Grinding Aid Additives for Dry Fine Grinding Processes

Review Article

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It is well known that attractive particle-particle interactions become more decisive with decreasing particle size. Especially in dry fine grinding processes, where small particles are produced within a dry environment by different types of mechanical stress, these forces lead to a variety of challenges, such as a complicated control of the powder behavior, a decrease of grinding efficiencies and production rates as well as obtaining high product finenesses. In order to control these forces, chemical liquid or solid additives – so called grinding aids – are added to the process in many industrial dry fine grinding applications. Even though the benefits of grinding aids have already been shown in various experimental studies and industrial applications, their selection and application is still mostly based on empirical knowledge. As shown in this review article, the variety of applied substances, ground materials and target finenesses, but also available mill types, process designs, mill and process parameters as well as analysis methods complicate the development of a comprehensive understanding. Within this article, we present the basic mechanisms of action of various liquid, gaseous and solid grinding aids. Subsequently, it is shown how grinding aid molecules interact with the solid particle surface, leading to decisive changes of the particle and bulk behavior. Based on various scientific studies it is shown, how this may affect the micro- and macro-processes inside the mill as well as the whole grinding plant operation. Finally, the current gaps of understanding are identified and critically discussed with a special regard towards a more efficient selection and application of grinding aid additives for future dry fine grinding processes.

1. Introduction

The history of grinding aids in dry grinding processes starts in the late 1930s with the application of the first commercial grinding aids in the cement industry [1]. Since that time, the importance of grinding aids in industrial dry fine grinding processes has strongly increased; so did the number of scientific papers dealing with this topic. Nowadays, grinding aids are widely established in the cement industry, but also in other industrial sectors such as in the field of ceramics or filler materials. The main objectives of a grinding aid application are either: a) increasing the production capacity, b) decreasing the specific energy consumption to achieve a certain product quality, c) achieving finer particles or d) improving the product quality in terms of enabling the use of lower-quality feed materials [2]. However, even though more than 100 scientific papers on that topic can already be found in the literature and a variety of grinding aids are currently applied in industrial processes, a comprehensive understanding of grinding aids is still missing. Despite the fact that their basic mechanisms of action are known nowadays, the application of grinding aids is still mainly based on empirical knowledge. Especially a time efficient grinding aid selection is still almost impossible, as several aspects come together making the derivation of the appropriate selection criteria very complex. Therefore, this review gives a comprehensive overview on the state-of-the-art technology and methods regarding grinding aids in dry grinding processes. The mechanisms of action for liquid but also gaseous and solid grinding aids are presented; dissolved chemicals, which are often used as a surface active compound in commercial liquid grinding aid blends, are hereinafter assigned to the group of liquid grinding aid additives. Furthermore, it is shown how these additives may influence the particle and bulk behavior in the case of different products. Subsequently, a variety of studies dealing with grinding aids in grinding processes are reviewed. The article distinguishes between different ground materials, fine and ultrafine grinding, a number of mill types as well as batch and continuous operated grinding processes. Also, an overview of the variety of substances as well as their impact on the grinding result is given. In addition to that, findings from industrial processes are evaluated. Simultaneously, the above-mentioned lack of understanding is discussed critically.

2. Mechanism of action

2.1. Liquid grinding aids

As mentioned above, the history of grinding aids in dry grinding processes starts in the late 1930s with the application of the first commercial grinding aid in the cement industry [1]. At the same time, the first studies concerning grinding aids in dry grinding processes appeared in the literature [3, 4]. In a first instance, it was assumed that grinding aids may act by bringing static charges of the same sign to the surface of the product particles [3]. However, this idea was soon abandoned again for various reasons, such as the fact that also non-ionic grinding aids cause very good grinding results. Already prior to these studies, Rehbinder [5] as well as Rehbinder and Kalinkovaskaya [6] created the basis for a later and more lasting, but also controversial theory. In fact, they investigated the impact of the adsorption of surface active substances on the mechanical properties of solid particles. By using sclerometer tests they showed that adsorbed surfactants reduce the surface hardness of different materials. They concluded that an adsorption-induced lowering of the particles surface energy reduces the fracture resistance of the solid matter. Also, they categorized these substances into two groups, namely (A) dissolved inorganic salts and (B) organic molecules with polar groups. Within the following decades, a variety of studies dealt with the investigation of the impacts of surface active substances on the mechanical properties (such as fracture, compressive and tensile strength) of particles and rocks. A detailed review of these papers was already presented by El-Shall and Somasundaran [7]. In the year 1958, Rose and Sullivan [8] were the first to extend the findings of Rehbinder to grinding processes in tumbling ball mills in order to explain the mode of action of grinding aid molecules in technical mills; making the “Rehbinder effect” also very popular in the field of grinding.

Simultaneously, a growing number of authors started to question the relevance of the Rehbinder effect for dry grinding processes, as they presented studies that revealed further aspects. For instance, Kennedy and Mark [9] observed an increase of dust formation when applying grinding aids, which was one of the first indicators regarding the fact that grinding aid effects are connected to a better particle dispersion. Furthermore, the reduction of ball-coatings by those additives was monitored, leading to a controversial discussion as to whether this may be the primary grinding aid mechanism [10]. In 1961, Mardulier [11] showed that polar additives are more effective than nonpolar molecules. He explained this finding by attributing higher affinities of the polar groups within the grinding aid molecule to the high energy sites on the surface of those particle which possess unbalanced valence force. In contrast to Rehbinder, he connected the reduction of surface energy by grinding aid molecules to a decrease of the inter-particle adhesion forces; instead of to a change of the fracture behavior. Also, he considered ball coatings as an extreme case of agglomeration. Thus, the prevention of ball coatings indeed contributes to the grinding aid mechanisms especially at high finenesses, but it is not considered as the major effect. Moreover, influences of grinding aids on the material recirculation in closed circuit grinding plants were shown by this author, indicating further impacts of these additives on the flow behavior of the material. At the end of the 1960s, von Seebach [12] showed that adhesion forces between cement particles can be reduced significantly by exposing the particles to vapors of liquid chemicals, namely ethylene glycol (see Figure 1). His work confirmed that grinding aids primarily act by reducing the adhesion forces between the particles. During the same period, Westwood [13-15] as well as Westwood and Goldheim [16] found that surfactants only reduce the particle strength, if the plastic deformation is important for the particle fracture. They thereby presented a further indirect disproof for the validity of the Rehbinder effect in dry grinding processes, because mostly brittle fractures are important for the technical grinding of inorganic materials in tumbling ball mills. Following, they introduced a completely new idea on grinding aid mechanisms. They suggested that the adsorption of grinding aid molecules leads to a hindered motion of the dislocations near the particle surface, thus, decreasing the plasticity of the material. The authors highlighted this effect as the main grinding aid mechanism, because this would lead to a more brittle character of the material. From the beginning on, this theory was doubted though since plastic material behavior would be required to explain this effect, which is actually not the case for most of the grinding processes in tumbling mills.

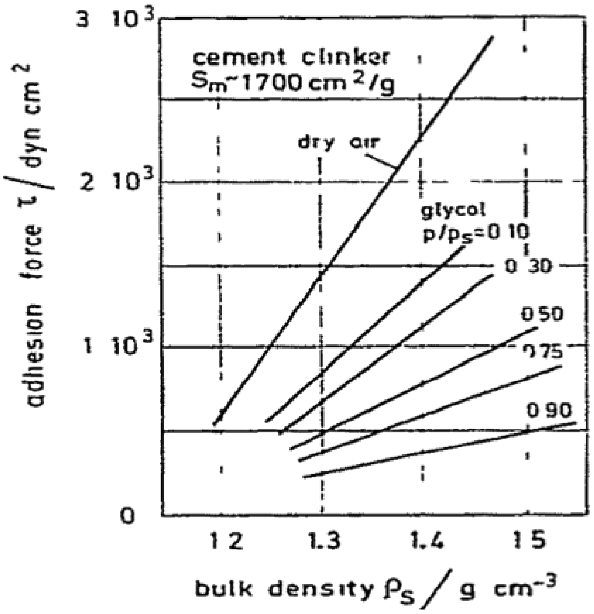

Figure 1: Impact of ethylene glycol vapors on the adhesion force of cement clinker particles [12].

In the 1970s, the relevance of both the Rehbinder as well as the Westwood effect for dry grinding applications was finally disproved. It started with the measurements of crack propagation velocities, as it was done by Schönert [17]. Even though Schönert actually did not focus on the investigation of grinding aids, he also lastingly changed the understanding of the particle breakage in the field of additive application. Studies like this indicated that the crack propagation velocities while particle stressing in technical mills are substantially greater compared to the spreading velocities of additive molecules over the particle surface. Thus, any surface active molecules are not able to follow the crack propagation fast enough in order to maintain those mechanisms proposed by Rehbinder and Westwood. Locher and von Seebach [18] directly showed that vapours of (liquid) chemicals do not improve the actual breakage event for brittle fractures. They also showed that grinding aids promote comminution by abrasion as the molecules prevent the (re)agglomeration of the fine abraded particles. Further detailed statements against the relevance of both effects, Rehbinder or Westwood, were also given by Somasundaran and Lin [19] and Ocepek and Eberl. [20]. Graichen et al. [21] as well as Graichen and Müller [22] showed experimentally that no impact on the breakage probability is seen when stressing single particles which were pre-treated with different chemicals. They also illustrated that this finding is valid for both compression and impact stressing. After those studies, it was widely accepted that grinding aids act by reducing the adhesive forces between the particles, and thus, by changing the agglomeration behavior of the powder as well as improving its state of dispersion and flow behavior [23]. Schubert [24] concluded, that thereby the micro-processes of the stressing events inside the mill are improved, leading to a decrease of energy losses especially for those mills in which particles are stressed as particle beds. Also, he attributed an improvement of the transport behavior in grinding plants as well as the prevention of material coatings on the milling equipment to the reduction of the particle-particle interactions.

In the middle of the 20th century, also the aspect of “stress corrosion cracking” was discussed to be responsible for the observed grinding aid effects [25]. This phenomenon describes the growth of crack formation along grain boundaries for certain kinds of materials which are exposed to tensile stresses within a corrosive environment. Several authors showed that especially materials such as stainless steel, aluminum or magnesium alloys and brasses are sensitive towards stress corrosion cracking when being placed in certain chemical environments (e.g. saturated vapors of ammonia or corrosive aqueous solution) [26]. However, whether this phenomenon is responsible for grinding aid effects in industrial dry grinding operations has not been clarified yet. Most likely, it can be neglected due to the same points that were made for disproving the relevance of the Rehbinder effect.

