Automated calorimetry - the missing link in quality control

thyssenkrupp Industrial Solutions and Calmetrix have partnered to develop polabcal - the first automated calorimeter for laboratory automation in the cement industry and other industries. polabcal provides rapid, accurate and numeric information on clinker and cement reactivity, so that data can be fed back to clinker and cement production. Calorimetric analyses closes a gap as thermal power, reactivity and compressive strength are closely linked.[1]

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Chemical/mineralogical process control in cement plants runs on a timescale of 30min to several hours. Only instrumental analyses can provide a sufficient number of data points. Increased usage of alternative fuels and raw materials (AFRs) complicates quality control. Trace elements (eg, alkalis, SO_3, MgO and P_2O_5) and process conditions (eg, kiln atmosphere and cooling conditions) modulate and often reduce reactivity of both clinker and cement. Quantitative XRD closes the gap between bulk chemistry and clinker and cement mineralogy. However, XRD does not provide reactivity data – reactivity can only be anticipated from mineralogical analyses by experienced users.

Compressive strength measurement is the common numeric value for cement reactivity. This physical testing is slow (days to weeks). Even one-day strength measurements are available only after two days (daily composite sample plus testing). Strength testing is costly as it requires normative sand and intense lab work. Compressive strength testing is loaded with a considerable error margin of 3-5 per cent. The timescale gap of physical data and chemical/mineralogical data calls for complex mathematical analyses to correlate both.

To predict compressive strength calorimetry is a cost-efficient tool with errors at less than one per cent, but it has rarely been used for correlation analyses with physical test results due to time requirements and missing numeric values.[1] Non-destructive physical testing techniques (eg, ultrasonic testing) do not reduce time demand for strength measurement but improve the cost of strength testing (less sand, less samples, less cubes/prisms).[2]

Introducing the polabcal

For the first time thyssenkrupp Industrial Solutions now offers an automated calorimeter as an add-on to its polab® laboratory automation portfolio. Calmetrix® developed I-Cal Flex for laboratory automation and contributed its experience in calorimetry of clinker and cement.

Figure 1: polabcal – the first automated calorimeter (with air-conditioned housing and PLC controller)

I-Cal Flex

Isothermal calorimeters monitor heat release from a hydrating cement over time[3]. The data is displayed either as a thermal power over time or as the cumulated heat release over time (see Figure 2). Thermal power shows a strong initial peak attributed to the initial hydration of C_3A and free lime (0-30min), a dormant period with little heat release after several hours (1-5h), a main peak reflecting the main hydration of calcium silicates (6-12h), possibly a sulphate depletion peak indicating the final consumption of the sulphate carrier (12-24h) and a long lasting slow heat release for conversion of less reactive constituents in cement. Any changes in the calorimetry curve can be attributed to a change in reactivity.

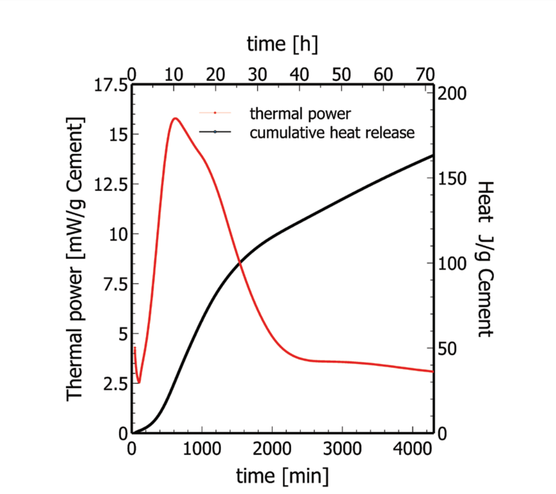

Figure 2: typical visualisation of calorimetric data as a thermal power curve and a cumulative heat release over time. The initial peak is cut and can only be seen if internal mixing cells are used

Today, calorimeters are charged manually by weighing the sample, filling the vial, adding water, mixing the water with the sample in the vial and inserting it into the calorimeter. The initial peak (first 30m, see Figure 2) can be resolved only in the internal mixing vessel. These vessels allow little control of the mixing process and are constrained for automation due to the lack of mechanical stability.

