



CEMENT ADDITIVES COMPREHENSIVE UNDER- STANDING OF GRINDING AIDS

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BUILDING TRUST





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Cement is vital for today's construction industry. The cost optimized production of quality cement which meets customer demands and standards as well as sustainability issues challenges every cement plant individually. Sika offers innovative cement additive concepts combined with a specialized technical support, targeting improved production rates, enhanced strength development and adjusted workability. The reduced utilization of energy and clinker contributes to the profitability of your business.

Grinding aids increase the productivity and cost-effectiveness of cement production.

A comprehensive experimental test program and a variety of computer simulations were used to determine the physical and chemical mechanisms of action.

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Comprehensive understanding of grinding aids

1 Introduction

Grinding aids have been used successfully for decades in cement production and many other areas, such as ceramics, pigments etc. The main effect is to reduce energy consumption and increase the grinding efficiency. Additional features can be improved – e.g. powder flowability and strength development of binders. There is surprisingly little verified knowledge about the way in which the substances contained in grinding aids act effectively. There are correspondingly many hypotheses in the scientific literature as well as in industrial practice. Starting from basic physical and chemical background, the laboratory screening process covering several hundred compounds and mixtures as well as extensive computer simulations (molecular modelling) [1, 2] provide a better understanding of grinding aids. This makes it possible to design new, more efficient, customized additives.

Experimental studies on the action of grinding aids during clinker grinding have been done to cover all types of organic, and some inorganic com-

pounds as well as various mixes and also at different dosage levels. The influence of the type, number and combination of functional groups as well as molecular weights of compounds over a wide range was investigated systematically. A detailed description of all the experimental and computational test results would go beyond the constraints of a single paper. This article will concentrate on the underlying phenomena and the new findings relating to the mode of action of grinding aids.

2 Basic physical and chemical principles

The first and second laws of thermodynamics suggest that everything tends towards a state with the lowest possible energy and the greatest possible disorder. A free-standing powder heap tends to become stable and spread out, i.e. to achieve the lowest possible energy and degree of order attainable under the given conditions. Energy reduction or higher randomness by itself can be the driving force for physical and chemical process, but combinations of both terms are more common: the free



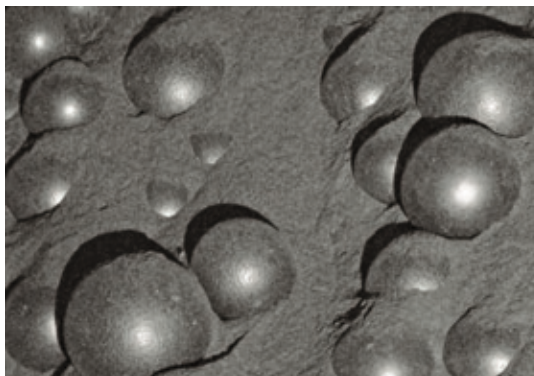
enthalpy or Gibbs energy tends towards the lowest possible value. Entropic contribution (the attempt to achieve disorder) is often substantially smaller with respect to the total energy contribution; therefore it will not be emphasized separately in this paper.

The milling media (balls) in **Figure 1**, which are coated by ground particles, represent a state of minimum energy of a system without grinding aids. Likewise the clean milling media in **Figure 2** represent a state of minimum energy of a system with grinding aids. Presence of grinding aid leads to a different minimum energy state [3].

2.1 Irreversible and reversible processes

As a rule of thermodynamics, chemical reactions only take place by themselves if this involves the release of energy (usually heat). They cannot therefore be reversed without external energy. This is also the case in the reaction of cement with water. Water from moist raw materials and from the injection of cooling water is usually present during the industrial grinding of cement, even without the use of grinding aids. Therefore it can be assumed that the surfaces of the majority of commercial clinkers are predominantly or even completely hydroxylated. This is also important because it assists the grinding, in other words water is a weak grinding aid. The chemical reaction of oxide ions (O^{2-}) with water (H_2O) to form hydroxide ions (OH^-) takes place irreversibly (**Fig. 3**).

Decomposition of organic compounds also takes place irreversibly. Compounds with boiling points of 50–400 °C, i.e. significantly below and above the grinding temperature, were tested (**Table 1**). Few organic compounds are stable above 200 °C temperature. They decompose, usually forming volatile secondary compounds. However, in the presence of air, in thin molecular layers and on inorganic materials, they can decompose at substantially lower temperature (e.g. 100 °C) within hours or days. Various internal investigations have shown that the usual grinding aids and also concrete additives are well able to withstand normal grinding conditions. Appreciable decomposition is, however, possible if the cement is stored for weeks



1 (l) The milling media (balls) coated themselves with cement if no grinding aid is used

2 (r) Grinding aids keep the milling media (balls) clean and increase the productivity

at above 50 °C temperature. This can occur if silos are filled with hot cement.

Mostly adsorption of grinding aids is reversible. As the binding forces are small at the usual mill operating temperatures (80–120 °C), adsorbed molecules can desorb from the clinker surface. The boiling points of liquids correlate with the intermolecular interactions (“strength of the adsorption of molecules on one another”). If the liquids are chemically similar, the strengths of adsorption on clinker surfaces correlate with the boiling points.

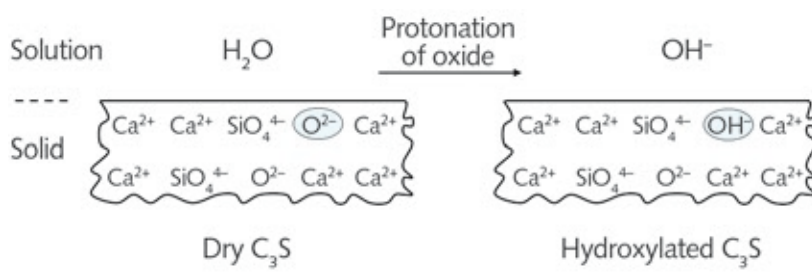
2.2 Dispersion mechanisms during grinding

Dispersion of organic molecules during grinding can occur via two basic mechanisms: gas phase transfer and surface contact transfer. This can easily be proved in simple grinding experiments in a closed batch mill. For instance various alcohols with boiling points below grinding temperature improve grinding efficiency significantly (**Table 2**). They are adsorbed so weakly due to the high volatility that they can still be smelt even on cold cement. It must therefore be assumed that they are dispersed, either partially or completely, via the gas phase.

On the other hand, polymers like polycarboxylate ethers (PCEs) also improve grinding efficiency significantly. PCEs can only evaporate with irreversible decomposition. During grinding, however, the molecules remain substantially intact [4, 5] – they retain their action as concrete plasticizers – so the evaporation mechanism can be excluded. Dispersion must be considered via surface contact transfer.

At this point, it should be pointed out that a plasticizing effect only occurred in trials with

3 Reaction on the clinker surface (tricalcium silicate, C_3S): water molecules (H_2O) react with top surface layer oxide ions (O^{2-}) to form hydroxide ions (OH^-) [2]



Tab. 1 Boiling point range of chemical additives used as grinding aids for clinker

Range of b.p. (boiling point) [°C]		Example		b.p. [°C]	Molecular formula	Molecular weight [g/mol]
< 100	Very low	Ethanol*		78	C ₂ H ₆ O	46
80–120	Grinding temperature					
100–200	Low	Propylene glycol	PG	188	C ₃ H ₈ O ₂	76
200–300	Medium	Diethylene glycol	DEG	245	C ₄ H ₁₀ O ₃	106
300 <	High	Triethanolamine	TEA	335**	C ₆ H ₁₅ NO ₃	149
150 <	Decomposition***	Polycarboxylate ethers	PCEs		C _{2x} H _{4x} O _x	25 000–50 000

* Ethanol and other very low boiling solvents are not used commercially.

