SINTEF Building and Infrastructure   Christian J. Engelsen

Quality improvers in cement making – State of the art

COIN Project report 2 - 2008

SINTEF

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COIN Project P1 Advanced cementing materials

SP 1.1F Reduced CO2 missions

COIN Project report 2 – 2008

Summary

It has been shown that the overall cement properties are interconnected and in many cases there is still potential for further production improvement by only optimising the different stages (e.g. separate grinding, mill operation etc.). This, in turn, indicates the potential for quality improvers to further optimise the production and improve the quality of the cement. It was found that the combination of certain alkanolamines (TEA and TIPA) with calcium nitrate gave considerable enhanced early strength. Probably the same effect will be found combining nitrate with the highly efficient grinding aid DEA. If quality improvers are used for clinkers that are mineralised with for example Zn, Ti or Cr, significant improvement can be achieved. The total improvement as decrease in clinkering temperature, increased Blaine surface and increased early strength can be measured and expressed in terms of decreased energy used pr. cubic metre of produced concrete.

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Foreword

COIN - Concrete Innovation Centre - is one of presently 14 Centres for Research based Innovation (CRI), which is an initiative by the Research Council of Norway. The main objective for the CRIs is to enhance the capability of the business sector to innovate by focusing on long-term research based on forging close alliances between research-intensive enterprises and prominent research groups.

The vision of COIN is creation of more attractive concrete buildings and constructions. Attractiveness implies aesthetics, functionality, sustainability, energy efficiency, indoor climate, industrialized construction, improved work environment, and cost efficiency during the whole service life. The primary goal is to fulfill this vision by bringing the development a major leap forward by more fundamental understanding of the mechanisms in order to develop advanced materials, efficient construction techniques and new design concepts combined with more environmentally friendly material production.

The corporate partners are leading multinational companies in the cement and building industry and the aim of COIN is to increase their value creation and strengthen their research activities in Norway. Our over-all ambition is to establish COIN as the display window for concrete innovation in Europe.

About 25 researchers from SINTEF (host), the Norwegian University of Science and Technology - NTNU (research partner) and industry partners, 15 - 20 PhD-students, 5 - 10 MSc-students every year and a number of international guest researchers, work on presently 5 projects:

- Advanced cementing materials and admixtures
- Improved construction techniques
- Innovative construction concepts
- Operational service life design
- Energy efficiency and comfort of concrete structures

COIN has presently a budget of NOK 200 mill over 8 years (from 2007), and is financed by the Research Council of Norway (approx. 40 %), industrial partners (approx 45 %) and by SINTEF Building and Infrastructure and NTNU (in all approx 15 %). The present industrial partners are:

Aker Solutions, Borregaard LignoTech, maxitGroup, Norcem A.S, Norwegian Public Roads Administration, Rescon Mapei AS, Skanska Norge AS, Spenncon AS, Unicon AS and Veidekke ASA.

For more information, see www.coinweb.no

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1 Introduction

Grinding aids are mostly organic compounds that are added to the clinker in the cement mill. Their main purposes are to reduce the energy required to grind the clinker into a given fineness and therefore increase the efficiency of the cement mill. Grinding aids have been used for more than 50 years and the most common additives can consist of glycols, alkanolamines and phenol-type compounds. In addition to increase the efficiency of the mill, some grinding aids also provide important positive effects on the final cement such as, rheology of the fresh cement paste or concrete and improved strength development. Grinding aids that provides these "extra" properties are called *quality improvers* or the name *performance enhancer* as we also may like to use.

The grinding technology of clinker in cement production is indeed important for several reasons. Firstly, the fineness (Blaine specific surface) of the finished cement is one of the main factors that are affecting the early strength development. Norcem produces rapid hardening cement (Norcem Industrisement) with a Blaine of 520 m^2/kg; commercially available in Norway. In order to achieve such high fineness grinding aids are used and in this particular case triethanolamine is used. In general, the energy consumption is linear up to a fineness of approximately 300 m^2/kg (Hewlett 1998). Above this level, the energy consumption increases progressively due to agglomeration in the cement mill and a higher amount of energy is lost in heat. This is usually taken care of by the use of grinding aids and also by optimizing the cement mill technology. The latter will not be considered in detail in this state of the art report.

Reducing energy consumption is therefore another main driving force in the field of cement mill technology. Approximately 35-40 kWh/t is required to produce Portland cement with a Blaine in the area of 300-340 m^2/kg (Hewlett 1998). For higher surface areas (e.g. Norcem Industrisement) the energy required is > 50 kWh/t. By the use of grinding agents the energy is reduced or the production rate is increased at the same energy consumption level. Moreover, energy saving is indeed important when producing blended cements. In the production of blast furnace slag cements the pure cement clinker is far more easy to size reduce compared to the slag. In Trenkwalder and Ludwig (2001) they estimated the power consumption to be 43 and 68 kWh/t for producing cement and slag meal (separate processes) with a Blaine of 300 and 400 m^2/kg respectively. Together with optimized mill technology they achieved reduction in the electric power consumption of 7% without the use of grinding aid. Including a suitable additive in such processes, the possibilities for further increase in the grinding efficiency are most likely present.

In summary, *conventional* grinding aids are used to increase the production rate in the cement mill. If such additions give beneficial chemical effects during hydration of the final cement (e.g. increased strength, improved workability etc.) the grinding aid is regarded as quality improver or performance enhancer. It is emphasised that several *conventional* grinding aids today are also claimed to give beneficial chemical effects to a certain extent.

2 Principle mechanisms and desirable effects of quality improvers

2.1 Mechanisms during grinding in the cement mill

The mechanisms in charge when improving the grindability of a clinker must be explained from a physico-chemical point of view. In general, the surfaces of the clinker particles are not in thermodynamic equilibrium due to the incomplete surface bonds, which lead to a free surface charge. As in all systems, the particles will try to approach equilibrium by lowering the free energy, which in turn is done by aggregation and adhesion to surfaces. When the clinker is entering the cement mill the particles are coarse and the energy considerations are not significant. As the clinker is size reduced during grinding, the free energy of the surface increases and the non equilibrium become significant. The aggregation and agglomeration will therefore become increasingly significant and the efficiency of the mill is reduced. This is shown in Figure 1b.

