

C	E	M
C	O	N

PROPER SETTING TIME AND WATER DAMAND BY SULPHATE OPTIMIZATION

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This paper reflects the utilization of Gypsum, Hemihydrate or Anhydrite in cement as compound to control the setting properties of the cement, its reaction and the related necessary Sulphate optimization to achieve the required cement properties in practical operation.

1) BASIC REACTION AND PURPOSE OF SULPHATE ADDITION TO CEMENT GRINDING

Sulphate (Gypsum, Hemihydrate and Anhydrit) is inter-ground with the clinker to avoid a flash set of the cement, - meaning the direct reaction of the C₃A with water to form the hexagonal shaped mineral Tetra-Calcium-Aluminate Hydrate (TCAH). This reaction would result in an immediate stiffening thus resulting in un-workability of the cement (or mortar).

In general the molecular ratio of SO₃ and C₃A admixed to in the cement mill is in the range of 1:1. Deviations from this ratio are caused by the impurity of the materials and the reactivity of the clinker. For this reason and due to the purity of the natural Sulphate materials as well as considering the different reactivity of C₃A (depends mainly on the alkali content of C₃A) 3-5 wt-% of Sulphates are added to the cement. Above molar ratio is the reason that SO₃ admixture is limited in almost every cement standard (e.g. ASTM, EN196, etc.).

The Sulphates and the C₃A immediately react in contact with water to form a mineral layer of Ettringite around the C₃A particles and thus cover and prevent the C₃A minerals from further reaction with water. No TCAH is formed.

a) Primary (initial) reaction

The Sulphates and the C₃A immediately react in contact with water to form a mineral layer of Ettringite around the C₃A particles (Ettringite hedgehog) and thus form a cover around the C₃A minerals and prevent further direct contact and reaction with water. Hence a flash set of the cement is prevented. The reaction equation is formulated as follows:



1 : 1 : 1 : 2 (Molar ratio)

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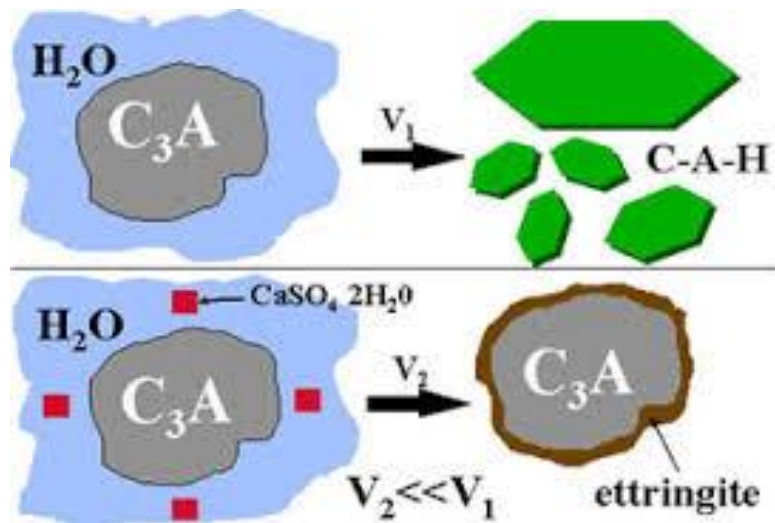


Fig.1: Reaction of C_3A without and with presence of Sulphate.