** Extrapolated value, according to other references 360 °C, decomposition ≥ 190 °C.

*** The decomposition velocity depends strongly on the compound and the conditions (temperature, oxygen availability, layer thickness, substrate). It starts for most organic compounds between 100–200 °C.

particularly high dosages of grinding aids. With commercial grinding aids containing PCEs, such as SikaGrind®-820, -840 and -870, the dosages typically used in cement production are not sufficiently high for a measurable effect.

The majority of commercial grinding aids have boiling points and decomposition temperatures that are significantly above the grinding temperature (e.g. PG, DEG, TEA, see Table 1). Their vapour pressures are low but sufficiently high that they are presumably dispersed via both mechanisms, gas phase transfer as well as surface contact transfer.

Adsorbed liquids on the clinker surface are in equilibrium with their gas phases. The vapour pressure depends on the boiling point, temperature and also on the solid, which is covered. In relative terms, propylene glycol (b.p. 188 °C) is distributed most readily, diethylene glycol (b.p. 245 °C) moderately and triethanolamine (b.p. 335 °C) least via the gas phase. The effective ratio of gas phase transfer to surface contact transfer is difficult to measure and not known. It depends not only on the grinding aid but also on the mill and the grinding parameters. Probably surface contact transfer is usually more important than gas phase transfer.

2.3 Surface energy and surface tension

Atoms, molecules and ions always interact with one another. Within homogeneous solids and liquids, the internal forces of opposite direction with equal magnitude cancel each other out. The formal energy is zero in the bulk. But at the interface, there is a resultant force directed inwards due to

cohesion (air-liquid interface shown in Figure 4, [6]). The energy of the top layer of surface atoms is above zero due to less binding sites. Solid materials possess surface energy and liquids also have surface tension. Nominally these two are identical due to same value and dimension. Surface tension is a common phenomenon. Therefore, small droplets are round and water striders as well as other small water-shedding objects do not become wet but “float” on the top of water (Fig. 5, [7]).

Work must be performed against the surface tension for the creation of additional surface area. The more finely a liquid is sprayed, the more pressure is needed at the nozzle. In the same way that a large number of fine liquid droplets have greater energy than a few large ones, dust also has greater energy than coarse powder. The major part of the energy consumed during the grinding process of cement is converted into heat, but a small fraction (≤ 0.5 %) is retained in the cement as surface energy (Table 3).

The behaviour of liquids on solid surfaces can differ widely. The droplet shape (Fig. 6) always corresponds to the lowest energy level of the system that can be reached. This depends on three factors: the surface energy (surface tension) of the liquid, the surface energy of the solid and the interfacial energy (the interactions) between the two compounds.

Liquids with high surface tension do not wet substance with low surface energy. Mercury forms beads on non-metallic materials. On the other hand, liquids with low surface tension spread out on substances with high surface energy. Penetrating oil penetrates into the finest cracks and eventually covers the entire work piece. In the same way, grinding aids distribute themselves over the entire surface of the clinker. However, on materials with low surface energy, such as plastics, they form shallow droplets, i.e. the surface is only partially wetted.

2.4 Reduction in the surface energy of clinker

The high surface energy of dry clinker is reduced to a certain level by hydroxylation. Further decrease is only possible through organic grinding aids (e.g. SikaGrind®). Organic additives do also work in pure form, but for technical and economical optimiza-

Tab. 2 Results of grinding experiments with clinker and solvents in a laboratory mill (sieve residue at 32 µm, fineness according to Blaine)

Water + ...	Boiling point [°C]	Res. 32 µm [%]	Blaine [cm ² /g]
Reference (pure clinker)		35.3	2325
Water	100	31.3	2710
Hexane	69	31.8	2645
Paraffin oil	170	30.7	2740
Mixture of aromatics	180	29.9	2740
Rape seed oil	360*	29.5	2785
Dioxan	101	29.8	2810
Acetone	56	29.5	2790
Ethyl acetate	77	28.3	2870
Isopropanol	82	27.0	2983
Diethylene glycol	245	27.3	2943

* Rape seed oil decomposes above 200 °C.

tions they are usually mixed with water. In both cases they act primarily by reducing the surface energy.

This process consists of three parts (shown in equation 1). In the presence of water and grinding aids, clinker attempts to lower its surface energy ($E_{s,c}$: surface energy of clinker). The surface of the grinding aid must be increased on the basis of energy gained through the reduction of the surface energy of clinker, i.e. the surface energy of the grinding aid ($E_{s,g}$) must be overcome. And the clinker/grinding aid interfacial energy ($E_{1c/g}$) must be negative or, at most, weakly positive.

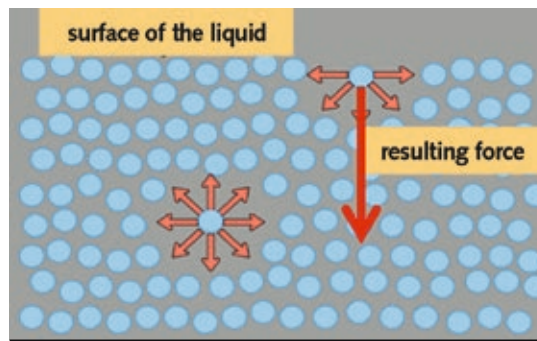
$$-E_{s,c} + E_{s,g} + E_{1c/g} = E_{s,CG} \quad (1)$$

If the surface energy of the clinker covered with grinding aid ($E_{s,CG}$) is negative, i.e. energy is released during the coverage, then the grinding aid spreads out even without any mechanical assistance. The contact angle of grinding aid on clinker is 0° (Fig. 6).

This means that grinding aids must not only reduce the surface energy of the clinker ($E_{s,c}$) but also adsorb sufficiently strongly on it (i.e. have a low interfacial energy $E_{1c/g}$). These two properties can only be partially combined with one another. Therefore it does not mean that the grinding aids with the lowest surface energy ($E_{s,g}$) perform best. Comprehensive experiments show that moderate values, i.e. the range from 30–50 mJ/m^2 , are the most suitable (Table 4).

2.5 Interactions between grinding aids and clinker surface

Nonpolar solvents, fuels and oils have low surface tensions and energies. They contain no or only weakly polar functional groups in the molecules and interact therefore only weakly with polar compounds. They are not miscible with polar water but do spread out rapidly on polar clinker surfaces. Because of the poor interaction with clinker they adsorb too weakly to form stable separating layers between particles. The clinker particles form agglomerates that are held together by strong polar interactions. Nonpolar liquids are therefore not suitable as grinding aids in spite of their low surface tensions (Table 2 and 4).



4 Diagram of different directional forces on molecules. Surface tension is the effect of one-sided forces on the surface [6]



5 Water striders are carried by the surface tension [7]

On the other hand, commercial grinding aids consist of nonpolar hydrocarbon skeletons as well as polar functional groups. The latter interact readily with clinker. The majority of active compounds are alcohols, i.e. they have polar organic hydroxide groups (R-OH). Triethanolamine (TEA) is a tri-alcohol and diethylene glycol (DEG) is a di-alcohol. Very good grinding performance is also achieved using some mono-alcohols, such as isopropanol. However, these are not used in commercial cement production because of their low boiling points ($< 100^\circ\text{C}$) (Table 2).

