

Optimization of Cement Sulfate

Part I - Cement without admixture

Introduction

In 1946 William Lerch published a paper on the optimum sulfate content in Portland cement, which demonstrated that the optimum sulfate content with respect to mortar strength correlated closely with heat of hydration measured by isothermal calorimetry, and also with the length change of mortar bars stored in water. Lerch concluded that a Portland cement with close to optimum sulfate content would display a calorimetry heat profile with the time of sulfate depletion occurring after the main silicate hydration peak. The results of Lerch were reviewed in light of the development of modern "easy-to-use" calorimeters and their potential usefulness for the cement industry.

Introduction

Sulfate is added to clinker in the manufacture of Portland cement for the purpose of retarding the hydration of the aluminate phase. Codes such as ASTM C150 and EN197 regulate the maximum sulfate expressed as SO₃ with respect to durability, but no SO₃ minimums are assigned.

An extensive study by William Lerch /1/ used isothermal calorimetry to study the influence of gypsum addition rates to a range of commercial clinkers on the hydration performance of corresponding Portland cements in terms of strength development and dimensional stability. It was concluded that the optimum sulfate content

for maximum strength usually correlates with minimum dimensional change during water storage.

The optimum sulfate content was easily identified by a calorimetry heat profile. Optimum sulfate with respect to strength development and dimensional stability occurred when the depletion of soluble sulfate used up by aluminate hydration occurred at a time later than the maximum heat evolution from the main silicate hydration peak, Figure 1.

Calorimetry heat profiles from hydrating Portland cement

Figure 1 shows an example of hydrating Portland cement with slightly higher than optimum sulfate content monitored at room temperature by an isothermal conduction calorimeter. Portland cement mixed with water initially displays a strong exotherm caused (A) by rapid dissolution and initial hydration of mainly the aluminate phase. If sufficient sulfate is available in solution, the hydration rate rapidly decreases (B) as aluminate reacts with calcium and sulfate to form ettringite. The formation of ettringite prevents so called "Flash Set" and allows the concrete to be transported and placed while it is still fluid. After some time the strength giving Alite hydration takes off, which results in a broad exotherm (C). "Set" usually occurs at the initial part of the Alite exotherm. The Alite and aluminate hydration continue in parallel until the mixture runs out of soluble sulfate (D), which initiates the forma-

Application Notes

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Paul Sandberg

Grace Construction Products,
W. R. Grace & Co. - Conn.,
62 Whittemore Avenue, Cambridge, MA 02140 USA
Phone: +1-617 498 4566
email:
paul.j.sandberg@grace.com

Fields of application

Cement hydration
Optimization of sulfate

Instrument configuration

3114 TAM Air

References

1. Lerch, William. "The influence of gypsum on the hydration and properties of Portland cement pastes", Proceedings, Vol. 46, of the American Society for Testing Materials, 1946.

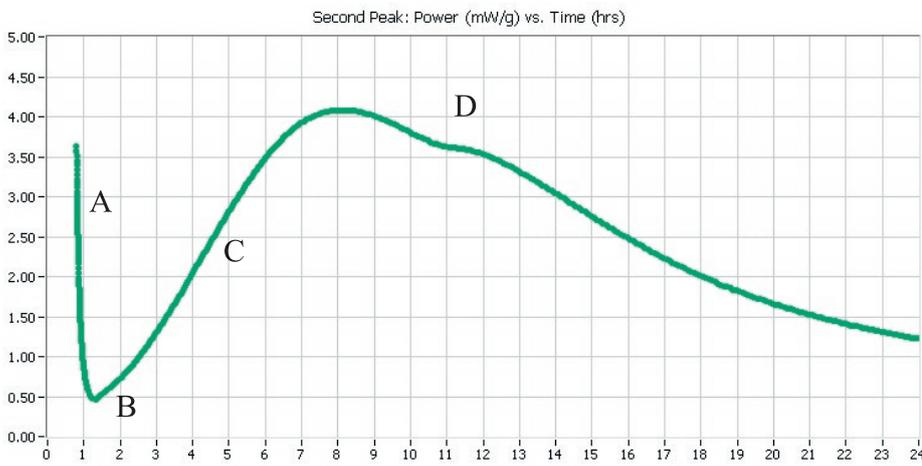


Figure 1. Example of normal hydration of Portland cement, featuring A) Initial heat evolution by dissolution of cement and initial hydration of aluminate and silicate. B) Dormant period associated with very low heat evolution indicating slow and well-controlled aluminate hydration. C) Heat evolution associated with strength developing tricalcium silicate hydration. D) Sulfate depletion