In the 1970s and 80s, a great number of authors dealt with the investigation of grinding aid impacts on dry grinding processes. Among the literature especially the works by Scheibe et al. [27] as well as Dombrowe et al. [2, 23, 28, 29] deserve to be highlighted. They performed several systematic investigations of various grinding aids within industrial grinding processes, but also regarding the basic grinding aid mechanisms. For instance, Dombrowe et al. [23] investigated the impact of grinding aids on the grinding limit of clinker grinding in laboratory ball milling. They showed that agglomeration and product adhesion are significantly reduced by grinding aids especially in the range of very fine particles in the lower micron range, leading to a shifting of the grinding limit towards higher product fineness. They also attributed these effects to the material transport inside the mill, which is strongly affected by the fine particle fraction (0 – 5 µm), and can thus be increased by grinding aids. Moreover, they showed that grinding aids are not only efficient in the lower micron range, but already increase the size reduction rate at the beginning of the grinding process. However, coarse grinding of clinker was found to be independent of the addition of grinding aids [28].

Several years later, Mishra et al. [30] as well as Weibel et al. [31] found by means of molecular simulations that the agglomeration energy between cement particles is strongly reduced by adsorbed grinding aid molecules. Thus, this finding indirectly confirmed that the surface energy of particles is in fact reduced by the adsorption of surface active compounds.

The authors also verified, that the polar parts of the additive molecule adsorb on the particle surface while the non-polar compounds further shield the particles (see Figure 2). The corresponding adsorption mechanisms are specifically discussed in a later chapter.

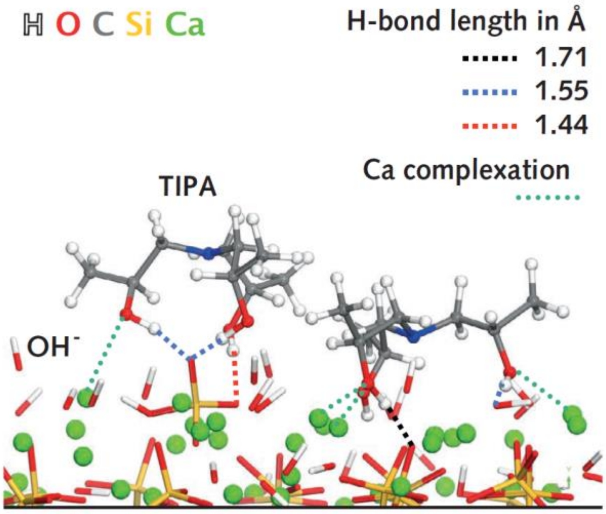

Figure 2: Adsorption mechanism of triispropanolamine molecules on a clinker particle surface, determined by molecular simulation [31].

The final experimental evidence, proving that liquid grinding aids truly decrease the surface energy of the product particles, was recently presented by Prziwara et al. [32] by means of inverse gas chromatography measurements. On the one hand, they showed that the reduction of the surface energy of ground limestone particles depends on both the kind and the concentration of the applied grinding aid. On the other hand, they confirmed the relation of surface energy and adhesion forces by presenting a very good correlation between the surface energy values and different powder properties like the agglomerate sizes as well as the powder flowability (see Figure 3).

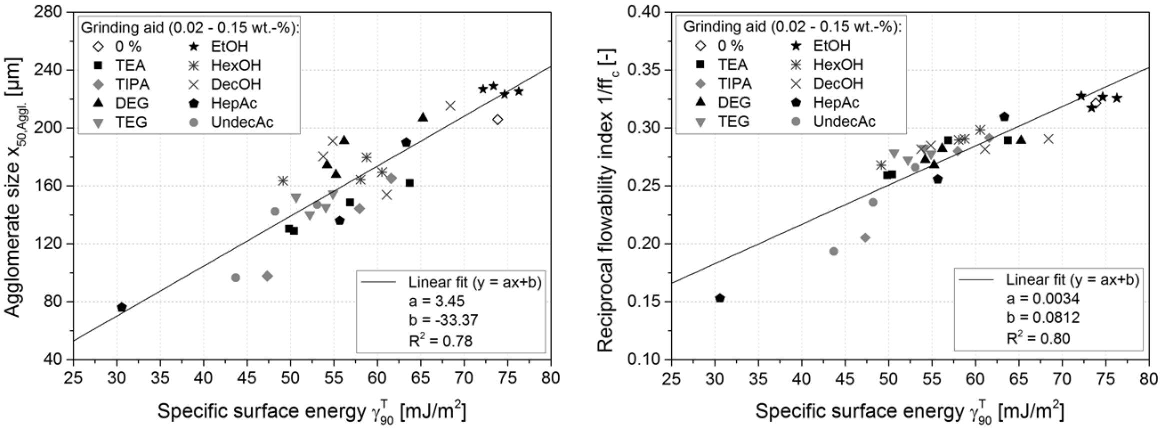

Figure 3: Relation of specific surface energy of the particles (measured by inverse gas chromatography) and agglomerate size (left, optical image analysis) as well as powder flowability (right, ring shear tester) for different grinding aids and additive concentrations [32].

2.2 Gaseous grinding aids

The mechanisms discussed above are in particular valid for all liquid as well as dissolved grinding aids. In both cases, the surface active compounds are present in the form of separated and freely movable molecules which are able to form adsorption layers on the product particles, and thus, decrease the adhesive forces between the particles. Generally, it can be assumed that similar mechanisms determine the grinding aid performance also for gaseous additives or vapors of liquid chemicals. For instance, the aforementioned study by von Seebach [12] clearly showed that also the adsorption of gaseous surface active compounds onto the particle's surface leads to a decrease of the adhesion forces between the product particles. In general, these effects can only be obtained as long as a sufficient number of molecules finally adsorb onto the particle surface, which is not necessarily the case for highly volatile gaseous compounds. Furthermore, the adsorbed grinding aid molecules are in equilibrium with their surrounding gas phase, meaning that adsorption capability also depends on ambient conditions like temperature and vapor pressure. For example, Buczek et al. [33] placed coal in an atmosphere of saturated surface active vapors for more than 24 h prior to grinding. Due to a sufficient adsorption under these conditions, they were subsequently able to show that even very volatile compounds like methanol and acetone but also ammonia and chloroform can act as grinding aids when dry grinding the coal. However, most of the industrial dry grinding processes are performed in open systems or even in air supported grinding plants, where high concentrations of additive molecules in the gas phase are hard to maintain. Also, high milling temperature (e.g. 80-120 °C for cement grinding) may impair the adsorption mechanism [31]. Thus, even conventional liquid grinding aids do partly desorb from the particle surface and are subsequently removed from the system with the mill air: For instance, Rechenberg [34] detected 2-13 % of the total additive amount in the exhaust air, while the higher values were measured in the case of higher product surface related grinding aid concentrations. The fact that high additive amounts inside the exhaust air are occurring especially at high applied concentrations may be the reason why Dombrowe et al. [23] only detected smaller amounts of approx. 2 % inside the exhaust air within their studies. These studies clearly show that the use of gaseous substances is principally possible, but often not applicable as the main part of the grinding aid amount is exhausted from the process without having brought its stabilizing effect. This may also be the reason why exclusive studies on gaseous grinding aids are hard to find in the literature.

2.3 Dry particulate grinding aids

A reliable description of the mode of action of dry grinding aids is more complicated compared to liquid (or gaseous) additives, since only a low number of corresponding studies are available in the literature. The situation is aggravated by the fact that different types of dry grinding aids may follow different mechanisms. Thereby, it needs to be distinguished between certain substances:

- Dry organic compounds with melting points slightly above room temperature, such as medium-chained alcohol amines and carboxylic acids
- Dry (mainly inorganic) particulate grinding aids having significantly higher melting points, such as inorganic salts
- Colloidal sub-micron particles

Chemicals with melting points slightly above room temperature do probably follow the same mechanisms as liquid and gaseous additives since the mill temperatures and especially short-term temperature peaks are often significantly higher. In combination with the afore-mentioned aspect, the intense stress and mixing inside the mill may help to break the initial particulate structure of the grinding aid and to spread the molecules within the particle bulk, respectively. Despite the initially restricted mobility of the molecules, the formation of adsorption layers similar to a liquid/gaseous additive may therefore be possible. The most famous of such compounds is stearic acid, which was shown to cause beneficial effects in dry grinding processes of both inorganic (e.g. cement [35], aluminum [36] or brass powder [37]) and organic products (e.g. chitosan [38]). Another important representative is triisopropanolamine, which is solid at room temperature but often leads to similar effects as liquid alcohol amines such as triethanolamine (see Figure 4). Such solid chemicals are often added in dissolved form, which further helps to dose the additive to the process and distribute the single molecules within industrial mills.

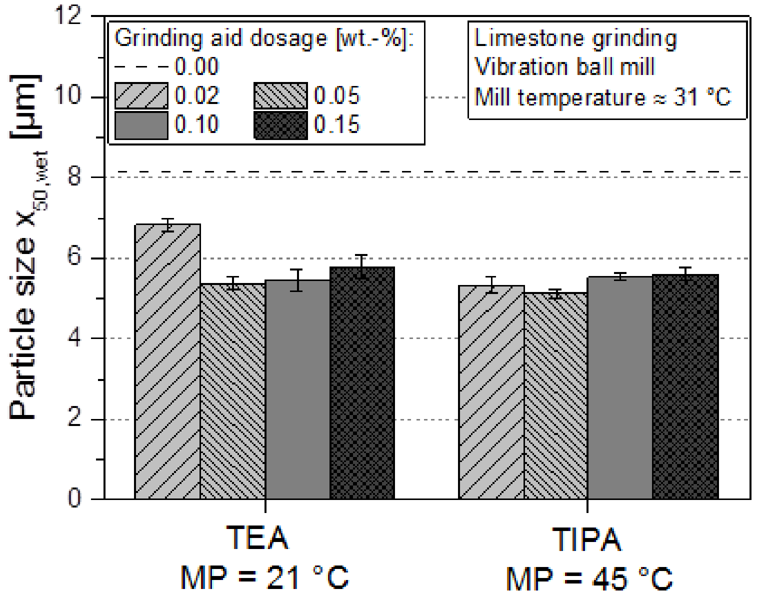

Figure 4: Grinding aid effects of Triethanolamine (TEA, melting point below room temperature) and Triisopropanolamine (TIPA, melting point above room temperature) for dry fine grinding of limestone (values taken from [32]).

