

GRINDING AIDS: A STUDY ON THEIR MECHANISM OF ACTION

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ABSTRACT

Most of the recent works [1] on cement additives focused the attention on their effectiveness on cement performances in terms of mechanical and rheological properties. Our ambition has been to watch deeply in the interface between the components of cement additive and the cement grain surface, in presence of small (cement grinding) and large (cement hydration) amount of water.

We could assembly data concerning mill output, specific surface area, particle size analysis, electrophoretic mobility and particularly microstructures of hydrated cement products investigated by Environmental Scanning Electron Microscopy - Field Electron Gun (ESEM – FEG). Even if this work is still in progress, we can make a reliable hypothesis about the pre-hydration of clinker during grinding process, which is deeply influenced by the presence of the active components (alkanolamines and glycols) of cement additive, or better of Grinding Aids (GA).

INTRODUCTION

The introduction of GA, started more than 50 years ago, has as ultimate task the prevention of cement particle re-agglomeration during and after milling process[2]. What makes GA application even more desirable is their significant effects on mechanical properties of cement, whose particle size distribution results narrower and shifted towards shorter diameters[3].

Their influence on cement chemico-physical behaviour has been attributed to the reduction of surface energy forces generated on cement grains during comminution. According to this thesis[4], GA are constituted of polar organic compounds such as alkanolamines, which arrange their dipoles so that they saturate the charges on the newly formed particle surface, reducing re-agglomeration. Nevertheless, this kind of additives results efficient even at very low dosage (< 500 ppm), which cannot give reason of a complete covering on cement particle surface, that is for a complete screening of the free charges. Moreover, it cannot give reason of their effects on subsequent mechanical properties of cement paste.

Various research groups followed different approaches to go further in the interpretation of the GA action. Some authors[5] have been involved in the analysis of alkanolamines and glycols based GA, extracted from dry cement by different technics. Besides the intrinsic difficulty in the extraction of this polar compounds, once they interact with cement, it has been hypothesized[5(a)] either an irreversible physic adsorption or a chemical interaction with cement salts, favoured by high temperatures (100-120°C) reached inside the mill during grinding process.

Much more interest has been shown on the influence of these alkanolamines or glycols as admixtures on cement hydration and strength development. It is well known[6], for example, and well accepted that alkanolamines (especially TriIsoPropanolAmine - TIPa) interact preferentially with iron based phases of cement[6(b)]. In the same way TriEthanolAmine (TEA) effect on cement setting time is still debated[1(a),7].

Our approach to the study of GA mechanism of action took advantage of our experience on cement behaviour during hydration and tried to focus the attention on the morphological effects of GA on cement.



RESULTS AND DISCUSSION

We set up a grinding procedure utilizing a lab mill, Bond type, in order to check the effectiveness of GA components we were going to study and to prepare all the samples we tested. Obviously our procedure has not much to do with the industrial process, since both particle size distribution and specific surface area result quite different in the two case. Nevertheless, we could easily verify its internal consistency.

We chose an Ordinary Portland clinker as reference substrate, whose specific gravity is $3,11 \text{ g/cm}^3$ and chemical composition, expressed in element oxides, is shown in **Table 1**.

Table 1 – Chemical Composition of the Reference Portland Clinker

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O
25,21	5,13	3,97	59,99	1,29	1,32	0,25	0,64

As grindability parameter we used Blaine Specific Surface Area (BSS) development during milling process. In **Figure 1** we show BSS development utilizing some typical raw materials of GA at the dosage indicated.