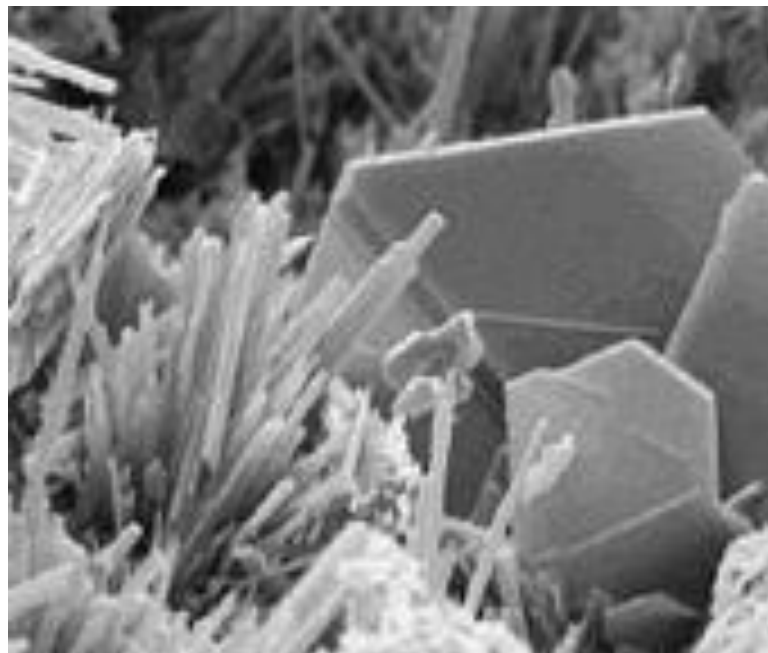
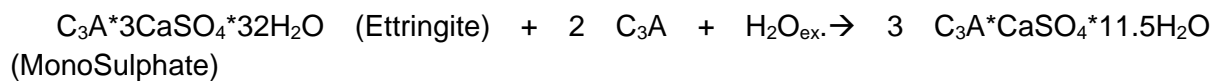


Fig.1: Electron microscopic pattern of Ettringite "hedgehog" covering C_3A next to Portlandite ($Ca(OH)_2$).

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b) Secondary reaction

After complete consumption (molar ratio 1:3) of the Sulphate by the Ettringite formation the concentration of the SO_4^{2-} ions in the solution is reduced below the stability of Ettringite and some Ettringite dissolves providing access of the remaining $2/3^{\text{rd}}$ of the covered C_3A to the water. Finally the complete Ettringite is dissolved and reacted with the remaining C_3A to MonoSulphate. This complete transformation from the start of the reaction is of practical relevance only in case of thermally treated precast concrete. The relevant reaction equation of the secondary reaction can be formulated as follows:



The primary and secondary reaction is also characterized by the typical heat of formation diagram of cement.

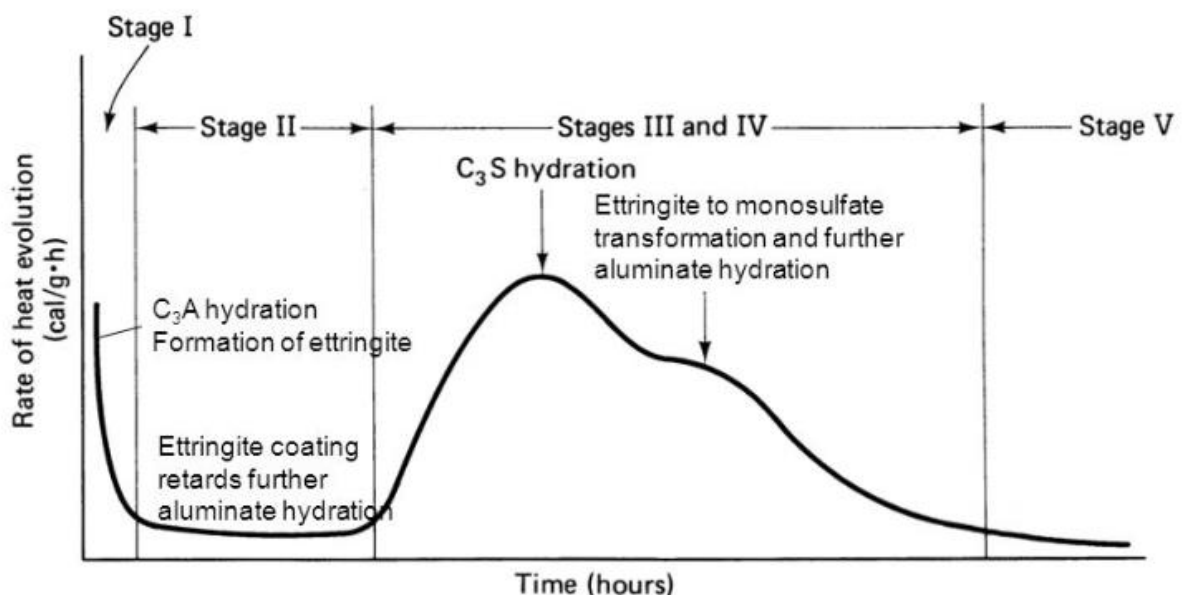


Fig.3: Typical heat of flow diagram of cement vs reaction time.