In contrast to that, the mode of action of those dry particulate grinding aids, which have significantly higher melting points (e.g. salts), may be completely different. Unfortunately, a comprehensive understanding of these additives is missing, as only a few studies deal with this topic. For instance, Pollmanns et al. [39] and Pollmanns [40] investigated the impact of high concentrations (20 wt.-%) of sodium chloride on the ultrafine (submicron) grinding of various inorganic materials (see Figure 5). They found that this additive leads to a strong increase of the product fineness for zinc oxide and zirconia, while it only causes medium and negligible effects for alumina and calcite, respectively. Thereupon, the authors assumed that the salt ions are incorporated into the solid surface, whereby free valence electrons are saturated, and thus, the tendency of agglomeration is reduced. However, they were not able to present evidences for this thesis. Similar effects were achieved by Ikizaki et al. when adding large quantities (≥ 8 wt.-%) of solid nitrates to dry ultra-fine grinding of either soda glass [41] or sericite [42]. The authors confirmed an exchange of potassium ions from the sericite with ions from the nitrate salts using XRD measurements. Therefore, they rather called this process chemically assisted dry comminution (CADC) instead of applying grinding aids. They also showed that the wet measured particle size and the BET surface of the product particles showed inconsistent trends [41]. This outcome indicates that particle agglomeration still plays a decisive role despite the application of this kind of additives.

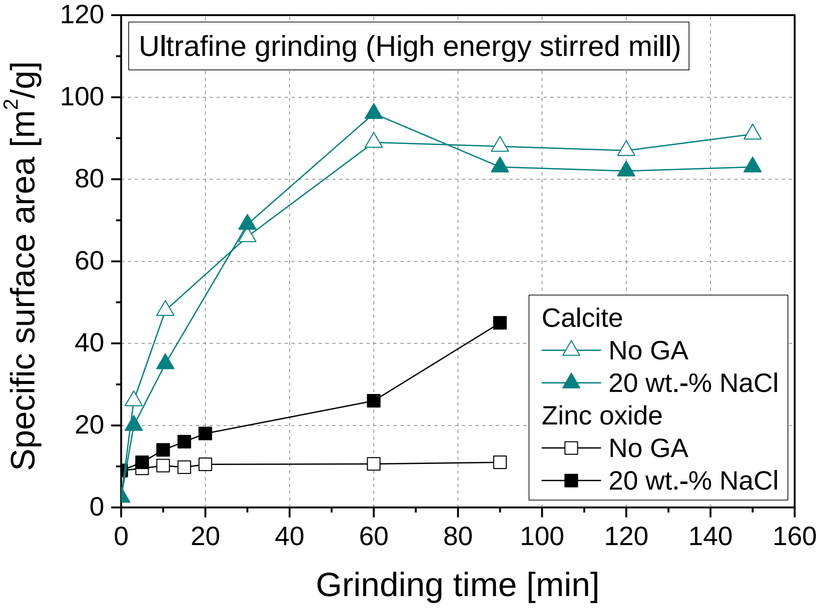

Figure 5: Impact of sodium chloride on dry ultrafine grinding of calcite and zinc oxide (values taken from [39]).

Generally, a different mode of action can be assumed for additives consisting of colloidal sub-micron particles. Here, the mechanisms may be similar to those ones of solid flow additives, which are widely used in many industries in order to control the mechanical properties [44] as well as the flow behavior [45] of fine cohesive powders. These flow additives – mostly ultrafine (guest) particles – are added to the process in order to adhere to the product (host) particles. Thereby, the guest particles act as spacers between the hosts particles, leading to an increased distance between the host particles, and thus, to a reduction of the attractive forces. Consequently, values like agglomeration, powder flowability and further bulk properties are directly affected by these additives. It can therefore be assumed, that solid flow additives – when added in appropriate concentrations – may lead to comparable effects like conventional liquid grinding aids.

Sweitzer and Craig [43] showed that colloidal carbon black increases the fineness of dry ground cement clinker, whereby a maximum increase of 49 % was found for an additive concentration of 1.28 wt.-% (see Figure 6). Also, they observed a sufficient reduction of the ball coating with the addition of carbon black.

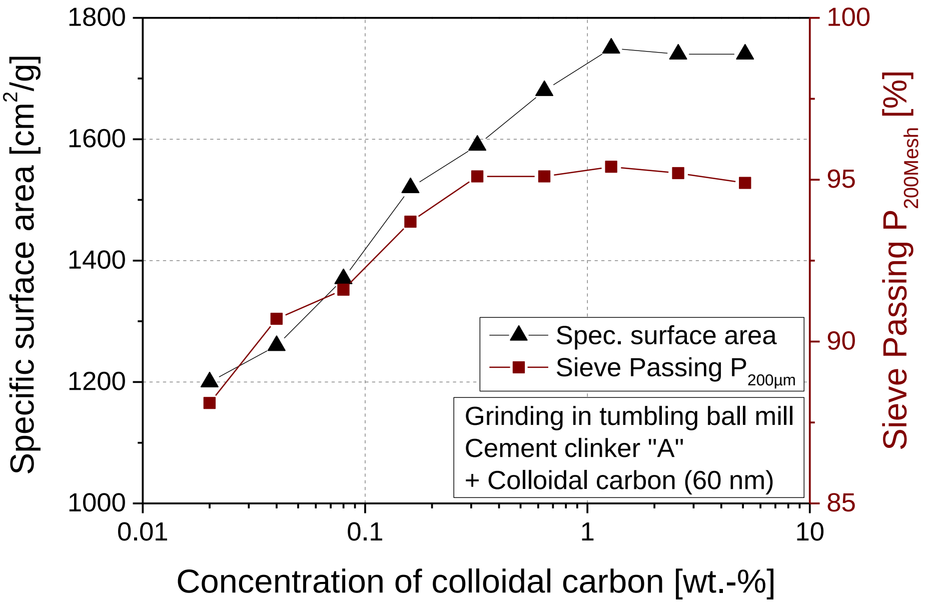

Figure 6: Specific surface area and sieve passing of ground cement clinker for different amounts of colloidal carbon black as a grinding aid additive (values taken from [43]).

In order to control the product behavior, a further special case can be found in the field of "co-milling" where particulate additives are applied to dry grinding processes. Co-milling basically describes the addition of solid additives to dry grinding processes in order to enable micronization and a simultaneous dry coating of the product particles. Nowadays, most of these applications can be found in the pharmaceutical industry where such additives are mainly added in order to decrease the cohesiveness of fine pharmaceutically active ingredients (APIs). Thus, the purpose of co-milling is rather to control the product behavior for subsequent process steps than to improve the grinding process. However, similar mode of actions as discussed above may lead to a reduction of the adhesive forces of the product particles. For example, Mullarney et al. [46] used different types of sub-micron silicon dioxide particles as additives for dry fine grinding of various active pharmaceutical components (APIs) in a “comil”. They showed that this kind of co-milling strategy is very effective in terms of a simultaneous dispersion of the nanoparticles as well as their dry coating onto the host particles, leading to an improved flow behavior of the APIs. Similar results were presented for co-milling of KCl particles in a continuous fluid energy mill using silica, alumina and titania nanoparticles as coating material [47]. Vogt et al. [48] presented that the co-milling of various poorly soluble drugs in a jet by using different excipients also leads to positive effects regarding the drug dissolution behavior. In other studies, Ibuprofen was successfully dry-coated in a fluid energy mill with both amorphous hydrophilic silica particles as well as water-soluble polymers as coating components [49, 50]. Here, it was also proven that dry coating does not only improve the flow and bulk properties of the ground drug particles, but also their later dissolution behavior. Han et al. [51] further showed that dry coating with nanosilica by co-milling leads to a reduced cohesion and improved flowability of the guest particles not only by creating nanoscale surface roughness, but also by passivating high-energy surface sites, and thus, reducing the surface energy of the milled material. Wang et al. [52] showed that excessive amounts of wax as coating material may also lead to negative effects on the particle size and the dissolution behavior of co-milled ascorbic acid particles. Even though no conclusions can be derived regarding the impact of those nanoparticles on the grinding process, accompanying and maybe less regarded effects on the grinding step are also possible. Thus, these studies may indicate further potentials especially regarding the optimization of dry fine grinding processes within the pharmaceutical industry.

2.4 Dispersion and adsorption of grinding aids

In industrial processes, grinding aids are commonly added to the material by dropping the chemical either onto the feed conveyor belt or directly into the milling chamber [53]. Scheibe et al. demonstrated that different addition strategies such as dropping, injecting or vaporizing have no significant impact on the grinding aid performance in tumbling ball mills, mainly because of the good mixing effect within this mill type. Weibel et al. [31] reported that the dispersion of the grinding aid within the product happens in particular via a) gas phase transfer and/or b) surface contact transfer. They affirmed this assumption with different observations: On the one hand, they found that the dry grinding of cement was significantly increased using various alcohols with boiling points below grinding temperature. At the same time, the authors noticed the characteristic odour of the alcohols coming from the cold cement, which indicates a high volatility of the chemicals as well as a weak adsorption. However, since the additives still increased the grinding performance significantly, they assumed that the grinding aid is distributed partially via the gas phase. On the other hand, the authors successfully applied polycarboxylate ether (PCE) as a grinding aid, which only evaporate under irreversible decomposition. This occurence is therefore a strong indicator for a surface contact transfer of the polymer. The authors concluded that conventional grinding aids such as glycols and alcohol amines have low but sufficiently high vapor pressures, so that their dispersion probably happens via both mechanisms. It can further be assumed, that chemicals having a lower boiling point are distributed via the gas phase to a higher extent than high-boiling compounds. However, the ratio of the gas phase and the surface contact transfer is difficult to characterize, not at least because of the overlapping impacts of the mill and the grinding conditions [31].

Different information can be found in literature regarding the optimum point of time of the additive addition. As mentioned above, Scheibe et al. [28] reported that positive grinding aid effects were not seen for coarse grinding processes. At the same time, they did not detect any negative effects when already adding the additive to the coarse grinding chamber either. In contrast to that, Nair and Paramasivam [54] found a slight increase of fines for the delayed adding of calcium stearate to ball milling of limestone. Hasegawa et al. [55] also achieved better results for a step-wise addition of the grinding aid during the ultrafine grinding limestone in a vibration rod mill. The inconsistencies of these studies may be explained by a study of Prziwara et al. [56] on the impacts of grinding aids on the dry stirred milling of limestone: The authors found that the strategy of adding the grinding aid only influences the grinding result, if an early (or delayed) addition of chemicals influences the flow behavior of the product in such a way, that the micro-processes inside the mill, and thus, the grinding conditions are changed. A detailed discussion of the impact of the additive on the stress behavior inside the mill is given in a later chapter.

Furthermore, Weibel et al. [31] discussed the impact of the surface energy of the solid as well as the surface tension of the grinding aid on the wetting and spreading behavior of the chemical on the solid surface. They stated that liquids with a low surface tension easily spread out on solid surfaces of high surface energy, as it is normally the case for grinding aids in combination with inorganic particles such as cement clinker. At the same time, the grinding aid molecules need to be adsorbed on the solid surface sufficiently, which is reflected by a low interfacial energy between additive and solid surface. Thus, chemicals with a low surface tension do not necessarily lead to the best performance. For instance, non-polar liquids spread out rapidly on polar surfaces due to their low surface tension. However, they are not applicable as grinding aids, because they do not adsorb adequately in order to form a stable adsorption layer on the solid surface.