By using grinding aids the organic additives are adsorbed to the surface of the clinker/cement particles. This reduces the energy needed to break down the particles and reduces the surface charge. The latter is thus preventing the cohesion of cement particles. The organic additives also change the electrostatic forces between the cement particles by reducing the attraction forces (Van der Waal) and increasing the repulsion forces. The effect of using a grinding aid is shown in Figure 1a. The additives are thus behaving as surfactants.
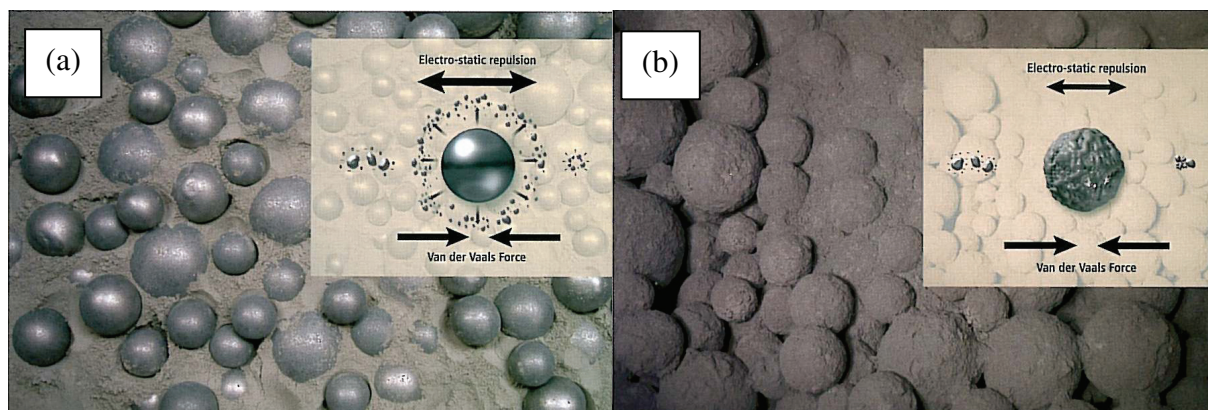
Figure 1 Principle of grinding cement clinker with (a) and without (b) grinding aid
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The energy supplied (grinding time) versus the surface area generated is usually linear up to a surface Blaine of 300 m²/kg before the agglomeration starts. With grinding aids this linear relationship is prolonged. The maximum surface Blaine achieved, i.e. optimum grinding time, is at the point where significant deviation from linearity is seen. This is showed in Figure 2a where 3 different glycols were tested as grinding aids (Teoreanu and Guslicov 1999). It can be seen that the linear area is significantly prolonged for a given dosage of additive and that serious non-linearities start when the Blaine specific surfaces were approaching 600 m²/kg. The reduction in evolved surface area is due to reduced activity of the surfactants as the surface area becomes too high. This is the stage where agglomeration and adherence to grinding media and walls of the cement mill starts. With respect to the dosage, an optimum dosage of additive exists for a given grinding time. The optimum dosage is achieved when a continuous monolayer is formed onto the particle surfaces (Teoreanu and Guslicov 1999). Higher additions will lead to lubrication effects that will decrease the breakdown of the particles and the efficiency of the mill decreases. In

Figure 2b large reduction in power consumptions can be seen due to increased grindability relative to the reference cement.

Figure 2 Evolution of specific surface as function of grinding time (a) and the specific power consumption with increasing Blaine (b). Results achieved for cement clinker ground with ethylene glycol (EG), propylene glycol (PG) and polypropylene glycol (PPG). (Teoreanu and Guslicov 1999).

Other considerations that can be taken into account regarding the grindability are the mineral composition of the clinker. Alite crystals are more elongated than belite. The more alite present in the clinker the easier it is to grind. The grindability of a clinker is determined by 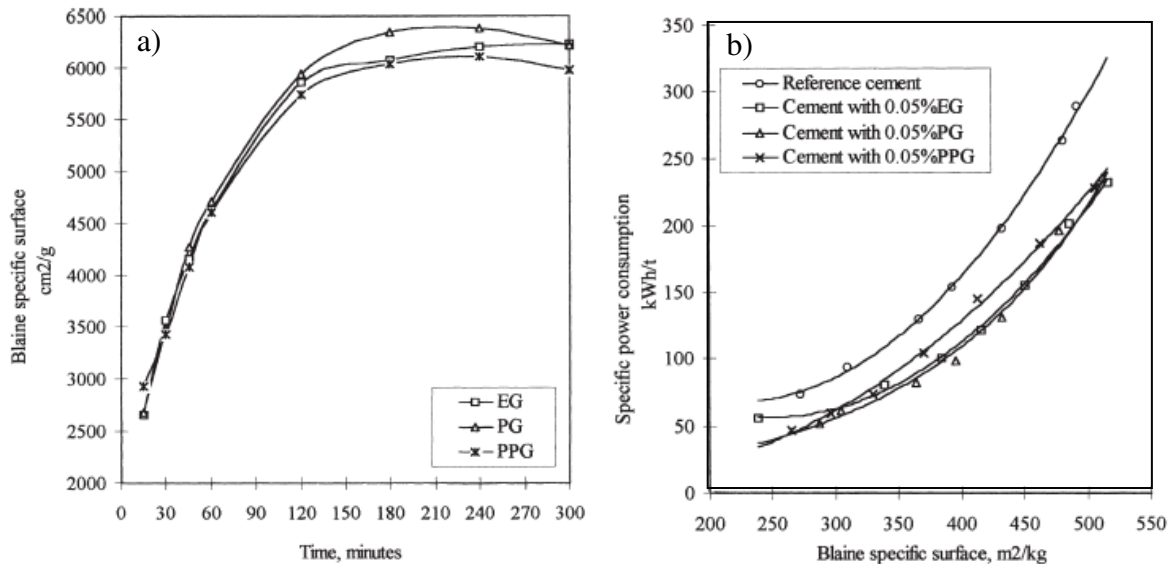the fracture energy and the size of the micro cracks present (Hewlett 1998) which in turn are dependent of the cooling regime applied to the clinker. Brittleness index values have been calculated for principle clinker phases to be 4.7 (C_3S), 2.9 (C_3A), 2.0 (C_2S and C_4AF). From this we also can deduce that C_3A is easier to grind than C_4AF. In addition, mineralising effects that influence the molten phase and are forming solid solutions with C_3S and C_2S will increase the grindability by reduced hardness of these phases (Opoczky and Gavel 2004).

2.2 Mechanisms during hydration

Many grinding additives are reported to give beneficial effects during hydration. The mechanisms can in general be explained as for the admixture used in concrete. The surface of the cement has a residual positive charge whereas sand and aggregates has a net negative charge. In addition water molecules are dipoles. The overall action of charged surfactants are that they arrange in such a way that opposite charges are cancelled out, i.e. decreasing the free energy (electric potential) of the system (Hewlett 1998). The additives used during grinding are, as explained in previous section, adsorbed to the surface of the cement particles. This means that the additives will have some action on the rheology of the concrete mixture and during hydration depending of the molecule structure. Triethanolamine (TEA), for example, is widely used as grinding additive and will in fact influence the hydration properties. In Figure 3 the differential heat of hydration is shown for cement ground with different concentration of TEA, i.e. the hydration heat for pure cement is subtracted. At the lowest dosage (0.015%) it behaves as an accelerator whereas retardation properties were found at higher dosages. From the appearance of the change in hydration heat, it is the hydration rate of C_3S that is altered. In the same figure we also can see that

TEA changes the hydration of C_3A (AFt formation). At a dosage of 0.015%, TEA is accelerating both the hydration of C_3S and C_3A.

