

MEASURING CASTABLE RHEOLOGY BY EXOTHERMIC PROFILE

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ABSTRACT

As castable placement technology advances, further information is needed to assess the rheological properties. Flowability, set time and strength-gain measurements have been successfully used to assess rheology, however a growing number of laboratories are supplementing these measurements with an Exothermic Profile measurement of the castable and also the raw materials used to formulate the castable.

The heat of hydration of Portland Cement and Calcium Aluminate Cement are on the same order at about 500 kJ/kg. Because Calcium Aluminate Cement releases this energy over a much shorter period of time, this reaction is easy to measure, even when the cement contents are low. Certain deflocculated castables also exhibit a heat rise during initial flocculation, well before hydration, marking the end of working time. Because these measurements can be automated with a thermocouple and a PC, the test is easy to set up and run.

Creating an exothermic profile on a neat cement paste gives information about the composition and reactivity of that cement and may be useful for QA purposes.

This paper will present practical examples of the above-mentioned topics and attempt to explain the reason for the occurrences. Results and discussion concerning the repeatability and reproducibility of these tests will also be presented.

INTRODUCTION

Both complex and simple castables utilizing calcium aluminate cements (CAC) as the binder undergo two visible reactions after water has been added. The first reaction is a flocculation reaction and is noted by a lack of mobility of the castable (end of working time) and/or a set by Vicat needle. This type of reaction can also be measured by the stiffness of the castable in a flexible container (e.g. cup). Once this reaction has

occurred, it is often referred to as “set” or “initial set” or “gelled”. After this reaction, a castable does not necessarily have sufficient mechanical strength to survive significant handling. Measured compressive strength numbers may only be on the order of about 1.5 MPa (220 psi). When this reaction is related to the initial dissolution of CAC, it can release a small amount of heat, which may be measured by a thermocouple.

The second reaction is the hydration of the cement with water. During this reaction, hydrates are formed through precipitation from solution. These hydrates grow in the liquid portion of the castable, converting liquid to solid and binding other materials in the castable together. This causes the castable to gain mechanical strength.

For this second reaction to begin, germination of nuclei from the saturated solution must occur within the castable. After these nuclei are formed, the hydration reaction begins and proceeds as described by Le Chatelier’s cycle. This cycle is a continuous dissolution of anhydrous cement and precipitation of hydrates and proceeds until all the anhydrous particles of cement exposed to water within the castable have been consumed (Figure 1).

The cement dissolution portion of the reaction is exothermic in nature. During this reaction, temperatures within the

castable can range from barely recordable (< +1°C above start temperature) to temperatures in excess of 130°C (266°F). The final temperature in the castable depends on many things, including:

- cement content (% by wt.)
- mineralogy of cement
- admixtures
- size of cast object
- shape (surface area) of cast object
- start temperature of mix
- temperature of surroundings
- thermal conductivity of aggregate system
- thermal conductivity of the environment

Confirmation of the timing of these reactions can be measured by inserting a thermocouple into the wet castable and measuring the temperature [1, 2]. Temperature can easily be logged by a PC and plotted vs. time to produce an exothermic profile (EP) of the castable under investigation. When run under standardized conditions, repeatable results can be generated and strength gain can be predicted for specific castable systems where a correlation has been established. On certain deflocculated systems, an initial rise in temperature is sometimes observed which can indicate the initial dissolution of cement and usually signals the end of working time.

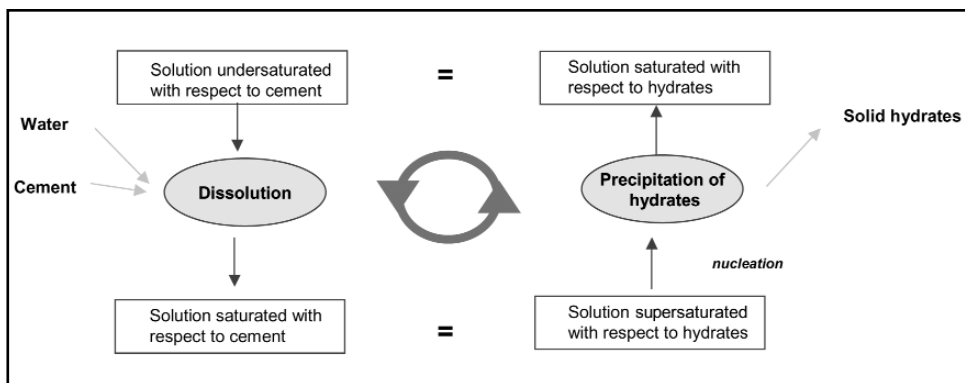
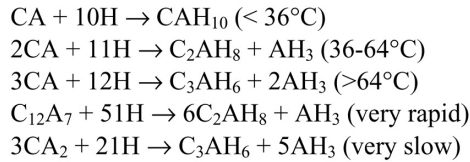