Dombrowe et al. [2] had a closer look into the optimum grinding aid concentration range. They characterized the coverage of cement particles with different primary alcohols by means of adsorption/desorption experiments. Thereby, they found that the amount of molecules within a monomolecular adsorption layer is rather a function of the number of hydroxyl groups than of the molar mass of the additive, indicating that grinding aid molecules adsorb onto the particle surface with their polar parts. Moreover, the authors showed that the adsorption energy is not an exclusive measure for the grinding aid performance.

By means of molecular simulations, Mishra et al. [30] showed that grinding aids like triisopropanolamine (TIPA), triethanolamine (TEA), N-methyl-diisopropanolamine (MDIPA) and glycerin orientate to a polar surface with the polar parts of the molecule, while the non-polar rest shields the particle. They found that adsorption onto cement surfaces happens by coordination of Ca^{2+} ions, hydrogen bonds as well as other polar interactions. Thereby, they determined higher adsorption energies on dry, non-hydroxylated surfaces. However, they further assumed that the adsorption of grinding aid molecules does not happen on freshly cleaved surfaces, since those surfaces can be assumed to relax immediately after breakage. The adsorption energy turned out to rather depend on molecule-solid interactions than on the volatility of the grinding aids. Thereby, they found the adsorption strength follows the order glycerin > MDIPA > TEA ≈ TIPA. In contrast to that, the reduction of the agglomeration energy, which was computed from the simulation results, turned out to follow MDIPA > TIPA > TEA > glycerin. On the one hand, the authors concluded that the adsorption strength is an important parameter regarding the formation of a stable adsorption layer. On the other hand, they stated that the agglomeration energy actually correlates with the experimental grinding efficiency rather than the adsorption energy. They also assumed that the binding geometry including the thickness of the adsorption layer leads to the better results obtained by the amines compared to glycerin. In agreement with that, Prziwara et al. [32] found that the surface energy of the limestone particles, which correlates with their tendency to agglomerate, is also reduced stronger by applying alcohol amines compared to glycols. Possible impacts of the molecular structure of the grinding aid are discussed in chapter 3.2.

2.5 Impact of grinding aids on particle and bulk properties

As described above, the reduction of the surface energy by grinding aids was recently proven experimentally by Prziwara et al. [32]. It was shown that the surface energy of limestone particles decreases with an increasing amount of grinding aid, as a more complete adsorption layer on the particles is achieved with sufficiently high grinding aid concentrations. Generally, the strongest reduction of > 50 % was achieved by carboxylic acids followed by alcohol amines, poly alcohols and mono alcohols. Simultaneously, both the cohesiveness of the powder as well as the state of agglomeration decreased with the reduction of surface energy. The authors attributed this to the relation of surface energy and adhesion forces between the particles. The first studies aiming to characterize the impact of surface active compounds on the adhesion forces between the particles were already presented much earlier [12, 29]. A further important study was presented by Spindler et al. [57] who measured the adhesion forces between limestone particles by an ultra-centrifuge method as a function of the amount of added hexanoic acid as a surface active compound (see Figure 7). On the one hand, they showed that the adhesion forces are reduced with a certain amount of hexanoic acid, leading to an optimum concentration at which minimum forces are obtained. The adhesion forces were shown to increase again above this concentration. On the other hand, they presented a very good correlation between adhesion forces and the powder flowability, which in turn reached maximum values in the range of low adhesion forces. They showed that the adhesion force, and thus, the grinding aid have a significant impact on the bulk behavior of the powder. In general, minimum adhesion forces are assumed to be achieved in the range of a mono-molecular adsorption layer which leads to best stabilization effect. At higher concentrations, excessive amounts of molecules cause capillary effects which again lead to an increase of the adhesion forces [31].

As the powder flowability is easier to measure than the adhesive forces between the particles, various authors have examined the impact of grinding aids on the flow properties of the ground material. Furthermore, the investigation of the powder flowability is of higher application-oriented importance, because the knowledge of this property helps to understand the impact of grinding aids on flow and transport processes inside the mill on both micro as well as macro levels. The relation of grinding aid, powder flowability and milling process is discussed separately in chapter 3.3.

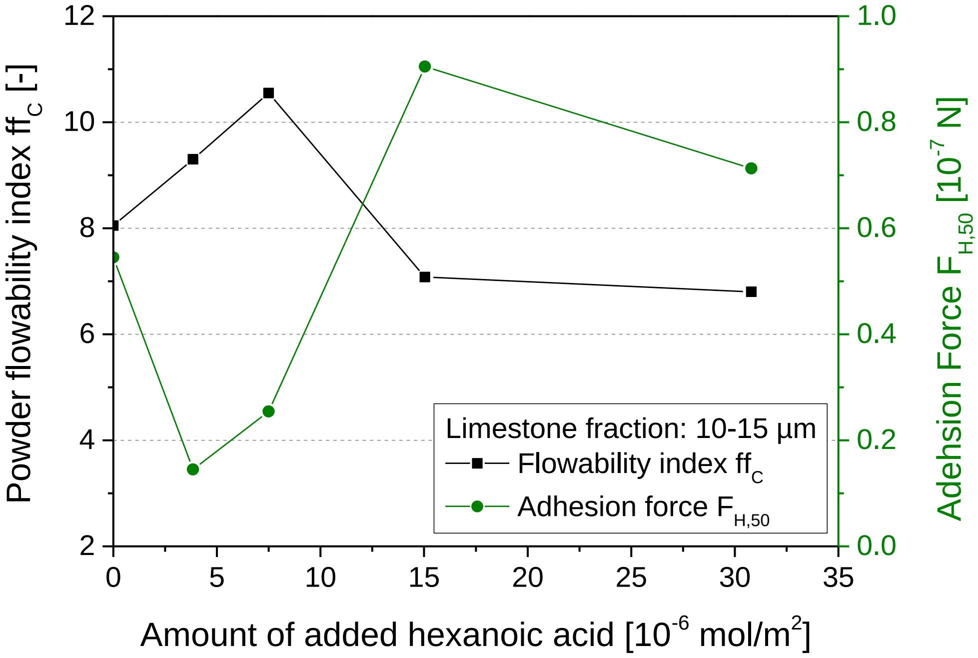

Figure 7: Impact of the amount of hexanoic acid on a) the powder flowability index ff_C of limestone particles and b) the corresponding adhesion forces between the single particles (data taken from [57]).

Unfortunately, there is still a very limited understanding to how far the powder flowability of a certain product is influenced by different types of grinding aids as well as grinding aid concentrations. The lack of comprehension may especially be caused by the complexity of overlapping parameters: Besides the chemical structure of the additive as well as the actual (and usually unknown) surface coverage, the flowability is also determined by a variety of partly unknown particle properties (e.g. particle size distribution, particle shape, particle roughness, moisture content or chemical surface properties). Also, the variety of used testing methods, like ring shear tests (e.g. [32, 56, 58]), Imse flowability tests (e.g. [23, 59]), Jenike shear tests (e.g. [54]), simple measurements of the static angle of repose (e.g. [60-62]) and recently also powder rheometry (e.g. [50]), make the development of universal rules even more difficult. Some of these studies indicate that a larger non-polar part within the grinding aid molecule may support positive effects on the powder flowability [23], possibly due to steric stabilization effects. However, molecules with a high fraction of non-polar to polar parts may require significantly higher concentrations: Larger non-polar parts reduce the density of anchor groups within the molecule, which is why a higher number of molecules is required to saturate the solid surface [32]. Other studies indicate, that carboxylate acids often lead to a stronger increase of the flowability especially for inorganic minerals (e.g. [32]). Recently, it was also shown that polymer-based grinding aids such as polycarboxylate ethers are very effective regarding the flowability enhancement, especially of cement powders [60]. Nevertheless, the specific interactions between the solid surface and the additive molecules may cause deviations from these trends.

Furthermore, grinding aids may cause further effects on other bulk properties like the compaction behavior [63, 64] or bulk density [63], which may also be relevant to optimize grinding operations. Unfortunately, only limited information on these aspects can be found in the literature.

3. Grinding aids in batch-wise grinding processes

3.1. Grinding results from laboratory investigations

Nowadays, grinding aids are mainly established in continuously operated industrial grinding processes. However, as laboratory mills are often seen as the more convenient tool for an efficient grinding aid screening, most of the present studies were carried out in batch-wise operated grinding devices on laboratory scale. Thereby, a variety of different mill types have been used so far. The majority of the investigations were done in mills containing loose grinding media such as tumbling ball mills, vibration ball and rod mills, stirred media mills, planetary balls mills or even more exotic devices like box mills. Batch-wise laboratory studies using mills based on differing stress mechanisms like high pressure grinding or (single particle) impact stressing are very rare.

Table 2 in the appendix summarizes a variety of chemicals that have successfully been tested as grinding aids in batch-wise operated laboratory mills. It is distinguished between the physical state (liquid/dissolved and solid) and the kind of grinding aid, the ground material as well as the used mill type. Also, results from studies dealing with ultrafine (uf) grinding into the sub-micron particle size range are specifically marked. In order to give an impression of the grinding aid performance, the relative increase of the product fineness ϕ_{GA} which was achieved by applying grinding aid application is calculated based on data from the present studies. The calculated values are listed together with the corresponding grinding aid concentration. The relative fineness increase ϕ_{GA} is defined as the ratio of the specific product surface area $S_{m,GA}$, that was achieved using a grinding aid, and the specific surface area $S_{m,ref}$ obtained from the reference comminution without any grinding aid under identical grinding parameters as well as similar grinding times or specific energies (see Eq. 1). The used values of the specific surface areas were mostly obtained from either BET or Blaine measurements.

$$\phi_{\mathrm{GA}} = \frac{S_{\mathrm{m,GA}}}{S_{\mathrm{m,ref}}} \qquad [1]$$

In many studies, only particle sizes or sieve residues instead of the specific surface area are used for quantifying the grinding aid success. In such cases, the fineness increase ϕ_{GA}* was calculated based on these alternative fineness characteristics. Thus, a direct comparison of the values ϕ_{GA}* with the surface-based values ϕ_{GA} needs be done with caution.