With the aid of computer simulations it has been possible to demonstrate that the molecules always turn their polar functional groups towards the clinker surface. Figure 7 shows two tri-isopropanolamine molecules on dry tricalcium silicate (C_3S , alite). The polar alcohol groups (-OH) partially offset the polarity of the clinker and the nonpolar hydrocarbon groups (R = alkyl, e.g. CH_3 or alkylene, e.g. $-\text{CH}_2-\text{CH}_2-$) shield it. The interactions, and therefore the attractive forces between the cement

	Energy per g cement [mJ/g]*	Energy per m^2 cement [mJ/m ²]*	Percent of grinding energy [%]
Grinding energy of cement (typical value**): 40 kWh/t	144000	240000	100.00
Surface energy of dry C_3S	800	1340	0.56
Agglomeration energy of dry C_3S	270	450	0.19
Agglomeration energy of hyd. C_3S	140	230	0.10
Agglomeration energy of hyd. C_3S with glycerine	70	120	0.05
Agglomeration energy of hyd. C_3S with MDIPA	30	50	0.02

* Typical surface of cement (BET value): $0.6 \text{ m}^2/\text{g}$. This corresponds to about $0.3 \text{ m}^2/\text{g}$ ($3000 \text{ cm}^2/\text{g}$) according to Blaine.

** The better the used grinding aid, the lower the energy consumption. The indicated rough value primarily visualizes the huge difference to the small surface and agglomeration energies.

*** Hydroxylated C_3S surface is denoted by hyd. C_3S .

Tab. 3 Grinding, surface and agglomeration energies of cement without and with grinding aids

Drop shape	Wetting	Contact angle	Interfacial energy	Example
	Non-wetting	~ 180 °	>>>> 0	Mercury on nonmetals
	Partial non-wetting	< 180 °	>>> 0	Water on Teflon
	Partial wetting	90 °	>> 0	
	Complete wetting	> 0 °	> 0	Grinding aid on plastics
	Complete wetting	~ 0 °	= 0	Grinding aid on clinker
	Spreading	0 °	< 0	Grinding aid on clinker

6 The drop shape depends on the interaction between liquid and solid surface

particles, fall with decreasing surface polarity. This minimizes the tendency to form agglomerates and maximizes the grinding output.

Comprehensive laboratory trials have not only confirmed suitability of well-known glycols and alkanolamines additives, but also provided consistent correlations between molecular structure and performance. The focus was on organic compounds with a well-balanced ratio of polar to nonpolar parts. Inorganic compounds assist the grinding only to a limited extent, but they can modify various other cement properties such as setting, initial and final strength in desirable way.

3 Surfaces without and with grinding aids

Figures 8-13 show various possible ways how new surfaces are formed and subsequent chemical and physical processes during grinding. Calcium oxide (CaO) is used in the diagrams for simplification instead of a clinker phase. Exposed surface ions are denoted with full charge (Ca²⁺, O²⁻) but the overall crystal is neutral, so no charges are marked in the intact crystal lattice. The lighter the colour of the squares in the diagrams the lower is the polarity. The thinner the green arrows, the weaker are the interactions between cleaved surfaces. A cleavage with significant charge separation (Fig. 8) is only possible in the complete absence of water and even then is very unlikely. Freshly cleaved polar surfaces relax immediately. Surface atoms repositi-

Tab. 4 Boiling point, surface energy (surface tension) and polarity of grinding aids (glycerine, DEG, PG) to show the deviation from other liquids

Liquid	Boiling points [°C]	Surface energy/ Surface tension [mJ/m ² or mN/m]	Polarity (Interaction)
Mercury	357	476	(Metallic)
Water	100	71	High
Water with surfactants	100	30	(Polar)
Glycerine	290	63	Medium
Ethylene glycol	196	48	
Diethylene glycol (DEG)	245	45	
Propylene glycol (PG)	188	36	
Ethanol	78	22	
Rape seed oil	360 (>200 dec.)	32	Low (Non-polar)
Diesel fuel*	200–300	28	
Hexane	69	18	
Liquid nitrogen	-196	9	Very low

* Diesel fuel consists of paraffin oil and aromatics (see Tab. 2).

tion themselves in accordance with minimum energy and optimized charge equilibration [2]. In the usual presence of water (or hydroxide ions) this takes place particularly rapidly as the hydrogen ion transfer (movement of protons), with half-lives in the pico-second range, is one of the fastest known chemical processes.

The propagation velocity of fractures in clinker is extremely high. Simulation results show that it reaches 11,500 km/h along the cleavage faces of alite mineral, which is almost ten times the speed of sound in air [8]. The spreading velocities (propagation) of liquids are substantially lower [8, 9]. Wetting velocities of 1 μm/s to 10 m/s (36 km/h), depending on the conditions (Fig. 6), are mentioned in [10]. Because spreading velocities are much slower than crack propagation velocities and surface relaxation and charge balancing happens quickly, it must be assumed that grinding aids are always, or to a very great extent, adsorbed on neutral surfaces (Fig. 9 and 10). This statement has not been directly proved for clinker but it is supported for all investigated ionic compounds. Organic acids and salts and quaternary ammonium compounds, that can counterbalance charges, perform worse than the corresponding alcohols. This contradicts the often postulated action of grinding aids by charge balancing.

Water, glycerine, diethylene glycol (DEG) and diisopropanolamine (DIPA) assist grinding in ascending order (Figs. 10-13). Water dissociates into positive hydrogen ions and negative hydroxide ions (H₂O → H⁺ + OH⁻, hydroxylation), which position themselves so that the surface polarity of the clinker is reduced. The alcohol groups (R-OH) of the grinding aids reduce the surface polarity further. The hydrocarbon parts (R, consisting of CH, CH₂ and CH₃) shield the polarity. The hydrocarbon parts of glycerine are small (shown in Fig. 11), of diethylene glycol moderate (Fig. 12) and of diisopropanolamine large (Fig. 13). The larger the hydrocarbon parts the smaller is the surface energy of covered cement particles and the better is the grinding effect.

Figures 9-13 show models that do not only correlate well with the practical experiments but also correspond to the molecular configurations that were found with molecular simulations (section 4). The forces of attraction between the ground cement particles as well as between cement particles and milling media (steel balls etc.) that, without the use of grinding aids (Figs. 9-10) lead to agglomeration and adhesion to the grinding media (Fig. 1) depend on the surface energy.

4 Molecular modelling (computer simulation)

Macroscopic properties, like temperature or particle fineness, are usually the consequence of various mechanical, physical and chemical processes and

are relatively easy to measure. On the other hand, it is often only molecular modelling that can provide an insight into specific values or trends such as adsorption energy, agglomeration energy and mechanism of molecular interactions on the surface. One familiar method is the Monte Carlo simulation based on the random principle. However, “molecular dynamics simulation”, which is more suitable for this purpose, was applied as part of a doctoral thesis financed by Sika Technology AG at University of Akron (USA) [1] and in cooperation with the Swiss Federal Institute of Technology in Zürich [2].

In the NVT ensemble molecular dynamics, the number of particles (N), the volume (V) and the temperature (T) remain constant throughout the simulation. The most important part of any atomistic modelling work is to use validated force field parameters, which should be consistent with physical-chemical properties for each compound in comparison to experimental measurements. We present simulation results of carefully validated models of cement minerals [2, 11].