Accelerators are generally divided into two subgroups. The first group comprise admixtures that increase the hydration of C_3A by interfering with the first ettringite formation and increase the dissolution of silica (e.g. alkali metal hydroxides). The other main group include admixtures that increase the hydration of C_3S by increasing the dissolution of lime (e.g. halide, nitrate, nitrite etc.). According to Hewlett (1998) the TEA additive increases the formation of C_2AH_8 and C_4AH_{19} (and therefore promoting conversion to thermodynamic stable hydrogarnet phase) and also increases the formation of ettringite.
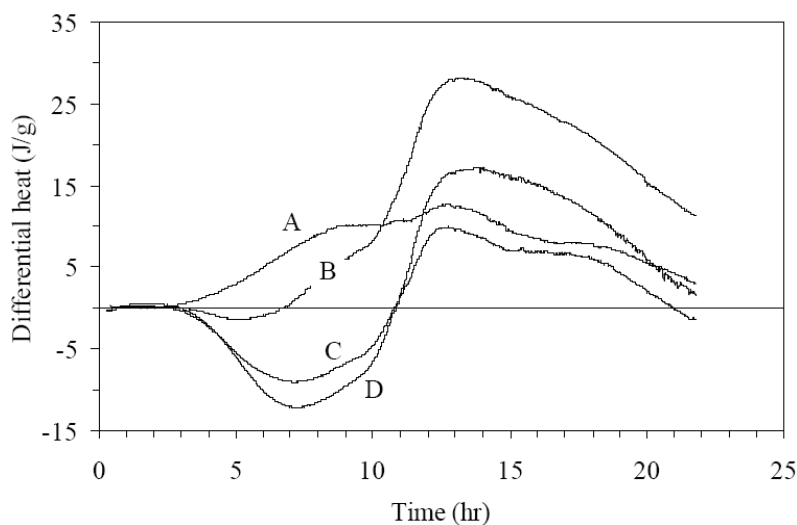
Figure 3 Hydration heat evolution for cement ground with various concentration of triethanolamine (TEA): 0.015% (A), 0.075% (B), 0.1% (C) and 0.15% (D). The hydration heat for pure cement is subtracted (Jolicoeur et al 2007).

2.3 Desirable effects

Using quality improvers in cement making affects various parameters as discussed above. The desirable effects can be summarised as follows:

- Increased grindability
- Increased or maintaining sufficient powder fluidity
- Workability/rheological effects
- Hydration effects: retarding/accelerating effects
- Increased strength

Increasing the grindability and powder fluidity are typical effects that are determined by grinding aids whereas rheology, hydration and strength development are affected by conventional admixtures (added to the fresh concrete mix). These effects, all together, recognise the quality improver or a performance enhancer added in the cement clinker mill.

3 Quality improvers tested for Portland cement

3.1 Polyol type additives

In a recent study, Jolicoeur et al (2007) investigated effects of glycols and compared the results with triethanolamine (TEA). The grinding aids tested are shown in Table 1. The ethylene glycol series have the structural formula of $HO-CH_2-CH_2[-O-CH_2-CH_2]_n-OH$ (n = 0, 1, 2 etc., gives EG, DEG, TEG etc.). Improved powder fluidity relative to TEA was not observed with the ethylene glycol series at a dosage of 0.1% as can be seen in Figure 4a.

The propylene glycol series have the structural formula of
$HO-CH(CH_3)-CH_2-[O-CH_2-CH(CH_3)]_n-OH$ (n = 0, 1, 2 etc., gives PG, DPG, TPG etc.) or illustrated as:

(PG)

(DPG)

(TPG)

For the propylene glycol (PG) series in Figure 4b, only the monomer (PG) achieved improved fluidity relative to TEA. In addition the effect of molecular weight can be seen as the fluidity decreases in the sequence of monomer (PG), dimer (DPG) and trimer (TPG).
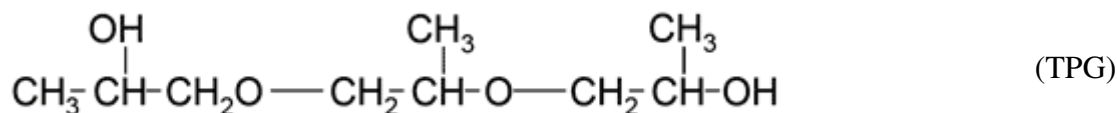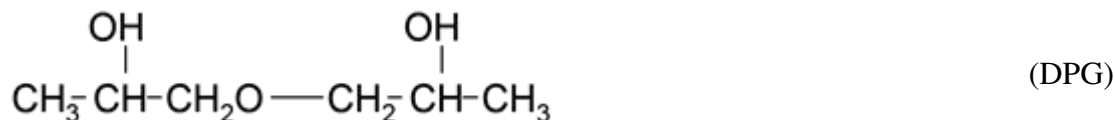
In Figure 4c the effect of aliphatic tail is shown for the diols at a dosage of 0.075%. Maximum fluidity was obtained with PG (1,2-propanediol) and 12HD (1,2-hexanediol). The effect is most likely caused by repulsion between particles and that the optimum is achieved with a certain size of the tail. PPT (polypropylene glycol triol) is also included in Figure 4c and the achieved high fluidity was not expected as Figure 4b showed fluidity decrease with increasing polymerisation.

In Figure 4d the effect of molecular structure is shown. The positions of the hydroxyl groups in butanediol seemed to be decisive as the fluidity index of the cement was 16 times higher when 2,3-butanediol (23BD) was used compared to the 1,4-butanediol (14BD). The effect of adding a methyl group to 2-methyl-1,3-propanediol (MPdiol) yielding 2,2-dimethyl-1,3-propanediol (DMPD) was found to largely increase the fluidity.

Table 1 List of different polyols given by Jolicoeur et al (2007)

Abbreviation	Name	Abbreviation	Name
TEA	Triethanolamine		
EG	Ethylene glycol	PG	Propylene glycol
DEG	Diethylene glycol	DPG	Dipropylene glycol
TEG	Triethylene glycol	TPG	Tripropylene glycol
PEG	Poly(ethylene glycol)	PPG	Poly(propylene glycol)
12HD	1,2-Hexanediol	12OD	1,2-0ctanediol
12BD	1,2-Butanediol	23BD	2,3-Butanediol
GLY	Glycerol	PPT	Polypropylene glycol triol
MPdiol	2-methyl-1,3-propanediol	DMPD	2,2-dimethyl-1,3-propanediol
LF2	Mixed EG-PG copolymer	LG650	Polypropylene glycol triol
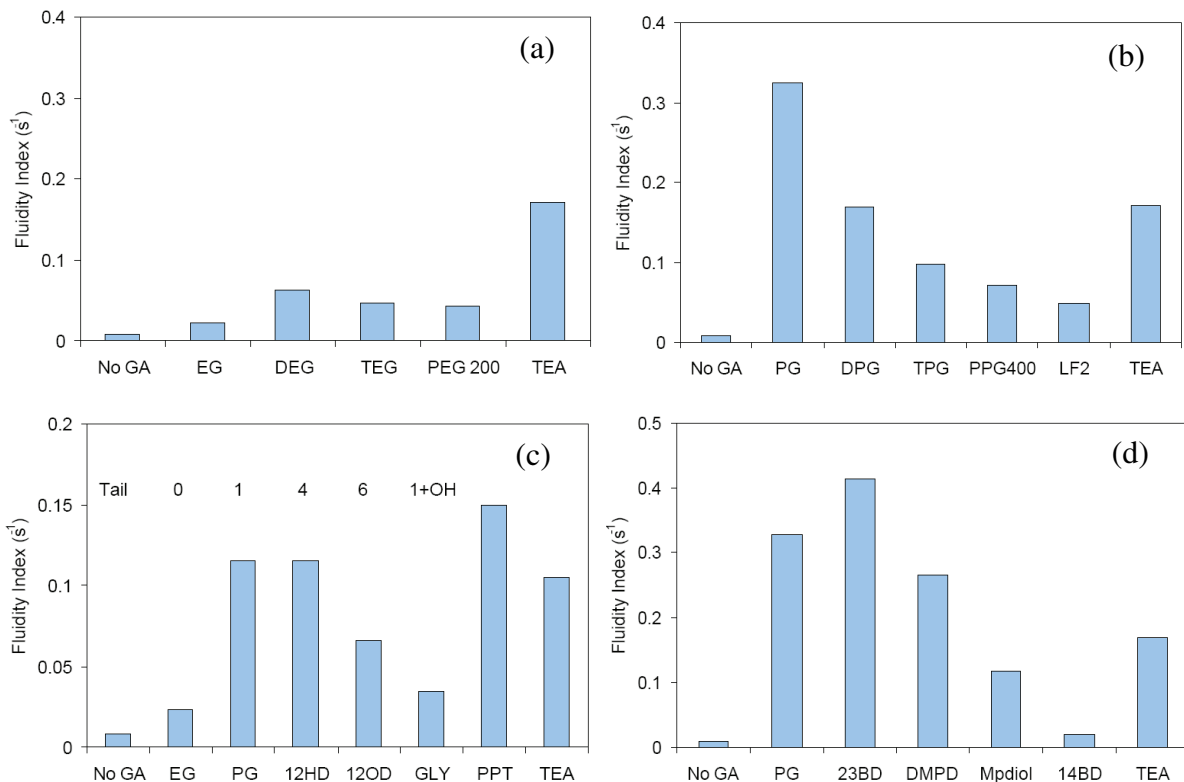
Figure 4 Fluidity of the cement ground with different glycol additives and its oligomers at dosages of 0.1%. No GA means cement ground with no grinding aid and serves as a reference: (a) ethylene glycol series, (b) propylene glycol series in addition to the EG-PG block co-polymer LF2, (c) effect of tail length for additives (0.075%) with adjacent hydroxyl groups, the triol additive PPT is also included, (d) effect of hydroxyl position in butanediol (BD) and addition of a methyl group to MPdiol yielding DMPD (Jolicoeur et al 2007).

