

“Optimization in the use of cement additives: effect of gypsum dehydration on the reactivity of performance enhancers”

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Experimental:

Sulphate sources:

Natural (mostly dihydrate) gypsum, collected from an Italian cement production facility, 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 the hemihydrate (bassanite) and anhydrous (anhydrite) calcium sulphate forms, 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) and thermogravimetric analysis (TGA – Netzsh TG209F1 Iris), so to confirm the effectiveness of the conversion of natural gypsum to the other desired forms. The resulting compositions are reported in the **table 1**, along with the respective SO₃ content.

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%
Hemihydrate	-	17,20%	77,10%	5,70%	52,67%

Table 1- Different sources of SO₃

Target cements:

Using a laboratory ball mill, cements with four different SO₃ content (0,7% - 1,4% - 2,1% - 2,8%) and, for each SO₃ content, different calcium sulphate form (dihydrate, hemihydrate and anhydrite) have been reproduced through intergrinding of clinker and calcium sulphate (grinding time has been kept constant).

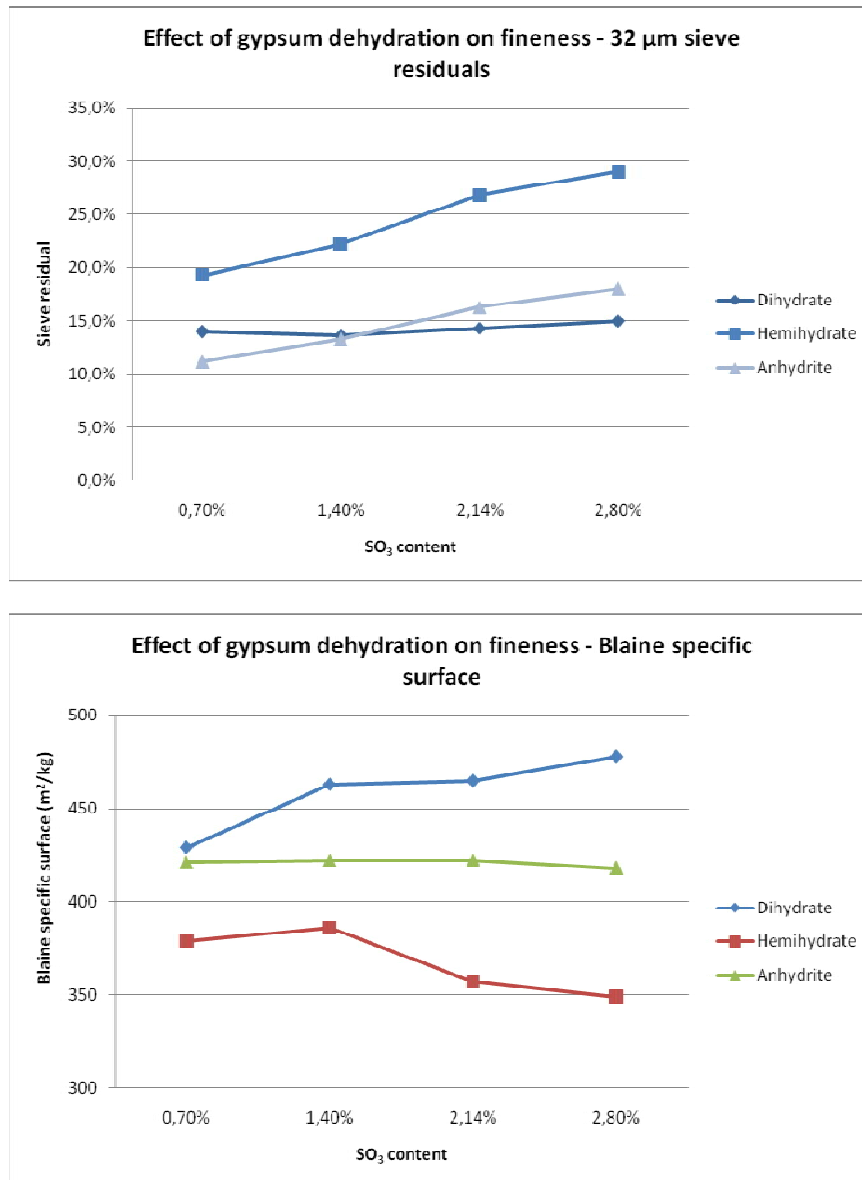
For each cement, mortar workability (flow) and compressive strengths have been determined in absence as well as in presence of two alkanolamine-based, commercially available, cement additives produced by MAPEI, namely the grinding aids/performance enhancers MA.G.A./C150 (improver of the early compressive strengths) and MA.G.A./C222 (improver of the late compressive strengths). Both products were added directly to the gauge water during mortar preparation at a dosage of 500 g/t (0,05%, based on the amount of cement). This has permitted us to focus on the chemical interactions in the cement/alkanolamine system without any influence deriving from the additive-modified particle size distribution. The chosen dosage is representative of a normal industrial usage (suggested dosage range for both products is between 300 and 500 g/t). Determination of compressive strengths and workability has been performed according to standards EN 196-1 and EN 1015-3 respectively. Fineness of the cements has been evaluated through the determination of the Blaine specific surface and air-jet sieving (Alpine LS-200 N).