Figure 13 shows the adsorption of diisopropanolamine (DIPA) schematically. The spatially correct arrangement of the similar triisopropanolamine (TIPA) on hydroxylated tricalcium silicate (C_3S , alite) is shown in **Figure 14**. Hydrogen atoms (H) from the alcohol groups of the TIPA form hydrogen bonds with oxygen atoms (O) of silicate and hydroxide ions. The calculated average bond lengths are shown in **Figure 14**. Oxygen atoms (O) of the alcohol groups of the TIPA coordinate with calcium ions (Ca) of the C_3S . Similar interactions and arrangements also occur with other clinker phases (C_2S , C_3A) and grinding aids [11, 12].

4.1 Adsorption energy of grinding aids on C_3S surface

The adsorption energies of various organic compounds on clinker surfaces were determined in order to clarify whether the grinding effect is dependent on the strength of adsorption. Instead of the route via the surface and interfacial energies (equation 1) of C_3S and grinding aid, there was direct simulation of the quantity of energy that is released during the adsorption of gaseous molecules on C_3S .

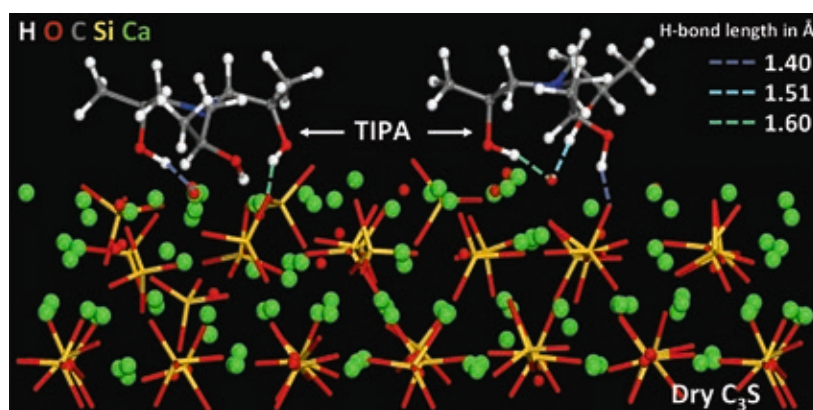
The sequence changes slightly depending on the conditions (**Fig. 15**, data in kcal/g of adsorbed substance). At 110 °C (383 K; typical grinding temperature) and with hydroxylated surface, TEA adheres the most weakly and glycerine the most strongly.

Adsorption energy on C_3S :

TEA < TIPA < MDIPA < glycerine

Grinding performance with clinker:

glycerine < TEA < TIPA < MDIPA



The grinding trials with clinker resulted in a different sequence of Blaine values and sieve residues (32 μm). Glycerine had the poorest effect and methyl diisopropanolamine (MDIPA) had the best. There is no correlation between adsorption energy and grinding performance. The grinding performance depends on other properties.

4.2 Agglomeration energy of C_3S and C_3A

Agglomeration energy can be understood as follows: the release of stored energy when two parallel relaxed cleaved surfaces come together or equally the required energy to separate them. Dry and hydroxylated tricalcium silicate surfaces (“ C_3S ”, “HC”) without and with various grinding aids were simulated in analogy with **Figures 9-13**. **Figures 16 and 17** show a monomolecular layer of glycerine in the confined and separated states between cleaved C_3S surfaces. The difference between the two calculated energy levels is the agglomeration energy. The distribution of the glycerine molecules in the separated state does not play a crucial role [2]. An example with equal distribution is shown in **Figure 18**.

The agglomeration energy (**Fig. 19**, data in mJ/m^2 of surface) correlates at 90 °C inversely with the grinding performance of clinker in the laboratory trials [2].

Agglomeration energy:

$C_3S > HC > HC\text{-glycerine} > HC\text{-TEA} > HC\text{-TIPA} > HC\text{-MDIPA}$

Grinding performance:

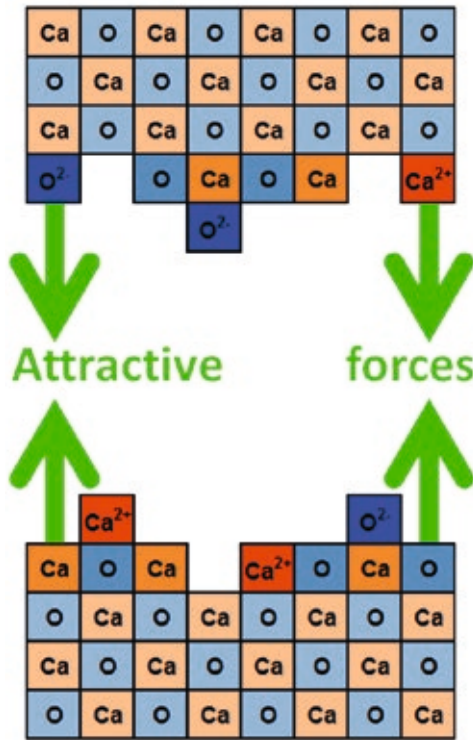
Clinker < HC < HC-glycerine < HC-TEA < HC-TIPA < HC-MDIPA

Not all clinker phases behave the same. In case of tricalcium aluminate (C_3A), the agglomeration energies and their ranking are partially quite different as is shown in **Figure 20** (data in mJ/m^2 of surface) [11].

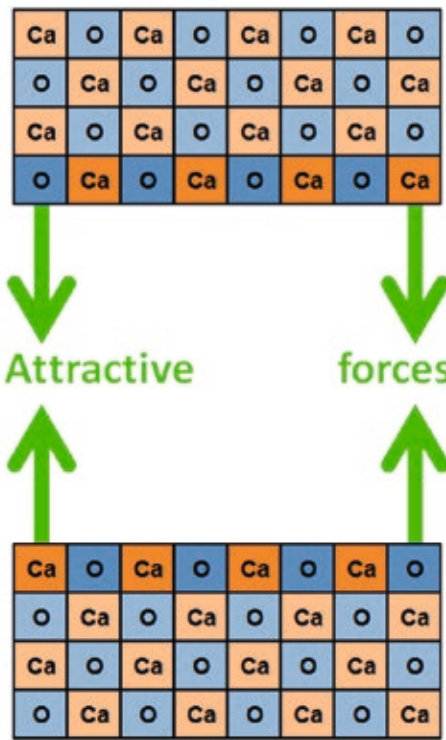
Agglomeration energy:

$C_3A > HC > HC\text{-TIPA} > HC\text{-glycerine} > HC\text{-TEA} > HC\text{-MDIPA}$

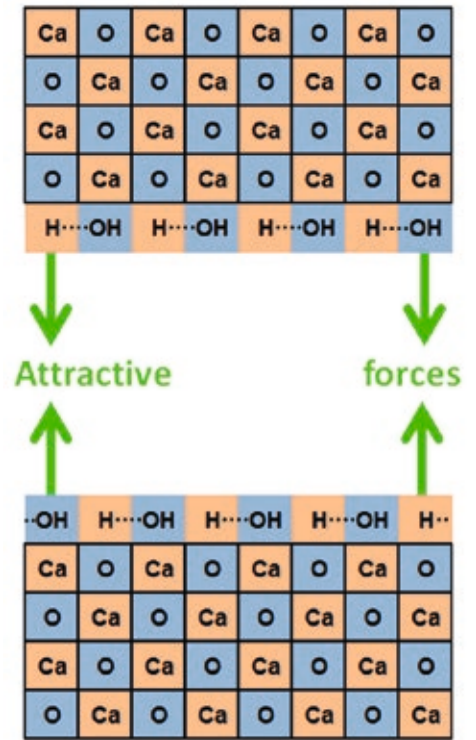
7 Interactions of two TIPA molecules (triisopropanolamine) on dry C_3S surface (tricalcium silicate, alite) [1]



