

Troubleshooting sulfate imbalance in mixtures with cement, supplementary cementitious materials and admixtures

Instruments to which this note applies: I-Cal 4000, I-Cal 8000, I-Cal 2000 HPC, I-Cal 4000 HPC, I-Cal 8000 HPC

Target use: Materials selection, mix design optimization, quality control cement, dry mortar, concrete

Introduction

Sulfate is added to Portland Cement to control the early aluminate reaction during cement hydration. Most standards prescribe sulfate optimization only at room temperature and in absence of Supplementary Cementitious Materials (SCM) or chemical admixtures, both of which are well known to affect the sulfate balance of any given cement. This application note describes a simple approach to gauge and optimize the added sulfate level in mixtures with cement, SCM and admixtures.

Figure 1 shows an example of a mortar mixture in sulfate balance with 25% Portland cement clinker replaced with fly ash and a gradually increased dosage of a dispersing admixture, tested in an isothermal calorimeter at 23 °C and a water/cement ratio of 0.50.

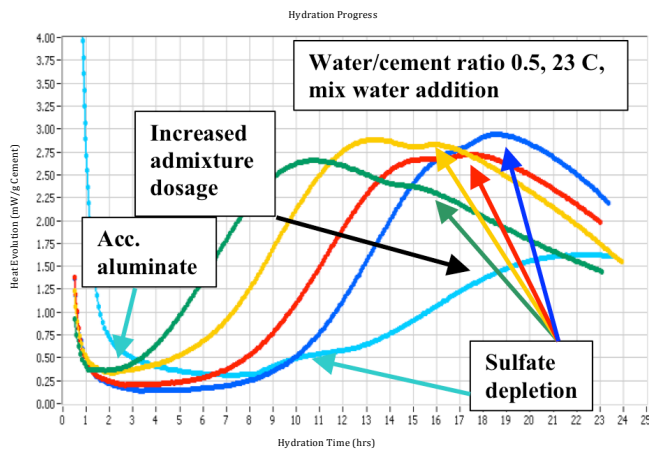


Figure 1. Graphical representation of Heat Flow normalized by weight of cement for a well balanced mixture with 25% Portland cement replaced with fly ash and a gradually increased dose of a dispersing admixture.

Note that the so-called “Sulfate Depletion” peak is not always visible in mixtures containing SCM or low aluminate cement. Even so, one can probe the sulfate balance of any mixture by gradually adding more of either an SCM or an admixture that affects the sulfate balance of the mixture. Some SCM’s such as most high calcium fly ashes (known as class C ashes) consume sulfate and thereby affect the sulfate balance of the mixture. Similarly, many admixtures such as dispersants and accelerators, as well as retarders affect the sulfate balance either directly by accelerating the aluminate reaction, or indirectly by improved dispersion and wetting of cement

grains. The example in Figure 1 shows a mortar mixture that is initially in sulfate balance at low admixture dosages (green, yellow and red curves). However at higher admixture dosages the mixture eventually becomes abnormally retarded (light blue curve in Figure 1). Also note the accelerated aluminate reaction at a very early age for the light blue curve.

Figure 2 shows an example of a mortar mixture with 25% Portland cement replaced with fly ash where the mixture quickly becomes under-sulfated with increased dosing of a dispersing admixture, tested in an isothermal calorimeter at 23 C at w/c 0.50.

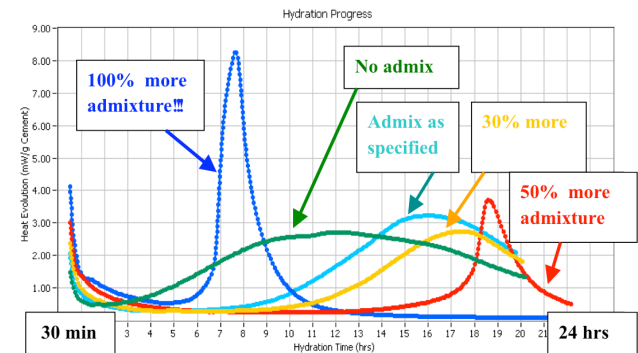


Figure 2. Graphical representation of Heat Flow normalized by weight of cement for an under-sulfated mixture with 25% Portland cement replaced with fly ash and a gradually increased dose of a dispersing admixture.

Note that the so called “Sulfate Depletion” peak is barely visible for the mixture without admixture (green) while even at low dosages of admixture the hydration profile appears compromised (light blue, yellow) relative to the shape of the mix without admixture (green). Such drastic changes in the hydration shape caused by incrementally higher admixture dosages is a classic sign of a mixture that is on the verge of becoming under-sulfated and often abnormally retarded. Compare the under-sulfated response in Figure 2 with the normal response in Figure 1.