Figure 1. Le Chatelier's Cycle

PRACTICE

Le Chatelier's principle as applied to simple calcium aluminate cement mortars produces hydration reactions with the following equations [3]:



Calcium aluminate cements currently on the market typically contain a mixture of soluble anhydrous phases, including C_{12}A_7 , CA and CA_2 . Individually, these phases react at different rates due to different solubilities. Once Le Chatelier's cycle begins and dissolution and precipitation are occurring simultaneously, the exothermic property of dissolution proceeds in such a way as to generate a measurable increase in temperature.

Exothermic Profile of Simple Mortar

Figure 2 shows a typical thermal profile of a 70% Al_2O_3 cement in a sand mortar (25% cement, ISO 679 sand and 12.5% water). One plot is of the thermocouple reading, which is embedded inside the mortar during hydration, and the other is the derivative of this temperature reading.

This cement is composed predominantly of CA and CA_2 . The internal temperature recorded by the thermocouple is constant at $\approx 20^\circ\text{C}$ until 220 minutes when the first hydrates begin to form. Up to 285 minutes we see the temperature increasing up to about 38°C . In this region we can observe the formation of CAH_{10} . Stopping the reaction and running XRD and DTA on the concrete have confirmed this is the predominant hydrate phase at this point during the reaction [4]. From 285 to 315 minutes the temperature further increases up to 65°C . In this region we can observe the formation of C_2AH_8 and AH_3 . After 315 minutes the temperature further increases up to 80°C . In this region the precipitation of C_3AH_6 and AH_3 are observed until 345 minutes when the reaction begins to slow as the anhydrous phase is consumed.

Both the slope of the temperature profile and the derivative of that profile with respect to time can note these three regions. Not only can we confirm the onset of hydration and therefore strength gain, but we can also derive some information about

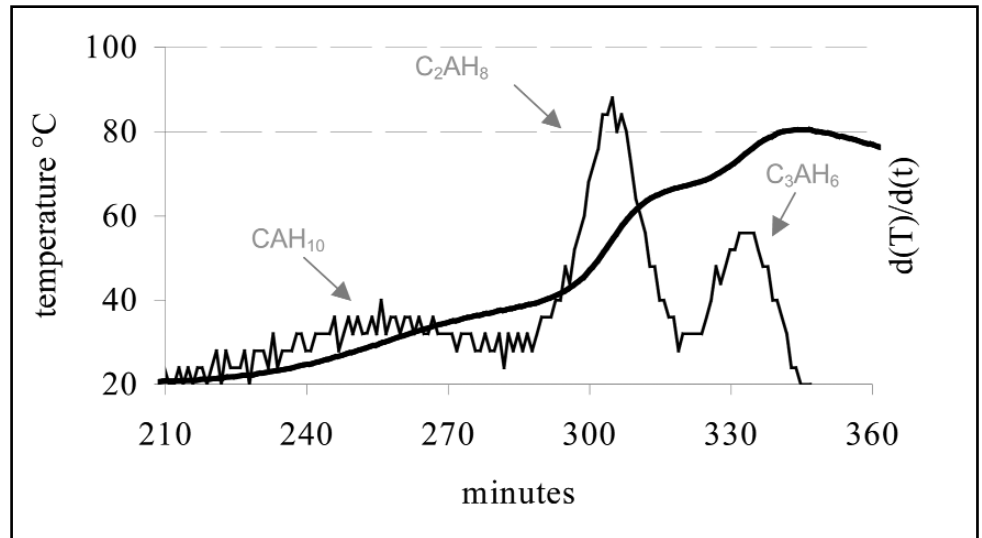


Figure 2. Thermal profile of alumina cement in sand mortar.