As seen in Table 2, a high number of researchers have already dealt with the investigation of grinding aids in laboratory experiments. Thereby, a variety of over 100 chemicals were successfully tested as additive for different particulate products. Naturally, the majority of the studies are located in the field of construction materials, especially because these materials are produced in large quantities while often demanding comparatively high specific energy inputs. However, also other inorganic products like alumina and quartz were investigated intensively. Other products like graphite, zirconia or zinc oxide and in particular organic materials like chitosan are in the minority among the tested materials. Independent of the ground material, mostly chemicals from the groups of mono alcohols, poly alcohols (mainly glycols), alcohol amines and carboxylic acids as well as their salts are suitable as grinding aids. In contrast to scientific laboratory studies, which often focus on the investigation of single grinding aid components, commercial grinding aid are usually provided as blends of these chemicals [65]. Recently, substances with a more complex chemical structure or chemical composition have succesfully been tested as grinding aids. For instance, waste products such as soapstock [66], sulfite waste liquor [67], waste cooking oil [68] and fly ash [69] were tested especially for economic reasons. Also, polymer-based grinding aids such as polycarboxylate ethers, which are already established as superplasiticizers in the concrete industry, are currently becoming more popular as grinding aids [31, 60, 70-72]. Schrabback [72] as well as Heller et al. [73] found that those complex molecules are in particular beneficial, when being applied together with common grinding aids.

Table 2 also indicates that it is hardly possible to derive any universal rules on mill- or solid-specific grinding aid effects based on these studies, even though the total scope of experimental results is very large. The reasons for the difficulty regarding a direct comparison of these various studies are very divers:

- The **diversity of ground products** including their mostly unknown surface properties makes the development of a comprehensive understanding even more difficult, especially regarding solid-specific grinding aid effects. This aspect is made even more complicated, as a variety of studies from the sector of construction materials do not focus on the grinding of a single material, but on the multi-component grinding of material mixtures. For instance, Teoreanu and Moanta [74] showed that different alcohol amines will lead to varying effects, depending on the content of granulated blast furnace slag within the cement blend. Moreover, the grinding aid performance can be influenced by the state of the material (fresh vs. aged) as shown by Dressel and Stark [71]. Thus, only a few studies indicate clear trends. For instance, the results of both Dombrowe et al. [23] and Sohoni et al. [67] show that alcohol amines are most effective for grinding cement while monocarboxylic acids are favorable for grinding limestone.
- **Grinding equipment:** Both of the aforementioned studies investigated grinding aids only in tumbling ball mills. To what extent the grinding aid performance may be related to the grinding mechanism as well as stressing conditions inside the mill, is nowadays still not really understood. The corresponding aspects are discussed separately within the next chapter, because this relation seems to be underestimated in most of the grinding aid application.
- **Measurement equipment:** In general, the usage of different measurement devices to quantify grinding aids effects on the product fineness makes a reliable comparison of these different studies partly very difficult. Especially values characterizing the specific surface areas, which are often obtained from Blaine measurements, can be seen critical. As shown by Graichen and Müller [22], significant differences between the particle size distribution and the Blaine surface are observed after applying grinding aids, because the adsorbed molecules tend to change the packing structure of the particle bed as well as its permeability, which directly affects the Blaine measurement. It was also shown that BET measurements are inaccurate when the samples are not prepared sufficiently by thermal conditioning prior to the measurement. This is due to the still adsorbed grinding aid molecules changing the nitrogen adsorption onto the particles, and thus, the measurement result [23, 75]. Dombrowe et al. [23] also assumed that grinding aids may affect wet particle size measurements, as they change the wetting properties of the particles. Therefore, they recommended to only use dry particle size analysis like sieving and air classification methods. Unfortunately, those methods are hardly appropriate for characterizing fine particle systems as well as fine fractions in particulate product.
- **Test evaluation:** In the field of industrial production, the specific energy demand, thus the amount of energy that is needed per product mass to obtain the desired

product fineness, is one of the most important parameters. Therefore, it should also be considered as the most important value to describe grinding aid benefits in batch-wise operated grinding experiments. However, a lot of studies are only based on grinding times as the measure to characterize the grinding success. Of course, some studies rather aim to describe basic phenomena, such as determining the impact of grinding aids on the particle and powder behavior (see e.g. [32]). Nevertheless, the universal illustration of the product fineness as a function of the specific energy demand would help to develop a comprehensive understanding of the grinding aid impacts on batch-grinding processes.

- **Fineness range:** The investigated product finenesses differ a lot among the presented studies, making a comparison of the results very difficult. A comparison of these studies indicates that grinding aid effects can be fineness-specific, which is not surprising as the adhesive particle forces become more decisive with increasing product fineness. As seen in Table 2, the relative increase of the product fineness is generally in the range of ϕ_{GA} = 1.0-1.5 for usual fine grinding (independent of the physical state of the grinding aid). In contrast to that, the benefits of grinding aid applications are much higher in the case of ultrafine grinding (uf), leading to ϕ_{GA} values of up to approx. 15. For instance, ϕ_{GA} values of 1.5 are achieved for the fine grinding of limestone, while in ultrafine grinding values of up to 2.7 are obtained. These results clearly show that the actual product fineness needs to be taken into account when comparing different studies. Moreover, these "fineness-effects" may also depend on the nature of the applied grinding aid. As an example, Figure 8 shows the grinding progress of cement clinker as a function of the specific energy consumption. When adding an amine-based grinding aid, ϕ_{GA} increases with the product fineness from initially 1.08 (≈ 2000 cm^2/g Blaine) to 1.5 (≈ 7500 cm^2/g Blaine). In contrast to that, ϕ_{GA} stays almost constant in the range of 1.2 while using a glycol-based additive.
- **Grinding aid concentration:** It is widely known that the grinding aid performance rather depends on the degree of particle surface coverage with grinding aid molecules than on the gravimetric grinding aid concentration (see e.g. [32]). In general, this value is not only affected by the grinding aid concentration itself, but also by the specific surface area of the product particles as well as other aspects like the purity of the added grinding aid or its molecular structure which determines the space requirement of each molecule on the particle surface. Obviously, finer products possess a larger specific surface area, which is why they demand a higher amount of grinding aid in order to be stabilized sufficiently. A similar trend can already be seen in Table 2: For instance, ultrafine grinding processes demand a significantly higher grinding aid concentration up to several percent related to product mass to achieve the desired grinding aid effects. In contrast to that, lower concentrations between 0.005-0.2 wt.-% are common for usual dry fine grinding processes within the lower micron range. However, as the aforementioned aspects

are not included in most of the studies, it is difficult to develop a comprehensive understanding of the optimum grinding aid concentrations. Moreover, several studies investigate excessively high concentrations, which certainly lead to certain grinding aid effects, but do not help to understand the selection of optimum concentrations (see e.g. [76]).

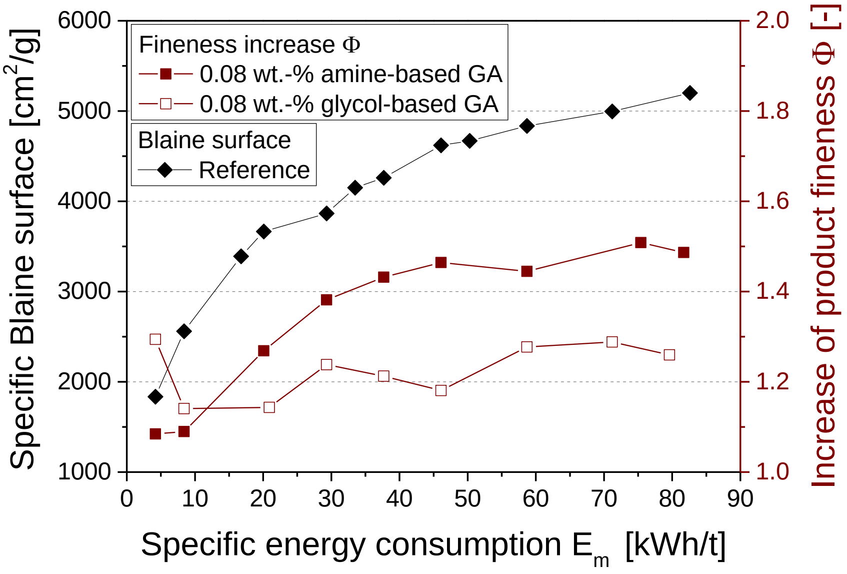

Figure 8: Evolution of the specific Blaine surface of cement as a function of the specific energy input, including the relative increase of the product fineness when applying amine- and glycol-based grinding aids (data taken from [77]).

3.2 Impact of the molecular structure on grinding performance

In order to enable an efficient grinding aid selection, many researchers addressed the question to which extent the grinding performance is correlated with certain chemical-physical properties of the additive. Scheibe et al. [27] carried out an extensive investigation of various grinding aids on the batch-wise grinding of cement clinker, quartz and limestone in the 1970s. They found that the impacts of the applied chemical on parameters like the product fineness or the material adhesions inside the mill depend on a complex relation between the ground material itself and the properties of the chemical. Thereby, they did not see a significant impact of neither the dipole moment of the grinding aid nor its solubility. In contrast to that, Paramasivam and Vedaraman [63] concluded that a high dipole moment, a high surface tension and a low vapor pressure (for low grinding aid concentrations) as well as a low viscosity (independent of the grinding aid amount) lead to higher product finenesses in the case of grinding limestone. Based on the results of grinding quartz, Hasegawa et al. [78] suggested that the product of dipole moment and molar mass may be a good indication for the grinding aid effectiveness. However, both approaches are not satisfactory for an efficient grinding aid selection, because the chosen properties do not include solid-specific grinding aid effects as shown by Scheibe et al. [27]. Also, the impact of the molecular geometry and further physico-chemical parameters are thereby not considered appropriately. Other studies revealed that even the adsorption energy is not an exclusive measure for the grinding aid performance [2].

Dombrowe et al. [23] also summarized a number of criteria for selecting grinding aids with a special regard on their molecular structure. They summarized that the chemical structure has a decisive influence on the grinding aid performance; this includes the kind and number of functional groups as well as the chain length of nonpolar parts within the molecule. They also showed that an asymmetrical arrangement of the polar groups within the molecule favors the effectiveness. However, they concluded that it is hardly possible to derive selection criteria based on these properties, also due to the fact that grinding aids may act solid-specific. They further showed that a high concentration of functional groups does not guarantee a high stabilization success, even though this may lead to a high surface coverage at the same time. For instance, the investigation of different carboxylic acids at a constant gravimetrical concentration revealed that the best effects on the grinding of limestone are obtained with medium-chained molecules (see Table 1). The authors also mentioned that the small effects of long-chained carboxylic acids (C_{12} and higher) at usually applied concentrations can be compensated by applying uncommonly high concentrations. It clearly shows that different additives demand other optimum concentrations.

Table 1: Impact of the concentration of carboxylic groups within monocarboxylic acids on the product fineness (undersize at 40 and 17 µm) as well as Imse powder flowability of ground limestone for different chain lengths (data taken from [23]).