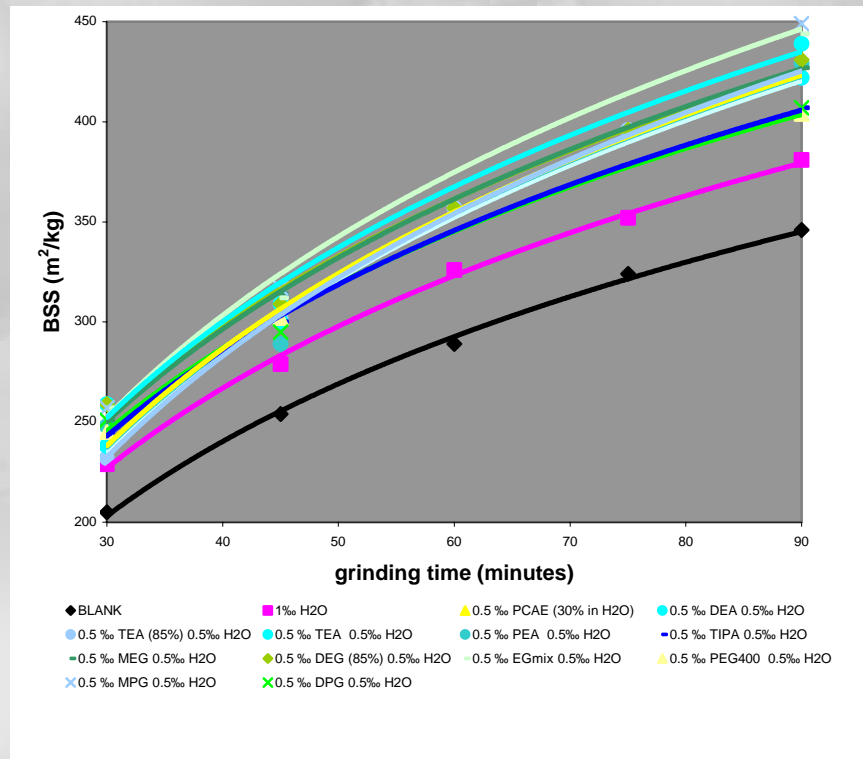


Figure 1 - Blaine Specific Surface Area Development of reference OP clinker ground in lab mill type Bond.

These data clearly show that water is a decent GA, as it is known since a long time[4], but other components such as ethylene- and propylene-glycols or ethanol- and isopropyl-amines give a much larger contribute. Also PolyCarboxylic Acid Esters (PCAE), largely utilized as superplasticizers in concrete prove themselves as good GA. This lead us to hypothesize that also the further contribution by small organic molecules such as alkanolamines and glycols does not come necessarily and only from a further electrostatic screening, but also from steric or chemical interactions with cement particles. These BSS data has been confirmed by accurate adsorption/desorption isotherms measurements and BET calculation, whose results are shown in **Figure 2**.



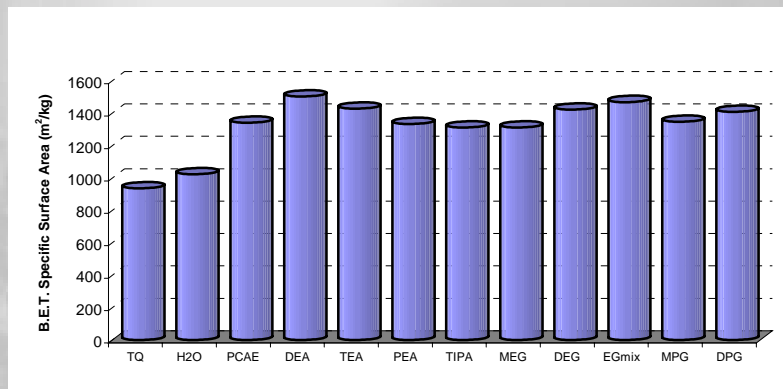


Figure 2 - B.E.T. Specific Surface Area of reference clinker powder after 90 minutes grinding

Also particle size analysis performed by mechanical Alpine sieve (Table 2) and laser light scattering of some of these samples give more or less the same trend.