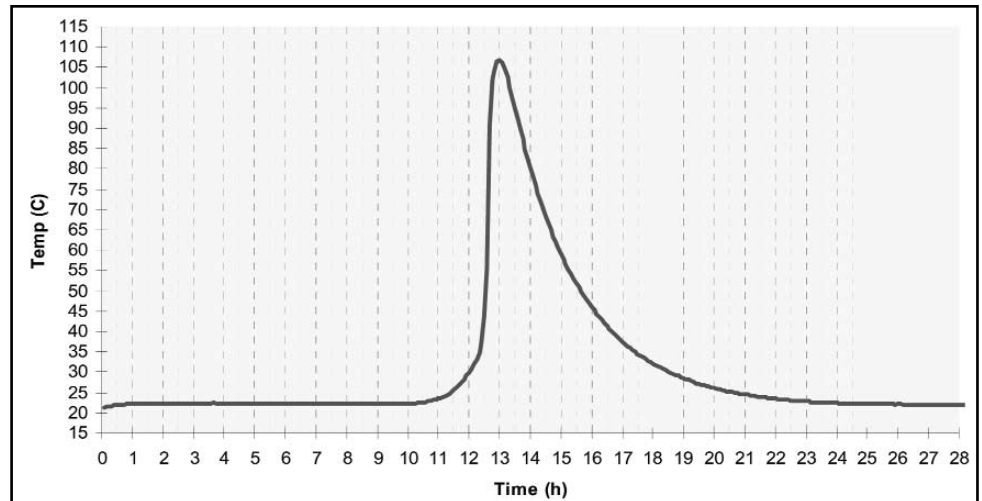


Figure 3. Neat paste exothermic profile.

the hydrate phases that are being formed by the temperature inside the castable.

Exothermic Profile of Neat Paste

It is interesting to now compare this mortar profile to an exothermic profile generated with the same 70% alumina cement in a neat paste formulation. Neat paste is a formulation of only cement and water. In this case the water is added at 25% of the weight of the cement.

Figure 3 shows no thermal activity (hydration) until about 11 hours, with a peak temperature occurring at about 13 hours. In contrast, the mortar peak temperature occurred at 5 1/2 hours. The reason for this slow activity in the neat paste is the lack of germination sites for the nuclei to start the hydration reaction. Without the heterogeneous nucleation sites provided by the normally present "other" castable raw materials, like aggregates, fines, etc., the

reaction must start from precipitates only. In this case, the hydration is controlled mainly by the mineralogical composition of the cement. Cements that contain a higher proportion of reactive phases, like C_{12}A_7 , would create an ionic solution higher in Ca^{2+} than that of CA or CA_2 . It is the ratio of Ca^{2+} to $\text{Al}(\text{OH})_4^-$ in solution that governs the rate of the formation of nuclei, assuming other parameters being equal.

Figure 4 exemplifies this difference in ionic concentration over time of two solutions; one exposed to laboratory prepared CA and the other to laboratory prepared C_{12}A_7 . In this extreme example, one can see that the ionic concentration of the two ionic species will be significantly affected by the composition of the anhydrous phase. As the mineralogy of the anhydrous cement varies, so should the ratio of ions in solution.

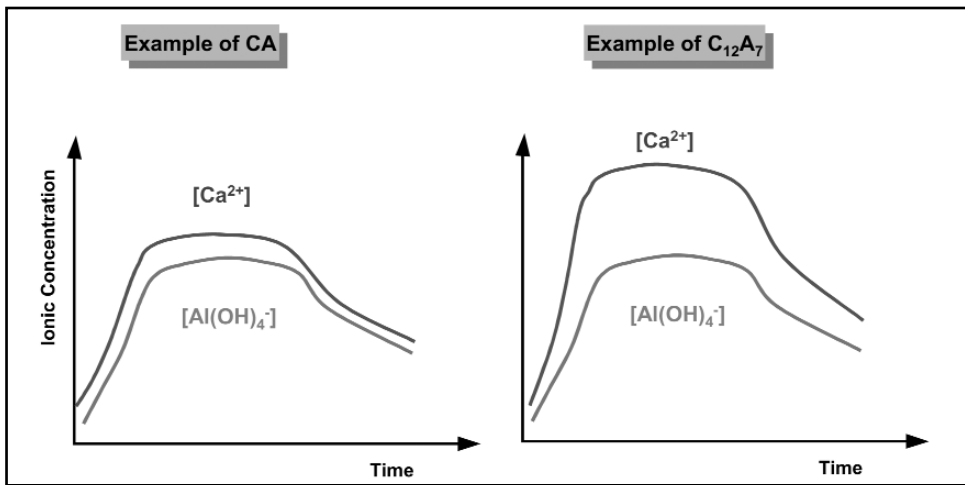


Figure 4. Schematic ionic concentration of two solutions.