Chain length	Conc. [mmol/kg]	Passing D_{40} µm [wt.-%]	Passing D_{17} µm [wt.-%]	Imse powder flowability [%]
C_2	8.3	88.5	67.2	85
C_3	6.8	87.6	67.3	87
C_6	4.3	89.2	68.4	98
C_8	3.5	88.6	66.1	87
C_{12}	2.5	84.6	68.5	85
C_{14}	2.2	74.4	63.0	40
C_{18}	1.7	73.0	58.0	38

Prziwara et al. [32] showed that the number of grinding aid molecules per solid surface (N_{GA}) is a better measure to describe the grinding aid performance than the gravimetric concentration. They also found that molecules with a high ratio of polar to non-polar molecules demand lower N_{GA}-values to achieve their maximum effects than molecules with a longer non-polar chain. The authors concluded that the number of polar groups determines the number of anchor groups for the adsorption. They stated that molecules with more than one anchor group lead to a more "flat" adsorption, and thus, to a higher surface coverage at a constant number of added molecules. However, it was also shown that these molecules do not necessarily achieve the best effects. Instead, the molecules leading to the strongest reduction of the surface energy of the particles turned out to be the most effective grinding aid additives regarding the prevention of agglomeration and the increase of powder flowability. Unfortunately, no method to approximate the reduction of the surface energy based on the chemical grinding aid parameters is known until now.

3.3. Importance of stress conditions inside the mill

Similar to the aspects discussed above, it is also almost unknown how the grinding aid performance is influenced by the selected mill and process parameters, and thus, by the stress conditions inside the mill. It may appear obvious that the micro-processes of the individual stress events inside the mills are affected by the grinding aids, since those additives are well-known to influence decisive product properties like the powder flow behavior and agglomeration. Therefore, it seems more than likely that the product reacts differently to certain stress situations, depending on its bulk and flow properties. However, only a very low number of authors have dealt with this question so far.

A reason for this may be the predominant role of tumbling ball mills in the cement industry especially within the last century. Thus, most of the grinding aid studies focus on this mill type, which makes it difficult to compare the grinding aid performance for different grinding mechanisms. Also, tumbling ball mills are usually operated within a narrow range of process parameters, since the choice of parameters like mill speed and ball size is strictly limited. This also restricts the stress conditions to certain boundaries. Within one of these studies, Dombrowe et al. [23] showed that the efficiency of grinding aids in tumbling ball mills is not affected by parameters such as mill speed, ball filling ratio, ball size, product filling and temperature. In contrast to that, Deckers and Stettner [79] revealed that the grinding ball size as well as the ball filling ratio influence the grinding aid effects.

A further hint regarding the change of friction and stress conditions as a consequence of the grinding aid application is given by the results of Moothedath and Ahluwalia [61]. They operated a lab-scale tumbling ball mill specifically at two completely different process conditions in order to comminute limestone predominantly by either breakage or attrition. Even though the experimental set-up of this paper is not always comprehensible, the results clearly indicate that grinding aids may have significantly different impacts on the grinding result depending on the stress conditions inside the mill. For instance, grinding aids like TEA and oleic acid showed different influences in attrition mode, while grinding in the common breakage mode was almost identical for both grinding aids.

A much clearer indication is given by Allahverdi and Babasafari [80], who investigated the effect of TEA on the comminution of cement in both a tumbling ball mill as well as vibrating disc mill. Therefore, they first identified those process parameters, which resulted in an identical Blaine value for both mills when grinding without any additive. Subsequently, they added TEA under the selected parameters. They found, that the use of TEA led to a stronger increase of the Blaine value in the case of the tumbling ball mill in comparison to the vibration disc mill (see Figure 9). This result clearly shows that the grinding aid efficiency is indeed a function of the stressing conditions provided by the mill. Similar to that, Nair and Paramasivam [81] found that the extent of enhancement within the grinding performance to grind calcite with calcium stearate as an additive varies for different media mill types.

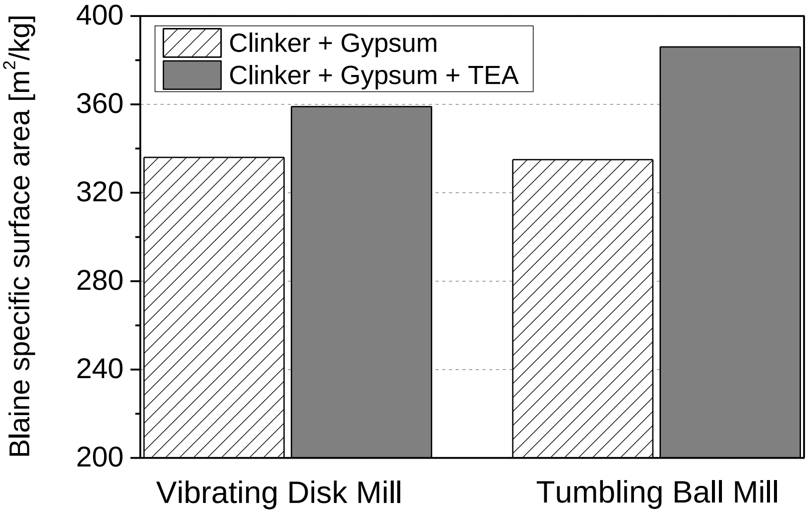

Figure 9: Impact of TEA on the grinding of clinker in vibration disc and tumbling ball mill, when grinding with mill parameter that lead to identical Blaine values without any additive (data taken from [80]).

Hoffmann and Bernhardt [82] showed that different carboxylic acids do not only improve the batch-wise high pressure grinding of limestone in a vertical rolling ball mill, but also reduce the power draw of the mill drive. The authors stated that the reduction of the adhesion forces by applying grinding aids leads to a decrease of the friction between the particles, which in turn, leads to an easier slipping and sliding of the particles within the bulk. They also assumed that this may further increase the grinding efficiency, because the increased particle movement may bring the particle bed closer to the more efficient conditions of single particle layer beds. This statement seems inappropriate for continuous processes, since it does not include the production capacity: In such cases, high transport velocities along the mill and low power draws of the mill drive may lead to low production rates, simultaneously. In comparison to roller mills, the power draw of a tumbling ball mill is only slightly affected by the adhesion forces of the ground particles, while the milling parameters play a larger role [82].

Oettel and Husemann [64] observed similar effects when they investigated the impact of the powder flowability on the comminution of limestone particles (40-50 µm) which were stressed batch-wise by high pressures within a force-controlled press. They specifically adjusted the powder flowability of the limestone by using different amounts of caproic acid and found that the particle stressing is significantly influenced by the powder flow behavior. Especially for only partially confined particle beds, the mass of particles that is captured beneath the piston decreases with an increase of powder flowability (see Figure 10). Depending on the geometry of the confinement, this increased product transport may also lead to a higher specific energy adsorption but a lower energy utilization at the same time. The authors clearly showed that the micro-processes are strongly influenced by the powder flow behavior while stressing, and thus, the applied grinding aid. In general, these finding indicate that the flowability does not only affect high pressure grinding, but also all of those grinding processes where the particles are stressed as particle beds.

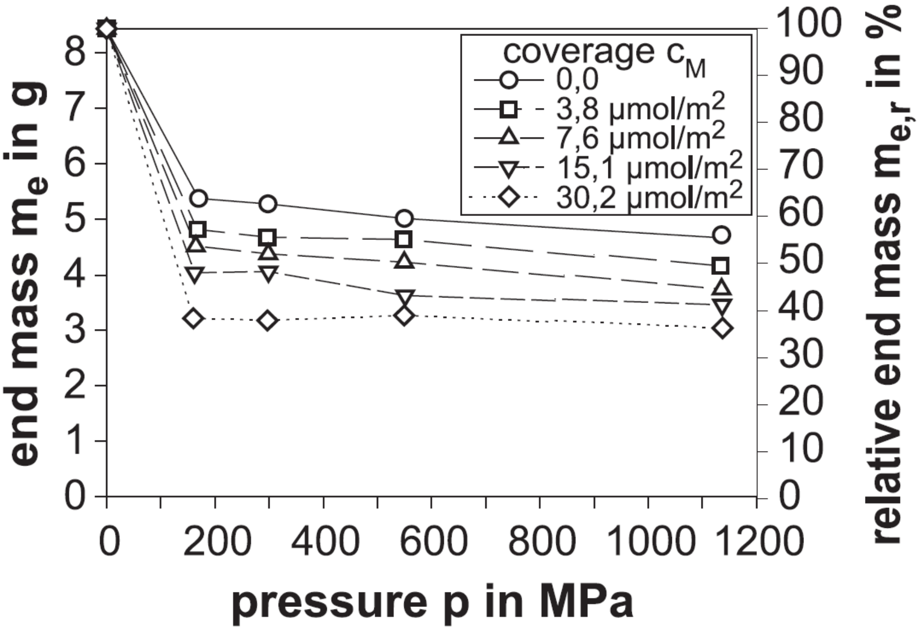

Figure 10: Impact on the amount of caproic acid on the capturing behavior of fine limestone particles in a high pressure grinding test (force-controlled press) using a partially confined particle bed [64].

Moreover, Recchi et al. [53] reported that traditional grinding aids such as ethanolamines, glycols or inorganic salts are surprisingly inefficient in vertical roller mills (VRMs), where grinding is also caused by high pressure stresses. Within this study, the authors achieved much better results by adding an innovative grinding aid containing high-boiling compounds and thickening agents by means of a new grinding aid dosing system. They assumed that the addition of the usual grinding aids directly inside the mill in combination with the higher mill ventilation of VRMs facilitates the early evaporation of the additive as well as its removal from the mill with the ventilation air. Indeed, mill ventilation is different in VRMs and may cause overlapping impacts on the grinding aid performance. However, since also traditional grinding aids have comparatively high boiling points (partly above 300 °C), it is doubtful that this mechanism alone causes the observed effects. Accordingly, Rechenberg [34] showed that the content of TEA or propylene glycol in the exhaust air of tumbling ball mills was independent of the temperature even up to clinker temperatures of 150 °C. In the case of Recchi et al. [53], the optimization of the VRM performance by adding high-boiling compounds and thickening agents may be an indication for a further aspect: It is conceivable that those kind of additives cause a more cohesive powder, leading to both a higher product retention time on the grinding table as well as an improved particle capturing under the grinding roll achieved by a more stable particle bed (compare high flowability investigated by Oettel and Husemann [64]). This would also explain why VRMs often demand the additional injection of water, which is usually assumed to "stabilize the particle bed". Unfortunately, there is a lack of studies on grinding aid effects in high pressure grinding systems, which is why this explanation should rather be seen as a thesis.

For batch-wise operated dry stirred milling, Prziwara et al. [56] found that the grinding result also depends on the product flowability which was specifically adjusted by different grinding aids. In contrast to VRMs, high flowabilities generally appeared to be more favorable in the batch operated stirred mill. The authors also showed that the powder flowability may have completely different effects depending on the process parameters of the mill and concluded that the flow behavior of the product powder determines the amount of particles that are captured between the colliding grinding beads (see Figure 11). Thus, the stress intensity as well as the product-related stress frequency inside the mill does not only depend on process parameters, but also on the applied grinding aid. The results indicate, that the grinding aid needs to be selected with a special regard to the stress conditions inside the mill, especially for those mills that enable very variable grinding conditions.