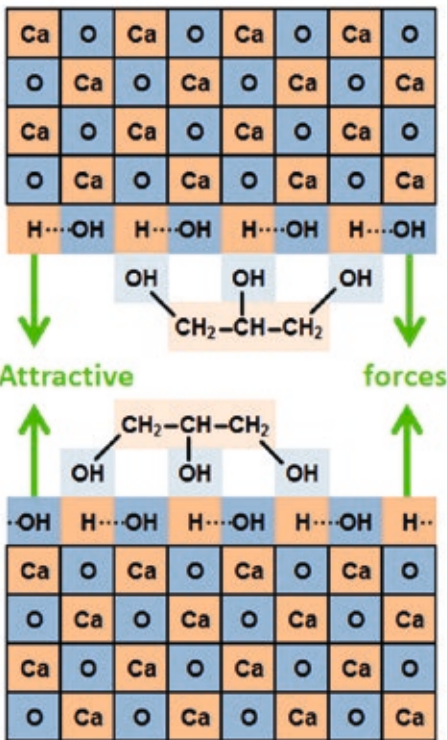
8 Energetically unfavorable, improbable fracture with partly separated charges



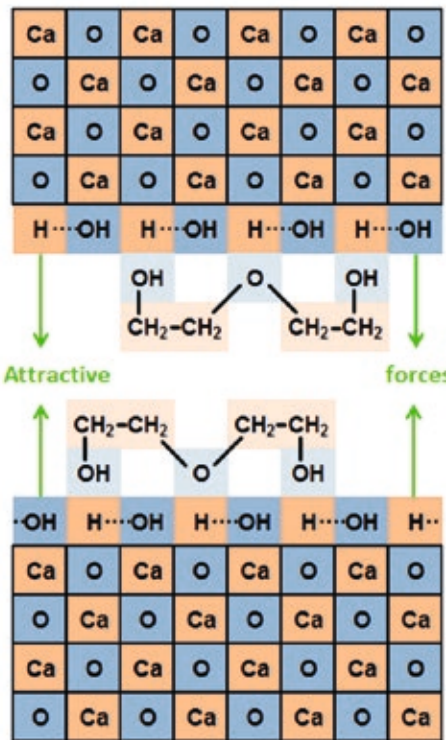
9 Fracture without water and grinding aid. The formed surfaces attract each other very strongly



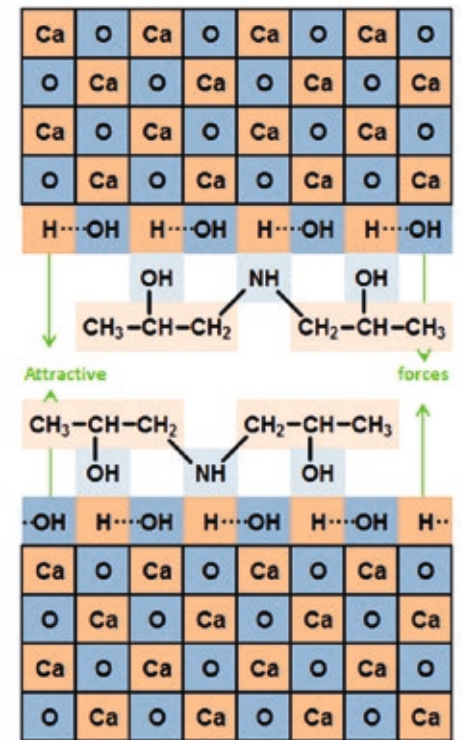
10 Fracture only with water. The formed surfaces attract each other strongly



11 Fracture with water and glycerine. The formed surfaces attract each other moderately



12 Fracture with water and diethylene glycol (DEG). The formed surfaces attract each other weakly



13 Fracture with water and diisopropanolamine (DIPA). The formed surfaces attract each other very weakly

C₃A surfaces covered with TIPA have higher agglomeration energy than C₃S surfaces covered with TIPA, while the opposite behaviour is obtained with all other organic molecules. And, even more important, the agglomeration energies of dry and

hydroxylated C₃A are almost double those of the corresponding values for C₃S. The beneficial effect of grinding aids is therefore substantially more marked with C₃A than with C₃S. This means that grinding aids can equalize to some extent the dif-

ferent grindabilities of the clinker phases and thus also of clinkers with different compositions.

The fundamentally different grindabilities of the different clinker phases are pointed out in [13] and [14]. According to [13] C_3S is the easiest to grind, C_3A is intermediate and C_2S and C_4AF are the hardest. The chemical composition and microstructure (e.g. porosity) also have an effect [14]. The computer simulations show that the effectiveness of grinding aids depends on the mineralogy, i.e. the percentages of the different phases. This is one of the reasons why, depending on the cement, grinding aids do not always have the same effect.

Grinding aids reduce the agglomeration energy in all cases. This leads to the central proposition of this article. The simulations establish the correctness of the hypotheses voiced decades ago that the grinding performance in the fineness range relevant for cement is directly dependant on the agglomeration formation [15, 16], i.e. the strength of the attractive forces between the particles or the agglomeration energy.

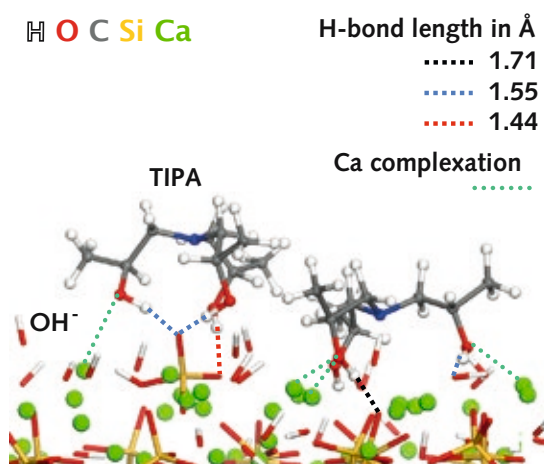
4.3 Molecular layer thickness

The effect of grinding aids (e.g. SikaGrind®) depends on the dosage level. An upper effectiveness limit was established with molecular modelling. This limit is reached when a monolayer of organic molecules lies between the clinker surfaces [2, 11]. More layers do not produce any substantial improvement but also no deterioration [2, 11]. For glycerine, for example, the distance between the highly polar C_3S planes caused by the mono-layer is 4 Å (Fig. 16). The agglomeration energy falls to half the value when compared with the hydroxylated C_3S surfaces. With more efficient grinding aids, such as MDIPA, it can be reduced still further down to a fifth of the value (Table 3, Fig. 19).

For an effective surface area of 0.6 m²/g (6000 cm²/g BET ~ 3000 cm²/g Blaine) a monolayer between the particles corresponds to a dosage of about 0.015% by weight of glycerine. The free particle surface area is only 50% covered (Table 5). Double the quantity (0.03%) is needed for complete coverage of the free surface area, which leads to a double layer for touching particles. Required dosage of organic compound is proportional to the cement fineness (Table 5). The theoretical results are compared with the experimental ones and discussed in the following section.

