Optimization of cementitious materials

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Introduction

Isothermal Calorimetry is emerging as a principal tool to directly measure the reactivity of materials and the rate of chemical reaction /1/. While isothermal calorimetry has been used for more than 60 years /2/ and is therefore not a new methodology, the rapid development of hardware, electronics and software has allowed for innovative equipment to enter the market at a very attractive cost compared to traditional test methods and equipment. The main benefits of isothermal calorimetry include very precise temperature control at a wide range of temperatures without the need for an air conditioned laboratory, low operational cost as sample preparation is simple and the measurements require little user intervention compared to traditional, manual tests.

Isothermal conduction calorimetry – basic principles

Most chemical reactions in cementitious binders release heat. The isothermal calorimeter continuously measures thermal power from a reacting sample kept at a user-defined near-constant temperature, allowing for a very precise "fingerprint" of the rate of chemical reaction. By integrating the thermal power over time one gets a measure of the overall degree of completion of the chemical reaction – heat of hydration - which for portland cement based systems correlates very well with compressive strength and other mechanical properties for a given mix design – Fig. 1.

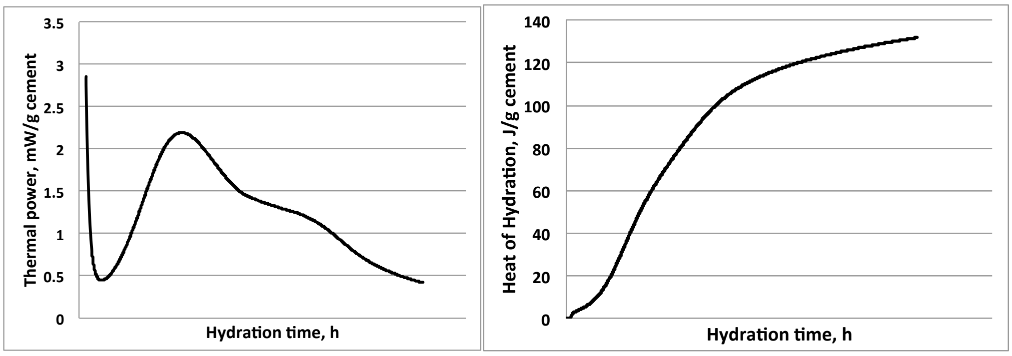

Fig. 1: Thermal power (left) and Heat of Hydration (right) of a portland cement based binder.

Temperature effects on the reaction rate of cementitious binders

Ambient temperature changes can have a strong impact on the rate of reaction of most cementitious binders, while the majority of standard performance tests of cementitious binders are only carried out at standard laboratory temperature. This represents a challenge whenever cementitious binders are mixed and cured outdoors. For example, most concrete today based on blended cements containing fly ash, granulated blast furnace slag and other so-called Supplementary Cementitious Materials (SCM) reacts much slower in the winter months compared to the summer. Isothermal calorimetry is an ideal tool to characterize such temperature effects as the user can perform tests at a wide range of temperatures, thereby simulating climate effects.

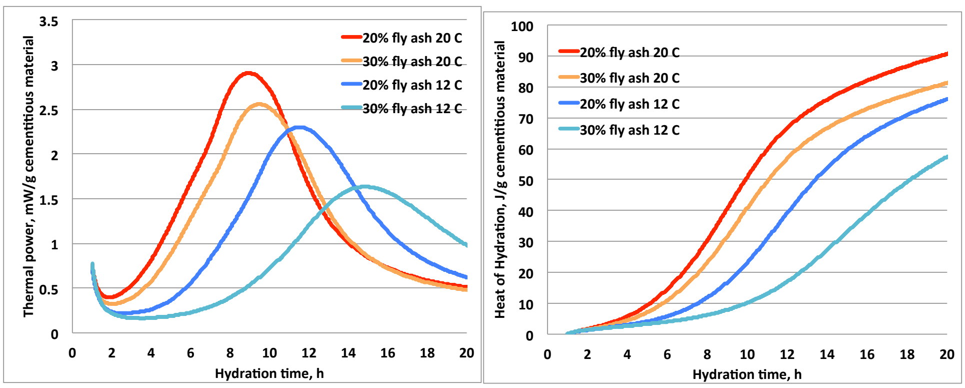

Fig. 2: Effect of temperature on hydration of blended cement with 20% and 30% fly ash. Left: Thermal power. Right: Heat of Hydration