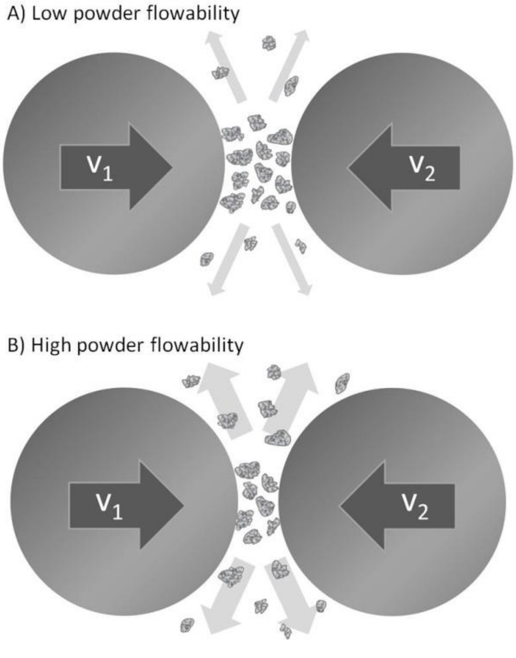

Figure 11: Influence of the powder flowability (specifically adjusted by diethylene glycole, DEG and heptanoic acid, HepAc) on the capturing of limestone particles between colliding grinding beads [56].

4. Grinding aids in industrial grinding processes

4.1. Transfer from batch to continuous processing

Laboratory experiments based on batch-wise operated mills are still the most common measure for selecting grinding aids and grinding aid concentrations. However, a reliable transfer of results obtained by batch-wise laboratory milling to continuously operated processes is hardly possible, as a number of overlapping parameters cannot be included in batch-wise experiments. Thus, remarkable differences regarding the grinding performance between laboratory experiments and industrial scale operations are very common. Assaad [83] showed that laboratory trials strongly underestimate the grinding aid effects in comparison to industrial grinding for cement grinding. Thereby, energy savings of 7-9 % were achieved in laboratory grinding, while doubling the amount of saved energy (13-18 %) in the industrial scale. Also, the particle size distribution varied between the different scales.

Results of different papers (see e.g.[2][58]) and own experience show that the most important impact is caused by the additive-induced change of the product flow behavior, which alters the retention time of the product material inside the mill. For example, Figure 12 shows that the concentration of TEA during the milling of cement in a continuously operated tumbling ball mill changes the transport behavior; among others by increasing the non-axial flow rate as well as the width of the residence time distribution (seen by the Bodenstein number which is equivalent to the Peclet number). By the combination of these effects on both the micro and macro level, a maximum product fineness is obtained at medium TEA concentrations [23]. In the worst case, high powder flowabilities may lead to an insufficient number of stress events on the material on its way through the mill. Obviously, such effects cannot be observed in batch-wise operated mills. Prziwara et al. showed that grinding aids causing high powder flowabilities are beneficial to batch-wise grinding of limestone in a dry stirred mill [56], while the same additives lead to an inferior process in the continuous single-passage grinding mode [58]. In contrast to that, Scheibe et al. [28] showed that grinding aid effects seen in laboratory tumbling mills can be transferred to industrial processes, at least in its tendency. However, they only investigated small concentrations of TEA, whereby the impact on the flow properties of the product is assumed to be very low. In a later paper, Scheibe et al. [2] clearly showed that higher amounts of TEA indeed lead to a reduced retention time within a passage-wise operated tumbling ball mill, especially due to the additive-induced increase of the powder flowability. They also stated that the addition of excessive grinding aid amounts above the optimum concentration leads to a decreasing grinding performance.

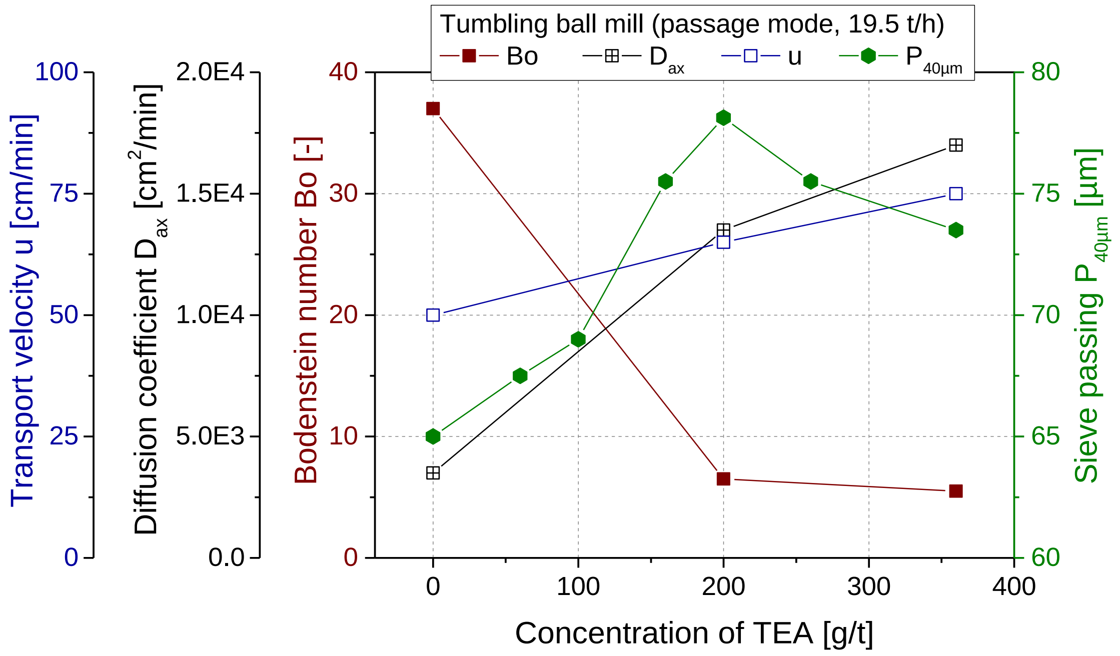

Figure 12: Impact of the TEA concentration on transport characteristics and grinding performance for milling cement in a passage-wise operated tumbling ball mill (values taken from [23]).

Besides the retention time inside the mill, further important aspects are the scale-dependent stress conditions inside the mill, the additional ventilation within continuous mills, the varying grinding temperature as well as the additional use of screening or classification devices [83]. Especially the use of screens and classifiers (especially when grinding in closed circuits) prevents the accumulation of very fine particles inside continuously operated mills. This in turn is an important issue within batch-wise milling experiments, because especially the fine particle fractions have a strong impact on the micro-processes inside the mill (see chapter 2.1). On top of that, grinding aids often have more decisive impacts on fine particles than on coarse particles. Thus, it is not surprising that the Bond Work Index (BWI) is often independent of the grinding aid [28], as the bond test includes the removal of fine particle fractions from the mill as well as its replacement with fresh material. Inspired by Bond, Assaad [84] developed a new laboratory method which aims for mimicking the industrial closed-circuit mode. The method also includes the periodic screening of the mill content in order to remove and analyze the fine particles. By repeating this procedure and balancing the fine and coarse fractions, the material circulation of a closed circuit process is simulated. The author found that the method gives a higher consistency of the grinding aid impacts obtained from laboratory and industrial grinding. However, it needs to be noted that this method does not consider impacts of retention time, classification efficiency or temperature, either. In a further study, Assaad [85] therefore investigated the impact of the grinding temperature on the performance of alcohol amine grinding aids in a laboratory tumbling ball mill. At least for these grinding aids, he did not find a significant influence of the temperature in the range of room temperature to 100 °C. How far this observation may be valid for other grinding aid types is difficult to say.

In addition to the actual grinding process, the classification step in closed-circuit mode may cause overlapping grinding aid effects, which are not considered by laboratory grinding tests. Especially grinding aids, which cause a strong reduction of the particle agglomeration, can bring further positive effects in closed-circuit processes. The impact of grinding aid additives on the classification process is discussed separately within the next chapter.

Altogether, it is still difficult to say in how far the grinding aid effects obtained from laboratory mills can be transferred to industrial-scale processes. The present studies indicate that the transferability probably depends on various material-related aspects (e.g. the impact of the grinding aid on bulk, flow and agglomeration behavior) as well as process parameters (e.g. process mode or differences of the milling conditions).

4.2. Further grinding aids effects in closed-circuit processes

As closed-circuit processes consist of different process units such as milling, classification, separation but also bulk and pneumatic conveying, grinding aids may lead to very divers and complex impacts on these industrial processes [2]. Besides milling, the classification step is assumed to be the most decisive process unit, because it determines the quality of the fine product. In addition to that, a bad classification performance may result in a high recirculation factor by increasing the reject flow of (agglomerated) fines to the mill, which in turn, directly affects the milling performance. Since grinding aids are known to influence the agglomeration behavior of the product, it seems obvious that these additives do also cause overlapping impacts on the classifier performance.

Scheibe et al. [2] were one of the first to show that grinding aids can also have positive influences on the air classification. For instance, the authors had a closer look to the classifier bypass, which is a measure to quantify the amount of fine particles that are mistakenly rejected by the classifier and led back to the mill. They demonstrated that this parameter is significantly reduced once a grinding aid is added to the process. For a constant product throughput, the material load of the mill is reduced, which results in both more efficient grinding conditions as well as a lower material recirculation. This in turn further increases the classifier performance. Sottili et al. showed that these aspects enable an increase of the overall production rate of 19 %, when applying 0.02 wt.-% of a commercial grinding aid blend in a closed-circuit tumbling mill cement plant. Simultaneously, the specific energy demand decreased of about 16 %. Due to the fact that the mean mill retention time decreased from 6 to 4.6 minutes with the addition of the additive, lower amounts of fine particles were produced in each grinding passage which is why the material recirculation almost doubled. Despite the higher resulting classifier load, they still detected higher separation efficiencies in the case of the grinding aid addition. As illustrated in Figure 13, grinding aid cause even greater improvements of the classification process (represented by higher yields of fine particles within the fine product) for higher specific material loads in the classifier chamber [23]. This clearly shows that especially the grinding operations with high material loads of the grinding plant can benefit from grinding aids.