5 Effects of grinding aid's dosage level

Without exception, the laboratory trials show that the grinding performance in the lower dosage range of grinding aids increases with further addition of grinding aid. In the upper range it flattens out [15] and at very high levels it even falls below the level without additives [9]. According to the literature the most favourable addition level generally lies, de-

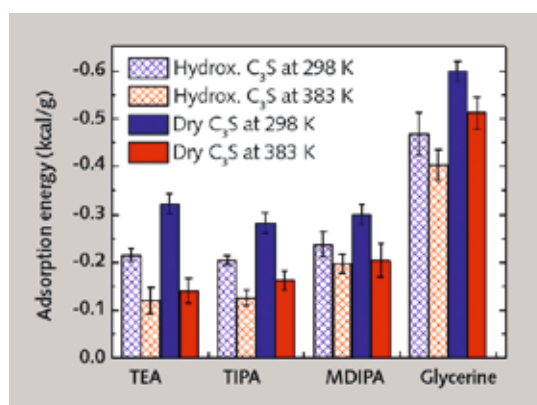


14 Two triisopropanolamine (TIPA) molecules on hydroxylated (OH⁻) tricalcium silicate (C_3S) surface. For simplification, only top layer of C_3S surface is shown

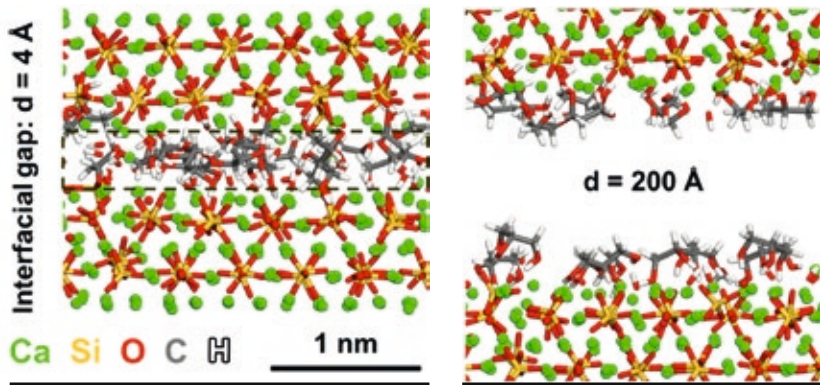
pending on the chemicals, at 0.01 to 0.1% by weight of organic compound [9]. This corresponds approximately to monomolecular coverage of the solid surface [9, 13, 17]. “The deterioration in the comminution result at excessive dosage level is attributed to the multimolecular layer on the solid surfaces. This can lead to the formation of capillary forces that favour agglomeration. The influence of the abrasive comminution component can be reduced by the lubricating effect and the powder flowability is so strongly increased that coarse particles are also discharged with the fine material” [9].

Plant trials by Sika show that dosage levels above the optimum amount can reduce the residence time of the cement in the mill in such a way that the material is inadequately ground. Optimum dosage levels and excessive dosages depend on the chemical structure of the added compounds and the local cementitious materials (clinker and supplementary cementitious materials) as well as on the fineness and the mill system (type and condition).

There are various reasons for the fact that the maximum effect calculated with molecular modelling is already achieved at the very low dosage level of 0.015% organic compound (Table 5). The simulations were carried out on smooth C_3S planes, but crushed clinker has unevenness, indentations and fine cracks in which organic molecules can accumulate. These are then absent elsewhere, espe-



15 Adsorption energies of triethanolamine, triisopropanolamine, methyl-diisopropanolamine and glycerine on dry and hydroxylated C_3S (tricalcium silicate) at 25 °C and 110 °C [2]



16 (l) Two C_3S surfaces with an intermediate monolayer of glycerine molecules [2]

17 (r) Two C_3S surfaces with an intermediate monolayer of glycerine molecules in separated state; both surfaces are half covered [2]

cially at exposed points. In practice, it is therefore necessary to increase the amount added in order to cover at least half the clinker surface. This is the only way to ensure that there is always a monolayer of organic molecules between touching particles (Figs. 16-18).

The speed of dispersion can also play a part. The higher the addition level of the grinding aid the more rapidly are newly formed clinker surfaces covered, the fewer or weaker agglomerates form and the finer or more productive is the grinding.

Simulations, trials and literature agree in suggesting that the technically maximum effect is reached when the clinker particles are separated from one another by at least one layer of organic molecules during the production. The quantity necessary for this depends on the required cement fineness or, more accurately, on the surface area to be covered (Table 5). On the other hand, the optimum addition level from the aspect of cost-effectiveness is obtained from the specific increase in production and the local conditions, such as energy, product and transport costs.

6 PCEs as grinding aids

Polycarboxylate ethers (PCEs) have been used with great success for a long time as concrete additives, e.g. in Sika® ViscoCrete® superplasticizers. However, their unique properties as cement additives were only recognized in recent years. In 2009, for example, Schrabback [18] showed how, for the same dosage level, an increase in production of 9 % could be achieved with a conventional grinding aid product but an increase of 16 % was achieved with one containing PCE.

On the one hand, PCEs work in a similar way to the low-molecular weight compounds. They partially compensate the polarity of the clinker surface through the coordination of their polar groups and they reduce it further through the shielding effect of their nonpolar alkylene groups. Though, in contrast to traditional grinding aids, PCEs contain no chemical groups of moderate polarity, in particular no alcohol groups, but only weakly polar ether groups and strongly polar acid groups or charged carboxylate groups.

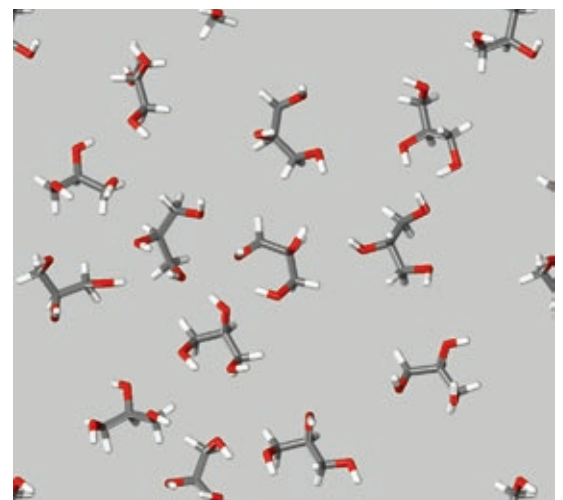
18 Distribution of glycerine molecules on approximately half covered clinker surface (top view)

The screening process, which covered several hundred compounds and mixtures, shows clearly that ionic compounds, such as pure acids, are not suitable as grinding aids. However, they are to be found in many commercial products as supplements, mainly to neutralize alkaline components. Whether they also have an appreciable effect on the grinding result and the manageability of the cement has not been finally clarified. However, the few acid groups of the PCEs, given their high molecular weights, do not explain the outstanding effect of grinding aids containing PCEs (e.g. Sika-Grind®-820, -840, -870).

Trials with other large and branched molecules, with and without charges, and computer simulations suggest that the good performance is a consequence of steric effects. But these are of a different type than those that PCEs deploy as concrete plasticizers. In the latter case the polyether side chains project far into the aqueous medium and prevent so the cement particles from coming too close. In the former case, during dry grinding both, the main chains containing carboxylate groups and the polyether side chains adsorb on the clinker surface [12, 19] (Fig. 21). However, the branching prevents flat adsorption of the entire PCE molecule. For steric reasons the distance between two clinker surfaces is 9 Å [12] (Fig. 22), i.e. twice as large as with glycerine (Fig. 16).