In section 2.2 we examined the triethanolamine (TEA) effect on hydration, see Figure 3. In regard to the fluidity of dry cement, PG and PPT (as the additive LG 650) were the most promising additives. The effect on hydration was therefore also tested for these additives by Jolicoeur et al (2007) in addition to glycerol (GLY) and glucose shown in Figure 5. The latter was included only for visualising a known retarder. It was demonstrated that these additives behaved as accelerators for both the silicate and aluminate phases. The accelerating effect of the PG additive lasted for almost 24 hours as can be seen in the thermogram in Figure 5.

From the mentioned study above it is quite clear that PPT and PG behaves as significant quality improvers as the fluidity was improved relative to TEA and accelerating hydration properties were demonstrated. (Teoreanu and Guslicov 1999) examined the grindability effects of EG, PG and PPG and found significant improvement in terms of Blaine specific surface and thus reduced power consumption, see Figure 2.
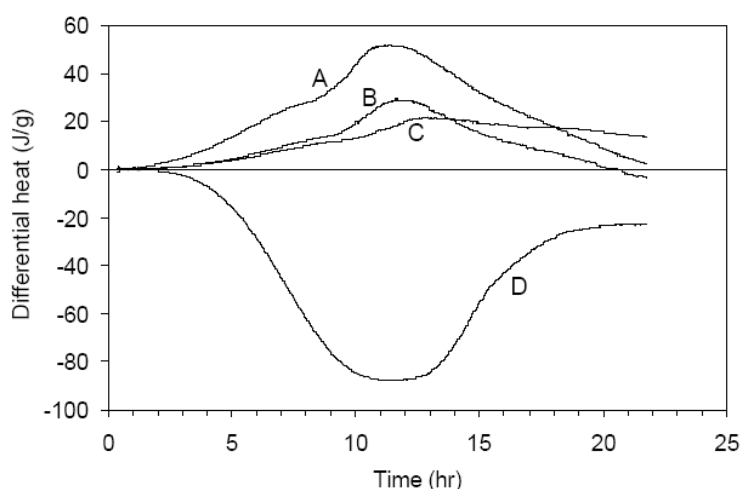
Figure 5 Differential heat of cement hydration. GLY (A), LG650 (B), PG(C) and Glucose (D). The dosage for PG was 0.1%; the dosages for the other additives were 0.075% (Jolicoeur et al 2007).

3.2 Alkanolamines

Alkanolamines are widely used as admixtures to concrete. Some of them (e.g. TEA) have also been used as grinding aids in the cement mill as discussed in previous sections. It is therefore important to explore their mechanisms during hydration in addition to their grinding aid effects. Structures of monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA) and triisopropanolamine (TIPA) are shown below:

MEA

DEA

TEA
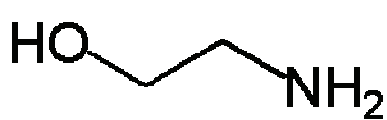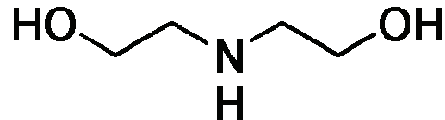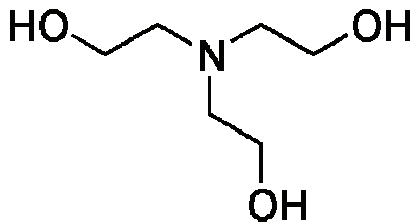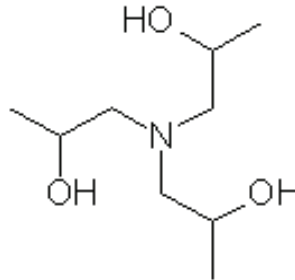
TIPA

TEA is a common grinding additive and its effects on the cement powder fluidity and the hydration are discussed in previous sections. The influence of cement hydration, however, is not straight forward as it acts as both retarder and set accelerator depending on the dosage. In Jolicoeur et al (2007) dosages in the range of 0.02-0.15% were used. At 1% TEA, strong accelerating effects are observed on cement hydration due to rapidC_3A hydration (flash setting) (Dodson 1990). Heren and Olmez (1996) studied the hydration and mechanical effects of the ethanolamines oligomers at dosages in the range of 0.1-1% added directly in the mixing water. They found the retarding effects of the ethanolamines decreasing in the sequence of TEA > DEA > MEA at all dosages (0.1-1%). Note that flash setting was not observed in these cases at 1% dosages, but keep in mind that white Portland cement was tested (low C_4AF). The effect on C_4AF will be discussed later. Lower strength was measured at early and late hydration for TEA whereas only slight reduction in early strength (3days) was observed for MEA. Note that the early strength of cement pastes with DEA was as high as the reference sample. In the same study published the following year (Heren and Olmez 1997), they also found that DEA and TEA did produce more porous pastes (larger size pores) although the general shape of the pore size distributions were the same. The pore structure of pastes containing MEA seemed to be close to the control sample.

