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POLABCAL: SPEED & ACCURACY

How automated calorimetry improves process control in calcium sulphate binder production and application.

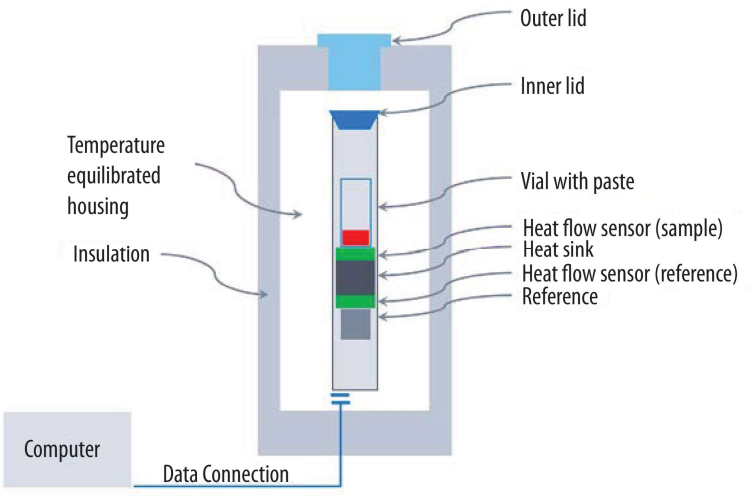
Calcium sulphate binders (CSB) are the principal constituents of stucco, wallboards, moulds for artwork and castings, and orthopedic casts. They are produced by the dehydration of natural gypsum, synthetic (usually flue gas desulphurisation (FGD)) gypsum, phosphogypsum, fluorogypsum and - with increasing importance - from recycled gypsum.

The reactivity of CSBs is controlled by phase composition, fineness, chemical admixtures such as accelerators and retarders, and/or seed crystals. Other factors that affect reactivity include temperature, the water/binder-ratio, the addition of foamers and the mixing process itself. The aim is to produce CSBs that have controlled water demand, workability and hardening properties.

Hydration of CSB starts within seconds of the addition of water due to the dissolution of gypsum and hemihydrate. The solution is saturated with respect to gypsum. During a subsequent dormant period, the reaction is dormant until the first gypsum seeds form. After this, the precipitation of gypsum accelerates. The resulting under-saturation of the pore fluid is compensated for by the further dissolution of hemihydrate. The reaction only stops when all hemihydrate is consumed. The hydration reaction is fully reversible, which makes CSBs ideal for recycling.

The aim, regardless of use, is a product of consistent reactivity that meets users' requirements. Testing of gypsum mixtures must be rapid and provide accurate data that can be used to adjust process control parameters, such that material losses and operational costs can be minimised.

Figure 1: Schematic design of isothermal calorimetric cell. The calorimeter is mounted in a thermostatic environment and records the heat produced by the sample.



Isothermal calorimetry

Isothermal calorimetry (Figure 1) is an analytical tool that follows the heat produced by chemical reactions over time. The thermal power during the hydration of gypsum is quantified by a heat flow sensor in a thermostatic environment. Thermal power is reported as a function of time. Various indices can then be evaluated, including peak maxima or total heat during a certain time interval.

When isothermal calorimeters are used in laboratory environments, the first 30-45 min are usually removed from every measurement as it takes this time for the sample to adjust to the temperature of the calorimeter. However, this is not possible for fast-reacting CSBs. This issue can be overcome by in-situ sample mixing inside the calorimeter, but this method requires extended thermal equilibration times and manual sample preparation.

Introducing the polabCal

Recently, thyssenkrupp Polysius and Calmetrix jointly developed an automated isothermal calorimeter known as polabCal for process control (Figure 2). This overcomes the thermal artifacts of standard calorimetry by preparing the sample in a thermally-controlled environment outside of the calorimeter. The temperature of the enclosure where the sam-