In contrast, completely flat adsorption is possible with linear molecules [12]. Figure 23 shows a polyethylene oxide chain with the same molecular weight as the polycarboxylate ethers in Figures 21-22. Because of limited computer capacity, polymers were just simulated with 1700 g/mol. Commercial PCEs for plasticizing concrete have typically 25 000-50 000 g/mol.

A specific steric effect occurs if branching makes flat adsorption impossible or if very long polymer chains overlap, i.e. with bulky or very large molecules.



6.1 Specific behaviour

All the trials confirm that PCEs alone do not work as well as good low-molecular weight grinding aids do [4]. This is in agreement with the computer simulations that organic intermediate layers of, for example, 4 Å are sufficient for good performance. If the same dosage level is used for PCEs then alongside areas with a fairly thick covering uncovered clinker surface occur. Additionally it is also likely that large polymers disperse more slowly.

Figure 22 shows that large molecules can theoretically not only separate clinker particles but also link them. However, polymer bridging is not likely. At overdosages of PCEs, cohesiveness of cement powder decreases significantly and powder flowability exceeds the required level. This can affect the grinding process and the cement handling.

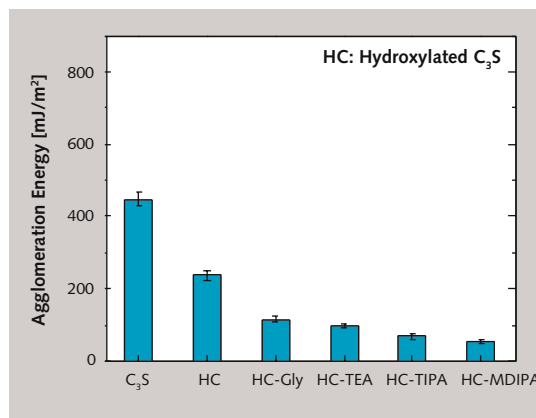
Thus, PCEs improve not only the grindability but also the flowability of cement. In addition to the steric effects this can be explained in the following way. When cement particles are pressed against one another the large PCE molecules are less easily displaced than the small more mobile molecules of the traditional grinding aids. This means that immobile PCE chains reduce more strongly temporary agglomerate formation and particle cohesion.

6.2 Mixtures of PCEs and low molecular weight compounds

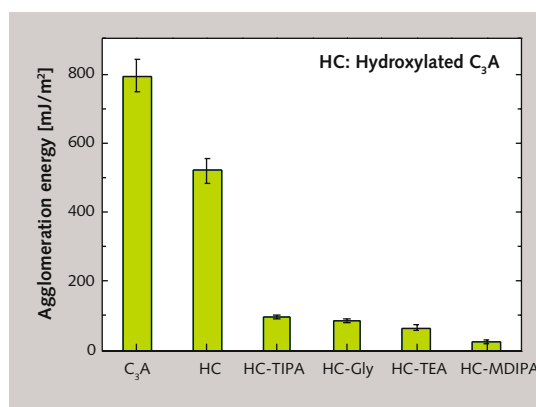
Commercial PCE-based grinding aids always contain low molecular weight compounds. Probably the former contribute to the success of such a formulation because of their steric effects and the latter because of the faster and better dispersion during grinding. Throughout the production process, they optimize particle spacing and the associated minimal agglomeration energy. Extensive studies with all ratios from pure PCEs to pure TEA and DEG have been published by Heller, Müller and Honert [4]. The technical and economical optimum ratios lie at different points. They depend on the compound, clinker, type of mill and mode of operation.

The investigations into which PCEs, which molecular details and which mixtures give the best result with respect to grinding and cement handling, and why, are continuing. Some observations and considerations indicate that it is particularly during the air separation process that PCEs develop their full effect. However, the now available experimental and theoretical research findings provide a good basis to further exploit the various benefits of PCEs as grinding aids.

Cement fineness (Blaine)	Half covering Monolayer between particles	Complete covering Double layer between particles
3000 cm ² /g	0.015 %	0.03 %
4000 cm ² /g	0.020 %	0.04 %
5000 cm ² /g	0.025 %	0.05 %



19 Agglomeration energies of dry and hydroxylated C₃S as well as hydroxylated C₃S with glycerine, triethanolamine, triisopropanolamine and methyl-diisopropanolamine at 90 °C (For numeric values see Table 3) [2]



20 Agglomeration energies of dry and hydroxylated C₃A as well as hydroxylated C₃A with triisopropanolamine, glycerine, triethanolamine and methyl-diisopropanolamine at 90 °C [11]

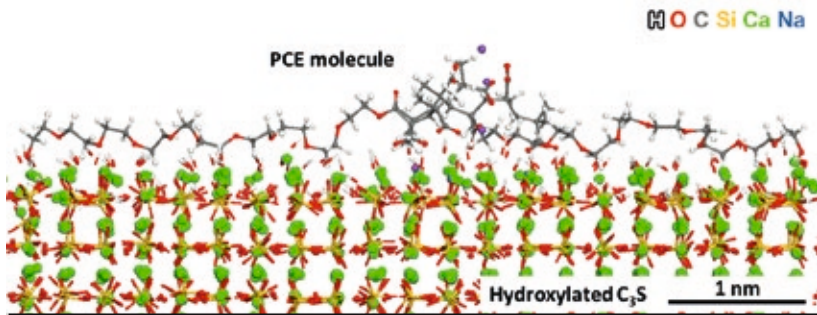
7 How do grinding aids work?

Based on results from comprehensive experimental tests and extensive molecular dynamics simulations, we present the crucial properties of grinding aids. There are consistent correlations between molecular structure and their grinding effectiveness. We also compare the gained understanding with previous attempts to explain the mode of action. This work resolves many discrepancies, which are described below as disproved and confirmed effects of grinding aids for cement.

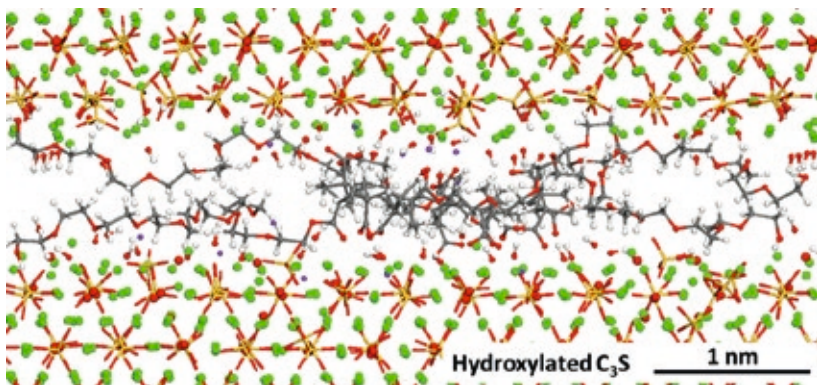
7.1 Disproved effects

- » Reduction of the crushing energy (Rehbinder effect)
The reduction of the mechanical toughness by surface-active compounds is not verifiable [9, 15].
- » Saturation of surface charges
There is no evidence of significant quantities of charges on clinker surfaces nor do ionic grinding aids have advantages over neutral ones.
- » Electrostatic repulsion
This force only opposes agglomeration in liquids. But in case of dry powders electrostatic