Aiad et al (2003) tested the rheological properties of PC (Portland Cement) and SRC (Sulphate Resistant Cement) pastes separately spiked with of MEA, TEA and PTEA (polymer) in the concentration range 0-2%. The study more or less confirmed the accelerating and retarding effects of the ethanolamines in terms of changes in the shear stress and viscosity. If we recall the retarding and accelerating effects on cement in Figure 3, Aiad et al (2003) demonstrated the importance of the phase composition of the cement. This is shown in Figure 6 where the shear stress in almost every cases decreases with increasing dose of admixture, which in turn show the retarding effects. Moreover, the decrease in shear stress is more significant in the SRC pastes. This is most likely due to the low C_3A content (2.6%) in the SRC used and therefore no accelerating effects, although not pointed clearly out by Aaid et al (2003). They conclude that ethanolamines influence the rheological properties of SRC pastes in the sequence of TEA > PTEA > MEA.
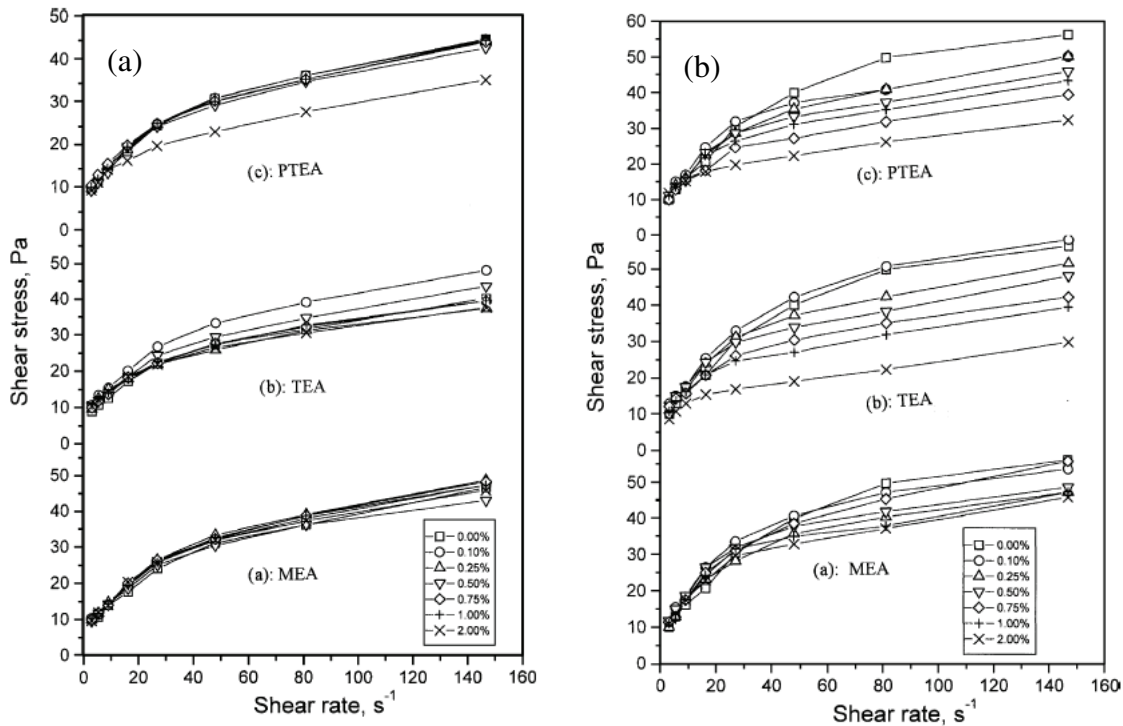
Figure 6 Shear stress as function of shear rate for OPC (a) and SRC (b) pastes admixed with MEA, TEA and PTEA (Aiad et al 2003).

TriIsoPropanolAmine (TIPA) is an additive that can be regarded as a quality improver. Gartner and Myers (1993) studied the effects of TEA and TIPA on hydration of cement mortar. They found in some cases increased 1 day strength of the mortar admixed with TIPA due to increased hydration of C_4AF. The mechanism was proposed to be that TIPA remained in solution (not adsorbed to surfaces as TEA) also after all the sulphates have reacted and that TIPA formed iron complexes that enhanced the transport of the ferric ions. Ichikawa et al (1997) confirmed the accelerated hydration of C_4AF by TIPA. They also showed that the amount of C_3S is important. The grindability of C_3S is higher relative to C_2S and fractures of the former grains are therefore expected to penetrate into the crystal. This causes interstitial phases (C_4AF) to coexist in the C_3S grains. This polymineralic C_3S favours both hydration of C_4AF and the C_3S in the presence of TIPA. In the same study it was also indicated that TIPA increased the limestone reaction in the formation of carboaluminates. Perez et al (2003) argued that the strength gain with TIPA was not caused by an increase in the hydration but rather by a modification of the cement paste - aggregate interface. Sandberg and Doncaster (2004), however, largely disagreed in this explanation and showed in their experiments results that supported increased hydration rate. In the very recent study of Aggoun et al (2008) TEA and TIPA was tested separately and also in combination with the set accelerator $Ca(NO_3)_2$ (calcium nitrate) in regard to setting time and strength development of two types of cement pastes.

The strength development results are shown in Figure 7 and significant increase in the strength at all ages was determined for both TEA and TIPA. The best results, however, were achieved with TIPA as emphasised by Aggoun et al (2008). Studying the results (Figure 7) in more detail it is apparent that TIPA is far more efficient at early age (185% strength increase after day 1 relative to control sample) for the cement sample rich in C_4AF (16%), not specifically pointed out by the authors (Figure 7b). In relation to the above discussions, this is a strong indication of accelerating the hydration of C_4AF keeping in mind that the *normal* cement consisted of ~9% C_4AF and thus achieved 90% strength increase relative to the control sample (Figure 7a). In regard to the dosage

used (0.05%), TEA is expected to have accelerating features which is in reasonable agreement with Jolicoeur et al (2007), see Figure 3.
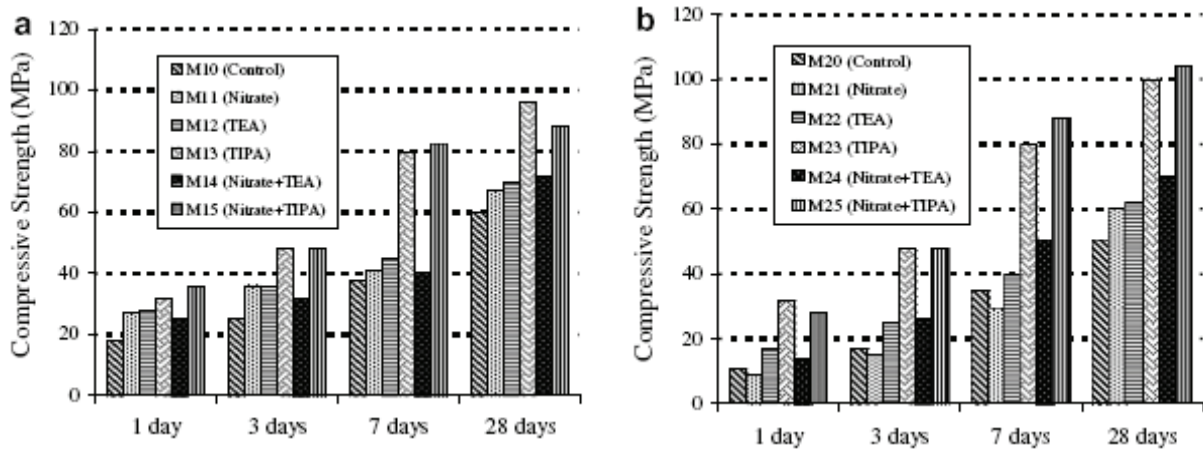
Figure 7 Strength developments for two different cement pastes with different admixtures, concentrations of 0.05% are used for TEA and TIPA and 1% are used for calcium nitrate. The principle mineral phases in the cements used were (a) C_3S (51%), C_2S (25%) C_3A (8.3%), C_4AF (8.9%) and (b) C_3S (52%), C_2S (23%), C_3A (2.8%), C_4AF (16%) (Aggoun et al 2008).