The immediate exothermic peak of heat of formation (stage I) is caused by the formation of Ettringite followed by a low flow of heat during the response period of stage II. After approximately 24 hours the C_3S reaction with Portlandite and water to form Calcium Silicate Hydrate Phases (CSH Phases) starts and dominates stage III. Within this long period of heat discharge by CSH formation the transformation reaction of the secondary reaction from Ettringite and remaining C_3A to Monosulphate takes place (stage IV). Finally at stage V the main exothermic reactions are concluded.

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The described reaction kinetics and thermodynamics (as per text book) is simplified and only valid in absence/exclusion of CO₂. Only small traces of CO₂ (in air or water) will cause much more complex reaction kinetics and thermodynamics with different final products. But for the general understanding the simplified reaction cycle is sufficient.

2) PROPERTIES OF SULPHATE PHASES

The following three major Sulphates and its main properties are relevant for cement production:

a) Gypsum (CaSO₄*2H₂O)

In the cement industry the expression Gypsum is often used for all Sulphates. However Gypsum in a mineral with 2 crystal waters structurally included. It is part of younger natural deposits. However pure Gypsum is mainly generated as precipitation Gypsum of industrial processes (e.g. phosphor Gypsum, desulfurization Gypsum of power plants, etc.). Gypsum is known in different crystalline modifications (α, β, γ-Gypsum). But for practical application in cement grinding with natural and industrial Gypsum this is of minor relevance.

Gypsum has a high solubility in water and is immediately available for the primary reaction of the Sulphate with the C₃A.

b) Hemihydrate (CaSO₄*0.5H₂O)

Hemihydrate is a Sulphate with reduced crystal water content. Although a natural mineral it is hardly dominant in natural Gypsum. Its stability is low. However it is important to the reaction of Sulphate with the C₃A of cement as it is formed in the cement mill process and has an important impact on the setting properties of the cement.

Hemihydrates have a very low solubility in water and for this reason its availability to the initial Ettringite formation is low. Nevertheless it reduced solution is maintaining the Ettringite formation and avoids early destruction of Ettringite.

The dehydration temperature of Gypsum which is of practical importance is dependent on the modification but mainly is in the range of 110 °C.

c) Anhydrite (CaSO₄)

Anhydrite Sulphate is without crystal water. Due to geological processes (sedimentation – pressure – tectonics) most natural Sulphates are of Anhydrite character.

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The solubility of Anhydrite in water is between Gypsum and Hemihydrate. Anhydrite is the most important Sulphate in practical cement technology.

3) SULPHATE OPTIMIZATION

Sulphate optimization is related to the Sulphate quantity and its phase composition in relation to the C_3A content and its reactivity in the cement to achieve the required setting properties which means to achieve the correct and complete reaction sequence of Ettringite formation.

a) Laboratory methodology by Rietveld XRD

The determination of the optimum quantity and phase composition (Gypsum, Hemihydrates and Anhydrite) in a particular cement can be carried out with the Rietveld XRD quantification methodology on hydrated and stopped cement samples. To do so:

- The crystallographic form of the C_3A in the clinker by XRD analysis should be determined (monocline vs orthorhombic C_3A). By this an estimation of the reactivity of the C_3A is possible.
- Ground clinker samples are to be mixed with different types of Sulphate and the Ettringite formation is to be determined by quantitative Rietveld XRD.

By this methodology the optimum quantity and mixture of Sulphate phases can be determined. However this laboratory methodology requires scientifically skilled personnel and equipment which is usually not available in a cement plant laboratory.