Table 2 - Progress Passing through Alpine Sieve with different Grinding Agents

Grinding Agents	Progress Passing (%)		
	32 μm	40 μm	63 μm
Blank	77,0	83,9	94,8
1,0 ‰ H₂O	80,0	86,8	97,2
0,5 ‰ H₂O + 0,5 ‰ TEA	95,2	97,7	99,5
0,5 ‰ H₂O + 0,5 ‰ TIPA	96,4	98,1	99,5
0,5 ‰ H₂O + 0,5 ‰ DiEthylenGlycol (DEG)	92,1	95,9	98,3
0,5 ‰ H₂O + 0,5 ‰ PolyEthylenGlycol (PEG) 400	84,8	90,6	97,6
0,5 ‰ H₂O + 0,5 ‰ PCAE	74,8	83,6	92,0

Evident exceptions are PCAE and PEG, which do not give good results in term of granulometry. We hypothesized that sliding friction generate local heat, which makes polymers on grain surface somehow sticky, preventing flowingness of cement powder.

In order to verify the electrostatic behaviour, we collect some data by electrophoretic light scattering on different cements with polar additive components. As a matter of fact Z potential can give some indication on GA influence on grain surface charges distribution (Figure 4).

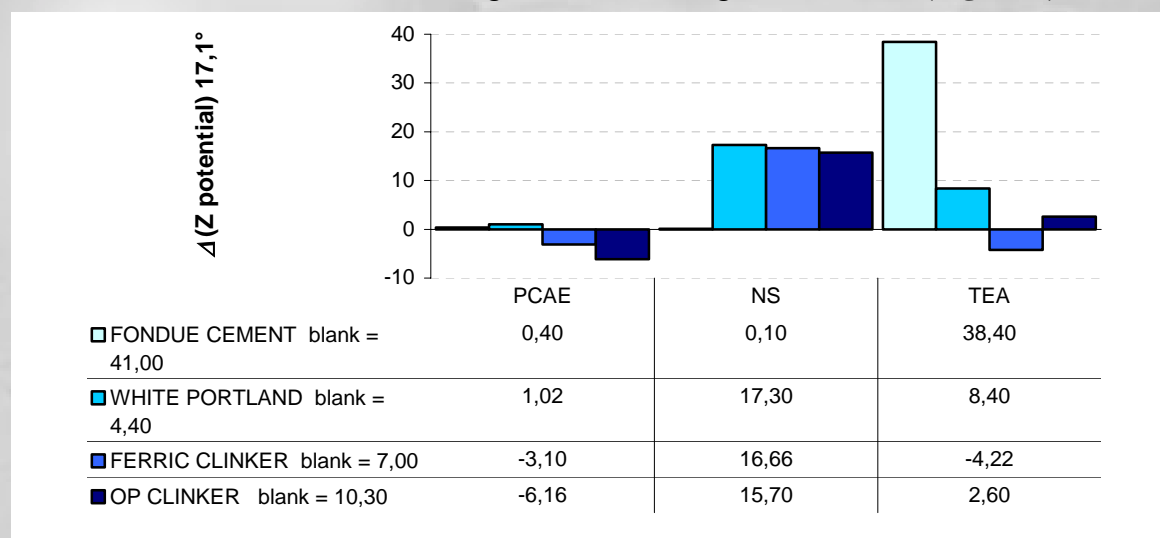


Figure 4 – Z potential variation due to some admixture components



We compared TEA, typical polar GA component, with two concrete superplasticizers admixtures such as PCAE and poly Naphtalene Sulphonate (NS), whose mechanism of action on cement paste is quite different. The former acts according to a steric mechanism coating cement grain, as it is evident from the negligible, eventually negative, influence on Z potential of any kind of cement powder. The latter, instead, induce a strong electrostatic interaction between its sulphonate groups and positive charges on grain surface. In this case GA action is somehow in between the two situations. When no ferric phase is present TEA acts as Z potential enhancer, while when it is present, as in Portland cement clinker, its effect is inverted. This can be explained by the well known chemical complex of TEA with ferric phase.

In order to make a definite breakthrough in this debated subject we exploited the potentiality of the ESEM-FEG morphological analysis to explore the microstructure of cement (and clinker) paste in the early hydration period. We used an Environmental Scanning Electron Microscope equipped with a FEG source (ESEM-FEG), which allows to study the samples without any previous treatment, like gold or graphite sputtering, and in the presence of some residual water. We chose working parameters (pressure = 6 Torr; temperature = 5°C), in order to discriminate the kind of water present in the sample. Under these conditions, it is possible to see only the water saturated with salts or bound to gel-like structures, while free water has a sufficient vapor pressure to be pumped away.

