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ABOUT THE REACTIVITY OF CALCIUM SULPHATE BINDERS

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Reactivitatea lianților pe bază de sulfat de calciu are o influență semnificativă asupra proprietăților lor de procesare. De aceea, în ultima perioadă, atenția se îndreaptă spre tipul şi cantitatea de aditiv şi modul de acțiune a acestuia asupra proprietăților produsului final.

Investigațiile efectuate au arătat că aceste influențe se manifestă în aproape aceeaşi măsură pentru toate grupele de lianți de tip sulfat de calciu (tencuieli din ipsos şi alfa-semihidrat ars la temperaturi joase, şi din anhidrit obținut la temperaturi înalte). Pentru a caracteriza reactivitatea lianților de sulfat de calciu, au fost efectuate, în principal, măsurători calorimetrice şi conductometrice.

The reactivity of calcium sulphate binders has significant influence on their processing properties. This leads to effects on the type and the amount of the additives to be deployed, and it affects the solid state properties of the constructive elements to be produced.

The investigations which were carried out showed that these interrelations are true to almost the same extent for all groups of calcium sulphate binders (plasters of paris and alpha-hemihydrate for low temperature burning, and anhydrite for the high-temperature range). In order to characterize the reactivity of calcium sulphate binders mainly calorimetric and conductometric measurements were carried out.

Keywords: calcium sulphate binders, reactivity, hydration

1. Introduction

Especially due to the varying heat transfer conditions in the burning system and because of the wide grain size distribution in the starting materials which contain calcium sulphate dihydrate, multi-phases form when these materials are dehydrated (except in the high temperature range). These multi-

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phase systems can consist of hemihydrate, anhydrite III, anhydrite II, and – under certain circumstances – they can also consist of the remains of the non-hydrated dihydrate (Fig.1). During the transition from one phase to another, it comes to a rearrangement of the crystal lattice, which is combined with the formation of lattice defects.

$$\mathrm{CaSO_4 \cdot 2\,H_2O} \rightarrow \mathrm{CaSO_4 \cdot 0{,}5\,H_2O} \rightarrow \mathrm{CaSO_4\,(III)} \rightarrow \mathrm{CaSO_4\,(II)}$$

$$\mathrm{DH} \rightarrow \mathrm{HH} \rightarrow \mathrm{A\,III} \rightarrow \mathrm{A\,II}$$

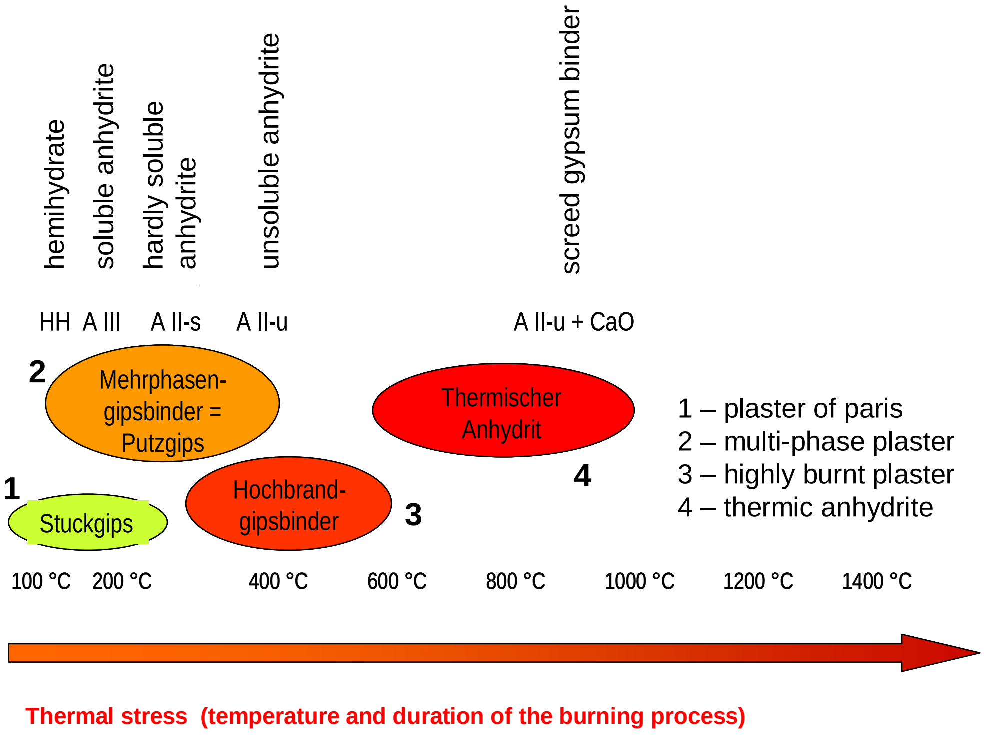


Fig. 1. Schematic illustration of the calcium-sulphate binders to occur at varying burning exposure

It is typical for the phases of the calcium-sulphate binders that have formed during dehydration - and which are able to set – to try and completely convert into the thermodynamically stable phase calcium sulphate dihydrate when they have contact with water.

The reaction rate of this process is significantly determined by the reactivity of the binders. The reactivity on the other hand, is above all dependent on the dehydration conditions (phase composition and lattice defects), the grinding (fineness), and the storage (ageing). But also the terms of creation and contaminations of the starting materials play a certain role.

During the dehydration of the starting material the crystal water escapes partly in an explosive manner. This leads to the formation of craters and cracks in the stucco particles and thus to a drastic increase of their inner (BET) surface (Fig. 2).

The higher surface energy of these rough, crypto-crystalline particles and also of the fine particles which were created by the grinding process leads to a stronger interaction with water. This stronger interaction manifests itself both in an increase of the reaction heat as well as in an increase of the solubility and the solubility speed. By means of conductivity measurements of suspensions one can make statements on changes of the solubility behaviour since there is an almost linear dependency between the ion concentration and the conductivity.

The reaction capacity of the calcium sulphate binders can be described directly by means of calorimetric measurements of both the totally released heat amount (reaction enthalpy) and the determined heat change per time unit (heat development rate or heat rate).