Besides the above described Rietveld XRD methodology other direct XRD techniques as well as indirect laboratory methods, e.g. SO_3 concentration measurement of cement solutions or heat flow calorimetry, etc. are available. However the Rietveld XRD methodology is to be considered the most direct and accurate measurement technique.

b) Field methodology

In practices the dehydration and transformation of Gypsum to a certain percentage of Gypsum (for fast reaction), Anhydrite (for extended reaction) and hemi hydrate (for final reaction) in the cement is carried out by the adjustment of the grinding temperature and retention time of the material in the cement mill. To do so the following methodology is applied:

- Determination of phase composition of Sulphate (Gypsum or Anhydrite) by chemical analysis.

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- Variation of cement outlet temperature (or mill gas outlet temperature) from 80°C up to maximum 120 °C and collection of representative samples. Variation steps should be within 5-10 °C.
- Variation of Sulphate addition to the cement.
- Analysis of water demand and setting time according to standard tests.
- Identification of optimum Sulphate concentration and mill temperature to achieve the required setting time and water demand.

If Anhydrite is used as Sulphate no dehydration reaction in the mill is necessary and only quantity of the Anhydrite has to be adjusted to meet the required setting time. Depending on the reactivity of the C₃A a certain over stoichiometric addition is often required.

In case of Gypsum an overdosing (too much Gypsum in the cement) have to be avoided. If Gypsum is transferred into Anhydrite or Hemihydrates, excessive Anhydrite might react with water and result in a reformation of Gypsum by rehydration. This reaction is resulting in early stiffening (setting) of the cement and is called “false set”.

This field methodology can be applied by analysis and equipment which is available in any cement plant laboratory and is using standard testing procedure. No specialized and/or scientifically qualified personnel is required.

c) Vertical Roller Mill (VRM) and Roller Press (RP) cements

Traditionally cements were produced applying ball mill technology. Today more energy efficient VRM or RP grinding technology with higher unit capacity and an improved flexibility towards product portfolio is used for cement grinding. However this technology sometimes results in severe quality problems of the cement. These are mainly problems concerning the setting time, workability and the related water demand even if mill outlet temperature and consequently dehydration of Gypsum into Hemihydrate and Anhydrite is suitably achieved.

Initially it was anticipated that the change of grinding technology from impact (in case of ball mill) to pressure (in case of VRM and RP) would cause a different shape of the cement particles. But by intensive studies no such difference of the particle shape could be identified between cement of the different grinding technologies.

Instead a difference in the steepness of the grain sized distribution was found. Ball mill cements usually achieve a steepness on a double logarithmic RRSB grain size distribution curve of 0.8 – 1. The grain size distribution of VRM and RP cements often indicate a higher steepness of 1 – 1.2 resulting in a more uniform and less flowable particle size distribution. Depending on the concentration and reactivity of the C₃A in the cement and the steepness of the grain size distribution curve setting time, workability and water demand problems are more or less dominant.

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Although a sulphate optimization should be carried out independent from the applied grinding technology above mentioned problems cannot be solved exclusively by sulphate optimization if caused by unsuitable steepness of the grain size distribution curve. In such cases technical measures to improve the steepness, e.g. partial recirculation of cement to the mill, optimization of separator operation, modification of air flow dynamics in the mill, etc. are to be considered.

4) CONCLUSION

In recent year's international clinker trading increased significantly. Cement manufacturers are using various clinker, Gypsum and additive sources. In addition the product portfolio of cement and related building material products increased. As a consequence the requirements to the quality control units to maintain constant cement properties, i.e. the setting time, water demand and workability whilst using different materials like clinker, Gypsum and additives are more demanding. Sulfate optimization procedures and practices are more frequently required and should be within the scope of services and know-how of every QC department.

Sulphate optimization of cements will result in:

- Optimum setting time and water demand.
- Avoidance of false set (overdosing of sulphate).
- Avoidance of flash set (under dosing of sulphate or unsuitable dehydration).
- Optimum utilization of sulphate as a raw material.

Sulphate optimization should be carried out in the following cases:

- Change of clinker source and clinker composition.
- Change of sulphate source or composition (e.g. natural vs industrial Gypsum).
- Change of grinding technology, e.g. from ball mill to VRM or RP.
- Commissioning of new cement and grinding plants.