

Influences of the type and amount of calcium sulphate on the reactivity of alkanolamine-based set accelerators/strength improvers

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Abstract

Since the discovery, in the second half of 19th century, that the addition of gypsum to Portland clinker allows a better control of cement setting, wide attention has been given to the study of the effects of calcium sulphate on silicate hydration. It is well known that calcium sulphate can control other mechanical performances, such as compressive strengths and dimensional stability, but the details of the mechanism of action are not completely understood. On the other hand, less attention has been focused on the influence of different types of calcium sulphate on the reactivity of organic additives. In this paper the performances of alkanolamine-based cement additives (widely used in cement manufacturing, thanks to their effect on grinding efficiency and clinker hydration) are described in function of the type and amount of sulphates.

Several cements with different SO₃ content coming from different types of calcium sulphate have been reproduced and the effect of alkanolamine-based set accelerators/strength improvers on cement hydration has been tested. The results clearly show that the type of calcium sulphate used (gypsum, bassanite, anhydrite) has a sensitive influence on the reactivity of organic additives. Particular attention has been given to the correlation between mechanical performances and mechanisms of cement hydration. On the basis of the data collected, some hypothesis on the interactions between organic additives, sulphate ion and clinker hydration are proposed.

Originality

The originality of the paper lies in the detailed study of the relations between the type and amount of calcium sulphate and the performances of cement additives in terms of compressive strength increase. As far as we know there are no papers dealing with this particular concept with specific reference to alkanolamine-based set accelerator/strength improvers.

Chief contributions

Grinding additives based on alkanolamines are commonly used worldwide during cement manufacturing and their effect on compressive strengths enhancement is crucial for the improvement of cement composition and clinker reduction. In our opinion the main contributions of this paper is to give practical advices about the relations between cement additive reactivity and sulphate type and amount. During industrial production the optimisation of organic additives in function of sulphate content is not usually carried out but, according to the results of our work, it can lead to further benefits.

Keywords: Grinding aids, alkanolamines, sulphates

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1. Introduction

The role of calcium sulphate as a setting-time regulator is widely known in the modern cement industry and has been already the subject of numerous studies. In addition to setting time, other crucial parameters such as compressive strengths and dimensional stability have been proven to be severely influenced by the sheer amount of sulphates which are introduced in the cement's recipe (Taylor, 1993). More in detail, the effect on the former has been summarized into the "Optimum Gypsum" parameter, a matter which has been deeply analyzed in previous works (Kanare et al., 1984). Nevertheless, the exact mechanism by which a certain amount of sulphates is able to maximise the cement's performance under this particular point of view, is still a fertile terrain for open discussions. Similarly, although grinding aids as well as performance enhancers based on alkanolamines are used worldwide in the cement industry, the mutual influence between alkanolamines and sulphates (amount as well as nature) on the cement quality has not been, to our knowledge, extensively investigated yet. Tri-ethanolamine (TEA) and Tri-isopropanolamine (TIPA) are today's most widely used alkanolamines. While the addition of both molecules during the cement grinding process (usually in very low dosages: only 0,01 to 0,05%) positively affects the resulting cement's particle size distribution, TEA and TIPA exhibit in most cases a different behaviour as performance enhancers. TEA is reported to accelerate the hydration of C₃A (Ramachandran, 1973). In literature there are some discrepancies about the influence on setting time and compressive strengths, probably due to the fact that the effect of TEA on cement hydration is strongly related to dosage (Dodson, 1990), but in the end TEA can be considered as an early compressive strength enhancer, particularly at dosages commonly used during cement production. The behaviour of TIPA has been described in details by Gartner and Myers. This molecule – a well known complexing agent for iron in alkaline media - is supposed to solubilise the layer of iron hydroxides resulting from C₄AF hydration, allowing a better reaction of silicates with water and increasing the late strengths. Although TEA can complex iron as well, it does not have effect on late strengths because it is rapidly subtracted from pore water by adsorption on hydrated phases. TIPA, probably thanks to its higher steric hindrance, remains in solution allowing a complete removal of iron hydroxides (Gartner et al., 1993).

2. Experimental

2.1 Preparation of the different sulphate sources

Natural gypsum has been crushed and heated in an oven at 140°C for 72 hours and at 500°C for 20 hours, in order to obtain dehydration to hemihydrate (bassanite) and anhydrous (anhydrite) calcium sulphate respectively. All the samples have been analyzed before and after heating by X-ray diffraction (XRD - PANalytical X'pertPro MPD), X-ray fluorescence (XRF – Brucker AXS S8 Tiger), thermogravimetric analysis (TGA – Netzsh TG209F1 Iris) in order to confirm the conversion of gypsum to other calcium sulfate forms. The compositions are reported in the table 1, along with the SO₃ content.

