Behaviour of calcined gypsum-based materials during setting

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Abstract. The behaviour at early age of several composed gypsum-based materials was investigated. The binary binder, composed of calcium sulphate hemihydrate and slaked lime, several ternary binders with different types of pozzolans were prepared, and their behaviour during setting was studied. Unrestrained volume changes of calcium sulphate-based pasts were measured by displacement of liquid, in which the specimens were submerged. The hydration heat of composed binders was measured by isothermal calorimetry. The behaviour of composed materials with different types of pozzolans was compared with the behaviour of calcined gypsum.

1. Introduction
Even if gypsum is one of the most environmentally friendly materials, because its low energy consumption at production and possibility to produce it from secondary materials, its utilization is restricted on the interior use only. When pure gypsum is wet, its strength decreases significantly and it starts to dissolve. To solve this problem ternary gypsum-based binders were developed. Ternary binders usually consist of calcined gypsum (calcium sulphate hemihydrate, pozzolan and activator of pozzolanic reaction (usually hydrated lime or cement). It was found, that these materials have better resistance against the water, because the insoluble phases are formed in them [1, 2]. These materials are studied intensively nowadays, but being relatively new materials, there is a lot of information missing yet. While the mechanical properties of ternary materials were studied by several authors as well as their durability in wet environment [3, 4, 5, 6], the behaviour of ternary materials at the early age was not studied very often. Singh and Garg [7] measured the setting times of secondary binder, composed of anhydrite and blast-furnace slag and they found, that the setting time shortens with increasing amount of slag. Garg, Jain and Singh [8] tested the ternary material, made from 30% of hemihydrate, 40% of fly ash and 30% of hydrated lime and they state, that the setting time of ternary binder was two times longer than setting time of pure hemihydrate. Hydration heat of composed calcium sulphate-based binders was studied very rarely. Guan et al. [9] studied the heat evolution of binary binder, prepared from calcium aluminate cement and flue gas desulfurization gypsum and found that the amount of gypsum strongly influences the hydration behaviour of the material and with increasing amount of gypsum the hydration is faster. Magallanes-Rivera and Escalante-Garcia [10] compared the results of isothermal calorimetry of commercial and fluorogypsum binders with different pozzolans and stated that the reaction of fluorogypsum is slower and less heat is liberated, but the final strength of fluorogypsum composites is higher.

The volume changes of materials during setting are also important, because they can influence significantly the properties of material in solid state. Cement based materials shrink during setting, due to the autogenous shrinkage. Immediately after mixing water and cement, a chemical shrinkage change
will occur due to the reduction in volume of the reaction products. Chemical shrinkage values for individual cement phases are given in table 1 and the total value of chemical shrinkage $V_{CS, cem}$ of cement can be calculated according equation (1).

\[
V_{CS, cem} = 0.0532 \, [C_3S] + 0.0400 \, [C_2S] + 0.1113 \, [C_4AF] + 0.1785 \, [C_3A]
\] (1)

The volume changes of gypsum during setting differ from the volume changes of cement. Calcium sulphate hemihydrate starts to shrink immediately after mixing gypsum with water and then it expands slightly. The shrinkage is caused by the chemical reaction between the water and hemihydrate, when the dihydrate is formed according equation (2). If equivalent volumes of the hemihydrate, water, and the reaction product (dihydrate) are compared, the difference $\Delta V_{cs,g}$ between the volume of the dihydrate formed and the equivalent combined volumes of the hemihydrate and water will be 7.11% (equation 3) [12].

\[
(CaSO_4)_{2} \cdot H_2O + 3H_2O \rightarrow 2CaSO_4 \cdot 2H_2O
\] (2)

\[
\Delta Vcs, g = \frac{(105.56+54.21) - 148.41}{(105.56+54.21)} \ast 100\% = 7.11\%
\] (3)

The setting expansion of gypsum is caused by the crystallization. Crystals starts to grow and intermesh and make the solid structure of gypsum. The structure after setting is therefore composed of interlocking crystals between which are micropores and pores containing the excess water required for mixing (figure 1). On drying, the excess water is lost, resulting in a porous structure.

![Figure 1. Setting expansion of hardened gypsum due to crystallization.
   a) Initial mix, b) crystal growth, c) close contact of crystals, d) expansion,
   f) termination of crystal growth [12].](image)

The volume changes of composed binders are therefore caused by several different processes. We found that behaviour of composed gypsum-based binders during setting is not described sufficiently yet, therefore we studied several composed gypsum-based binders at the early age. Volume changes during setting, hydration heat and setting times of three ternary calcium sulphate-based binders, one secondary binder and were measured and compared with behaviour of calcined gypsum.
2. Materials

Three ternary, one binary gypsum-based and one pure gypsum paste were prepared. The main component of all pastes was commercially obtained calcined gypsum (producer Rigips, s.r.o., Czech Republic). The mineral composition of calcined gypsum, determined by XRD is in table 3. As a pozzolan additives the crushed ceramic, silica fume (SF) and granulated blast-furnace slag (GGBS) were used. Crushed ceramic powder was obtained from regional producer of bricks (Heluz, Czech Republic) as a waste product from the ground brick production. The dust was sieved through the 250 µm sieve in order to exclude big particles. Silica fume and granulated blast slag were commercial products also (producers Stachema, Czech Republic and Kotouč Štramberk, Czech Republic). As an activator of pozzolanic reaction the slaked lime (producer Vápenka Čertovy Schody a.s., Czech Republic) was used. Mineral composition of slaked lime is in table 3. The amount of amorphous phase, determined by XRD analysis is given in table 4.

