₆ (see grey dashed line in Fig. 3). The analysed slight CA₂ increase during the first 4 h is an artefact caused by a water film on top of the samples below the Kapton film. Since the water film usually disappears by consumption of water with the beginning of the hydration reaction the first dissolution of crystalline CA₂ is detectable after 4 h. The heat flow, however, indicates a hydration reaction starting immediately after water addition. Firstly, the heat flow slowly increases until 2 h and then the preliminary heat flow event abruptly starts with its maximum after 2.5 h (see the vertical dotted line in Fig. 3). The only explanation for this heat flow is the dissolution of amorphous CA₂ before crystalline CA₂. Our theory is supported by the occurrence of crystalline bonded water at 2.5 h, detected by ¹H-TD-NMR (see vertical dotted line in Fig. 3).

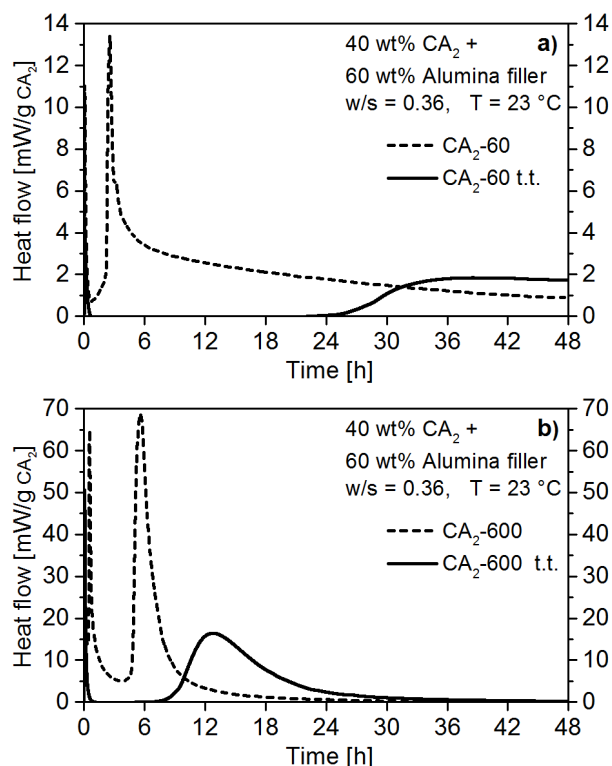


Fig. 2: a) Heat flow curves of CA₂-60 before (dashed line) and after (solid line) thermal treatment. b) Heat flow curves of CA₂-600 before (dashed line) and after (solid line) thermal treatment. Data recorded at a TAM Air calorimeter using internal stirring.

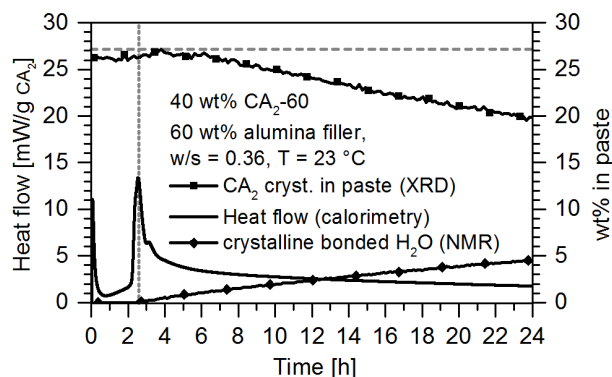


Fig. 3: Decrease of the amount of crystalline CA₂ in the paste as determined by in-situ XRD (the initial amount of 27.1 wt% is indicated by a grey dashed line), formation of hydrate phase as observed by in-situ ¹H-TD-NMR and heat flow of a hydrating paste of CA₂-60 at 23 °C. The time of the maximum heat flow as well as the starting time of hydrate phase formation is highlighted by a vertical dotted line at 2.5 h.

Influence of prolonged milling on CA hydration kinetics

In Fig. 4 the heat flow curves of CA-3 and CA-70 are shown. The BET surface area of CA-3 is very low (0.27 m²/g) and also the amount of an X-Ray amorphous fraction is supposed to be quite low. Due to coarse particles in the sample the quality of the diffractograms is not good enough for quantitative XRD analysis. The main hydration period of the coarse sample CA-3 is starting 6 h earlier in comparison to CA-70 which is in excellent accordance with data published by Klaus et al. [1]. The reason for the retardation is still unclear. The heats of hydration (see Fig 5)

indicate a higher hydration degree of the fine sample after 30 h which was also described by [1].

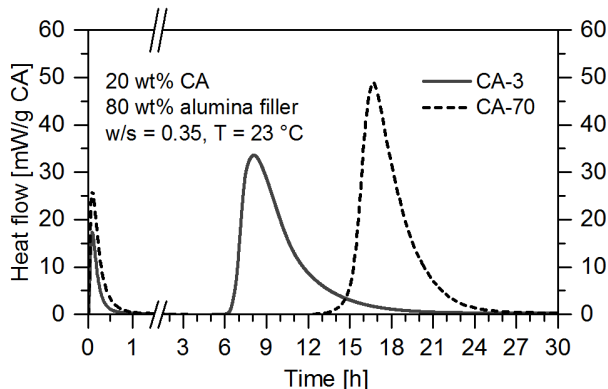


Fig. 4: Heat flow curves of CA-3 and -70.