Table 1- Sources of SO₃

| Type of calcium sulphate | CaSO ₄ · 2H ₂ O | CaSO ₄ | CaSO ₄ · ½ H ₂ O | CaCO ₃ | SO ₃ |
|--------------------------|---------------------------------------|-------------------|--|-------------------|-----------------|
| Natural | 80,00% | 15,00% | - | 5,00% | 46,05% |
| Anhydrite | - | 94,00% | - | 6,00% | 55,31% |
| Bassanite | - | 17,20% | 77,10% | 5,70% | 52,67% |

2.2 Reconstruction of target cements and evaluation of mechanical properties

Using a laboratory ball mill cements with four different SO_3 content (0,7% - 1,4% - 2,1% - 2,8%) and, for each SO_3 content, different calcium sulphate form (gypsum, bassanite and anhydrite) have been reproduced through intergrinding of clinker and calcium sulphate (grinding time has been kept constant). Intergrinding gypsum is far more effective than interblended (Tang et al., 1992), but intergrinding of clinker and gypsum makes practically impossible to have similar clinker fineness and particle size distribution as gypsum amount is changed. With this in mind, cements with the same composition have been reproduced by blending the same clinker and calcium sulphate previously ground. This allows us to compare the effect of chemical additives also on cements with the same clinker particle size distribution.

For each cement, mortar workability (flow) and compressive strengths have been determined in absence as well as in presence of standard-grade tri-ethanolamine (TEA) and tri-isopropanolamine (TIPA) added directly in the mixing water during mortar preparation at a dosage of 500 g/t – 0,05% (based on the amount of cement). Determination of compressive strengths and workability has been performed according to standards EN 196-1 and EN 1015-2 respectively. Fineness of the cements has been evaluated through the determination of the Blaine specific surface and air-jet sieving (Alpine LS-200 N).

2.3 Hydration study

Hydration of cements have been studied with X-Ray Powder Diffraction, TGA and measurements of the specific surface of hydrated cement paste through the BET method (Coulter Beckman SA 3100, N_2 adsorption). Samples of cements have been mixed with water (same water/cement as mortar determination), with and without the addition in mixing water of TEA and TIPA. To obtain results for the quantitative analysis, the hydration has been stopped grinding the sample in a solvent and separated samples were prepared for each chosen hydration time. Powder diffraction data were collected with a PANalytical X'pertPro MPD diffractometer with theta–theta geometry equipped with an X'Celerator detector working with the $\text{CuK}\alpha$ radiation (1.54184 Å) in the 2theta range 5–80, a step size of 0.017° 2 theta and a scan step time (s) of 102,1. All data collections were performed at room temperature with back-loading sample holders to avoid preferred orientation of crystallites. Data were analysed by the Rietveld method (Rietveld, 1969) using the Bruker AXS software package TOPAS 4.2 operated in the fundamental parameters mode (Cheary *et al*, 1992, Coelho, 2000, BRUKER AXS, 2003).

3. Results and discussion:

3.1 Effect of the SO_3 source on the cement fineness:

In Figure 1 the Blaine specific surfaces for every cement reproduced by intergrinding are reported. In the case of natural gypsum, increasing the SO_3 content translates itself into an almost linear increase of the Blaine specific surface, while in the case of bassanite a progressive decrease of Blaine can be noticed, as reported by other authors (Frigione, 2002). Using anhydrite, increasing the SO_3 content translates itself into a situation which is the exact opposite of what has been observed in the case of natural gypsum: the Blaine specific surface remains almost constant while the sieve residuals suffer a substantial increase. This means that, with strong dependence to the amount of SO_3 , dehydration of natural gypsum during the cement production process may bring to substantial effects on the measured cement fineness.