Hydration of cements has 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, N₂ adsorption). Samples of cements have been mixed with water (same water/cement ratio 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. Samples for BET analyses have been manually crushed and its hydration has been stopped through solvent-quenching.

Results:

Effect of gypsum dehydration on the cement's fineness and coating-related issues:



Dehydration of natural gypsum and the consequent formation of hemihydrate and anhydrous CaSO₄ exerts a significant effect on the cement's particle size distribution. This effect may be summarized in the following key points:

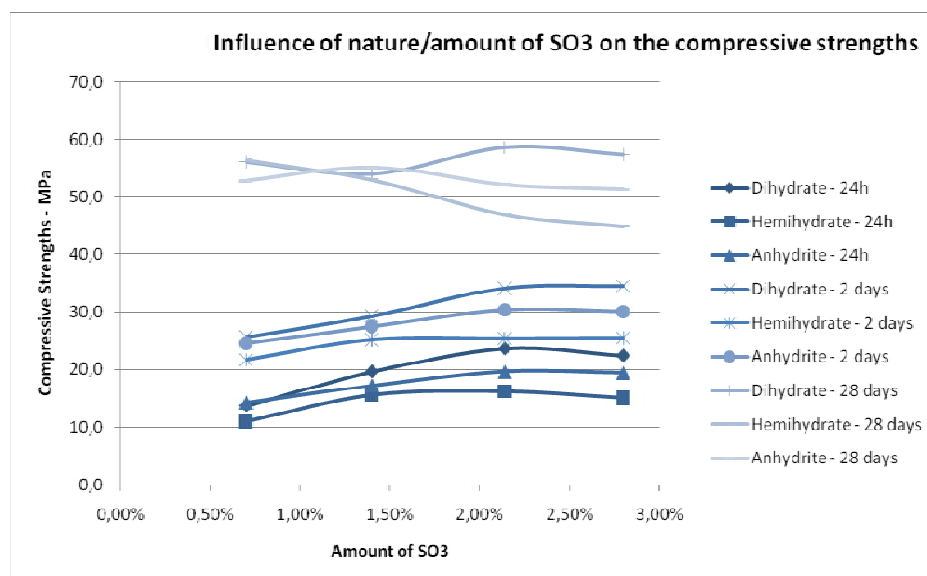
- Increasing the amount of natural gypsum determines an almost linear increase of the cement's Blaine specific surface. On the other hand, sieve residuals seem not to be affected by such variation.

- As the amount of hemihydrate CaSO_4 increases, the Blaine specific surface seems to be on a descending trend. Sieve residuals, on the other hand, increase significantly.
- Finally, as the amount of anhydrous CaSO_4 increases, a constancy of the Blaine specific surface coupled with a modest, yet linear increase of the sieve residuals can be observed.

These observations bring us to the conclusion that, depending on the total amount SO_3 , partial –or total– dehydration of the starting natural gypsum during the grinding process may indeed severely influence the cement's particle size distribution, thus providing very different values of specific surfaces and sieve residuals while maintaining an identical grinding time (i.e. energy which is introduced to the grinding system). Such effect is also reflected industrially, where the dehydration of natural gypsum is usually associated with a higher degree of coating on the mill balls. Such effect has an obvious negative impact on the cement production process, which can be minimized through the addition of the correct products (e.g. grinding aids).

Effect of gypsum dehydration on the compressive strengths and influence of cement additives:

Early compressive strengths data concerning mortars prepared in absence of additives added in the gauge water have followed in almost every case the typical trend of the *optimum gypsum*, with an optimum SO_3 content between 2,1% and 2,8%. This can be clearly seen in the following graph (Figure XX).



It is interesting to note how, while dehydration of natural gypsum does not determine a significant shift of the optimum gypsum % at the early ages, the situation is quite different at the late ones: here the optimum gypsum value for dihydrate and hemihydrates CaSO_4 are substantially different.

Introduction of cement additives to such systems has determined a series of interesting effects: more in detail, the influence of MA.G.A./C150 and MA.G.A./C222 on the mortar compressive strengths (expressed as compressive strengths increase in % with respect to the reference mortars prepared in absence of additives) are reported in figures 3, 4.