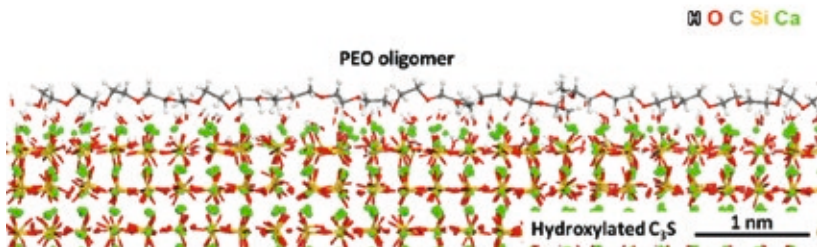
Tab. 5 Required grinding aid dosage (g glycerine per g cement) for covering the cement surface



21 PCE (polycarboxylate ether) molecule on hydroxylated clinker (C_3S) [12, 19]



22 PCE (polycarboxylate ether) molecule between hydroxylated clinker, distance of the two C_3S surfaces: 9 Å [12]



23 PEO (polyethylene oxide) molecule on hydroxylated clinker (C_3S) [12]

interactions (repulsions and attractions) must be as small as possible.

- » Strength of adsorption
The strength of adsorption of compounds does not correlate with the grinding performance [2].

7.2 Confirmed effects

- » Reduction of surface polarity
Grinding aid molecules, with their polar and nonpolar parts, compensate and reduce the polarity of the clinker surfaces to a considerable extent.
- » Reduction of surface energy
In parallel with the polarity there is also a reduction in surface energy.
- » Reduction of agglomeration energy
The agglomeration energy correlates inversely with the grinding performance. The lower the forces of attraction between two surfaces the fewer and smaller agglomerates form and the

more efficient is grinding. This is the main mode of action of grinding aids [15, 16].

- » Steric effects
PCE molecules do not only plasticize fresh concrete through steric repulsion but also reduce agglomeration during grinding through their spatial conformation. However, the molecular mechanisms with dry cement particles are completely different from those in wet concrete.
- » Dispersion via gas phase
Many compounds with boiling points below the grinding temperature that are not used because of their volatility perform well in closed mills. Also traditional grinding aids (e.g. DEG and TEA) have vapour pressures that are sufficient for a certain degree of gas phase transfer.
- » Dispersion through surface contact
Various compounds that only evaporate with decomposition perform well. Evaporation can be excluded because PCEs, for example, retain their concrete-plasticizing effect [4, 5]. Presumably contact dispersion is the more important transfer mechanism for all common grinding aids even though it is slower.
- » Water solubility
The majority of good grinding aids contain water for both technical and economic reasons. Water increases the safety (higher flash point) and is itself a weak grinding aid. It also assists the rapid and uniform dispersion of the organic compounds.
- » Synergistic effects of mixtures
There are mixtures that are of technical, of economical or of combined interest, especially those containing PCEs [4, 18].

8 Conclusions

A whole series of underlying effects and molecular as well as material properties play various roles during grinding with grinding aids. Reliable performance predictions are possible when the relative importance of the effects and interactions are known and understood. Usually, the best compounds are those that represent a balanced compromise concerning the different requirements.

Through a skilful combination of compounds, as it is the case in commercial products, it is possible not only to optimize the grinding performance but also to adjust many other properties, such as powder flowability, early and final strength development and the workability of mortar and concrete. New dimensions with respect to production efficiency are being achieved, especially with grinding aids like SikaGrind®-820, -840 and -870 that contain PCEs.

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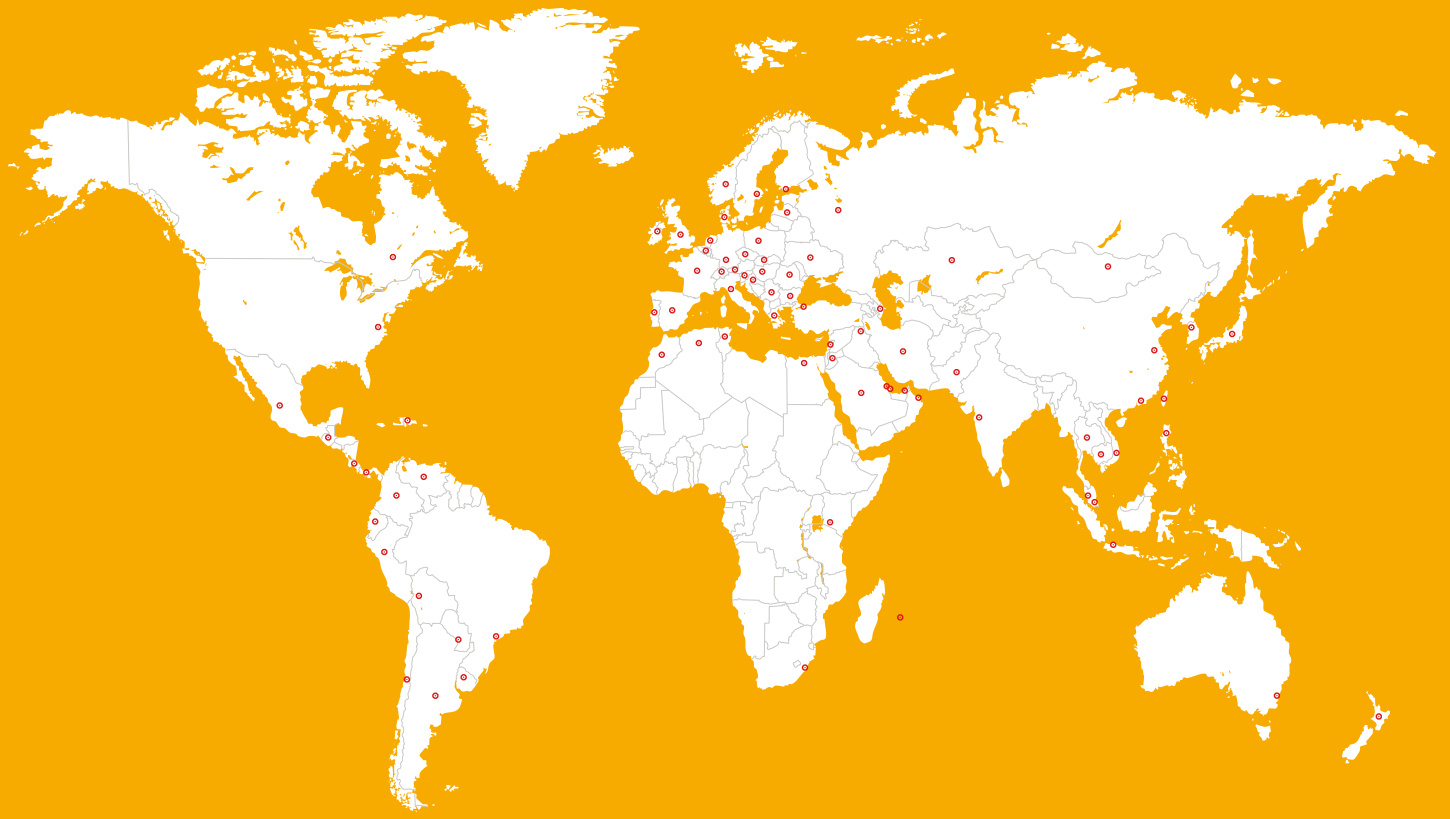


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