Fig. 2 shows an example for a fly ash blended cement with 20% and 30% fly ash tested at 12 °C and 20 °C, respectively. Isothermal calorimetry makes it very easy for the user to not only understand such temperature effects, but also to test for remedies when needed, such as the use of an accelerating cement additive, and/or finer cement grinding during winter months. Furthermore, one can calculate apparent activation energies simply by testing a given binder at different temperatures and assuming a first order reaction, which is generally useful for predicting temperature effects on most cement, concrete and dry mortar formulations.

Direct measurement of the pozzolanic reactivity of fly ash

The increasing demand for substitution of Portland cement clinker with fly ash and other SCM's creates a challenge as it is difficult to directly measure the reactivity of the SCM with traditional test methods, given that its rate of reaction is usually very slow and affected by the properties of the Portland cement component in the mix. Isothermal calorimetry offers the possibility to measure the reactivity of the SCM ***directly***, without the heat flow contribution from the Portland cement component, by reacting the SCM in a pre-defined simulated "Portland cement environment" that represents the chemical environment defined by available Portland cement based materials /3/. Fig. 3 shows an example with two different fly ashes reacting in a simulated "Portland cement environment" with a variable alkali content. The alkali greatly affects the dissolution of the potentially reactive glassy phases in most SCM's.

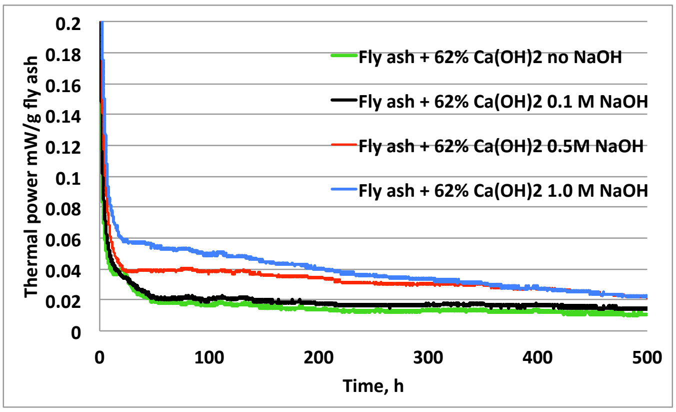

Fig. 3: Direct reactivity of fly ash in a simulated Portland cement environment with excess calcium hydroxide and variable sodium hydroxide concentrations.

Sulfate optimization of Portland cement based binders

The concept of sulfate optimization of Portland cement to minimize the aluminate reaction at early age and thereby maximize strength development is well known /2/. However, sulfate optimization is becoming increasingly challenging as modern binders make use of greater amounts of supplementary fuels, SCM and chemical additives, most of which have a strong impact on the sulfate optimum /4,5/. Traditional methods involving strength development of standard mortar or concrete are often too crude as they typically do not factor in the effect of temperature, chemical additives and, more importantly, temporary early age effects on aluminate reactivity that strongly impact rheology and workability. Here again, isothermal calorimetry offers outstanding possibilities as most if not all such effects can be tested for locally, without the need for a traditional laboratory. The isothermal calorimeter itself is "the lab". Fig. 4 shows and example with concurrent measurements of compressive strength of standard mortar, and isothermal heat of hydration of cement paste with different sulfate additions. The results clearly show the excellent potential for using heat of hydration obtained by isothermal calorimetry to define the sulfate optimum. Once the optimum has been defined, it is very easy to check for deviations from optimum simply by daily QC monitoring of the positioning of the so-called "sulfate depletion" peak, Fig. 5. Of course, by using isothermal calorimetry one can then easily also test for the effect of temperature and chemical admixtures, both of which usually have a profound impact on the sulfate balance of a cementitious mixture. Finally, by carefully measuring the very early reactivity of mainly the aluminates during the first hours, one can also detect and monitor potential performance shortcomings related to aluminate-induced workability issues, which are an often unintended consequence of the ever increasing demand for higher reactivity and lower fuel costs in cement manufacture – Fig. 5 (right).