**Table 3.** Mineral composition of used calcined gypsum and slaked lime.

| Mineral             | Bassanite CaSO₄·1/2H₂O | Anhydrite CaSO₄ | Gypsum CaSO₄·2H₂O | Calcite CaCO₃ | Portlandite Ca(OH)₂ |
|---------------------|-------------------------|-----------------|------------------|---------------|---------------------|
| wt %                | 74.2                    | 7.3             | 0.9              | 3.4           | 6.5                 |

2.1. Composition of tested pastes

Composition of ternary pastes was designed in such way, that the amorphous phase in each paste was the same and the amount of hydrated lime (as activator of pozzolanic reaction) was the same also. By that, the comparability of achieved results was ensured, even if the reaction of GGBS is slightly different than reaction of silica fume and crushed ceramic. The amount of amorphous phase was derived from the amount of amorphous phase in the ternary binder with 10% of metakaolin, which was found as an optimal in previous research [1]. The detailed description of used materials design is in [13]. Binary paste without pozzolan and pure gypsum paste were prepared as reference materials. The amount of water in the mixtures was determined by the flow test (flow value was established to be between 185 to 190 mm). Compositions of designed materials are in table 5.

**Table 4.** Amount of amorphous phase in pozzolans.

| Pozzolan            | Silica fume SiO₂ | Granulated blast slag | Ceramic powder | % by mass |
|---------------------|------------------|-----------------------|---------------|-----------|
| Amorphous SiO₂      | 90               | 87.7                  | 45.3          |

All pastes were prepared in the same way. All dry components were thoroughly mixed together (by hand) and then they were added into the measured amount of water during 15 seconds. The paste was then mixed by hand for 1 minute and immediately used.
Table 5. Compositions of tested pastes.

| Pozzolan | Gypsum   | Slaked lime | Water/binder ratio |
|----------|----------|-------------|-------------------|
| SF       | Silica fume | 8.5         | 81.5             | 10 | 0.8  |
| CC       | Crushed ceramic | 16.8     | 73.2             | 10 | 0.7  |
| BS       | GBS       | 8.7         | 81.3             | 10 | 0.75 |
| GL       | -         | -           | 90               | 10 | 0.73 |
| G        | -         | -           | 100              | -  | 0.67 |

3. Measuring methods

3.1. Isothermal calorimetry
Hydration heat was measured by the isothermal heat flow calorimeter KC 01 [14]. The measurement was performed with a 1 g sample of dry mixture in a cylindrical copper vessel of inner diameter 8.25 mm and height 70 mm, with a tight rubber plug. After inserting the copper vessel with the solid sample into the stabilized calorimeter, a weighted syringe with water has been placed near the reaction vessel, and so was a plastic tubule intended for paste mixing. The calorimeter with the solid sample and liquid components was left to stabilize the temperature (25°C). After about 1 h of stabilization, the calorimeter was opened and water was inserted into the vessel. The paste was mixed for 30 s by rotation of the plastic tubule mixer and then the vessel was closed by a rubber plug.

3.2. Setting times
Setting times of all materials were tested by Vicat apparatus with needle according the EN 13454-2 [17]. The needle was indented into material with the interval 1 min.

3.3. Volume changes
Unrestrained volume changes of gypsum-based pastes and mortars were measured by displacement of liquid, in which the specimens were submerged. The fresh paste was poured into the thin rubber membrane, which was tightly tied and submerged into the vessel, filled by the silicone oil. The vessel was closed by specially adapted lid with tightly embedded glass capillary and plastic overflow pipe (figure 2). The system was filled by oil to the required level and sealed. The level of liquid was recorded by time lapse camera for one hour with the first snap at 5 min after mixing. The obtained images were manually evaluated and the level of liquid was determined for each picture (figure 3). The tested material was dried and its dry mass was recorded.

Sometimes water is used in this experiment, but some authors state that the rubber membrane is not absolutely waterproof [15] and water can penetrate into the sample during experiment. This is generally not a problem for gypsum-based materials, because water uptake starts after relatively long period of submersion (days) [16] and the hydration processes in gypsum are significantly faster (usually less than two hours). We used silicone oil in order to avoid the volume changes of water with the temperature rise, because the setting reaction of gypsum is exothermic and large amount of heat is generated.