In theory the hydration heat can be calculated from the standard formation enthalpies of the substances taking part in the reaction. Assuming the following values by HENNING:

$\Delta H_0 (CaSO_4 \bullet 2\ H_2O) = -2023$ kJ/mol
$\Delta H_0 (CaSO_4 \bullet 0{,}5\ H_2O) = -1574$ kJ/mol
$\Delta H_0 (CaSO_4\ (III)) = -1420$ kJ/mol
$\Delta H_0 (H_2O) = -286$ kJ/mol

the following reaction enthalpies unfold (in relation to the amount of the corresponding starting material):

$$CaSO_4 \bullet 0{,}5\ H_2O + 1{,}5\ H_2O \rightarrow CaSO_4 \bullet 2\ H_2O$$
$$\Delta H_R = -20 \text{ kJ/mol} = -138 \text{ J/g}$$
$$CaSO_4\ (III) + 0{,}5\ H_2O \rightarrow CaSO_4 \bullet 0{,}5\ H_2O$$
$$\Delta H_R = -11 \text{ kJ/mol} = -81 \text{ J/g}$$
$$CaSO_4\ (III) + 2\ H_2O \rightarrow CaSO_4 \bullet 2\ H_2O$$
$$\Delta H_R = -31 \text{ kJ/mol} = -228 \text{ J/g}$$

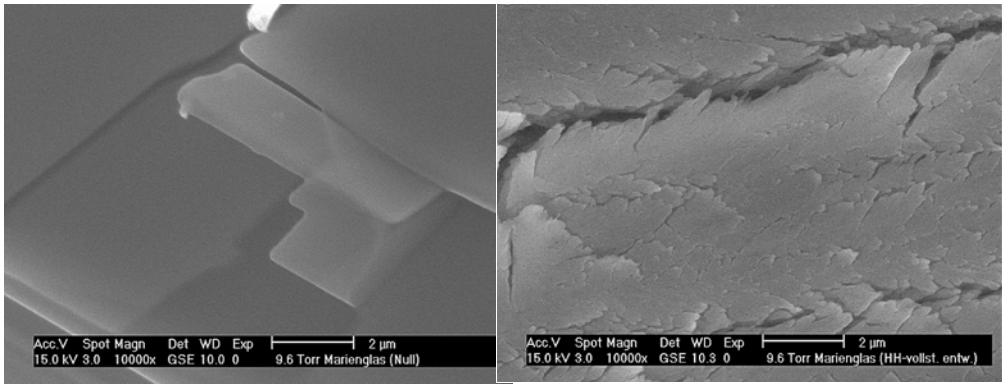


Fig. 2. Change of particle surface as a consequence of the burning process, exemplified on mica: left dihydrate, right hemihydrate

In the last 50 years numerous scientific papers [1-14] have been published on the hydration and setting behaviour of calcium sulphate binders. In these papers very divergent data is given as far as the hydration heat of hemihydrate is concerned. The range is between 111 and 134 J/g for the beta form, whereas for the alpha form the data ranges between 100 and 118 J/g. The reasons for these differences can be found with certainty in the varying sample preparation.

Thus, it is the aim of this paper to show the effects of different formation and storage conditions on the reaction capacity of calcium sulphate binders exemplified by means of selected investigation methods.

2. Experimental - Investigation Methods

Prerequisite for the hardening of calcium sulphate binders is their hydration. Since these reactions take place under heat release, calorimetric investigations are a very good choice in order to describe the kinetics. The dissolution behaviour is an important factor for the speed of this process. By means of conductivity measurements the dissolution behaviour can be characterized.

Conductometry

The electric conductivity of solutions or suspensions is almost linear to the concentration as far as diluted solutions are concerned. Calcium sulphates with their sufficiently low solubility are therefore predestined for the conductometric characterization of their dissolution behaviour (dissolved amount and dissolution speed). The gypsum binder is strewed into de-ionised water very quickly (approx. 3 s). The measurement is carried out at a water-binder ratio of 20 at constant stirring speed (magnet stirrer) in a carefully tightened beaker. The measurement is taken by means of a temperature-compensated conductivity meter cell. All data relate to 25 °C.

Calorimetry

The reaction behaviour with water is investigated by means of a differential calorimeter (ZIAC-D calorimetry system DC-I/IN). The shown results are recorded by a calorimeter in isoperibol control mode. Measurement is taken on a sample amount of 5.00 g having a water-binder ratio of 1.0.

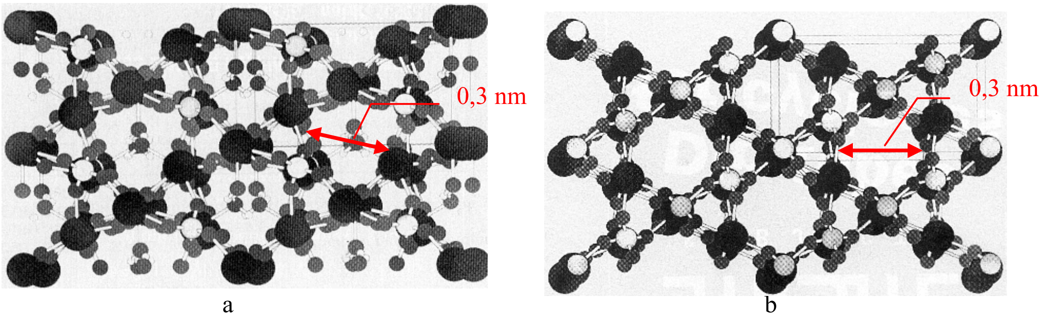
Hydration Process

The progressing hydration process of the calcium-sulphate phases can be described by their hydration degree. In order to do so, at time t, the amount of water necessary to form gypsum out of the calcium-sulphate capable to set, is divided by the amount of water necessary for complete hydration.

3. Results and Discussions

Effects of the Dehydration Conditions - Role of Anhydrite A III

In the structure of the hemihydrate the crystal water is present in structure channels, within the gypsum in layers. When the crystal water is removed out of the structure channels by thermal stress, the soluble anhydrite A III forms. In the crystal lattice this phase is only slightly different from the calcium-sulphate hemihydrate and is therefore capable of taking up water molecules again, immediately. ($CaSO_4 \cdot n\ H_2O$ where $n = 0\ldots\ 0.03\ldots\ 0.63$). –Fig.3.



a b

Fig. 3. Structure model of hemihydrate (left) and anhydrite III (right) [11]

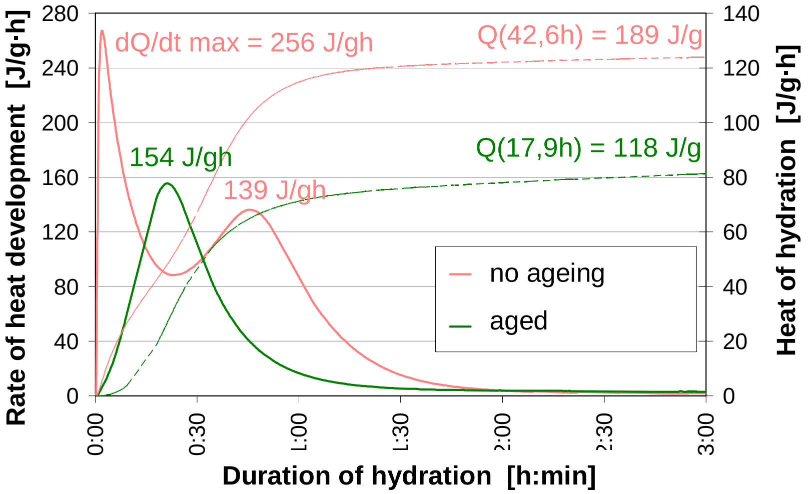


Fig. 4. Effects of ageing on the heat development of a multi-phase gypsum binder (lab burning: 10 h/ 250 °C) as a consequence of the complete conversion of the anhydrite III (75 %) into hemihydrate

The results illustrated in Fig. 4. show that even exposure to air humidity evokes significant changes. This is because the A III is completely decomposed on the one hand, but also because the particle activation (surface energy) which is initially there, is reduced by recrystallisation on the other hand. There is no other explanation for the big difference between both determined heat amounts. The enormously high amount of hydration heat released by the freshly burned binder – which has not been described in the literature, so far, must be seen taking this aspect into account.