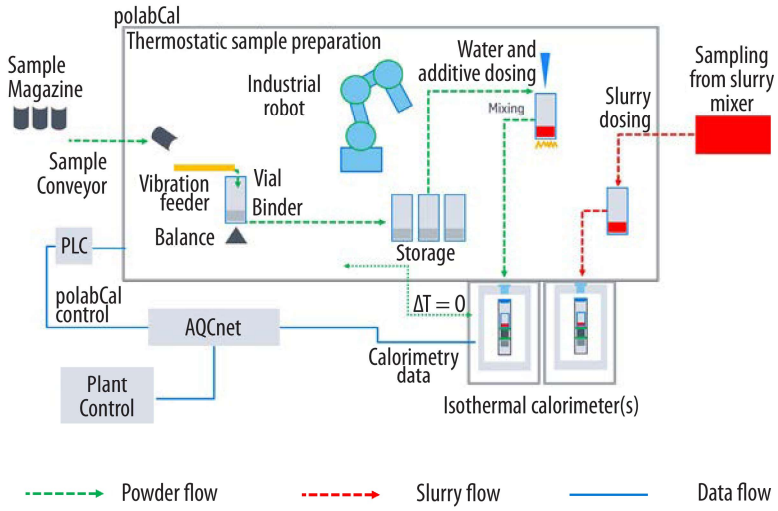
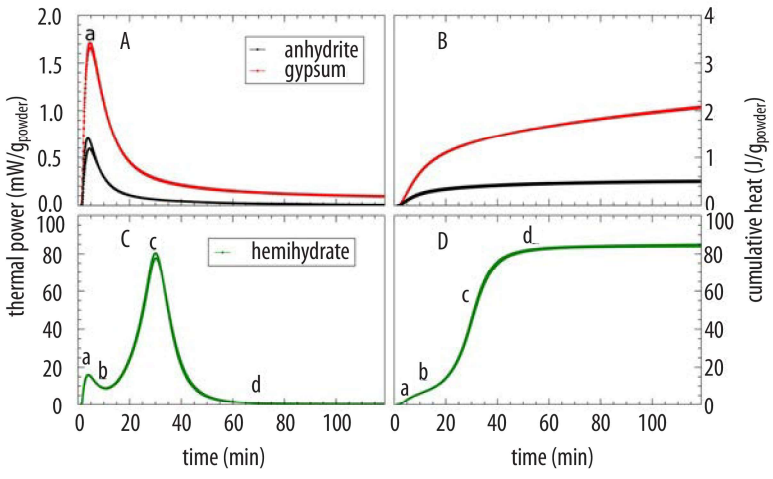


Figure 2: Schematic view of polabCal. The sample preparation is carried out with robotic handling in the thermostatic enclosure. The rectangle shows the extent of the enclosure.

ple is prepared is thermally equilibrated to be the same temperature as the isothermal calorimeter. This eliminates the need for initial temperature equilibration.

The samples are transferred automatically from an external sample magazine into the temperature-controlled enclosure. Inside the enclosure, sample handling is conducted by an industrial robot. Sample weight is measured by a balance inside the enclosure. Waiting positions ensure that the sample is in thermal equilibrium.

Figure 3: A-B: Dissolution of gypsum and anhydrite. At (a) maximum dissolution heat (B) cumulative heat during dissolution. **C-D:** Hydration of hemihydrate (see text for a-d). All in duplicate.



Just before the sample is inserted into the calorimeter, hydration is triggered by the addition of activation fluid (usually water). The water is injected by a precision syringe pump into the vial. The water volume is calculated using the powder weight to maintain a predefined water/powder ratio. Data recording starts from sample mixing to obtain the calorimetric baseline before the sample arrives at the measurement position, 40s after the addition of the water.

Up to 16-18 samples per hour can be dosed into vials and placed in an intermediate store. Final sample throughput depends on how long the user wants to analyse the samples for, as well as the number of available calorimeter cells. Typical installations provide 8-16 measurement positions for parallel measurement. All data is continuously transferred and analysed to be available for process control even before the measurement is completed. A special design can also collect slurries from an industrial slurry mixer for instantaneous analysis.

Examples using polabCal

All measurements described below have been made in a polabCal at 20°C from 5g samples and 2.5mL water (water/powder ratio = 0.5). All graphs display original data normalised to powder weight, without further data smoothing or processing.

Sulphate minerals in isothermal calorimetry: Figure 3 A-B displays isothermal calorimetric measurements of thermal power and heat for natural gypsum and natural anhydrite. Gypsum and anhydrite release very little heat during initial dissolution (note x-axis scale). After 5 min, the peak (a) marks a solution saturated with respect to gypsum. The thermal power of these samples decay steadily and no further heat release is seen over 24 hours (not shown). All measurements were duplicated, confirming the good repeatability of heat of dissolution to within 0.1-0.2mW/g of powder.

The heat release pattern for hemihydrate (Figure 3 C-D) starts with high intensity. During this initial dissolution (a), the solution becomes super-saturated with respect to gypsum. In the dormant phase with little activity, gypsum seeds form (b). The reaction then accelerates when gypsum precipitation increases (c). During this period, precipitation of gypsum and dissolution of hemihydrate are balanced. When the system runs out of hemihydrate (d) the reaction stops after about 60 min, no further heat release is observed. The heat release of the hemihydrate sample is about 40 times the heat release of gypsum and anhydrite.