This powerful technique enabled us to observe directly the “supramolecular structures” forming on the surface of a cement grain, when it comes in contact with water, and to follow the details of the hydration process. We developed the following model mechanism of cement hydration, based also on our preceding observations[8].

When the cement comes in contact with water, we observe the almost immediate formation of a gel on the grain surface. This gel, based on complex sulfoaluminate hydrates, is rich in water and salts. It exerts a barrier effect and governs the mass flow between inner part of the grain and pore water, thus controlling the hydration of silicate phases.

This gel evolves with time, getting “structured” and forming colloidal crystals that connect cement grains. All additives and admixtures that work on the plastic phase of cement paste interact with this gel and become part of it, modifying its structure in terms of quantity and quality. These modifications also depend on the chemical composition of the cement itself.

After an intermediate phase when the gel appears partially destructured, the first gel converts to a second one, from which calcium silicate hydrates (C-S-H) and ettringite form, not by precipitation but by mineralogical growing, probably influenced by free hydrated lime.

On one hand, the structures that arise from the second gel account for cement mechanical properties. On the other hand, timing and mode of the second gel “growth” strongly depend on the characteristics of the first gel in terms of thickness, chemical composition and stability. In the light of these considerations, we suppose that all kind of admixtures work on the first gel.

The hypothesis of a chemical composition based on sulfoaluminate hydrates comes from the fact that aluminate phases (C₃A and C₄AF) are the first to react with water, forming the corresponding aluminate hydrates, and that sulfate is present as a consequence of gypsum (or other forms of calcium sulfate) dissolution.

The delayed setting of cement is then caused by the formation of the gel, a form of colloidal ettringite, and not by precipitation of ettringite itself. Its distinct long hexagonal rods appear only after few hours from the beginning of the hydration, as a consequence of the sulfoaluminate gel transformation.

The relative amounts of Ca²⁺, Al³⁺ and SO₄²⁻ changes with time, modifying the “permeability” of the gel and allowing the hydration of the silicate phases, that proceeds toward the inner part of the cement grain. This means that the C-S-H structures grow from and through the gel layer, rather than precipitate from the external pore water solution.

Since the gel forms within few seconds and covers completely cement grain, it actually represents the grain surface when water is present, and any substance added to the cement must interact with the gel.



This means, for example, that during industrial grinding process of clinker, carried out in presence of water and GA, we just have the conditions for a preliminary hydration of clinker: in fact the addition of aqueous additives, the high temperature (up to 150°C) and the presence of steam promote the hydration of clinker grain. For this reason in our investigation on the “mode” of action of alkanolamines based GA we focused our attention on morphological modifications of hydration products of clinker and cement. As a matter of fact, only small amounts of GA (3-5‰) are usually added into the mill, but they become significant, if we consider that only the 2-5% of clinker participate to the hydration process.

In this paper we describe only the effect of alkanolamines on morphological structures of calcium aluminate hydrates by ESEM-FEG analysis, also compared with PCAE used as a GA.

In order to emphasize additives action, we used in our experiments the clinker ground in the lab mill without gypsum.

As we can see in **Figure 5**, the dry clinker powder, ground with or without additives, does not show any particular morphological structure of hydrated products.