Dehydration under low thermal stress

When gypsum binders are produced in the low-temperature range (≤250 C) under atmospheric (dry) burning conditions, the resulting products mostly show a high reactivity. These low-temperature gypsum binders are called plaster of paris and consist mainly of beta hemihydrate and soluble anhydrite (anhydrite III). They can also have low shares of dihydrate remains or already hardly dissolving anhydrite (anhydrite II s). The conversion conditions, here, influence the phase composition of the gypsum binders, the number of defects in the crystal lattice of the involved phases, as well as the size and shape of the particle surface developing. Even low shares of the highly reactive anhydrite III lead – at increased water consumption – to a stronger heat release. The beta-hemihydrate of such binders is unstable in comparison to aged materials - or alpha-hemihydrate produced with care under saturated steam conditions – and thus highly reactive.

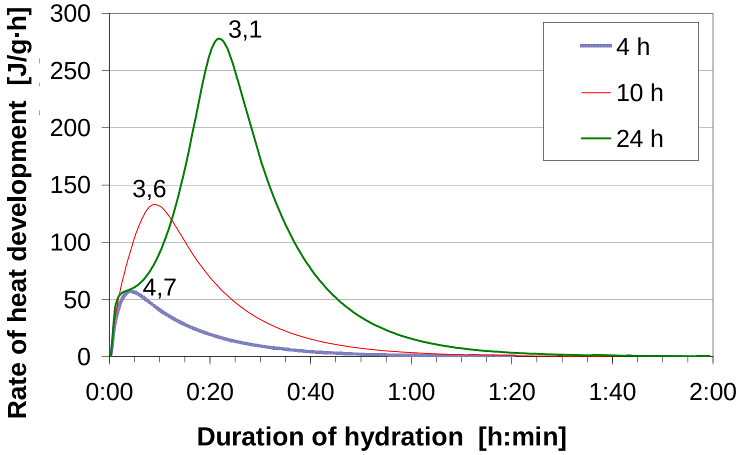


Fig. 5. Calorimetric description of the hydration of incompletely dehydrated lab binders
(burning temperature: 110 °C, burning duration: 4, 10, and 24 h)

phase composition:				
	110 °C / 4 h:	88 % DH;	12 % HH;	0 % A III
	110 °C / 10 h:	62 % DH;	38 % HH;	0 % A III
	110 °C / 24 h:	10 % DH;	90 % HH;	0 % A III

Under special conditions in the lab an FGD-Gypsum was dehydrated stepwise but completely. Fig. 5 illustrates the accelerating influence of the remaining dihydrate. With the gypsum share decreasing (as a consequence of the stronger conversion of the starting material into hemihydrate) the maximum hydration speed of the hemihydrate is expectedly reached at later stages. For these A III – free samples the determined reaction heat values are in correspondence with the hemihydrate share. But also the incomplete formation of the hemihydrate crystals which are still in the formation process, and which will complete themselves only with the complete conversion of the dihydrate (here after 24 h), could contribute to the increased reaction intensity.

For this purpose and in order to compare the reaction intensity, the maximum heat development rate of the respective phase able to set, was divided by their share in the binder. In Fig. 5 the determined characteristic values are placed at the curve's maximum.

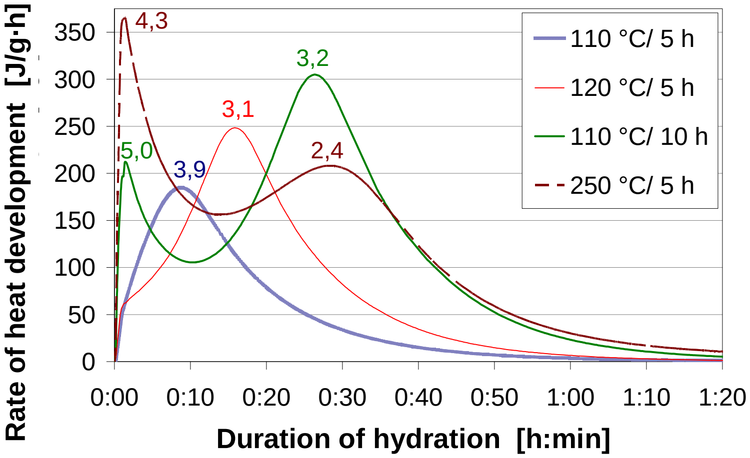


Fig. 6. Hydration curve of special lab binders (burning temperature: 110, 120 and 250°C
and burning duration of 5 or 10 h respectively, basis FGD-gypsum)
in dependence of the phase composition
110 °C / 5 h: DH – 54 %; HH – 46 %; A III – 0 %
120 °C / 5 h: DH – 21 %; HH – 76 %; A III – 3 %
110 °C / 10 h: HH – 57 %; A III – 42 %; A II – 1 %
250 °C / 5 h: HH – 2 %; A III – 87 %; A II – 11 %

Fig. 6 and 7 show calcinations in the low-temperature range produced in the lab with an increasing share of anhydrite III. Due to the complete conversion of the dihydrate into phases of the calcium-sulphate able to set, the hydration accelerating influence is missing and the hemihydrate reaction begins later as far as the dihydrate-free samples are concerned.

When sufficient anhydrite III forms due to burning stress (please take notice of the changed production conditions of the lot in Fig. 1), the reaction kinetic of the hemihydrate changes. On contact with water, A III reacts immediately and under strong heat release into hemihydrate. As a result of this reaction, immediately after strewing, a first peak occurs in the calorimeter curves (Fig. 7). At the same time one can observe, however, that the second curve maximum of the measured curves occurs at different times.

