Using calorimetry to understand pozzolanic reactivity of fly ash or other supplementary cementitious materials

Instruments to which this note applies: All Calmetrix I-Cal HPC isothermal calorimeters

Target use: Fast and convenient assessment of pozzolanic reactivity of fly ash in concrete.

Introduction

Fly ash activity is commonly tested in a mixture with Portland cement, which makes the resulting "activity" result heavily dependent on the chemistry and activity of the Portland cement itself. Furthermore, the heat from fly ash hydration is very low compared to that of Portland cement, thus making it difficult to measure the fly ash activity directly with calorimetry in a mixture of Portland cement and fly ash.

This application note describes how to use isothermal calorimetry to measure the hydration activity of fly ash directly in a simulated Portland cement environment, i.e. an environment that contains the relevant chemistry provided by a Portland cement, but without the actual hydration of Portland cement. This method provides a direct pozzolanic activity test of fly ash using isothermal calorimetry, which can be performed at a wide range of temperatures and without the variability or noise that would result from the presence of Portland cement.

Methodology

The approach outlined in this application note uses heat of fly ash hydration as a test method for fly ash activity in a well-defined chemical environment, excluding any interference from Portland cement clinker. While the pozzolanic activity is normally referred to as the ability of the pozzolanic material to react with calcium hydroxide to form calcium silicate hydrates, the presence of highly soluble alkalis, e.g. sodium and/or potassium, is critical. After a few hours of cement hydration, the soluble sodium and potassium are balanced by hydroxide ions in the pore water, thereby largely controlling the pH of the pore water. This is important because the pH in turn strongly impacts the dissolution of the amorphous phase in the fly ash, which is a necessary step before the pozzolanic reaction can take place.

A mix of calcium hydroxide and sodium hydroxide will provide a reproducible environment of the chemistry that unfolds the pozzolanic reaction and can therefore be used as a simulated Portland cement to measure fly ash reactivity.

Most cements generate a pore water in the range of pH 13-14 depending on the soluble alkali content of the cement and the water-cement ratio. Most fly ashes themselves contain soluble alkali, such that the pH driving the dissolution of the amorphous phase is typically above pH 13.

Experimental set-up

The following is an experimental procedure used to test two samples of low-calcium fly ash:

- Set the temperature of the calorimeter at 20.0 °C and let it stabilize for at least 24 hours
- Weigh 31 g calcium hydroxide and be pre-mix with 50 g mix water directly in a Calmetrix I-Cal HPC sample vial, together with sodium hydroxide, if any
- Leave the calcium hydroxide – water mixture inside the calorimeter to pre-condition its temperature to 20.0 °C.
- Once the water – calcium hydroxide slurry reaches thermal equilibrium in the calorimeter, remove the sample vial quickly from the calorimeter and mix 50 g fly ash into the water – calcium hydroxide slurry for 60 seconds, using a disposable plastic spoon that is left inside the sample vial after mixing.
- Close the vial and load it into the calorimeter and log the signal for 3 weeks at 20.0 °C

The heat of activity is very low for low calcium fly ash. Therefore, it is always a good idea to ensure the highest signal-to-noise ratio, for example, by using the largest possible quantity of fly ash in the sample, which in then will effect a higher signal. In this regard it is often best to prepare two samples for each calorimetry test: one sample with a slightly smaller mass of fly ash using internally equilibrated mix water and a disposable spoon left inside the sample cup as for the examples above, in order to accurately capture the initial reactivity. A second calorimetry sample with the maximum possible fly ash mass in the sample cup, which implies that the fly ash – calcium hydroxide mixture be prepared externally in a larger mixing bowl to facilitate proper mixing. It is also best to minimize any noise by ensuring that the laboratory temperature is well controlled, and that the calorimeter is not placed in direct contact with an air flow or any other source of heating / cooling. This guarantees the lowest noise and best baseline stability.

Example: reactivity of a low calcium fly ash

In this example, two samples of low calcium "class F" fly ash (labeled "NTPC" and "TANDA") were tested for pozzolanic activity with calcium hydroxide and various concentrations of sodium hydroxide in the mix water at a fixed water-to-solids ratio of 1.0 for 3 weeks at 20 °C without the presence of Portland cement in an I-Cal 8000 HPC isothermal calorimeter. Sodium hydroxide was added to the mix water at zero, 0.1, 0.5 and 1.0 M, representing cement pore water of pH 13 – 14.

Figures 1-2 show the activity of the two fly ash samples in presence of excess calcium hydroxide and a variable concentration of sodium hydroxide (0, 0.1, 0.5 and 1.0 M, respectively). Figures 3-4 show a close-up of the same results during the first two days.