Figure 7 also show interesting combinations of calcium nitrate with TEA and TIPA. The latter combination gave strength improvement in the same range as for TIPA alone. In regard to the setting, TEA and TIPA did not reduce the initial and final setting times. In combination with calcium nitrate, however, both admixtures achieved considerable reduction in setting time (35-70%). Kuroda et al (1986) tested a combination of calcium nitrite, calcium rhodanate and TEA in total concentration of 1% at 5 and 20°C. They found accelerated initial and final setting at both temperatures in addition to increased early strength at 20°C.

From the results shown above, alkanolamines undoubtedly serve as strength enhancers. In regard to improving the grindability and preserve sufficient powder fluidity for the additives under consideration, there are not many systematic studies available in addition to those already mentioned. Bravo et al (2003), however, carried out grinding experiments with glycols (MEG, DEG, PEG, MPG and DPG), alkanolamines (DEA, TEA and TIPA) and a superplasticizer (Poly Carboxylic Acid Esters, PCAE). In regard to the BET specific surface area, considerable increase was achieved for all additives as shown in Figure 8.

Figure 8 BET specific surface area after grinding clinker powder for 90 minutes admixed with different grinding aids (Bravo et al 2003).

Granulometric experiments carried out with mechanical sieves also showed improving results relative to the reference clinker except for PEG and PCAE in particular. The authors hypothesized that the pol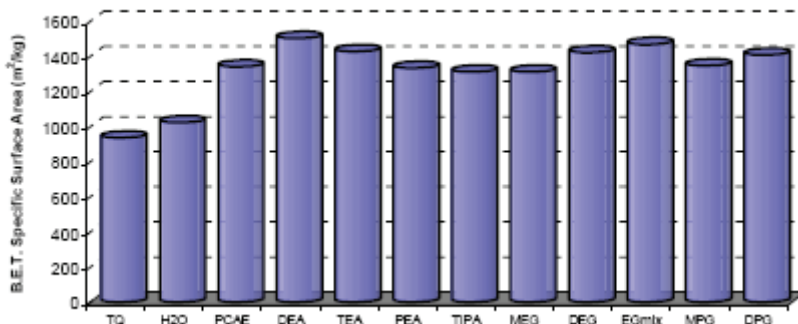ymers on the surface tend to make the clinker grains sticky causing agglomeration. The sieving analysis in regard to PEG (also for DEG) were in accordance to what Jolicoeur et al (2007) reported some years later in their fluidity experiments, see Figure 4a. It is therefore important to evaluate not only the particle surface evolution with grinding time, but also evaluate how the cement powder behaves in a more practical way by for example simple fluidity experiments on the dry cement.

Performance enhancers (quality improvers) are supposed to increase the efficiency of the cement mill and at the same time preserve sufficient *"workability"* of the dry cement i.e. not giving rise to problems like clogging during storage, packing or offloading from bulk transportation. In addition, the additives shall enhance the rheological and strength properties for fresh and hardened concrete respectively. In regard to the latter, a *"true"* quality improver must increase the early strength due to a chemical effect and not only due to increased fineness of the cement. There are not many studies where both the cement powder and concrete properties are studied, in particular where the additive is added in the grinding process. The results of Jolicoeur et al (2007) and to a certain extent Bravo et al (2003), however, are nice examples where the quality improvers have been added in the *"mill"* for investigation of both properties. In the latter study, only the hydration properties of TEA were determined.

From Figure 8 we also note that DEA gave interesting results. We know from Heren and Olmez (1996) that retarding effects was measured in the decreasing sequence of TEA > DEA > MEA for white Portland cement. The observed retardation was due to the high admixed content (0.1-1%) and the fact that the samples contained only 0.9% C_4AF. In lower admixed concentrations, DEA might have the same accelerating properties as TEA, and can thus be regarded as a quality improver as well.

3.3 Patents

Several patented grinding aid formulations exist which claim to improve the cement clinker grinding process. In Gartner et al (1991) the TIPA containing additive had improved grinding effects on blended cement and it was a strength enhancer at 7 and 28 days. The requirement was that the clinker should contain at least 4% C_4AF. The recommended dosages were additions to the cement in an amount up to 0.2%, preferably less than 0.1%, and most preferably between 0.005% and 0.03%, based on the weight of the cement. Moreover, Cheung and Gartner (1995) formulated a quality improver that is claimed to increase the early strength. The grinding aid was composed of a mixture of C_2 -C_3 alkylene glycol and corresponding oligomers in combination with carbon powder in weight ratios of from about 1:0.01 to 1:0.5.

Jardine (2007) combined a diamine (e.g. tetrahydroxylethylethylene diamine) with an alkanolamine (e.g. TEA, TIPA, DIPA etc.) and the grinding improvements are larger compared to these additives added separately. In regard to the mixing dosages to achieve favourable early strength, experiments showed that optimum mixture was 20-30% tetrahydroxylethylethylene diamine and 70-80% diethanolisopropanolamine (DIPA). The addition dosage was in the range 0.04% to 0.06%.

The few patents shown here describe the wide range of possibilities in quality improver formulations. Very often the key factor is to find the optimum mixture blends.

4 Quality improvers tested for blended cements

4.1 Fly ash

An interesting study has been carried out by Lee et al (2003). They studied the effects on strength by adding separately triethanolamine (TEA), Na_2SO_4 and K_2SO_4 to the mixing water of fly ash mortars. The results for TEA can be seen in Figure 9 and show that TEA contributed positively to the strength development. In the same study they measured the evolution of ettringite in the corresponding paste samples and found only a small increase at day 1 compared to the reference. The increase in early strength for mortars admixed with TEA cannot be caused by increased hydration of C_3A (ettringite formation) as were the case for mortars admixed with Na_2SO_4 and K_2SO_4. Lee at al (2003) also found that TEA (0.03%) reduced the total porosity by increasing the number of smaller pores.
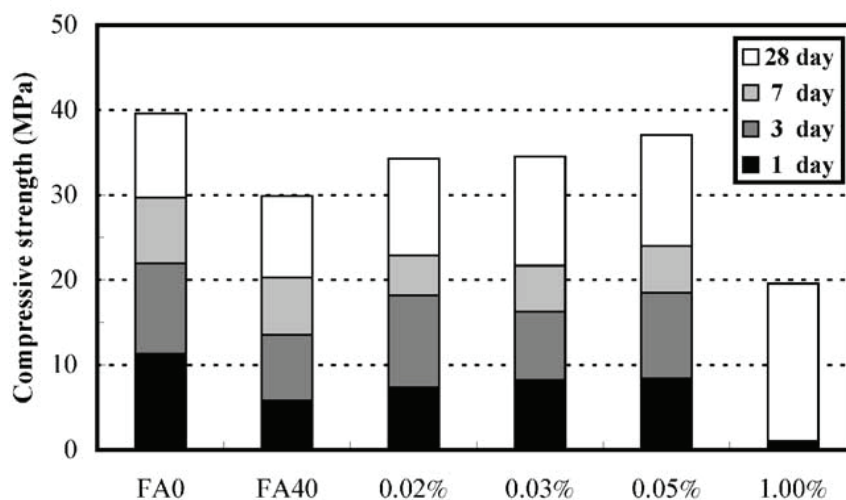

Figure 9 Compressive strength of cement (FA0) and cement with 40% fly ash replacement (FA40) mortars. The FA40 samples are admixed with 0-1% triethanolamine (Lee et al 2003).