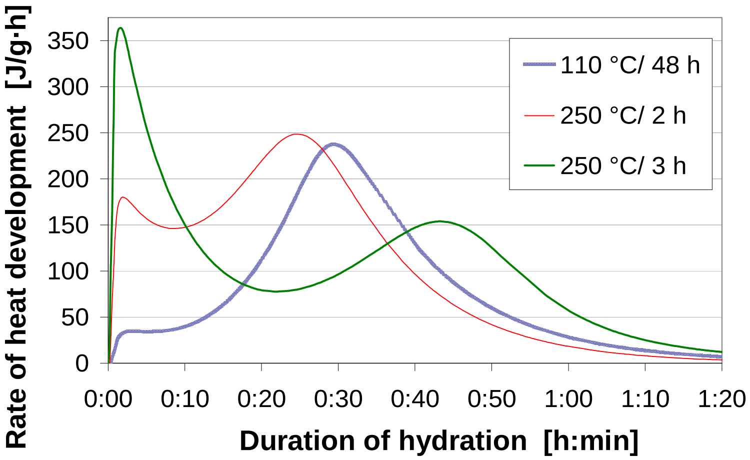


Fig. 7. Hydration curve of several multi-phase gypsum binders produced in the lab on FGD-gypsum basis in dependence of the phase composition
110 °C / 48 h: DH – 3 %; HH – 77 %; A III – 18 %; A II – 2 %
250 °C / 2 h: DH – 4 %; HH – 52 %; A III – 41 %; A II – 3 %
250 °C / 3 h: A III – 85 %; A II – 15 %

The characteristic hemihydrate reaction is thus postponed to a later stage with the share of A III in the starting material increasing. At the same time, the determined maximum heat rate for this section of reaction decreases. Both phenomena prove that extremely high A III contents have a delaying effect on the hydration process.

This statement can also be followed looking at Fig. 6 (comparison of curves 110/10 and 250/5). The hemihydrate peak of sample 250/5 which is exclusively evoked by a hemihydrate from anhydrite III, shows a significantly weaker reaction intensity than the curve (110/10) which results from a binder with an an almost equal share of hemihydrate and A III.

Dehydration at higher thermal stress

When the dehydration of calcium-sulphate dihydrate takes place at higher heat supply, at first there forms a multi-phase gypsum binder with varying shares of hemihydrate (HH), soluble anhydrite (A III) and anhydrite A II. In order to formally characterise the reaction behaviour the A II is subclassified in two "forms": in the relatively reactive share which converts within 72 h into dihydrate, the hardly soluble anhydrite (A II s), and the comparatively inert share, the insoluble anhydrite (A II u) which does not convert under given conditions (burning conditions and grinding fineness) within 72 h into dihydrate.

Multi-phase gypsum binders which were dehydrated at 400 - 500 °C from coarse grain material consist of HH, A III and A II s. Finer shares can already be A II u at this temperature and longer burning duration.

When you look at the hydration progress of a test series in which the lots were fired over varying times at 400 °C (from an alpha-HH on REA gypsum basis), a decrease in the conversion degree can be observed with the burning duration increasing (Fig. 8). This tendency can be followed over the entire hydration time – the turnover equals after 72 hours the addition of HH, A III and A II s. The phase composition of the used samples can be seen in Table 1.

This reduced reaction capacity with the thermal stress increasing in the case of multi-phase gypsum binders can also be shown by means of calorimetry after already shorter reaction times (Fig. 9). The reaction heat released within the first three hours results especially from the phases HH and A III.

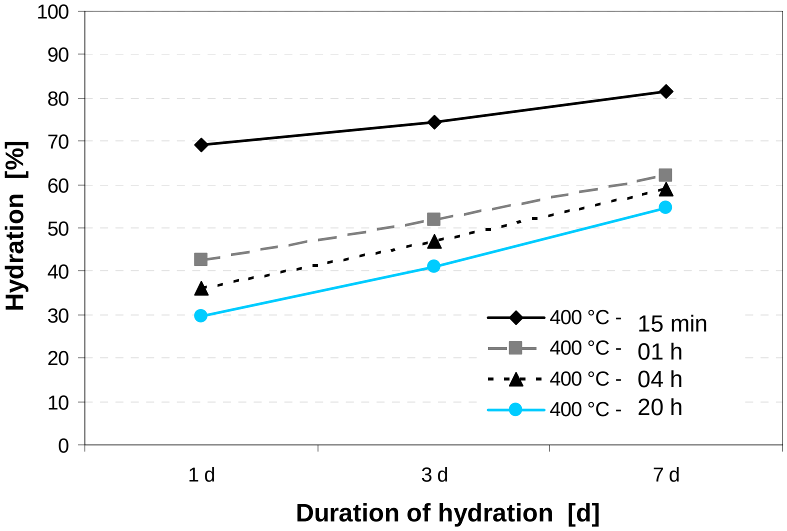


Fig. 8. Hydration progress of multi-phase gypsum binders in dependence of the dehydration regime

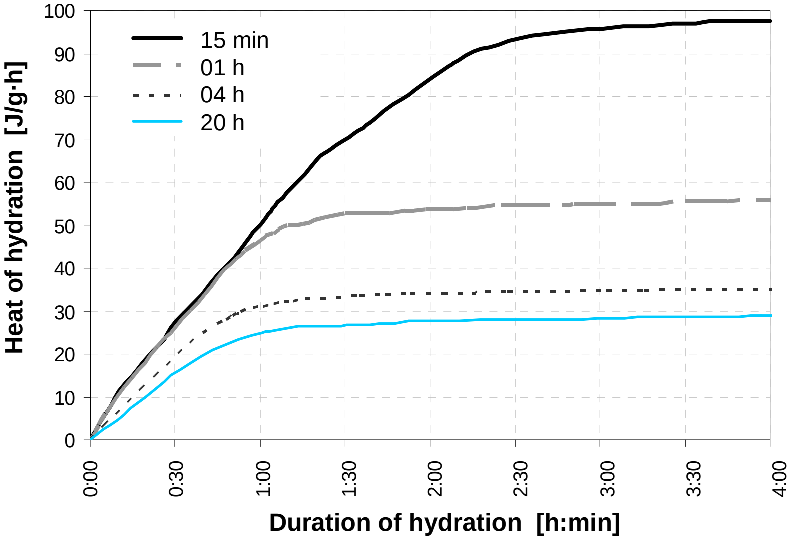


Fig. 9. Dependence of the released reaction heat in the hydration process of multi-phase gypsum binders in dependence of their dehydration regime at 400 °C

Table 1

Phase composition of lab burnings (multi-phase gypsum binders) in dependence of the burning duration (dehydration temperature 400 °C)

Phases	400 °C / 0.25 h	400 °C / 1 h	400 °C / 4 h	400 °C / 20 h
Hemihydrate	27,2	6,1	6,8	6,7
Anhydrite III	36,2	24,6	17,0	12,2
Anhydrite II s	12,2	14,1	14,2	11,8
A II u + others	24,4	55,2	62,0	69,3

With the burning stress increasing, the shares of HH and A III decrease until they are completely disappeared. Only anhydrite II continues to form whereas the relations move more and more towards A II u (highly burnt plaster, thermal anhydrite)

The decreasing reaction capacity of highly fired calcium-sulphates can be demonstrated by their dissolution behaviour shown in Figs. 10 and 11. It can be acted on the assumption that all lab burnings used here – taking the error margin into account – consist exclusively of A II u. Thus, the reduced interaction with water at increasing thermal stress (dissolution inhibition) can either be caused by a reduced number of defects in the A II – lattice and/or by a reduction of the reaction surface of the particles. Investigations on highly fired gypsum gravel show a decrease of the BET-surface at very high burning degrees (Table 2).