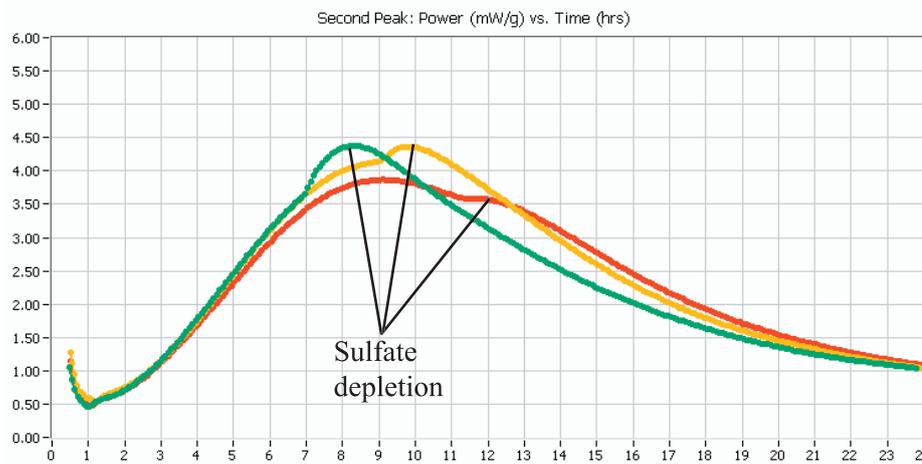


Figure 2. Effect of SO₃ content in a Portland cement on the timing of sulfate depletion. The cement used meets the specification for ASTM Type I Portland cement, BSA 380 m²/kg. A. Clinker ground to Blain Surface Area 400 m²/kg with 2% SO₃ interground as plaster (total 2.4% SO₃), B. Clinker A with 0.5% SO₃ added to cement as plaster (total 2.9% SO₃), C. Clinker A with 0.5% SO₃ added to cement as plaster (total 3.4% SO₃).

tion of aluminates with less sulfate than ettringite.

Laboratory screening of optimum SO₃ for a Portland cement by isothermal calorimetry

Figure 2 shows how Lerch's criteria - sulfate depletion peak to occur after the main silicate peak - can be used for a rapid indication of the optimum sulfate content of a laboratory ground clinker.

Evaluation of laboratory results and further field tests for sulfate optimum

The results of the laboratory screening shown in Fig. 2 indicate that

2.5% added SO₃ might be sufficient to bring the resulting Portland cement to optimum SO₃ level. At this stage a field trial would be recommended, since several factors may cause cement manufactured in the field to perform different as compared to the laboratory ground cement. Such factors include:

- Sulfate becomes more effective if interground (as compared to simple addition to cement)
- The mill circuit in the field is probably very different from the lab. This results in a different particle size distribution, and hence a different reactivity of the cement. The net result is likely a different optimum SO₃ for the field cement.

- The solubility of different sulfate forms depends on the manufacturing conditions.

Figure 3 shows the results of a field trial in which cements were produced at increasingly higher dosages of gypsum into the mill, which resulted in a range of total SO₃ contents. The variation in response reflects the natural variation in cement composition.

Selecting a target SO₃ based on isothermal calorimetry.

The optimum SO₃ for production would be selected using knowledge on the variability of total SO₃ in the finished cement. This variability may be influenced by the accuracy of the gypsum dosing system, alkali in raw materials, SO₃ in fuel, etc. The example in Fig. 3 indicates that 2.8% total SO₃ would be sufficient to delay the sulfate depletion peak until more than 2 hours after the maximum of the main silicate hydration peak. The target total SO₃ of the cement would be chosen to ensure that 95% of the cement produced has 2.8% or higher total SO₃.

It is also important to consider how the cement is used in the local market place. Most concrete is produced with admixtures, both chemical admixtures (water reducers, accelerators, retarders, etc.) and mineral admixtures (granulated slag, fly ash, natural pozzolans, etc.) In general, the use of admixtures leads to a more rapid depletion of soluble sulfate. Therefore, as a rule of thumb, the conversion peaks should appear no earlier than 2 hours after the maximum of the main silicate hydration peak to allow for common, general use of admixtures with the cement.

Final remarks

In practice the method for determining the gypsum addition rate is often based on an evaluation

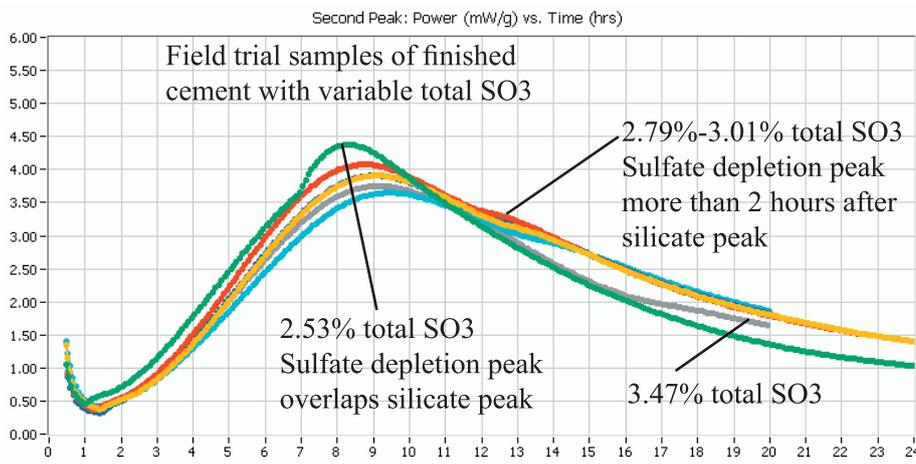


Figure 3. Cements produced in a field trial, tested by isothermal calorimetry. Based on Lerch's approach, optimum total SO₃ is in the range 2.8-3.0% SO₃. The cement used meets the specification for ASTM Type I Portland cement, BSA 370-400 m²/kg. Note

of several factors such as gypsum and clinker costs, the response of the main concrete customers to strength and dimensional stability, and local state/DOT/AASHTO directives. However, the calorimetry serves as an excellent indication as to the approximate values to aim for to avoid setting time and admixture incompatibility issues. Furthermore, the calorimetry can be used to assess the efficiency of any changes made to the cement production, such as changes in gypsum type or changes in raw material or fuel that may influence the reactivity of the aluminate phase and thereby the demand for soluble SO₃