Bouzoubaâ et al (1998) studied the high volume fly ash cements with respect to grindability and mechanical properties of the corresponding mortars. The clinker, fly ash and gypsum were interground in the portions 43.7:55:1.3. The grinding aid was a superplasticizer (sulfonated naphthalene formaldehyde condensate). Three different types of fly ash were used. In Figure 10 the grindability results in terms of Blaine surface are shown for Portland clinker and one type of fly ash blended clinker (Sundance FA) using the superplasticizer (SP). Considerable effect of SP was determined for the normal Portland clinker and more limited, but significant, effect was achieved for the blended clinker. The mechanical properties were improved with SP due to increased fineness. However, at a given Blaine (4500 cm^2/g) the strength development did not improve with SP for blended cements. For the Portland cement at the same Blaine an interesting comparison can be made as they added SP to the mixing water and to the laboratory mill. Although the conditions were not exactly the same, i.e. the cement contents were 315 and 240 kg/m^3 when the SP was added in the mixing water and the laboratory mill respectively. Moreover, the SP dosage was 0.7% compared to 0.9% in the mill. The compressive strength results achieved were not different with a slight increase at 7 and 28 days strength in the latter case. In regard to quality improvers, this study indicates that effects found when the additive is mixed with the hydration water also can be found when the additive was included in the grinding process. However, the authors emphasise that comparison is difficult and further research should be carried out. It is emphasised that when testing quality improvers, the addition should be made in the grinding mill.
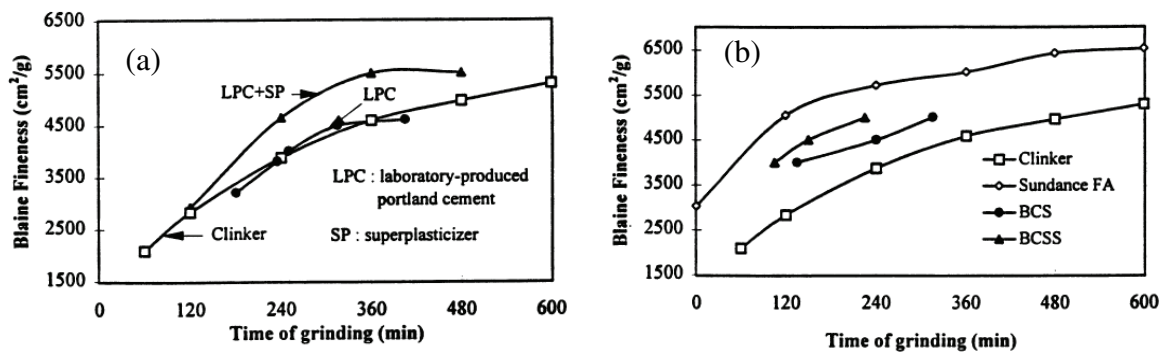
Figure 10 Blaine development as function of time. (a) Laboratory produced Portland cement with and without 0.9% superplasticizer. (b) BCS: Blended cement made with Sundance FA, BCSS: Blended cement made with Sundance FA and 0.9% superplasticizer (Bouzoubaâ et al 1998).

4.2 Slag cements

In the early study by Tachihato et al (1984) it was found a strength increase of 40% was found after 7 days for a Portland cement mortar with 70% slag and 0.5% TEA. Grinding of granulated blast furnace slag (GBS) is more energy demanding compared to grinding pure Portland clinker. In Trenkwalder and Ludwig (2001) they optimised the production of slag cements by separating the grinding of cement clinker and GBS in the Karlstadt cement works. Without any grinding aids, at least not reported, they managed to reduce the total electric energy consumption for cement grinding by 7% for all slag cements produced i.e. for the types CEM II/A-S, CEM II/B-S and CEM III/A-C. In addition, the workability and the strength development was improved. Improving the former property also reduce the use of plasticizers. In Erdogu et al (1999), grinding of cements blended with either 25% of GBS or natural pozzolan was studied in terms of intergrinding and separate grinding of the ingredients. They concluded that for producing the cement with natural pozzolan, intergrinding was less energy consuming than separate grinding for a given Blaine of 3500 cm^2/g. The interground pozzolan cements produced higher strength at all ages (1-90 days). Moreover, they also found that the intergrinding process consumed more energy than separate grinding for production of the slag cements at the given Blaine. The latter was due to coarser particles at the highest particle size range (60-90μm). These mentioned studies remind us that several factors need to be considered in order to obtain the desirable product produced at optimised conditions.

Padovani and Corcoran (2004) tested quality improvers for GBS cements. In the first part of the study, they tested the grindability and the mechanical strength of 4 different slags used in commercial production of slag cements in central Europe. Different results were obtained which also was the case when the specific slags were tested as finished slag cements (CEM III/A 32,5R) prepared in laboratory. It was also emphasised that the slags with high strength were those which contained the highest glass content. In the second part, the additives MAGA/C098, MAGA/C150 and MAPE/S500 were tested, all commercial products of Mapei. Unfortunately, the "active" ingredients were not reported and only the datasheet of the former was available. According to the safety data sheet, MAGA/C098 consisted of diethylene glycol (7-10%) and ethanediol (7-10%). Moreover, the exact additive dosage was not reported.

The quality improvers were tested on the 4 slag cements prepared in laboratory complying to CEM III/A 32,5R (50% GBS and 5% gypsum). The results are shown in Figure 11 and we note a significant effect for MAGA/C098. The improved early strength for this additive is due to the increased fineness and is therefore only considered as a grinding aid. This was also pointed out in Revuelta et al (2003). The two other additives tested, shown in Figure 11, achieved even higher strength development due to chemical interaction during hydration and are therefore considered as

quality improvers. Hydration temperatures measurements of one slag cement showed, however, that MAGA/C098 had almost identical temperature profile as MAGA/C150 (GA+).
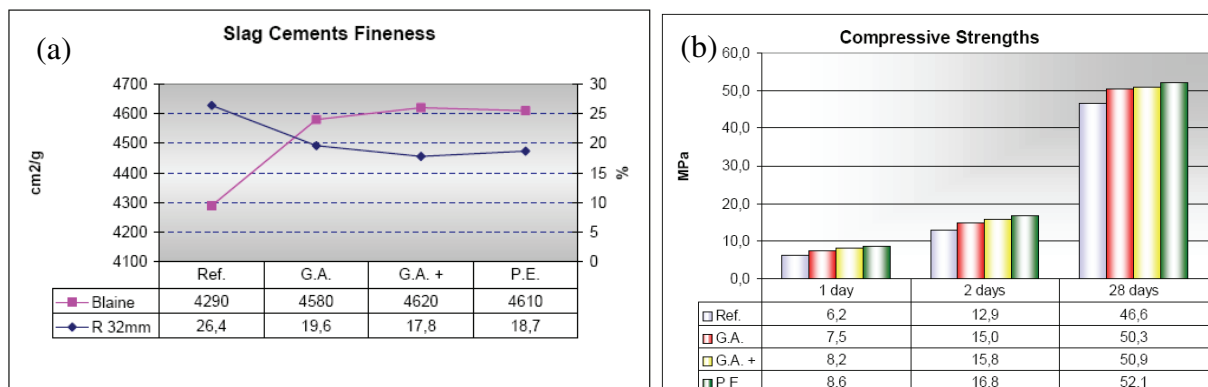

Figure 11 Fineness achieved for a given grinding time obtained (a) and compressive strength (b). Each measuring point is given as the average of a reference clinker prepared with 4 different commercial slags and with different quality improvers; Ref (without additive), GA (MAGA/C098), GA+ (MAGA/C150) and PE (MAPE/S500) (Padovani and Corcoran 2004).