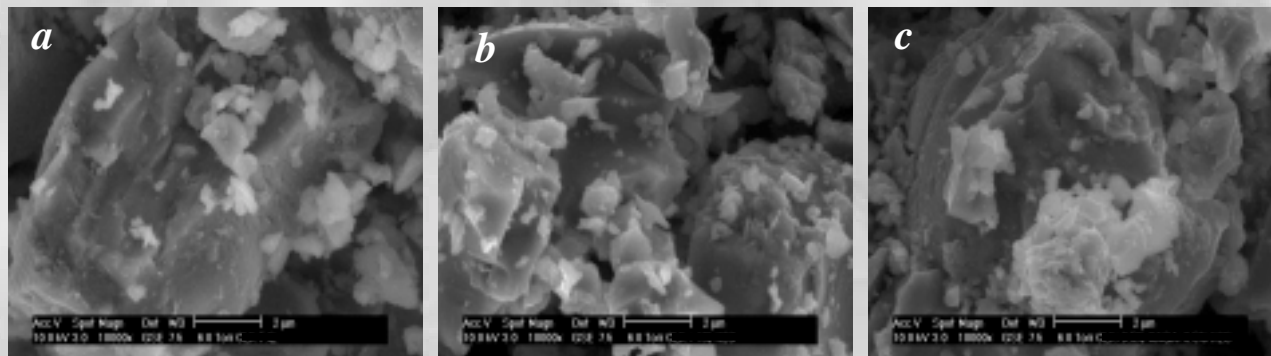


Figure 5 - ESEM-FEG images of a Portland dry clinker grain ground with: a) no additive; b) 1,0 ‰ H₂O; c) 0.5 ‰ H₂O + 0.5 ‰ of TEA.

In our opinion, this is an effect due to a mechanical action of grinding media, which break the hydrates that, therefore, become too small to be seen by ESEM-FEG analysis.

When we analyzed the morphological structures of a ground clinker paste, with a water/clinker ratio of 0.4 (**Figure 6**), we noticed that the clinker grains look still well separated, but covered with pseudo-regular gel-like structures, which cannot be observed on the dry powder. It is well evident that the gel formed by the paste of the clinker ground without GA (**a**) is less structured than the one of the clinker ground with TEA (**b**).

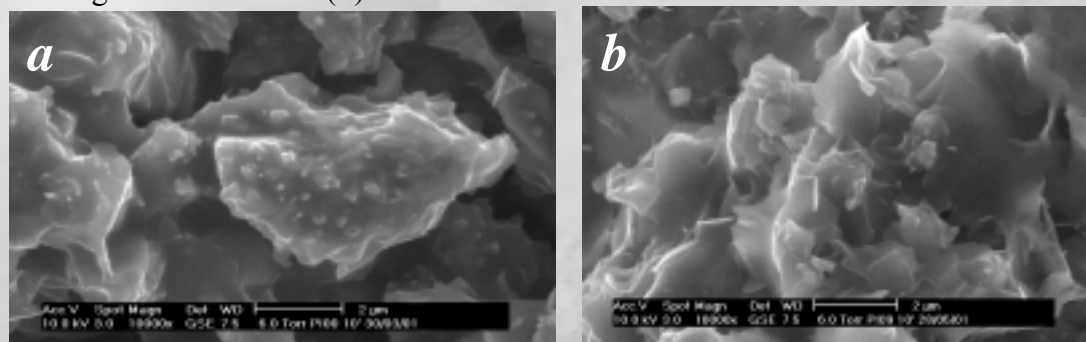


Figure 6 - ESEM-FEG images of a Portland clinker paste (w/c = 0.40) ground with: a) no additive; b) 0.5 ‰ H₂O + 0.5 ‰ of TEA.

The chemical composition of this gel is based on aluminate hydrates: in fact the aluminate phases (C₃A and C₄AF) are the first to react with water, forming the corresponding aluminate hydrates which directly interact with TEA[7].

We think that water is able to point out the structures of calcium aluminate hydrates already formed in the mill during grinding process.



A great surprise comes from the morphological analysis of a clinker ground without GA and pasted with water and TEA ($w/c = 0.4$, TEA = 0.5% w/w on the clinker), as shown in **Figure 7**.