The I-Cal Flex is a new development with a versatile design that allows for easy integration into an automated system (see Figure 3). Channels of I-Cal Flex can be replaced individually without removing the complete calorimeter. The latter maximises absolute operation times and minimises time loss for eventual maintenance/replacement and reduces maintenance costs. Furthermore, measuring cells are completely independent and cross-talk between neighbouring cells is eliminated.

Automated sample preparation

The polabcal (see Figures 1 and 4) receives samples either from the lab automation system directly (robot, handling device) or manually from a turntable magazine. The sample code, sample preparation, measurement and data evaluation are added from the proprietary control software.

Automated unattended calorimeters require the translation of manual procedures to automatic procedures. polabcal is housed and air-conditioned to maintain all materials, water and installations at constant temperature. Inside polabcal a turntable-magazine (manual/robot operation) holds samples ready for unattended sample start. A dosing system fills samples by weight or by volume into a vial. Water addition is adjusted to the sample weight. After closing the lid, the vial is transferred to a high-shear vibrating mixer with high reproducibility and later to I-Cal Flex. Temperature equilibration of both the polabcal and I-Cal Flex facilitate an immediate start of the measurement. The short and exactly reproduced delay from sample reparation to measurement assures a reliable recording of the initial peak (see Figures 5a and 5b). Within a few hours – sometimes even sooner – the operator can use measured reactivity data for control decisions. After the measurement the vial is disposed and the calorimeter is ready for the next sample. The calorimeter is supervised by automation software with embedded analytic modules based on thyssenkrupp Industrial Solutions' edge device technology.


Figure 3: I-Cal Flex calorimeter in automated operation. Each cell is operated by polabcal and can be exchanged individually for maintenance

Automated data evaluation

Today, calorimetric data is evaluated by visual inspection of samples relative to each other. Numeric analyses of calorimetry data are rare.[1] Only low-heat cements are tested for their absolute cumulative heat release over time.[4]

Automated calorimetric analyses require a new approach in data evaluation. Two approaches are possible:

1. a numeric approach where parameters like maximum heat release, changes in slope, slope over time and heat release after a certain time are collected from the calorimetric curves
2. a chemometric approach where calorimetric curves are quantified by shape similarity relative to their next neighbours of known data.

All parameters read from the curves are transferred into the cloud or a database for analysis. Finally, each measurement is stored in a fileserver. Time stamp and material code make each analysis unique. The complete data set can be analysed for chemical/mineralogical parameters driving reactivity.

Quality of automated sample preparation

Two important factors for sample preparation are repeatability and accuracy. Figure 5a highlights the superior data quality from automated sample preparation. The benefit is even more apparent if compared to Figure 2 corresponding to manual sample preparation. The area seen in conventional calorimetric measurement is shown in blue. In contrast, if polabcal is used the initial peak is measured accurately (insert in Figure 5a).

Figure 5b shows repeated measurements of the same cement. It is obvious that the initial peak is measured accurately. In addition, all data is reproduced with minimum deviation, giving access to reliable evaluation of the data, as well as accurate translation to numeric parameters and actions.