Table 2

Dependence of the BET-surface after burning of gypsum gravel (approx. 10 mm)

Burning conditions	Gypsum stone	150 °C / 2h	400 °C / 2 h	600 °C / 2 h	700 °C / 2 h	800 °C / 2 h	800 °C / 6 h
BET - surface	1,6 m^2/g	9,9 m^2/g	12,1 m^2/g	8,6 m^2/g	4,2 m^2/g	2,2 m^2/g	1,7 m^2/g

Within 7 days only a maximum of 1.5 % of the fired A II – lots converted into dihydrate. Thus, an exact distinction of the investigated samples illustrated in Figs. 10 and 11 was not possible by means of calorimetric measurements.

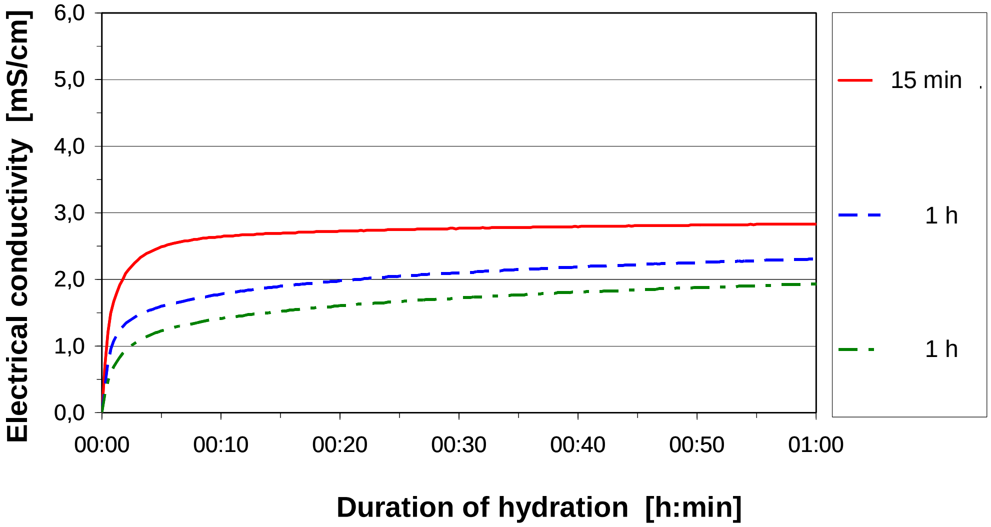


Fig. 10. Conductivity measurements on hydrating calcium-sulphate binder suspensions (l/s = 20); the used highly fired gypsum binders were produced at 800°C and varying burning duration

The screed gypsum described in the literature (extremely high dehydration temperature of gypsum) owes its reactivity the fine grinding of the created anhydrite (A II u) on the one hand, and its alkaline excitation (CaO) on the other hand. Such an excitation could not be measured in our lab experiment on samples with 800 °C and 1100 °C.

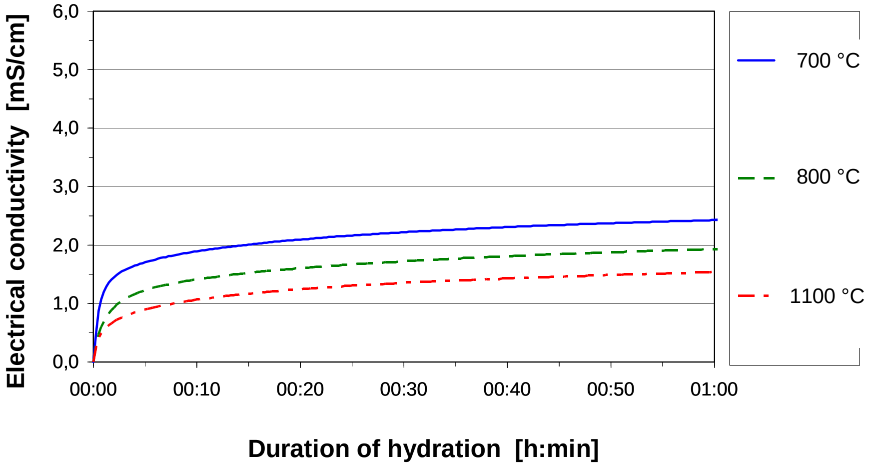


Fig. 11. Conductivity measurements on hydrating calcium-sulphate binder suspensions (l/s = 20); the used highly fired gypsum binders were produced at varying temperatures for 20 h

Influence of ageing

The term 'ageing' of calcium-sulphate binders means their decreasing reactivity, combined with a gain in stability as far as their processing properties are concerned, which is connected with the aforementioned decrease in reactivity.

The particles of the gypsum binders fired under 'dry' conditions are – among other things for the reasons mentioned above – nanoporous from the surface towards the interior. Therefore, the entering of air humidity into the structure channels of the anhydrite III and consequently its conversion into hemihydrate becomes possible in very short time. This decomposition of the A III causes a much more stable processing of the plaster of paris.

On the other hand the cavities in the particles which are formed during burning have an influence on the humidity adsorption. For example, for a freshly fired gypsum binder (1 h / 350 °C) a pore volume of 0.035 cm^3/g was determined. The pore diameters for this sample were mostly in the range between 3 and 40 nm. According to [20] or the Thomson-equation, respectively, the beginning of the capillary condensation at 20 °C can be estimated for the following capillary diameters - in dependence of the relative humidity (rel. hum.): 40 % rel. hum. – up to 2.3 nm, 81 % rel. hum. – up to 10 nm, 95% rel. hum. – up to 42 nm. The water condenses as well between the phase interfaces of the particles (gore having the same dimensions). In this 'liquid' water, the especially strongly activated areas of the binder particle dissolve and it comes to crystallization of gypsum on the particle surface.