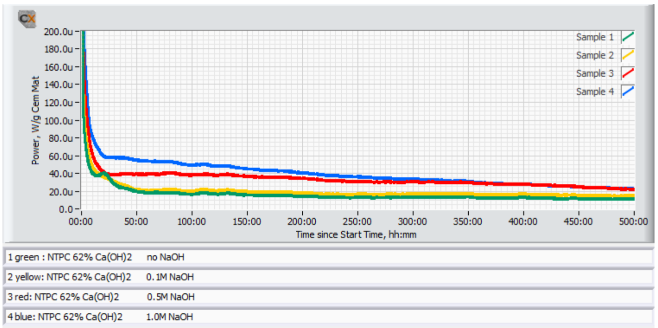

Fig 1. Power (rate of reaction) by weight of fly ash A (labeled "NTPC") during 3 weeks of hydration.

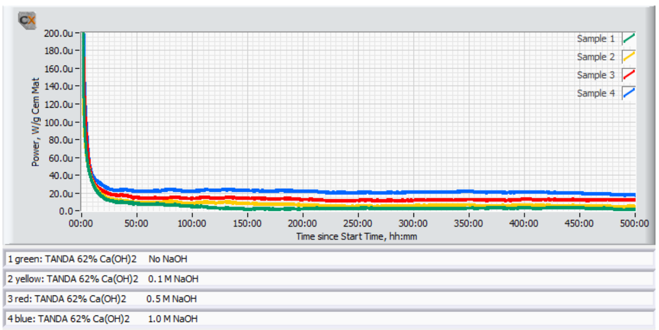

Fig 2. Power (rate of reaction) by weight of fly ash B (labeled "TANDA") during 3 weeks of hydration.

Results and discussion.

For the more reactive NTPC fly ash in Fig. 1 & 3, the effect of higher sodium hydroxide concentrations was quite substantial. However, for the much less reactive TANDA fly ash in Fig. 2 & 4, the sodium hydroxide concentration did not impact reactivity – in this case probably because the TANDA fly ash contains less of the pozzolanic amorphous phase.
Overall, the NTPC fly ash was considerably more active compared to the TANDA fly ash in all conditions tested.

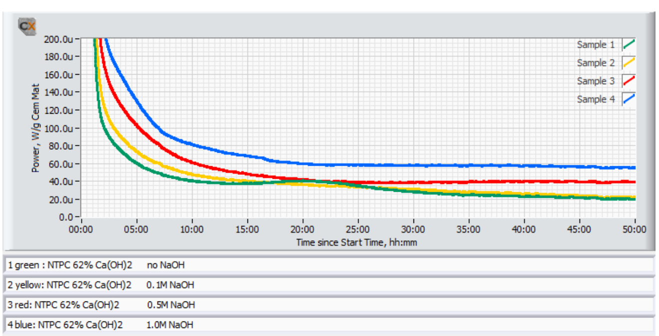

Fig 3. Power (rate of reaction) by weight of fly ash A (labeled "NTPC") during the first two days of hydration.

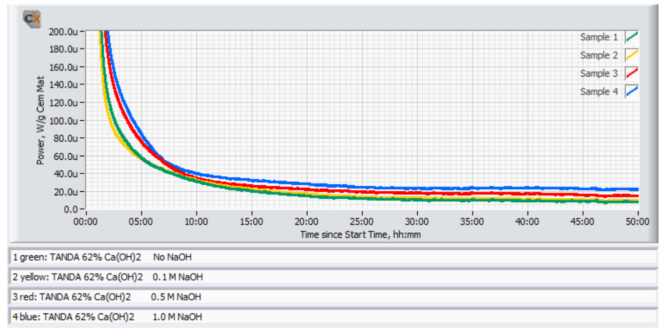

Fig 4 Power (rate of reaction) by weight of fly ash B (labeled "TANDA") during the first two days of hydration.

Conclusion

Isothermal calorimetry is a powerful tool to measure the pozzolanic activity of fly ash as a function of temperature in a "simulated Portland cement environment", emulating the fundamental elements normally provided by Portland cement. The use of a simulated Portland cement environment without actual Portland cement is often preferable as it excludes any thermal noise that would result from the hydration of the Portland cement itself.
It may be of interest to explore the effect of temperature on the pozzolanic activity. I-Cal HPC calorimeters are well suited for such studies, given their built-in precision temperature control that effectively eliminates the need for a larger climate control chamber for tests at different temperatures.

References

Zhang, T., Yu, Q., Wei, J., Gao, P., Zhang, P., 2012. Study on optimization of hydration process of blended cement. J Therm Anal Calorim, 107, 489–498

Kocaba, V., 2009. Development and evaluation of methods to follow microstructural development of cementitious systems including slags. PhD thesis No. 4523, École Polytechnique Fédérale de Lausanne, Switzerland, pp. 239.

Zhang, Y., Sun, W., Liu, S., 2002. Study on the hydration heat of binder paste in high performance concrete. Cem. Concr. Res. 32, 1483-1488.

Snellings R, Mertens G, Elsen J., 2010. Calorimetric evolution of the early pozzolanic reaction of natural zeolites. J Therm Anal Calorim. 101, 97–105.

Gruyaert E, Robeyst N, De Belie N., 2010. Study of the hydration of Portland cement blended with blast-furnace slag by calorimetry and thermogravimetry. J Therm Anal Calorim. 102, 941–51.