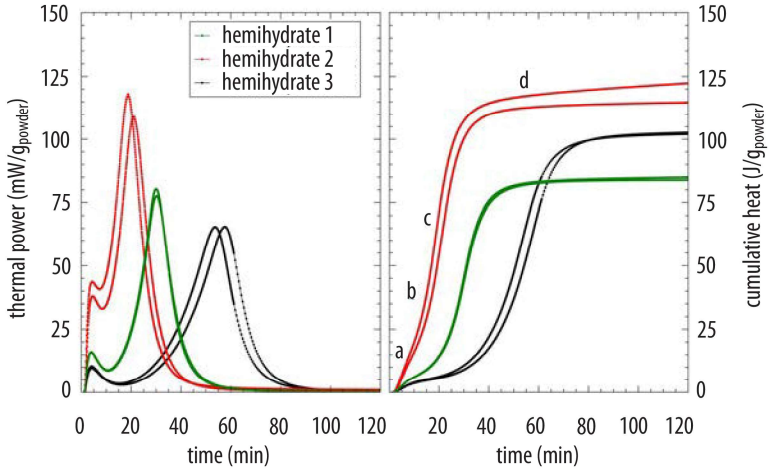


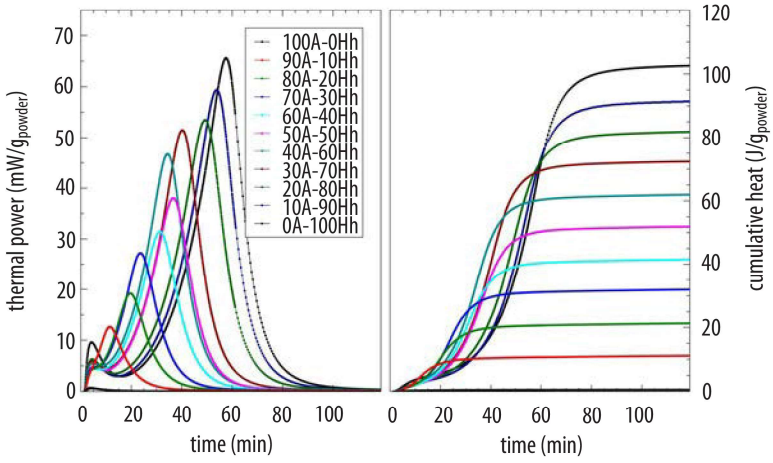
Figure 4: Analysis of three hemihydrate samples with polabCal.

Figure 4 A-B compares different hemihydrates. As can be seen, the course of the reaction remains the same, but reactivity and kinetics vary from sample to sample. Hemihydrate 2 reacts much faster and at higher intensity relative to hemihydrate 1. Finally, hemihydrate 3, which was stored in bags for a long period prior to measurement time, has a dormant period with a low intensity and an extended reaction time. There can be several reasons for the differences seen between the results for the three hemihydrate samples: sample purity, fineness, as well as chemical admixtures or seeds added.

Table 1: Correlation analyses of the calorimetric parameters versus hemihydrate content.

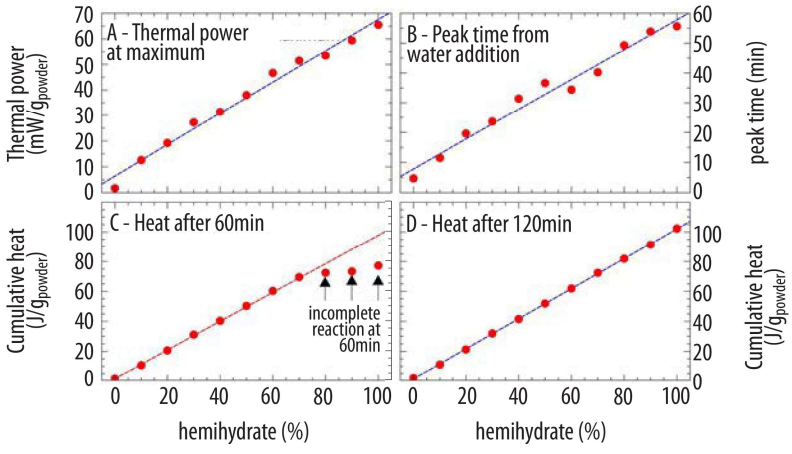
Y = mx + b	Thermal power max (mW/g powder)	Time from water addition (min)	Cumulative heat at 60min (J/g powder)	Cumulative heat at 120min (J/g powder)
Intercept	-9.5805	-14.0672	-1.3696	-1.5497
Slope	1.611	1.9525	1.0221	0.9951
Correlation coefficient	0.9927	0.9877	0.99991	0.99994

Below - Figure 5: A-B: polabCal measurements of anhydrite (A) / hemihydrate (Hh) blends. The peak maximum is shifted with increasing hemihydrate content. The cumulative heat curves are stacked linearly with the anhydrite sample being the lowest and the hemihydrate sample the highest.