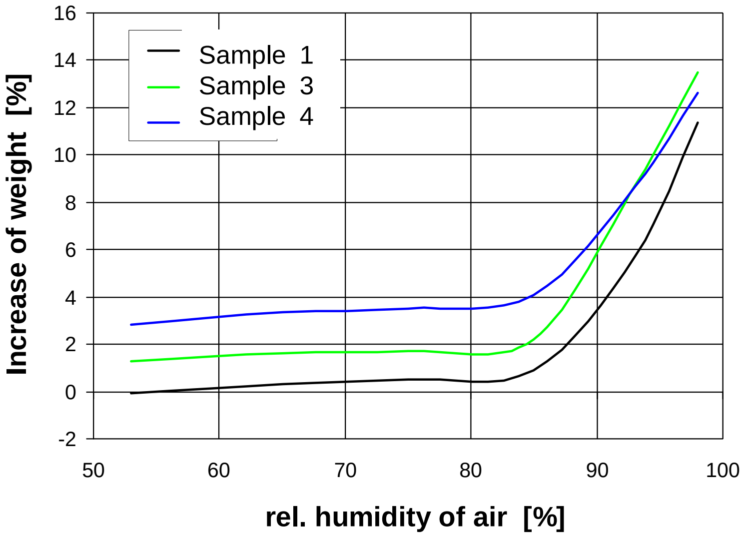


Fig. 12. Humidity take-up of several plasters of paris after 7 d storage in dependence of the air humidity at 20 °C

Fig. 12 illustrates that a relative air humidity of approx. 80 % is required for a significant capillary condensation as far as plaster of paris particles are concerned.

Changes concerning natural anhydrite

Finely ground anhydrite binders adsorb water molecules on the particle surface as well. In the 'liquid' water it comes to a hydration reaction and thus to gypsum formation. It is interesting to see here, too, that with reaching approx. 80 % air humidity, this humidity again and again 'condenses' in the particle interspaces which thus allows a progressing of the hydration reaction (Figs. 13 and 14). Due to the well-known low reactivity of natural anhydrite (A II u) against water, the fineness of the binder as well as the humidity supply are the determining factors for the adsorption of air humidity.

This is also in compliance with the well-known fact that the hydration progress and thus the hardness of natural anhydrite products are dependent especially on the grinding fineness. Fig. 14 shows new formations of gypsum on anhydrite grains caused by high air humidity.

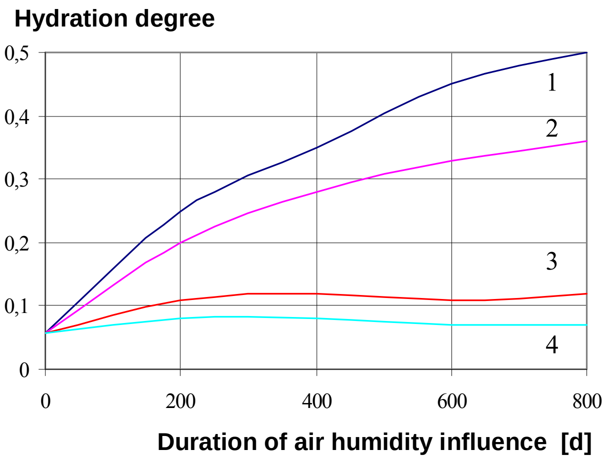


Fig. 13. Hydration progress of a finely ground anhydrite binder influenced by air humidity according to [7] (due to the mountain's humidity the hydration degree of the starting material was 0.056)

1 – 100 % rel. hum. 2 – 95 % rel. hum. 3 – 79 % rel. hum. 4 – 58 % rel. hum.

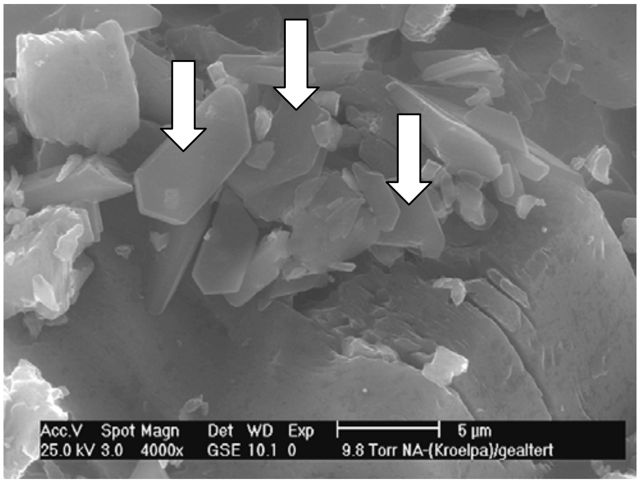


Fig. 14 Finely ground natural anhydrite (Krölpa: Zechstein I / Werra-anhydrite) with leaf-like new formations of gypsum (see arrows) on the particle surface (storage: 28 d at 20 °C at 98 % rel. hum.)

Changes on calcium-sulphate dihydrate

After having shown the interaction of calcium-sulphate binders and air humidity, the following question arises: in the case of finely ground dihydrate (gypsum), does the particle activation (surface energy) – which is exclusively caused by grinding - reduce under the influence of air humidity?

In order to answer this question, the influence that dihydrate has on the setting process of plaster of paris was investigated. Very finely ground gypsum stone particles serve as vaccination crystals; they are known as effective accelerators. Thus, a decrease of their particle activation should result in a reduced acceleration of the hardening process. For this reason finely ground gypsum stone was exposed to varying air humidities over a longer period of time.

The hydration behaviour (investigated by means of calorimetry) proves that air humidity during storage reduces the effectiveness of the finely ground gypsum stone as accelerator (Fig. 15). The maximum of the heat development rate is reached comparatively later. The released heat amounts, too, prove a faster hydration for the gypsum stone sample used as accelerator and which was stored in an air tight container. The total heat amount was expectedly not influenced.

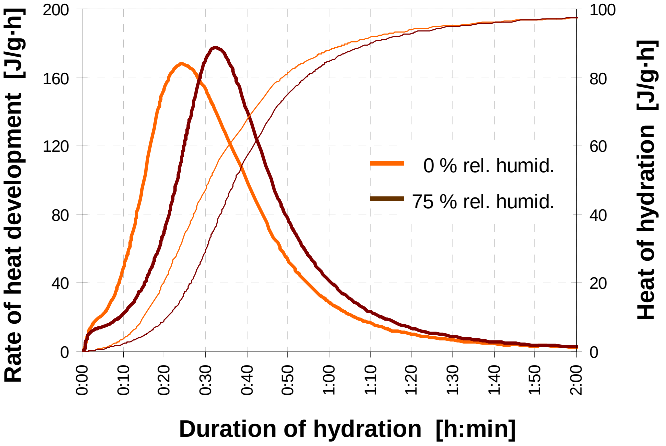


Fig. 15. Hydration curve of a plaster of paris under addition of finely ground gypsum stone (0.2 %), which was exposed to varying storage conditions for approx. 110 d: a) in a closed container; b) exposed to 75 % rel. hum.