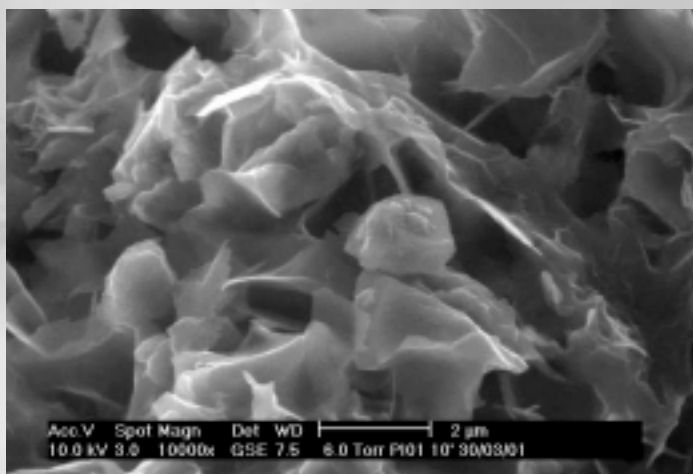


Figure 7 - ESEM-FEG image of a clinker ground without GA and pasted with water and TEA ($w/c = 0.4$, TEA = 0.5% w/w on the clinker).

Comparing **Figures 6b** and **7**, we can deduce that TEA produces the same kind of calcium aluminate hydrates added both into the mill and into the mixing water. This observation suggests that the clinker maintains a “memory” of the manufacturing process. The shape of these hydrates looks like the hydration products of C_4AF , synthesized in our laboratory (**Figure 8**).



Figure 8 - ESEM-FEG image of synthetic C_4AF paste ($water/C_4AF = 0.4$).

Figure 9 shows the gel formed during the hydration of a clinker ground with PCAE, with a water/clinker ratio of 0.4; as we can see, this gel does not show typical morphological changes on aluminate hydrates, even if grinding process data indicates the efficiency of this admixture as a GA.



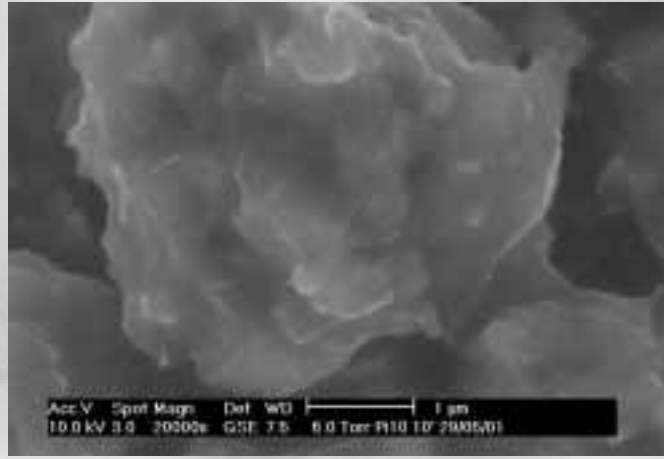


Figure 9 - ESEM-FEG image of a clinker ground with 0.5% of PCAE + 0.5% of H₂O and pasted with water (w/c = 0.4).

Considering that, when PCAE is used as a superplasticizer, we observe a huge formation of structured gel (**Figure 10**), we can hypothesize that PCAE actually works on sulfoaluminate hydrates, that we can call colloidal-ettingite, rather than on aluminate hydrates.

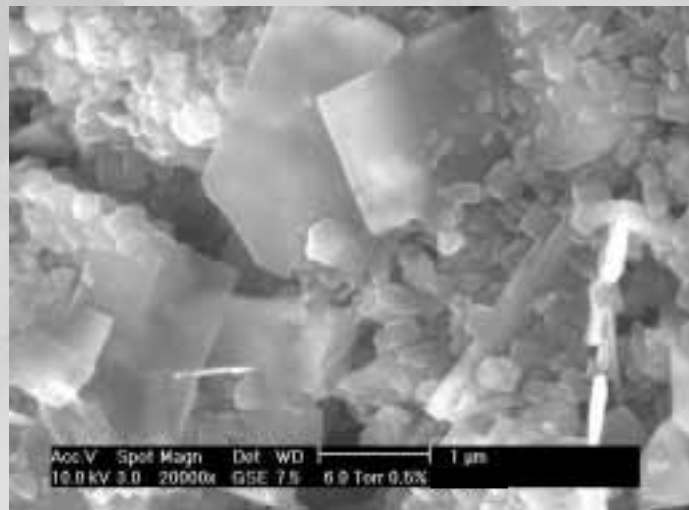


Figure 10 - ESEM-FEG image of an OPC type I paste (w/c = 0.35), with the addition of 0.5% (w/w on the cement) of PCAE.