Accuracy of polabCal: The accuracy of polabCal measurements was tested with blends made from anhydrite and hemihydrate (Figure 5A-B). The thermal power of the peaks increases linearly with increasing hemihydrate content. At the same time, the second peak is shifted to occur later. Cumulative heat release increases with hemihydrate content. Figure 6 A-D was used to retrieve numerical values for a correlation of data from calorimetry (thermal maximum, peak time from water addition and cumulative heat after 60/120 min) (Figure 6 A-D).

Thermal power (A) and time of peak after water addition (B) and the cumulative heat after 120s (D) correlate well with the hemihydrate content in the sample. This is a clear indication of the superior quality of the analysis. The cumulative heat after 60 min is affected by the incomplete hydration for hemihydrate content beyond 70-80% (Figure 6C). This is also seen in Figure 5 by the slope of cumulative heat release. The correlation data is shown in Table 1. The regression covered the complete range of the blends except cumulative heat 60 min, which was only correlated for hemihydrate less than 80%.



Left - Figure 6: Correlation analyses of calorimetric data with hemihydrate content for samples in Figure 5. The cumulative heat after 60 minutes is incomplete for high hemihydrate samples.

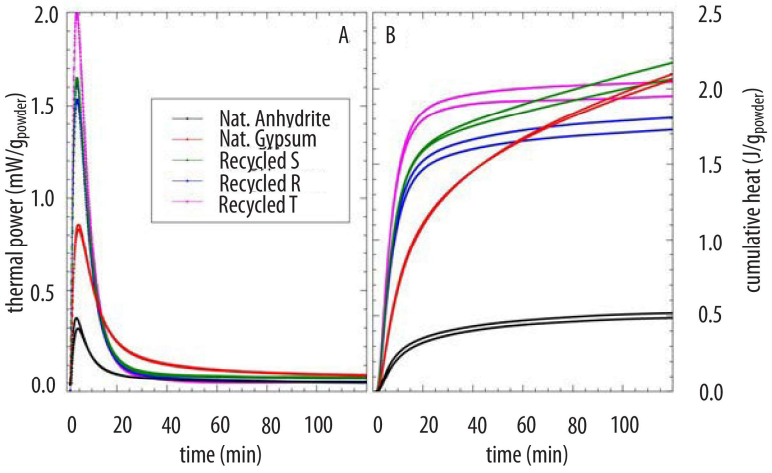


Figure 7: Heat of solution for recycled gypsum samples compared to natural gypsum. All recycled gypsum samples show an increased solubility in water.

Variability of raw materials: Recycled gypsum will become more important in CSB manufacturing. Figure 7 shows the dissolution heat curves for natural anhydrite, natural gypsum and three recycled gypsum products. Natural samples generate less thermal power during dissolution compared to all recycled gypsum samples ('Recycled S, R and T'). None of the samples in Figure 7 shows relics of hemihydrate (double peak in Figure 4). The increased solubility of the recycled gypsum could be due to either particle size, residual chemical additives or increased seed formation. Only two of the samples – natural gypsum and recycled gypsum S - also display a minor heat release over time.

Control cycles

The experiments presented in Figures 3-7 demonstrate the analytical performance of automated calorimetric analyses with materials from gypsum and stucco production. In all experiments, materials were changed to provoke differences in the analytical results. The most important point is shown in Figure 6, where a variation in hemihydrate content is linearly correlated with analytical results. This numeric information can be used to adjust process parameters like temperature, additives and residence time during hemihydrate production (Figure 8).

Hemihydrate can also be quantified in CSB applications. An example is plasterboard manufacturing, which requires large volumes of hemihydrate to react in a very short time. This process requires high frequency numerical data. In process control for CSB reactivity, this can be used as the main signal which is constrained by operational parameters like raw materials and process conditions, and economic parameters like cost and quality (Figure 8). The polabCal can rapidly visualise reactivity changes to return observations to the manufacturing process, like changing chemical additive dosages and/or seed concentration to maintain a targeted reaction rate of the product and to avoid losses during production.

Conclusion

The polabCal offers a fast way to quantify the reactivity of CSBs and is easily applied to determine the solubility of raw materials and the reaction kinetics of CSBs. Accurate numerical data is the key to implement automatic isothermal calorimetry as a tool in process control for both hemihydrate manufacturing and hydration kinetics of hemihydrate binders.

Figure 8: Process control cycle for plasterboard production. A frequent analysis of the CSB is used to maintain the production along a constant reactivity by adjusting additives, binder content and seed crystals.