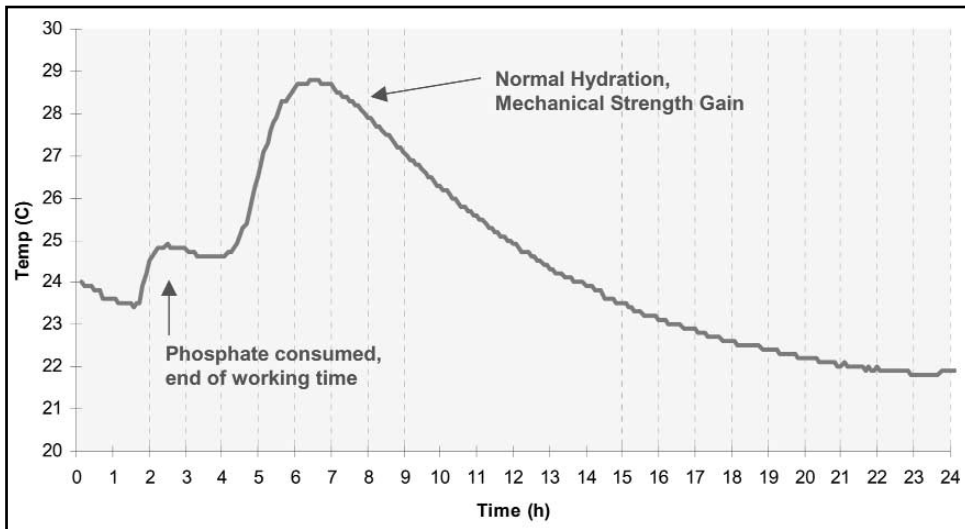


Figure 5. Exothermic profile of low-cement castable.

Table 1. Low-cement castable composition.

Sintered Alumina Aggregates (6 mesh and finer)	80%
Reactive Alumina	10%
Fume Silica	5%
CA Cement (70% Alumina)	5%
Sodium Tripolyphosphate	0.03%

It is for this reason that neat paste exothermic profiles can be useful to gauge the variability of the mineralogical composition of cement. In an exothermic profile of neat paste, the time to peak temperature is easy to read, as it is a very sharp peak. Lafarge Calcium Aluminates has reported that this time to peak value varies from approximately 9 to 24 hours depending on the reactivity of the cement. While this “time to peak temperature” value does not correlate to normal setting and strength gain numbers, it has been useful to predict the performance in a deflocculated castable system. Within lab repeatability studies have shown that on 10 specimens of the

same sample, a standard deviation of 0.2 hours is normal.

Exothermic Profile of Low Cement Castable (LCC)

The exothermic profile produced by placing a thermocouple into low cement castable is dependent on many things. Because other raw materials and the environment can control the reactions generated by the cement, proper controls must be in place to create repeatable results. The size of the sample and the insulation around the sample can also affect these results. If the castable contains very little cement, a larger sample will probably be required to gen-

erate enough heat to be measured by this method. Figure 5 shows an exothermic profile generated by a LCC with the composition shown in Table 1.

Upon inspection of this profile, two peaks are evident. The first peak is believed to be caused by a reaction of the phosphate and the silica fume, complexing the dissolution of the CA cement [5, 6, 7]. This complexing blocks the normal dissolution of the cement until the phosphate is consumed and then releases the CA into solution. Laboratory investigations have shown that this first peak strongly correlates to the working time of deflocculated castables. It has also been observed when working with aged castables that the first peak can disappear or that both peaks can be significantly moved to the right, indicating that reactions have been delayed or severely diminished.

The second peak in this profile shows the normal hydration reaction that occurs with CAC. As with other systems containing CAC, it is after this peak that full mechanical strength is obtained.

In this system the exothermic profile can be especially useful as it can give an indication of both the working time and the setting time of the castable in one automated test. Since admixtures can move these two reactions individually, this test can be useful to gauge the use of different admixtures on a given system. The effect of ambient temperature on working time and strength gain can also be studied with this method by allowing the specimens to cure in different environments.

Figure 6 shows exothermic profiles generated by a dose rate scan of a polyacrylate additive applied to an alumina-magnesia castable system. This example was also chosen as it was run in a 35°C environment. Note that the 0.01% addition rate had no effect on the control and that the 0.02% addition rate only changed the amount of heat released. In contrast, the higher dose rates have clearly shown a delayed dissolution of the cement, a retardation of the formation of nuclei and hence the onset of hydration.