Since it is well known that TEA based GA also improve the cement performances, especially compressive strengths at 24 hours, we tested the effect of this component on the clinker mixed with the gypsum (as in Portland cement) during hydration. This behavior is reflected in the temperature profile experiment. We recorded the temperature variation of two different “cementitious” pastes: one is a mixture of clinker ground with TEA and 5% of gypsum, the other is a mixture of clinker ground without GA and 5% of gypsum. Both mixtures were hydrated with a water/cement ratio of 0.5. As shown in **Figure 11**, two distinct peaks are present: the first one is very sharp and can be ascribed to the formation of hydrated sulfoaluminate phases, which is a quite exothermic reaction; the second peak is broad and is related to the formation of free lyme and C-S-H, which develop the mechanical properties of cement.



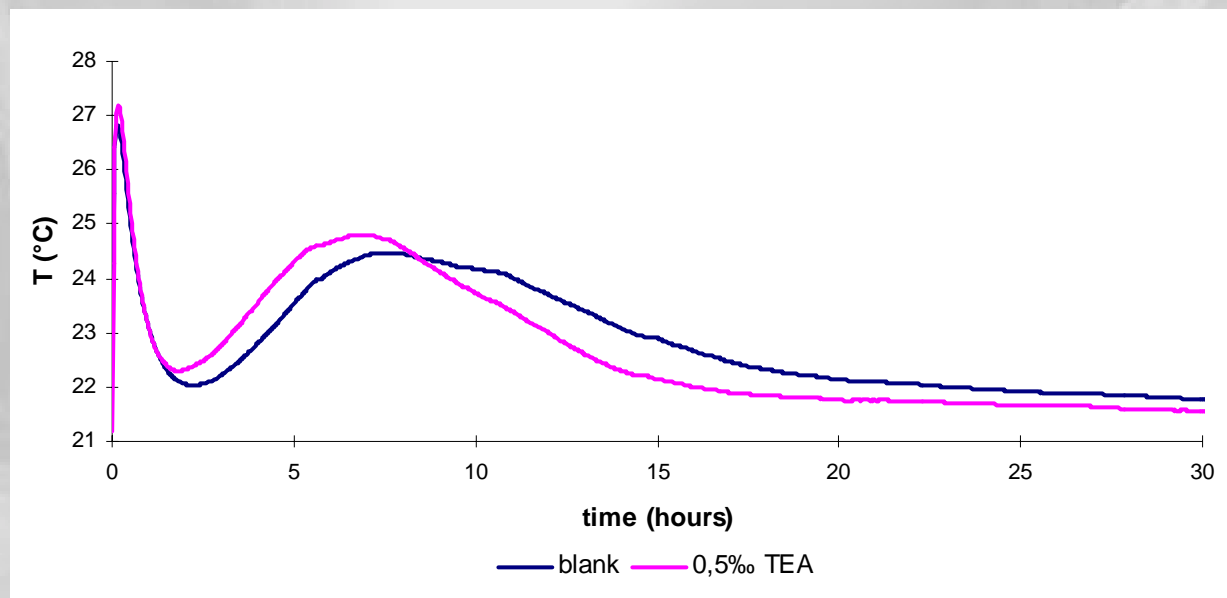


Figure 11 – Temperature profile of clinker hydration with 5 % gypsum and w/c = 0,5

From these analytical data it becomes apparent that TEA acts as an accelerator of C_3S hydration, then enhancing compressive strength of cement at the early ages. Morphological analysis of the two pastes reveals that the sulfoaluminate gel is the same in term of structures, which means that addition of gypsum hides any qualitative information. But, comparing structures at the same time of hydration, in the case of clinker ground with GA, C_3S hydration, and so the growth of C-S-H, is clearly faster and at 4 hours we already note the complete cross-linking of the grains by the structured gel.