Water glass (WG) has also been investigated as quality improver for GBS cements in India by Roy at al (1998). For the slag cement (50% slag and 4% gypsum) the Blaine increased from 3650 (0% WG) to around 4100 cm^2/g (1.5% WG) for the same grinding time. In terms of compressive strength 1% WG was found to be the optimum dosage. For slag substitution of 30-80% the early strength (1, 3 and 7 days) was always higher with 1% WG relative to no addition keeping in mind that the Blaine values were kept at the same level (3500-3600 cm^2/g). The authors indicated that WG activated the pozzolan reactions occurring in slag cements.

4.3 Other studies

The effect of various grinding aids on the separate grinding of limestone, quartz and Portland cement clinker were investigated by Sohoni et al (1991). In this study TEA, MEG, DEG, oleic acid (OA), sodium oleate (SO), sulphite waste liquor (SWL) and dodecylbenzene sulphonic acid (DBS) was tested. Nearly all the additives were effective as grinding aids for Portland clinker and limestone (SO, DEG and DBS not tested for limestone; OA and SO not tested for Portland clinker). Hardly any grinding effect was seen for quarts. The grinding effect of gypsum on the Portland cement clinker was also shown in this study. An addition of 4.3% (normal dosage area) showed Blaine improvement comparable to clinker ground with 0.04% TEA and no gypsum addition. Adding gypsum to the latter further increased the Blaine, but not in an additive way.

Hrazdira (1990) tested the grinding effects of TEA, Abeson-TEA (dodecylbenzenesulfonic acid-TEA), amorphous SiO_2 and Sodium Lignosulphonate (SL) in gypsum free cements. The dosages were 0.05% for the two former and 0.3% for the latter additives. In regard to grindability of the cement Abeson-TEA produced the narrowest particle size distribution. The viscosities of the corresponding pastes were decreasing in the order of TEA > Abeson-TEA > LS > $SiO_{2[am]}$. The initial set was 39 and 49 min. for pastes with TEA and Abeson-TEA respectively, and more than 100 min. for the others. The paste strength development (1-180 days) was, however, significantly higher for the Abeson-TEA paste. Again we see the accelerating effects of TEA and its derivatives at a certain dosage level (0.05%). Note that the cements used in this study were gypsum free (total SO_3 of 1.05%) and the hexagonal aluminate (C_2AH_8 and C_4AH_{19}) phases are expected to develop in stead of ettringite. In Hrazdira (1992) the properties of gypsum free

cements clinker grinded with Abeson-TEA was further studied. In regard to the compressive strength, an optimum dosage was found for a given Blaine.

5   Proposals for activities

Based on the studies discussed in this report several additives are interesting. Triisopropanolamine (TIPA) is already a well known quality improver and in combination with nitrate it gave excellent early strength development. The conventional grinding aid TEA proved to be a strong quality improver also in combination with nitrate. We suggest to further investigate these combinations. In this respect it is proposed to also combine DEA with nitrate. Some studies showed that DEA had even higher grinding effects than TEA.

The testing should emphasise fluidity and grinding for the chosen additive or combination of additives. The choice must also be based on the recommendations and conclusion in the state-of-the-art report on accelerators (Myrdal 2007). It is therefore considered important to link the research on grinding aids with potential strength enhancement properties to the R&D activities on accelerating admixtures for concrete. In any case it is recommended to test the features (grindability and hydration) of a quality improver by including the additive in the milling procedure.

An interesting activity will be to look at the overall effect of mineralisers together with quality improvers. From Engelsen (2007) it is known that certain trace elements (e.g. Cu, Cr and Zn) have considerable mineralising action during clinker burning. Opoczky and Gavel (2004) showed that the certain metals also have positive effects on the grindability. Considerable increase in specific surface (Blaine) was achieved for Zn, Cr and Ti added as 0.1% oxides as shown in Figure 12.

If for example a clinker is prepared with the use of the mineraliser(s) containing Zn, Cr, Cu and Ti, an improved grindability should be the results. This mineralised clinker can be further optimised by applying the appropriate quality improver depending on the desirable properties of the final cement. The rheological properties of the corresponding cement paste should also be measured in addition to the final strength in the paste, mortar and concrete form. The documented improvements from the mineralising, grinding and final concrete stage should be calculated in order to visualize the total effect.
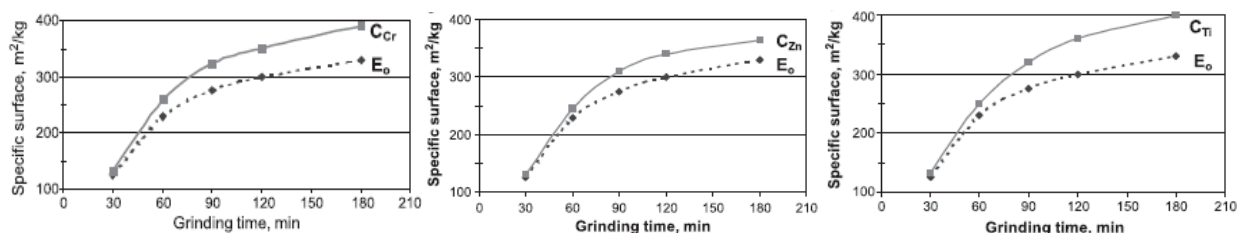

Figure 12 Blaine as function of grinding time for Portland clinker mineralised with Cr, Zn and Ti compared to a Portland clinker without mineral addition during burning (E_0). The content of mineralisers added to the raw materials was 0.1% as oxides (Opoczky and Gavel 2004).

The proposed activities are also valid for blended cements (slag, fly ash and limestone). In for example Tsivilis et al (1999), they optimised the clinker and limestone quality together with the optimum limestone content. They found that 10% limestone content in the cement gave comparable strength values as for the pure cement provided optimised conditions without the use of organic grinding aids. The potential for further substitution, maintaining the sufficient properties of the cement by applying a quality improver system, are proposed to be carried out. Most grinding aids/quality improvers also are effective for limestone.

6   Conclusion

It has been shown that the overall cement properties are interconnected and in many cases there is still potential for further production improvement by only optimising the different stages (e.g. separate grinding, mill operation etc.). This, in turn, indicates the potential for quality improvers to further optimise the production and improve the quality of the cement. It was found that the combination of certain alkanolamines (TEA and TIPA) with calcium nitrate gave considerable enhanced early strength. Probably the same effect will be found by combining nitrate with the highly efficient grinding aid DEA. If quality improvers are used for clinkers that is mineralised with relatively small amounts of for instance Zn, Ti or Cr, significant improvements can be achieved. The total improvement as decrease in clinkering temperature, increased Blaine and increased early strength can be measured and expressed in terms of decreased energy used pr. cubic metre of produced concrete.

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