General effects

When one produces a lab binder at extremely low temperature supply, it is possible to make an A III – free sample with high shares of residual dihydrate. When exposed to very high air humidity (98 %) it comes to a formation of ageing dihydrate in areas of capillary condensation. Within 14 days only a small share (namely 3 % of originally 62% hemihydrate) converted into gypsum. The formation of additional 3 % of dihydrate to the still existing 38 %, led – as expected - only to a slightly earlier hydration. However, the intensity of the hemihydrate reaction is significantly weaker after ageing. The characteristic maximum of the heat development rate is reduced by approx. 35 % whereas the phase able to set is only reduced by 3 % (Fig. 16).

Thus, the reduction of the particle activation of the binder caused by the burning process can undoubtedly attributed to the humidity adsorption and subsequent recrystallisation.

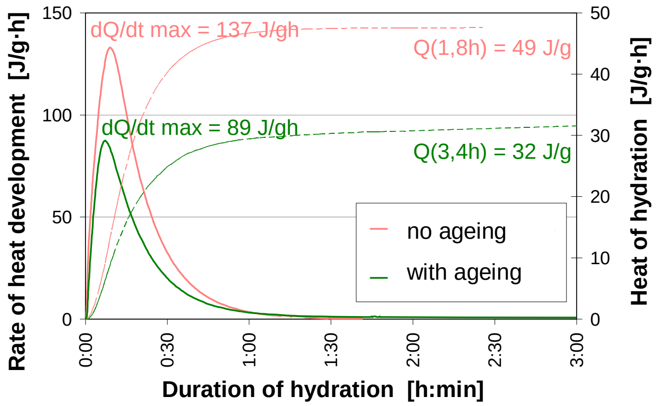


Fig. 16. Reduction of the hydration heat of a not completely dehydrated calcium-sulphate binders (lab burning: HH – 62 %, no A III) as a consequence of ageing (14 d at 98 % rel. hum./ 20°C) at a slight reduction of the HH-content to 59 %

The application of the Rietveld-refinement in the XRD-analysis of the samples shows in one example the decrease of the lattice dilation (micro strain) and at the same time the increase of the crystallite size of the hemihydrate as a consequence of ageing (Fig. 17). Also for anhydrite A II such a tendency could be found. This 'relaxation' in the crystal lattice caused by ageing leads to a reduced reactivity of the calcium-sulphate phases towards water and confirm the statements made on Fig. 10.

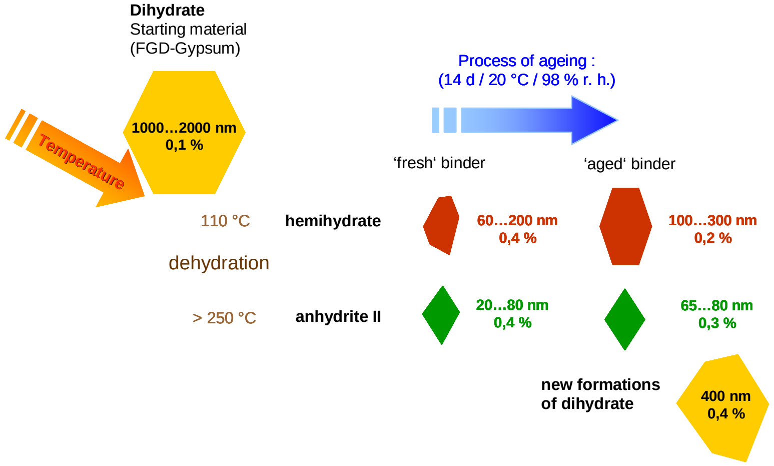


Fig. 17. Crystallite size and lattice dilation in the production and ageing process of calcium-sulphate phases Results of the Rietveld-refinement in XRD-investigations

Influence of the grinding fineness

The influence of the grinding fineness on the reaction capacity of calcium-sulphates shall be shown in the following two examples. For this purpose an industrial plaster of paris and a natural anhydrite were milled after buying by means of a disc swing mill in three steps. The changed characteristics are given in Table. 3.

Table 3

Characteristic values of the REA-plaster of paris and the natural anhydrite in varying grinding finenesses

	Fineness	1	2	3
	Grinding energy	low	middle	high
REA-plaster of paris	Specific surface acc. to BET [m²/g]	5,3	5,7	6,2
	Specific surface acc. to Blaine [m²/g]	0,1	0,4	0,9
Natural anhydrite	Specific surface acc. to BET [m²/g]	0,4	1,1	6,5
	Specific surface acc. to Blaine [m²/g]	0,1	0,4	1,2

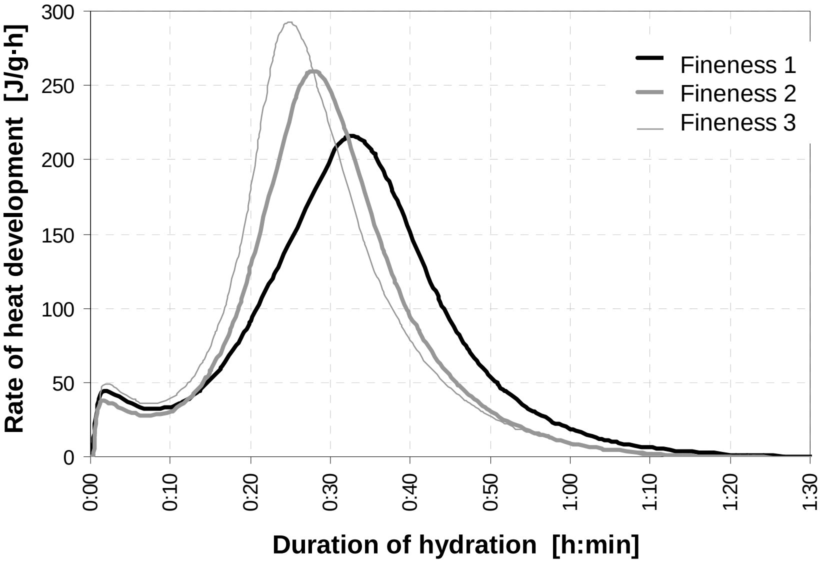


Fig. 18. Change of the heat development rate over the hydration time for the REA-plasters of paris having varying grinding finenesses (l/s = const.=1)

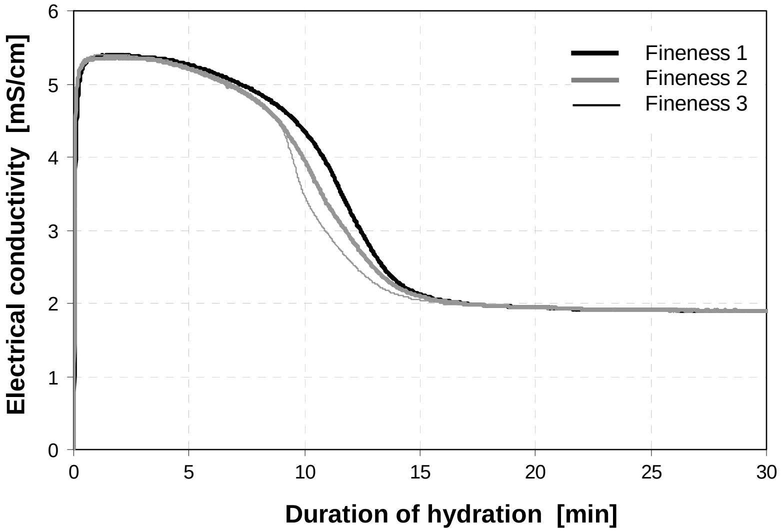


Fig. 19. Change of electrical conductivity over the hydration time for the REA-plasters of paris having varying grinding finenesses (l/s = const. = 20)