The response seen in Figure 2 calls for a follow-up test matrix where soluble sulfate is added to the cement prior to testing, typically 0.5-1.0% calcium sulfate hemihydrate or dihydrate calculated as SO₃ by weight of cement. Figure 3 shows an example where 1.4% SO₃ as calcium sulfate hemihydrate was added to the cement prior to testing of the same binder and admixture combinations as in Figure 2.

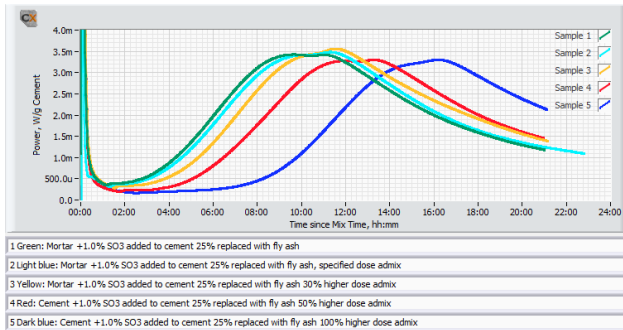


Figure 3. Effect of sulfate addition to cement prior to testing of the same mixtures as in Figure 2.

Note that the substantially improved hydration profiles in Figure 3 as compared to Figure 2 confirm that the mixtures in Figure 2 were indeed under-sulfated in presence of admixture. The sulfate addition test is critical as there could be other reasons not related to sulfate balance for the poor hydration performance in Figure 2. The fact that the mixtures improved to a normal hydration profile when additional sulfate was added prior to testing indicates that the mixtures tested in Figure 2 are susceptible to abnormal retardation and potentially poor workability retention as a consequence of sulfate imbalance. See Sandberg and Roberts [1] and ASTM C1679 for further details.

The mixing method is often critical for the hydration response of mixtures with chemical admixtures [2]. As most admixture chemisorb on the cement surface, the mixing / shearing action typically will cause very different responses in concrete or mortar, compared to cement paste. Whenever possible, it is strongly advised to prepare and test mixtures with chemical admixtures as close to the real application as possible. With the recent development of large cell isothermal calorimeters such as the Calmetrix I-Cal line of calorimeters, it is easy to test mortar or even concrete for sulfate balance in an isothermal calorimeter without having to remove any aggregates.

Test Protocol – chemical admixture dosage ramp

1. If not already at isothermal conditions, set the calorimeter to the desired test temperature and wait for at least 16 hours, preferably 24 hours for the calorimeter to stabilize.
2. Select a binder of interest, optionally with cement or cement clinker replaced with SCM
3. Prepare mixtures as close to the intended application as possible – e.g. avoid cement paste if the intended application is mortar or concrete.
4. Prepare and test replicate mixtures with increasing doses of chemical admixture, starting from below the normal / typical dose to at least 2 x the typical dose. If the mixture tends to bleed or segregate as a consequence of admixture overdose, keep mixing

until immediately before sampling to minimize variability in binder content in the actual samples tested.

5. Repeat step #4 with soluble sulfate added to the binder prior to mixing. (For example add 1.0% sulfate measured as % SO₃ by weight of cement.)
6. Evaluate the test results as shown in Figures 1-3. If the results from Step #4 are similar to Figure 1 with no apparent benefit when adding soluble sulfate in Step #5, then this is an indication that the selected mixture is in sulfate balance and appears to be robust with respect to normal variations in the field.
7. If the results from Step #4 are similar to Figure 2 with significant benefit when adding soluble sulfate in Step #5, then this is an indication that the selected mixture is NOT in sulfate balance and either a different admixture or binder, or both, should be considered and steps 2-5 should be repeated with the alternate binder/admixture.
8. If the results from Step #4 are similar to Figure 2 but with NO significant benefit when adding soluble sulfate in Step #5, then this is an indication that while the selected mixture probably is in sulfate balance, there is some other cement-admixture incompatibility issue and therefore either a different admixture or binder, or both, should be considered and steps 2-5 should be repeated with the alternate binder/admixture

Conclusion

Calorimetry is a very useful technique for troubleshooting of sulfate imbalance of cement in presence of SCM and or chemical admixture.

Admixture and/or SCM dosage ramps are easy and convenient to perform with calorimetry. When performing the dosage ramps, it is imperative to always overdose relative to the intended dose to gage the risk for unexpected retardation in the field. Additional sulfate addition tests are highly recommended whenever hydration curves appear unusual, in order to diagnose the underlying mechanism.

References

1. Sandberg, P., Roberts, L.: Cement-Admixture Interactions Related to Aluminate Control. Journal of ASTM International, June 2005, Vol. 2, No. 6 Paper ID JAI12296
2. Farrington, F.A.: Evaluating the Effect of Mixing Method on Cement Hydration in the Presence of a Polycarboxylate High-Range Water Reducing Admixture by Isothermal Conduction Calorimetry. Proceedings, ICCI, Montreal 2007.