CONCLUSIONS

Exothermic profiling of hydraulic minerals and the castable systems created from them can reveal useful information about the reactions present in these systems.

In the laboratory, this method is normally automated and if the environment is stable,

can produce results not generally subject to operator and equipment error. Only the thermocouples need to be calibrated. This technique can be used as a research and development tool to generate profiles of castables being optimized for admixture interaction. The addition of an accelerator or retarder can effect significant changes in the exothermic peak times and temperatures. As the castable can easily be stored in environments of different temperatures, studies could also be done on the effect of temperature on the system under investigation.

When designing experiments, one should keep in mind that the following variables can significantly affect the results of the profile: size and shape of specimen, thermal conductivity of specimen, starting temperature of the mix, temperature of the surroundings and the thermal conductivity of the surrounding medium.

Exothermic profiling could also be used as a quality control tool to verify the setting time of manufactured castable, troubleshoot problem castables and to screen reactive raw materials for use in these systems.

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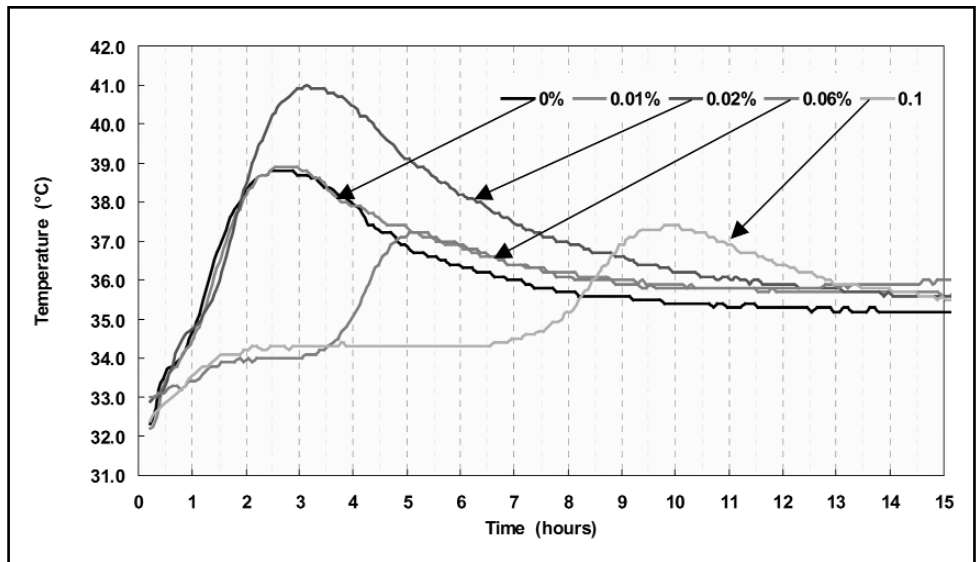


Figure 6. Effect of polyacrylate addition to exothermic profiles.

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From the Editor Continued from Page 4

reentry conditions at McDonnell Douglas; the simulator in its most primitive designs consisted of ganged arrays of torches which moved toward refractory candidates at a rate that duplicated the heating rates of reentry. Many commercial refractories were tested in those early studies and some of them could have been made to work. The ablation design was eventually selected because the glass fiber-polymer composites did not have joints and had the capacity to function as a very efficient thermal blotter. Another of the early designs involved carrying enough water on board to cool the reentry surfaces by evaporation! Refractory scientists also worked on the refractory coatings that were used to cover the metal surfaces of the early capsules. Through many years the launch pads were paved with aluminosilicate refractories which were flooded with H₂O to absorb much of the thermal energy of lift-off.

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Robert E. Moore, Editor

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with numerous years of practical experience to quickly analyze a customer's problem and resolve it—often without leaving their computer chairs! Furthermore, internet web training sessions are on the horizon with interactive refractory consultation for rapid failure analyses and repair regimens.

Meanwhile, the global refractory community is becoming more cohesive. International refractory symposiums, seminars, and expositions are escalating. Worldwide coordination of refractory technology, material standards, and installation specifications is progressing. For instance, the American Petroleum Institute (API) has issued an industry wide document that provides universal guidelines for the installation, inspection and testing of monolithic refractory linings in refining and chemical processing facilities. This document resulted from the collaboration of several experienced specialists involved in worldwide refractory installations. It can be the forerunner of additional universal specifications and standards that insure quality global refractory installations.

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