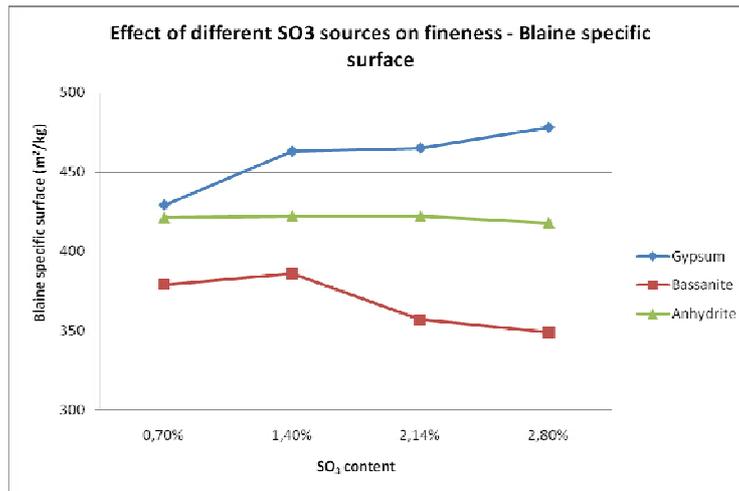


Figure 1 - Effect of different SO₃ sources on fineness

3.2 Effect of the SO₃ source on mortar workability

Data about mortar workability (flow), both on cements prepared by intergrinding as well as blending, have substantially confirmed a trend that we have observed also during previous trials: as can be seen in the Figure 2, increasing the SO₃ content in the case of hemihydrate calcium sulphate (bassanite) determines an almost linear ($R^2 = 0,9902$) decrease of the workability of the corresponding mortar. This trend is usually explained through the fact that increasing the amount of SO₃ in the case of bassanite could favor recrystallisation of dihydrate gypsum (secondary gypsum), a process which is known to be kinetically preferred with respect to the precipitation of ettringite (Frigione, 2002). Theoretically, adding an improver of the C₃A reactivity (such as TEA) and thus increasing the formation rate of ettringite would ideally enhance the mortar's workability. This is in fact what has been observed, as can be seen in the Figure 2 below.

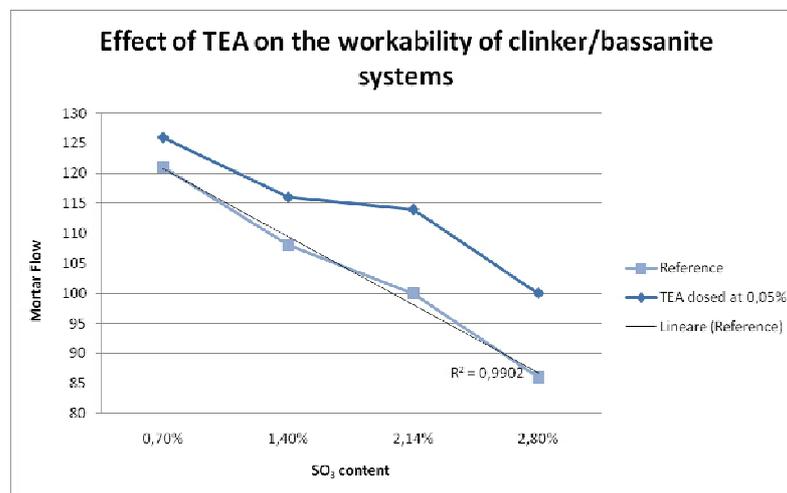


Figure 2 - Effect of TEA on workability

3.3 Influence of the SO₃ source and alkanolamines on the compressive strengths

Early compressive strengths data concerning mortars prepared in absence of alkanolamines in the mixing water have followed in almost every case the typical trend of the *optimum gypsum*, with optimum SO₃ content between 2,1% and 2,8%. Effects of TEA and TIPA (expressed as compressive

strengths increase in % with respect to the reference mortars prepared in absence of alkaolamines) are reported in figures 3, 4 and 5.

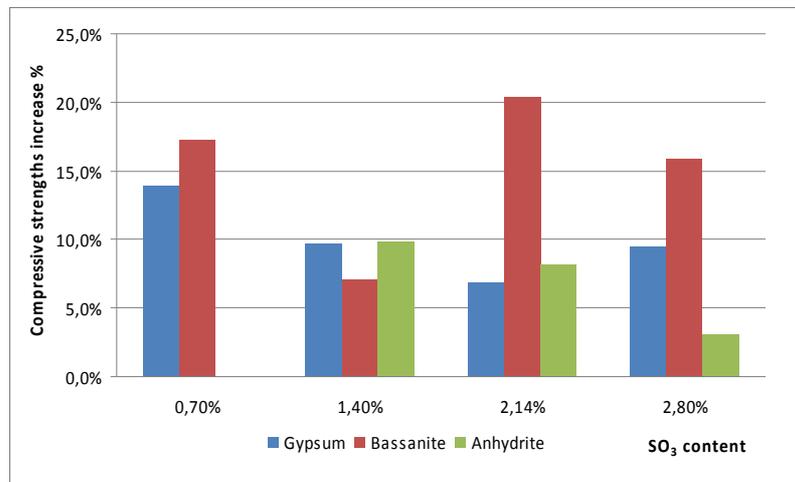


Figure 3 - Effect of TEA on 24 hours strengths - Cements prepared by intergrinding of clinker and gypsum