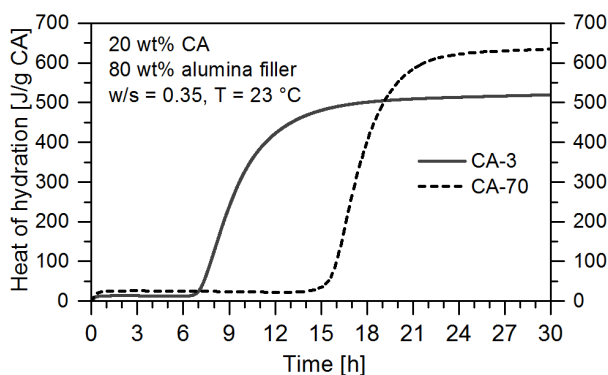


Fig. 5: Development of the heat of hydration of CA-3 and -70.

The very fine samples CA-600 and CA-1200 which contain major amounts of amorphous phase showed a hydration behaviour similar to the less intensively milled samples (see Fig. 6). However, the reproducibility of heat flow was quite unsatisfactory. This might be a result of a too low amount of filler in the paste. The main difference with regard to coarser CA samples are significantly higher initial heat flows as well as a continuous heat flow during the whole induction period (see Figs. 6 and 7). The total heat of hydration after 30 h considerably increased in the very fine samples indicating a higher hydration degree. This is in good agreement with the results by [1].

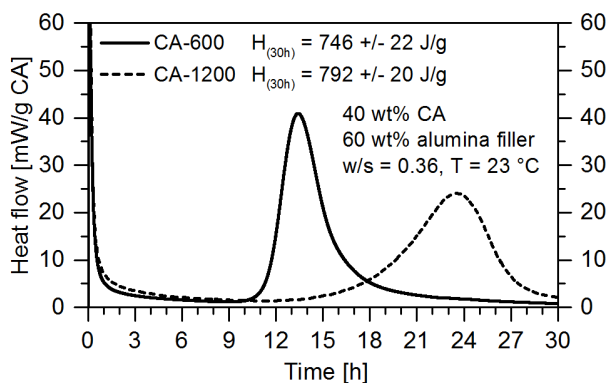


Fig. 6: Heat flow curves of CA-600 and -1200.

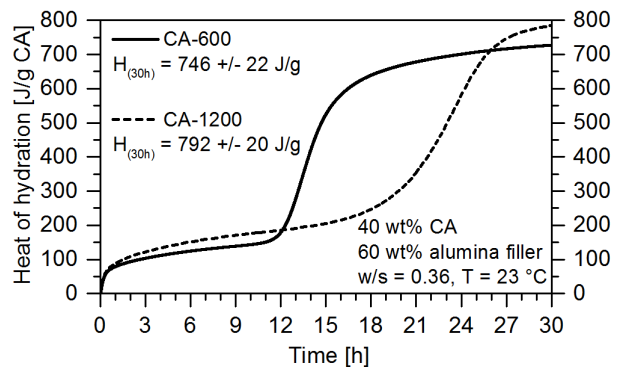


Fig. 7: Development of the heat of hydration of CA-600 and -1200.

CONCLUSIONS

Prolonged milling has substantial different effects on the microstructural properties and hydration kinetics of CA and CA₂. The hydration behaviour of CA does not significantly change although an unexpected retardation with increasing fineness was observed. In contrast, the hydration behaviour of CA₂ is dramatically changed and highly dependent on the degree of crystallinity, to be precise, the amount of X-Ray amorphous phase and the BET surface area.

REFERENCES

- [1] Klaus SR, Neubauer J, Goetz-Neunhoeffer F. How to increase the hydration degree of CA – The influence of CA particle fineness. *Cem. Concr. Res.* 67 (2015) 11-20.
- [2] Song TW, Choi SH, Han KS. Activation of hydraulic properties of the compound CaO·2Al₂O₃. In: Mangabhai RJ, editor. *Calcium Aluminate Cements*, Proceedings of the International Symposium, 1990, London, p. 372–377.
- [3] Banawalikar DG, Narayanan S, Majumdar SD, Chatterjee AK. New generation binders for monolithics. *Proceedings of the UNITECR 1997*, New Orleans, p. 1305-1314.
- [4] Moehmel S, Gessner W, Olieuw G, Rettel A, Seydel R. Investigations on the hydration behaviour of clinker phases of high alumina cements. *Proceedings of the UNITECR 1991*, Aachen, p. 147-150.
- [5] Gessner W, Moehmel S, Rettel A, Bayoux JP. The influence of a thermal treatment on the reactivity of calcium aluminate phases. *Proceedings of the UNITECR 1997*, New Orleans, p. 109-116.
- [6] Goetz-Neunhoeffer F, Klaus SR, Neubauer J. Kinetics of CA and CA₂ dissolution determined by QXRD and corresponding enthalpies of reactions. In: Fentiman CH, Mangabhai RJ, Scrivener KL, editors. *Calcium Aluminates*, Proc. Int. Conf., 2014, 54-64.
- [7] O'Connor BH, Raven MD. Application of the Rietveld refinement procedure in assaying powdered mixtures. *Powder Diffr.* 3 (1988) p. 2-6.
- [8] Jansen D, Stabler C, Goetz-Neunhoeffer F, Dittrich S, Neubauer J. Does ordinary Portland cement contain amorphous phase? A quantitative study using an external standard method. *Powder Diffr.* 26 (2011) p. 31-38
- [9] Hueller F, Ectors D, Neubauer J, Goetz-Neunhoeffer F. Influence of crystallinity and surface area on the hydration kinetics of CA₂. *Cem Concr. Res.* 89 (2016) 136-144.
- [10] Hertel T, Neubauer J, Goetz-Neunhoeffer F. Study of hydration potential and kinetics of the ferrite phase in iron-rich CAC. *Cem Concr. Res.* 83 (2016) 79-85.