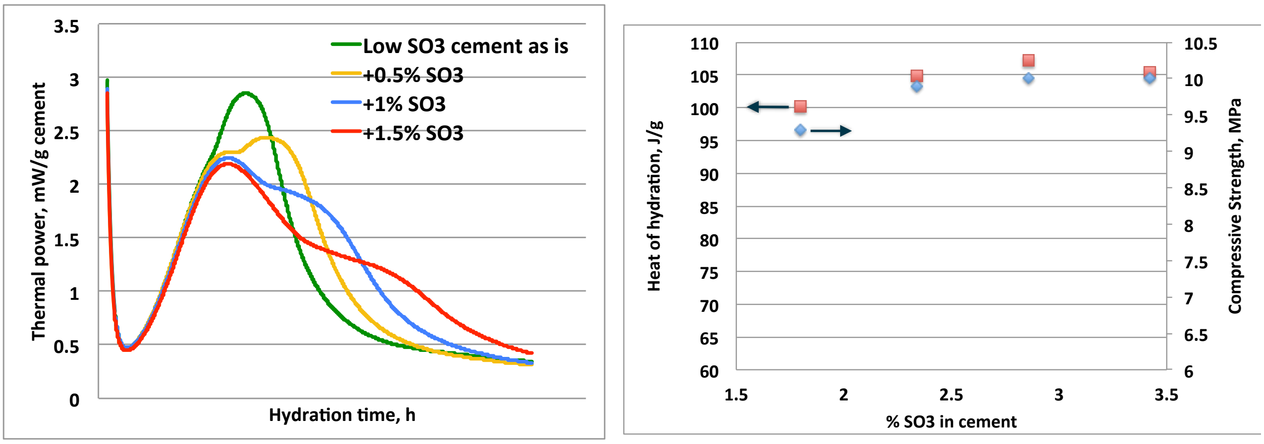

Fig. 4: Sulfate optimization tests by isothermal calorimetry. Left: Thermal power. Right: Heat of hydration compared to compressive strength

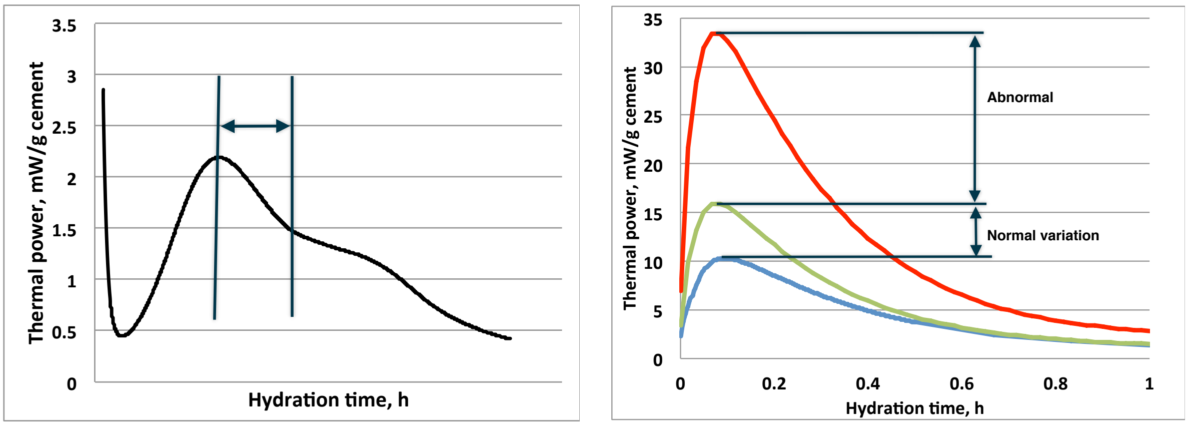

Fig. 5: QC testing: Left: Elapsed time between the maximum of the main peak and sulfate depletion based on results from the optimization in Fig. 4. Right: Very early reactivity. Note the difference in scale.

References

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