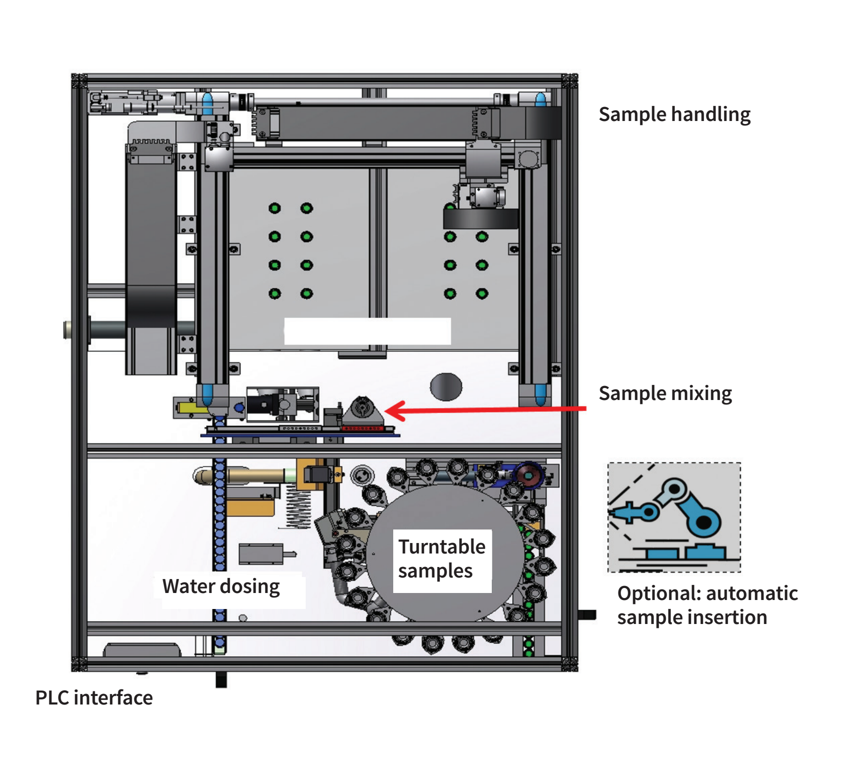

Figure 4: drawing of polabcal without housing to show the modules inside. Each step needed for sample preparation for calorimeters was translated into an automatic routine to improve sample preparation and transfer times from one step to the next

> *"Automated calorimetric analyses will facilitate a fast and considerably shortened data acquisition of calorimetric data."*

Depending on the required signal, either the first peak can be used standalone or data from longer measurement times can be included in the data evaluation. As repeatability is high, one can conclude that observed differences in shape correspond to differences in reactivity. This data correlated with process data, chemical and mineralogical data can be used for process control.

The missing link

Knowledge of clinker and cement reactivity is the missing link between plant quality control and physical testing of cement. Automated calorimetric analyses will facilitate a fast and considerably shortened data acquisition of calorimetric data. polabcal will allow correlation of clinker and cement reactivity with any analyses in the system (raw meal, hot meal, clinker, raw materials) to improve understanding of how to increase clinker reactivity – based on actual measured data. All this works from the front end of the cement production process with sufficient times to react. This link from process to physical data is a breakthrough in cement plant quality control. ■

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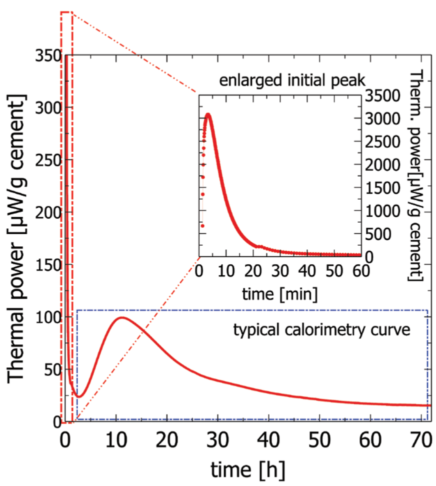

Figure 5a: thermal power pattern collected from polabcal. The graph shows a typical calorimetric measurement including the area usually seen in isothermal calorimeters. The insert shows the added benefit of routine initial peak measurement in polabcal and I-CAL Flex due to the speed of sample preparation

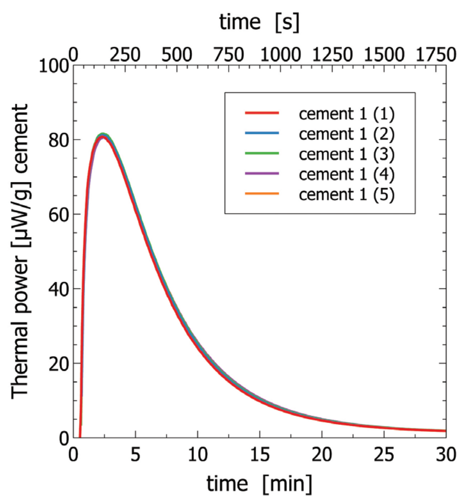

Figure 5b: repeatibility of polabcal measurement of five identical cement samples (only initial peak is shown)