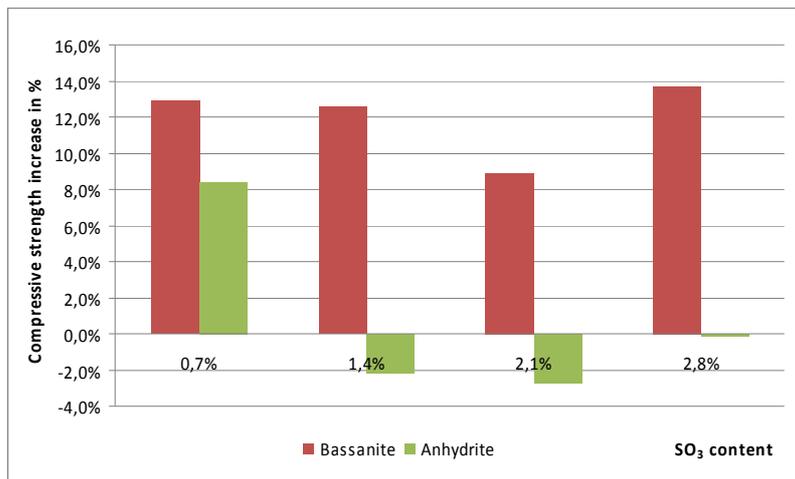


Figure 4 - Effect of TEA on 24 hours strengths - Cements prepared by blending of ground clinker and gypsum

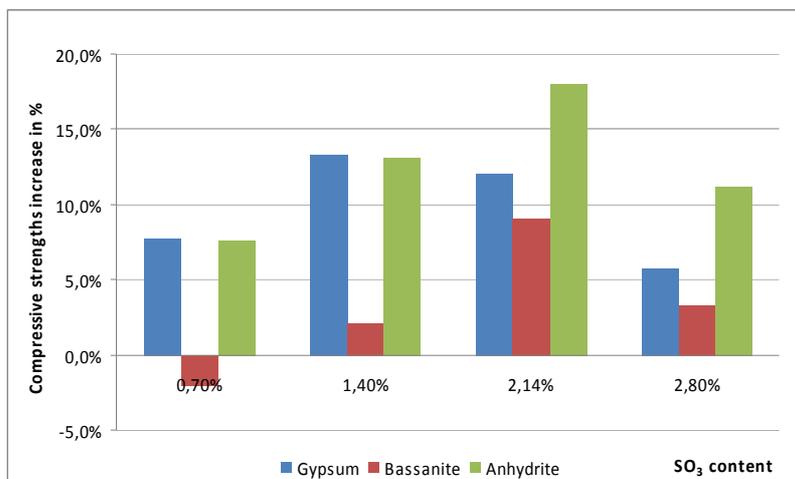


Figure 5 - Effect of TIPA on 28 days strengths - Cements prepared by intergrinding of clinker and gypsum

As could be reasonably expected, also in this case triethanolamine generally acts as an improver of early strengths. Additionally, it is noteworthy how the effect of alkanolamines on the development of compressive strengths (early as late) follows a pattern which is similar to the Optimum gypsum trend, in which there is indeed a certain SO_3 amount which is able to further maximize the effect of the single alkanolamine. More interestingly, we have noticed that the effect of TEA and TIPA can be different if different sulphate sources are used. In details:

- if bassanite is used, the % strength increase at early ages obtained with the addition of TEA in mixing water is more evident, while in the case of clinker/anhydrite systems this effect is less pronounced. This is particularly clear in Figure 4, referring to cements prepared by blending, where the clinker particle size distributions is always constant. The clinker/gypsum system places itself in an intermediate situation.
- On the other hand, TIPA is significantly less efficient in increasing late strengths when bassanite is used as a source of SO_3 .