With this work we have shown that alkanolamines interact with calcium aluminate hydrates, inducing morphological changes on the gel that covers clinker powder. In our opinion these structures could be the key point of clinker particles dispersion during grinding process and of their fluidizing effect. Therefore we can hypothesize both an electrostatic and a steric repulsive effect on the cement grain, probably related to the different chemical composition of the gel.

CONCLUSIONS

According to these results GA, in particular alkanolamines, influence the early period of clinker and cement hydration and induce morphological changes in calcium aluminate (C_3A and C_4AF) hydrates gel. We can also remark that clinker undergoes a pre-hydration reaction when it is ground in the presence of water and GA, and that it somehow keeps memory of the effect of alkanolamines on the hydration products formed during the milling process. This study is part of a more general investigation, whose target is to evaluate the chemical composition of the gel and to clarify the “mechanism of action” of other classes of admixtures on the formation of the gel. At present time we are studying the characterization of the first gel. A direct chemical analysis (by ESEM-EDX or XRD) is not possible because the “structures” are too small (< 100 nm) and the gel layer is very thin (10-100 nm): in these condition the influence of the matrix (the cement grain) is too strong.



EXPERIMENTAL

1. Materials

Beside the reference Portland clinker describe before, an OPC type I cement have been used, whose chemical composition, expressed in element oxides, is reported in **Table 3**.

Table 3 – Chemical Composition of the Reference Portland Clinker

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O
20.98	4.64	1.89	63.79	2.05	3.33	0.20	0.84

For Z potential measurements we utilized also other commercial cements: a fondue, a white Portland cement and a ferric clinker.

Alkanolamines and glycols used in our experiments are commercial products and they have been added by a sprinkler inside the mill or mixed with water before addition to cement in the concentrations indicated. The PCAE superplasticizer is a laboratory test product (MW ≈ 50.000 D), while NS comes from our production.

2. Chemical analysis (ICP-AES)

The sample is subjected to acid attack with concentrated HCl in a Parr bomb, using a microwave oven. The solution is filtered, diluted and analyzed by atomic emission spectroscopy on a Varian Liberty 220 ICP-AES.

3. Grinding process

For grinding experiments a laboratory mill type Bond for clinker grindability test has been used: rounds/minute = 70; grinding media = 32,5 kg (balls Ø = 17-40 mm). 2 kg of clinker is loaded after comminution to a grain diameter < 3 mm.

4. Blaine specific surface area measurements

After 30, 45 and 90 minutes a sample of 5 g of clinker is taken from the mill and its specific surface area is measured according to EN 196/6 (Blaine method).

5. BET surface area measurements

For the measurement of BET surface area of ground clinker powder a COULTER SA 3100 porosimeter has been utilized. Sample weight is 10 g and adsorbate gas is an He/N₂ mixture.

6. Alpine mechanical sieving

20 g of ground clinker is analyzed by an air-jet Alpine sieve 200 LS-N

7. Z potential measurements

For the measurement of Z potential of cement powder a COULTER DELSA 440 Multi-angle electrophoretic light scattering analyzer has been used. The sample powder has been dispersed in phosphate buffer pH 12 (12 mS).



8. ESEM-FEG analysis

The samples have been analyzed by scanning electron microscopy, without any previous treatment. We have used a Philips XL30 ESEM-FEG (Environmental Scanning Electron Microscope, equipped with a Field Emission Gun) in secondary electron mode. The instrumental configuration allows us to obtain a much higher brilliance of the electronic source than the one of an ordinary SEM, and to work in low vacuum conditions (6 Torr), with a voltage of 10kV, at a temperature of 5°C.

9. Temperature profile analysis.

The temperature variation during the first 24 hours of the hydration period is continuously recorded by a TESTO 781 digital thermometer, equipped with a TESTO DQF 826 probe (sensitivity: $1/1000$ °C). The probe is kept into the cement paste (500 g cement) immediately after mixing the cement with water. The system is kept in a thermostatic bath maintained at 20°C (reference temperature).

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