Each material was measured three times at least. Measured values of volume changes were related to the mass of the dried sample and mean values were calculated.
4. Results and discussion

4.1. Heat evolution

The rate of heat evolution during the first two hours after mixing is presented in figure 4. The shape of all curves (with the exception of calcined gypsum paste) is similar to each other. There are two significant peaks. According to Fischer [18] the first peak, developed immediately after addition of water, is due to the wetting heat together with the heat of conversion of anhydrite III to hemihydrate. The second peak, which starts with a short delay after the first peak, represents hydration of hemihydrate to dihydrate. Similar shape of hydration curves was observed by Tydlitat et al. [14] and Singh and Middendorf [19]. In the calcined gypsum paste the first peak is missing, there can be seen only slight decrease of the line, which is in agreement with the results, obtained by Lewry [20]. This is caused by the fact, that the conversion of anhydrite II to hemihydrate does not start yet, because no activator was added and change in the heat rate evolution was caused by the wetting heat only. The second peak of pure gypsum is the earliest (20 minutes), which corresponds with the fastest setting times of calcined gypsum paste.

For the composed materials the first peak occurs between 2 to 3.5 minutes and the second peaks are achieved at about 30 minutes. After 2 hours the heat evolution is minimal and the main hydration reactions of calcium sulphate are finished. The hydration of pozzolans does not play role at this period, because it is significantly slower (days). Nevertheless, the pozzolans and lime serves as activators of anhydrite hydration and therefore the first peak in the composed binders is more pronounced than peak in the gypsum paste. The activation by slaked lime is less intense than activation by pozzolans and therefore both peaks occur later and the first peak is lower.

The amount of cumulative heat, evolved during first two hours of hydration is in direct proportion with the amount of gypsum in the mixture, as can be seen in figure 4. It confirms the fact that only reaction of gypsum occurs at the first two hours.
4.2. Setting times
The setting times are given in table 6. Generally, setting times of all materials are short. Setting of pure gypsum is fastest, as expected. The initial setting time increases with the decreasing amount of gypsum, but it does not exceed 15 minutes in all materials. The total setting time ranges from 3 minutes to 4.5 minutes and is longer in the materials with lower amount of gypsum.

The setting times are shorter than expected according the calorimetric results. It can be caused by the definition of setting times obtained by standard Vicat test, which is originally designed for cement-based materials and mechanism of gypsum setting is different from setting and hardening of the cement.

Figure 4. Heat flow evolution of tested materials.

Figure 5. Relationship between the cumulative heat and amount of gypsum in material.
Table 6. Setting times.

| Material | CC  | SF  | BS  | GL  | G   |
|----------|-----|-----|-----|-----|-----|
| initial setting time [min] | 14  | 14.5| 12.5| 11.5| 8   |
| final setting time [min]   | 18.5| 17.5| 16  | 15.5| 11  |

4.3. Unrestrained volume changes

Volume changes of all tested materials can be seen in figure 6. The character of changes of all materials is similar. Firstly, the volume decreases, which is caused by the chemical reaction between the gypsum and water, as explained in the Introduction [12]. Then the volume starts to increase due to crystallization of gypsum. The local minimum corresponds with the initial setting times. The maximal values are achieved at the time of the maximal hydration heat evolution, found by the isothermal calorimetry. After achieving the maximal expansion, the volume of all material starts to decrease again and for all material the decrease was not finished at the end of measuring (e.g. after one hour). The final decrease of volume could be assigned to the continuing crystallization. Some experiments had to be terminated earlier, because the level of the liquid decreased under the lower end of the glass capillary.

The volume changes of pure gypsum are significantly lower than volume changes of all composed materials and occur earlier then in the composed materials, which corresponds with the shorter setting times and also with the peaks on the calorimetric curve. The biggest volume changes can be seen in the binary paste and in the paste with the silica fume, e.g. in materials with highest amount of gypsum and the smallest volume changes occur in the paste with lesser amount of gypsum. The results do not correspond with the fact, that changes of pure gypsum are smallest, but the mechanism of setting in the pure gypsum and composed materials is different. The presence of slower reacting components (either lime or pozzolans) affects the crystallization of gypsum and causes less compact structure.

There is necessary to point out, that the results of repeated measuring of the same material differ in relatively large range. The measuring was apparently affected by the amount of air in the sample and in the vessel itself, even if we tried to drive out all the air bubbles from the oil during the filling period.

![Figure 6. Volume changes during first hour.](image)

5. Conclusions

The behaviour at early age of several composed gypsum-based material was studied by the means of isothermal calorimetry, measuring of setting times and volume changes during setting. The results were compared with the behaviour of pure gypsum paste. According the isothermal calorimetry, the most of the heat is developed during the first two hours after mixing. The heat evolution is fastest in
pure gypsum and also the cumulative heat, evolved at two first two hours is biggest. The hydration of composed materials is slower and the cumulative heat corresponds with the amount of gypsum in each of them. It could be concluded, that only reaction of calcium sulphate phases occurs at the first two hours. The lime and pozzolan components do not react during that period, but they serve as activators of anhydrite conversion into hemihydrate. They also act as retarders of setting. Their presence in the materials causes the bigger volume changes during setting in comparison with volume changes of pure gypsum, because they interfere with the formation of more dense crystal structure.

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