In Table 2 TGA and BET data referring to pastes prepared with anhydrite and bassanite cements are shown. Bound water in the range 250-400°C (usually associated to water in C-S-H) is similar in all cements, but the effect of the addition of TEA in cements with anhydrite is a more evident reduction of $\text{Ca}(\text{OH})_2$ (portlandite) formation. This can be associated to a higher Ca/Si ratio in C-S-H, usually associated to lower mechanical performances (Kanare, 1985). On the other hand, BET shows a marked increase if TEA is added in bassanite systems, indicating a higher specific surface of hydrated product. The better effect of TEA as a strength enhancer in bassanite containing systems, could thus be explained with a different microstructure of calcium silicate hydrates, rather than with differences in the hydration degree.

Table 2 – TGA/BET analysis of clinker/sulphate/TEA systems

| SO_3 source | Additive | Bound water 250-400°C according to TGA | $\text{Ca}(\text{OH})_2$ according to TGA | % reduction of $\text{Ca}(\text{OH})_2$ formation with TEA | BET m^2/g | % increase BET with TEA |
|----------------------|----------|--|---|--|----------------------------|-------------------------|
| Anhydrite | - | 2,6 % | 14,6 % | - | 19,0 m^2/g | - |
| Anhydrite | TEA | 2,4 % | 12,2 % | - 16 % | 19,2 m^2/g | + 1 % |
| Bassanite | - | 2,7 % | 13,7 % | - | 20,4 m^2/g | - |
| Bassanite | TEA | 2,5 % | 11,9 % | - 13 % | 22,6 m^2/g | + 11 % |

Table 3 – XRD/BET analysis of clinker/sulphate/TIPA systems

| SO_3 source/content: | Additive: | Time elapsed: | BET m^2/g | % increase BET with TIPA | % hydration C_4AF |
|-------------------------------|-----------|---------------|---------------------------|--------------------------|-----------------------------------|
| Anhydrite/2,1% | - | 28 days | 13,2 | - | 0 % |
| Bassanite/2,1% | TIPA | 28 days | 26,0 | + 97 % | 75 % |
| Anhydrite/2,1% | - | 28 days | 16,5 | - | 0 % |
| Bassanite/2,1% | TIPA | 28 days | 28,6 | + 73 % | 63 % |

According to the literature (Gartner, 1991), both XRD and TGA analysis of samples hydrated with TIPA show an acceleration of the hydration of C_4AF and a higher hydration degree of C_3S (higher production of portlandite, higher amount of bound water and higher decrease of C_3S content). A general tendency of TIPA in accelerating the conversion of ettringite to monosulphate, hemi- and

monocarbonate can be noticed as well. In table 3 details on BET and % hydration of C₄AF (as evaluated through XRD on hydrated cement pastes) are reported. In case of cements prepared with anhydrite, there is a higher consumption of C₄AF and a marked increase of the specific surface of the hydrated products. This is coherent with the better performances obtained by the addition of TIPA in cements prepared with anhydrite.

The accelerating effect of TEA on the hydration of C₃A evidenced by several authors (Ramachandran, 1976, Dodson, 1990) may be explained considering that TEA is an effective chelating agent in alkaline media not only for Fe³⁺, but also for Al³⁺ ion. This has been also demonstrated through the use of ¹³C NMR spectroscopy (Scott et al., 1990). Complexation of Al³⁺ may increase the dissolution rate of C₃A. The morphology of early hydration products (in terms of growth of large crystals or formation of an amorphous layer of ettringite and calcium aluminate hydrates) reasonably depends on the rate of Ca²⁺, Al³⁺ and SO₄²⁻ supply to the solution. The supply rate of these ions is linked to reactivity of C₃A and calcium sulphate. As already summarized by other authors (Frigione, 2002), rheological and mechanical performances of Portland cements can be explained in terms of relative reactivity of aluminates and calcium sulphate. In the same way, microstructure of C-S-H and compressive strengths may be linked to morphology of early hydrates, thus explaining the differences in reactivity of TEA and TIPA in case of different sulphate sources.

4. Conclusions

Cement blends with different types and amounts of SO₃ sources have been reproduced and their respective physical/mechanical properties have been evaluated in presence and in absence of the alkanolamines TEA and TIPA. The known fact that cement fineness is strongly influenced by the source and amount of SO₃ has been observed also in this work. Additionally, it has been noted that mortar workability severely decreases in the case bassanite is used as SO₃ source. The hypothesis that an enhancer of the C₃A reactivity could improve this situation has been demonstrated through the addition of TEA. The effect of both TEA and TIPA as compressive strengths enhancers has been investigated with the aid of XRD, TGA and BET analysis. The results seems to indicate that the quality –and not the sheer quantity- in terms of morphology of the resulting hydrates could well be the explanation of the different behavior of TEA and TIPA in case different SO₃ sources are used.

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