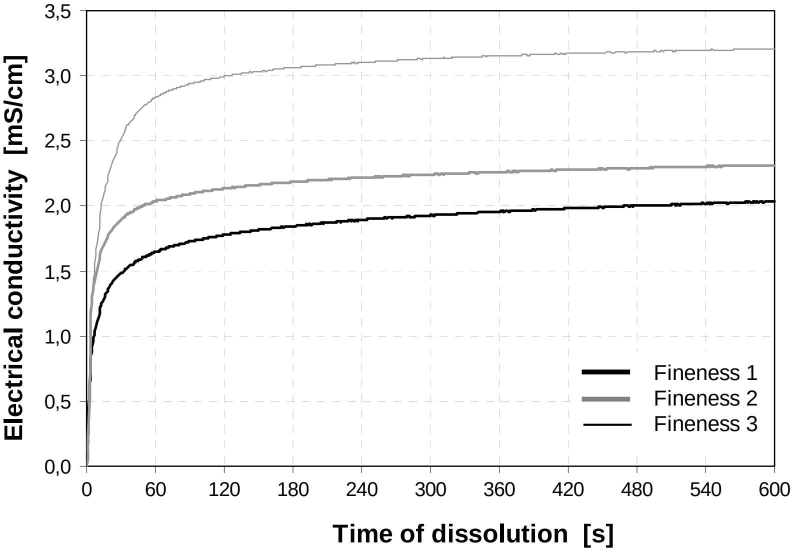


Fig. 20. Change of the electrical conductivity over the hydration time for the natural anhydrite having varying grinding finenesses (l/s = const. = 20)

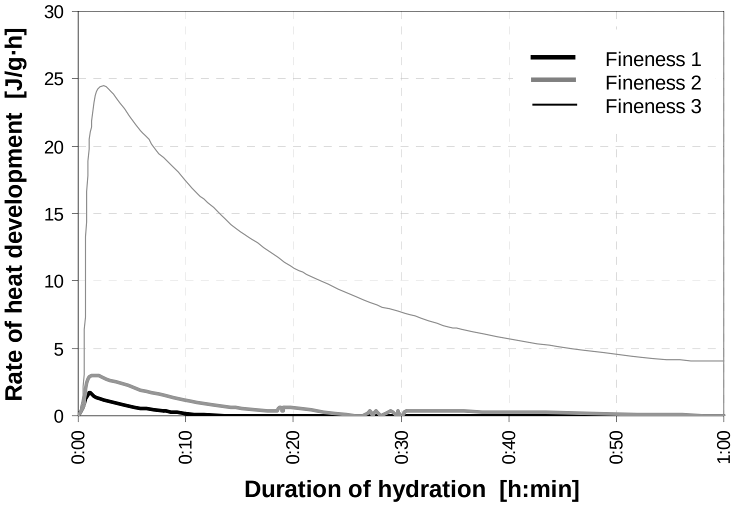


Fig. 21. Change of the heat development rate over the hydration time for the natural anhydrite having varying grinding finenesses (l/s = const. = 1)
Q_r = 0,2 J/g (fineness 1); Q_r = 0,8 J/g (fineness 2); Q_r = approx. 10 J/g (fineness 3)

The milling leads – as expected – to an earlier and more intense reaction of the hemihydrate with water. (Fig. 18). This is also shown by the corresponding conductometric measurements (Fig. 19). After reaching the saturation concentration of the hemihydrate (here almost identical for the varying finenesses), the conductivity of the suspensions decreases faster - as a consequence of a hydration reaction - in the case of more finely ground plaster of paris, than in the case of the less finely ground binder. This proves the faster conversion of hemihydrate into dihydrate.

As far as the finely ground natural anhydrite is concerned one can observe an increase in the reactivity, too, as a consequence of grinding. A significantly higher dissolution speed of finer particles is clearly to be seen (Fig. 20). The results of the calorimetry show (Fig. 21) that - despite the fine grinding – the hydration process of the inert natural anhydrite in pure water (without excitation salts) does not start within the first hour. The heat released within the first hour can thus be attributed exclusively to humidifying and dissolution effects (dissolution of the crystal lattice and solvation).

4. Conclusions

In the framework of this paper it is shown that calorimetric and conductometric measurements are especially appropriate to characterise the reactivity of calcium-sulphate binders.

Above all the phase composition and the lattice defects that form due to dehydration and fine grinding, influence the reaction capacity of calcium-sulphates.

Longer storage in tightly closed containers leads to a lower decrease of the surface energy; exposure to air humidity, however, can significantly reduce the reactivity.

These mechanisms are illustrated schematically in Fig. 22.

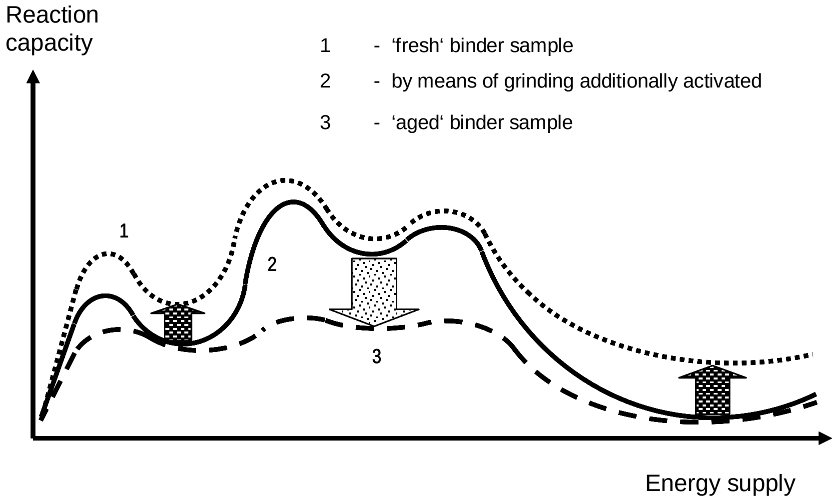


Fig. 22. Reactivity of the calcium-sulphate phases in dependence of thermal stress
1 – Increase as a consequence of fine grinding; 3 – Reduction caused by ageing

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