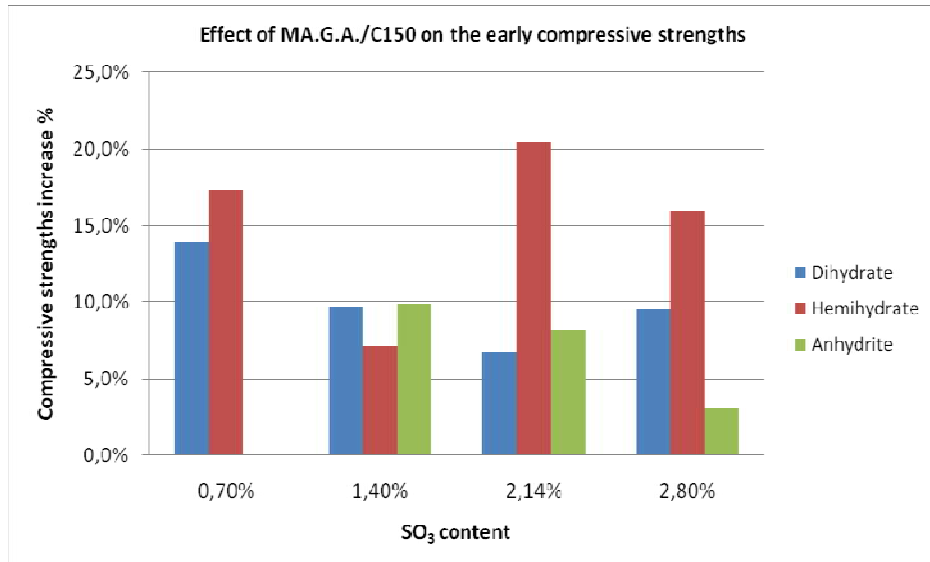


Figure 1 - Effect of **MA.G.A./C150** on 24 hours strengths - Cements prepared by intergrinding of clinker and gypsum

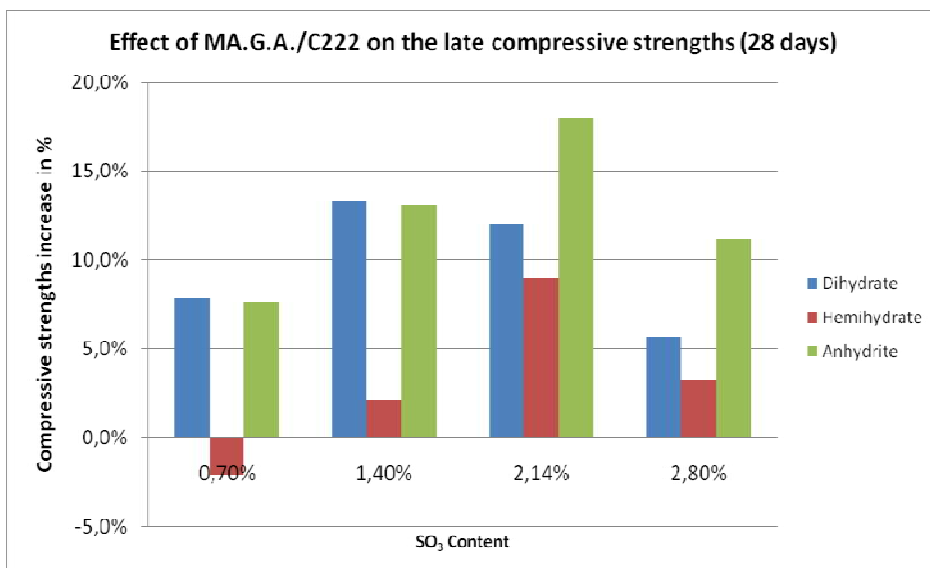


Figure 4 - Effect of **MA.G.A./C222** on 28 days strengths - Cements prepared by intergrinding of clinker and gypsum

Taking into account these results, the following observations can be made:

As could be reasonably expected, MA.G.A./C150 generally acts as an improver of early strengths, while MA.G.A./C222 mainly improved the late ones. Additionally, it is noteworthy to see how the effect of both additives on the development of compressive strengths (early as late) follows a pattern which is similar to

the *Optimum Gypsum* trend, in that there is indeed a certain SO_3 amount which is able to further maximize the effect of the performance enhancer.

More interestingly, we have noticed that the effect of both additives can be different if different sulphate sources are used, i.e. when partial or total dehydration occurs. In details:

- if natural gypsum is partially dehydrated to the hemihydrates form, the strength increase in % at early ages obtained with the addition of MA.G.A./C150 in mixing water is more evident, while in the case of clinker/anhydrite systems this effect is less pronounced. The clinker/gypsum system places itself in an intermediate situation.
- On the other hand, MA.G.A./C222 seems to be particularly effective in increasing late strengths when anhydrite (completely dehydrated natural gypsum) acts as a source of SO_3 , and less when hemihydrate CaSO_4 covers this role. Again, natural gypsum places itself in an intermediate situation.

Conclusions:

The experimental evidences that were collected during the present research clearly show how dehydration of natural, dihydrate, CaSO_4 during the grinding process is indeed able to influence crucial cement quality parameters such as fineness and, even more importantly, compressive strengths. Moreover, the efficacy of grinding aids/performance enhancers seems to be heavily related to the source, as well as sheer amount, of SO_3 . More in detail, it has been observed how improvers of the early compressive strengths seem to be particularly effective as dihydrated CaSO_4 becomes partially dehydrated to the corresponding hemihydrates form, while improvers of the late compressive strengths provide the best results when a complete dehydration of the SO_3 source takes place. Applied to an industrial production scenario, these results indicate how a deep understanding of the gypsum dehydration degree that is occurring in each production line appears to be quality-wise necessary.