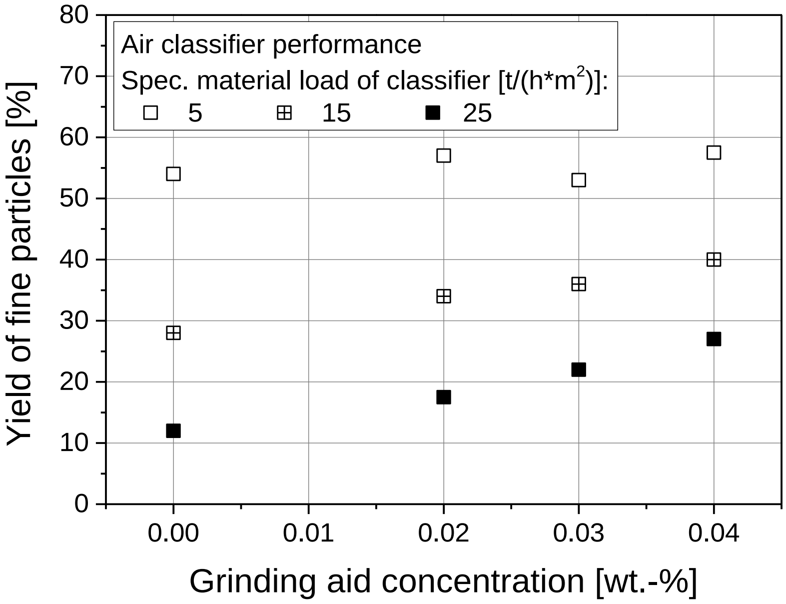

Figure 13: Yield of fine particles as a function of the grinding aid concentration for different specific material loads in the classifier chamber (data taken from [23]).

Toprak et al. [86] also showed that different grinding aids have a positive impact on the classifier bypass. Within their study, in particular grinding aid blends containing alcohol amines and hydroxyl amines caused a significant decrease of the bypass from initially 22.6 % to 15.7 % and 15.6 %, respectively. Toprak et al. [87] repeatedly identified a reduction of the by-pass through the addition of grinding aids in a further study, while they did not observe a significant change of the separation sharpness. Unfortunately, they did not give any information on the material loads of the classifier air. Therefore, it cannot be excluded that the experiments were carried out in an operating range, where grinding aid effects are rather low (compare Figure 13). Other mixtures containing modified amines or PCEs only caused medium effects. However, it is difficult to evaluate the impacts of these chemicals on the classifier performance solely based on these results, since the applied concentration was not held constant for the different additives. Furthermore, no information about the concentration of the active component within the used additive blends was given. This may explain opposing trends presented by other authors.

For instance, Mishra et al. [88] found that – in contrast to batch-wise milling – PCE containing grinding aids are favorable in closed-circuit grinding compared to TEA, which they attributed to superior effects of PCEs on the classification process. However, no evidence for this assumption is presented. In a recent study it was also shown that TIPA is more effective regarding the reduction of by-pass values compared to TEA and diethylene glycol, whereas the separation sharpness only slightly changed with the grinding aids [87]. In the case of ultrafine classification of limestone, Husemann et al. [75] showed that the addition of 0.7 % of stearic acid increased the mass of fine particles < 1 µm inside the fine fraction significantly.

Moreover, Scheibe et al. [2] stated that bulk conveying may be more difficult when grinding aids are applied, especially for a resulting increase of the powder flowability in combination with a steep conveyor belt. In contrast to that, pneumatic conveying is usually easier when grinding aids are added. Sottili and Padovani [89] also mentioned that the use of grinding aids can lead to a higher filter load as well as a lower grinding media wear, but without presenting experimental data for that.

4.3. Results from continuously operated grinding processes

Most of the available studies on the investigation of grinding aids in continuously operated grinding plants focus on closed-circuit operations with tumbling ball mills. For instance, Sottili and Padovani [90] showed that industrial closed-circuit grinding of cement clinker using a tumbling ball strongly benefits from grinding aid applications. Within their study, the use of grinding aids led to a decrease of the medium retention time of the material inside the mill by 25 %, which in turn, resulted in a 100 % increase of the product recirculation. Nevertheless, the overall process performance was not negatively affected by that, as the production rate was increased by 10-30 % [90] or even 25-40 % [89] at a constant product quality. For a comparable closed-circuit tumbling mill grinding plant, Lai et al. [91] achieved enhancements of the cement production rate of up to 23.5 % by adding PCE-based grinding aids. Similar enhancements up to 20 % were also reported by Schrabback [72]. Toprak et al. [86] were able to increase the production capacity of a 4500 cm^2/g Blaine cement up to 24 % with the addition of appropriate grinding aids containing either alcohol amines, hydroxylamine or mixtures of PCEs and amines. The authors also reported that the material circulation load significantly decreases as a consequence of the grinding aid additive addition. Similar results were demonstrated by Dombrowe et al. [23], where the addition of grinding aids led to a decrease of the circulation factor from 5 to 2-3.

An investigation on VRMs was carried out by Pohl et al. [92]. They achieved an increase of the production capacity from 70 to 90 t/h for the production of CEMII-32,5 cement by applying glycols as a grinding aid. Thereby, a simultaneous reduction of the specific energy consumption from 19,7 to 18,5 kWh/t (exluding energy demand for the pneumatic transport) was accomplished.

Grinding aids were also investigated in continuously operated dry stirred mills in open-circuit mode (passage grinding). Altun et al. [93] showed that triisopropanolamine-based (TIPA) grinding aids leads to a higher reduction of the specific energy demand for clinker grinding than additives based on glycols or TEA. They achieved the best effects with grinding aid concentrations of 0.1 wt.-%, which is comparatively high for the obtained Blaine surface < 3000 cm^2/g. Whether dry stirred mills generally demand higher grinding aid concentrations than conventional ball mills is difficult to say, as the author only described “TIPA-based” grinding aids without giving further information about the content of the surface active component within the used grinding aid blend. Furthermore, the authors showed that the material load inside the mill decreased with increasing grinding aid concentration for a constant product throughput. Thus, grinding aids also affect the ball-to-powder ratio inside the mill, which may be a further positive effect at higher additive concentrations. According to calculations done by the authors, the lower mill hold-ups also indicate reduced mean mill retention times, which normally counteract a high size reduction. Nevertheless, the best grinding performance was achieved with high additive concentrations. Prziwara et al. [58] investigated the impact of the powder flowability, which they specifically adjusted with comparatively high concentrations of different grinding aids, on the open-circuit grinding of limestone. In contrast to the aforementioned study, they used a special stirrer design, which is equipped with an additional classifier wheel in order to hold back the grinding beads inside the mill. As mentioned before, they found a significantly higher grinding efficiency in the case of low powder flowabilities. Surprisingly, higher mill hold-ups were found for the powders with high powder flowabilities, which the authors attributed to additional impacts of the internal classifier wheel. The comparison of the two studies indicates, that grinding aid effects may also depend on certain constructive elements of the mill, such as the design of the mill outlet.

Further grinding aid studies on continuous grinding processes were carried out for jet opposed mills. For instance, Schwarzwälder et al. [94] presented a reduction of the specific energy demand of 83 % and 62 % by applying grinding aids in the ultrafine jet milling of a ceramic pigment and a metal oxide, respectively. For the fine grinding of a hydraulic bonding agent they still found a decrease of the specific energy by 56 %. Unfortunately, the authors do not give any information on the ground materials, the kind of grinding aids or their concentration. Thus, it is hardly possible to obtain any important information on grinding aid effects in opposed jet mills from this study. This is also the case for a study on jet mills by Miranda and Yilmaz [95], who determined a strong increase of the product throughput (up to several 100 %) when grinding a ceramic oxide by means of an additive, but without giving important information on the product, grinding aid or process parameter. Results presented by Godet-Morand et al. [96] demonstrated, that the grinding aids success also depends on the product particle size. In the best case, they also obtained very high production rate increases of 88 %. Husemann et al. [75] showed that the product particle size is not significantly affected by the addition of 0.7 % stearic acid as additive for the ultrafine grinding of limestone in a jet opposed mill. Unfortunately, the authors did not present any data regarding the impact of the stearic acid on the resulting product throughput or energy efficiency. Altogether, it can be seen as a kind of predicament that three out of four present studies reveal huge potentials of grinding aid applications in jet opposed milling, but without paying more attention to this topic; such as performing further systematic investigations or just giving more information on the used additives. Since other studies on grinding aid effects in jet mills are hard to find, future systematic investigations on this topic would be highly appreciated.

5. Influence of grinding aids on product properties

As surface active grinding aids mainly stay adsorbed on the product particle surface even after grinding, further impacts of the additives on the final product properties or processing properties of the ground material are not surprising. These effects are especially well-known in the field of construction materials. However, they are not the main focus of this review paper. Thus, the most important of these aspects are summarized briefly within the following chapters, since they may limit the choice of appropriate grinding aids but also cause significant benefits regarding the product quality.

5.1. Construction materials

Especially in the field of construction materials, the effects of remaining grinding aid molecules on the handling properties of the ground materials along the further processing as well as on the final product characteristics are crucial. The reason is that they may exclude even those additives, which lead to promising grinding results. Therefore, a variety of studies have already investigated the impact of grinding aids on these aspects. The most important effects may be roughly divided in three different groups:

a) Processing properties: As shown in various studies, grinding aid molecules maintain their stabilizing effects even after mixing the ground particles with water. This of course significantly influences the rheological properties of the particulate paste, such as the viscosity and the spreading behavior as well as the water demand (e.g. [97-99]).
b) Chemical hydration reaction: In the field of cement chemistry, the influence of chemical additives on the chemical hydration reaction when mixing a fine particulate binder (such as cement clinker) with water and other filling materials as well as fine and coarse aggregates is of major interest. The kinetics of these reactions primarily determine the setting behavior of the paste, and thus, its processability especially in terms of time for mixing, transporting, placing and compacting. The impact of remaining grinding aid molecules on the hydration reaction and the subsequent

setting behavior was already investigated and discussed within a variety of studies (e.g. [70, 71, 100-102]).

c) Hardening of the paste as well as strength development and final strength of the building component: As a consequence of influencing the hydration reaction as well as the reaction products, grinding aids may also change the strength of the final building component. In fact, the majority of those scientific papers, which investigate grinding aid impacts on the dry grinding of cementitious materials, evaluated the influence of the additives on the strength development simultaneously (see e.g. [93, 100, 103].

5.2. Other examples

Other impacts of grinding aid molecules on the product properties, apart from the construction sector, are only reported sporadically. For instance, Toraman et al. [104] showed that color properties like the lightness, the total color difference or the whiteness index of ground calcite are influenced by certain grinding aids. These effects are also independent of the obtained product fineness. Badjena [37] also reported that grinding aids influence properties like shinning and leafing characteristics in the case of brass particles and pigments. Here, smaller concentrations (0.1 %) of stearic acid led to the best results. The author also observed changes of the particle shape, while more equiaxed shapes were obtained with stearic acid. For the grinding of graphite particles, Hayashi [105] showed that certain grinding aids like tri-sec-butylaluminate and octofluoropentanol cause a thinning of the flaky graphite particles (see Figure 14). The authors attributed this to chemisorption of the grinding aid molecules on the broken bond planes, which in turn may facilitate the fracture of particles along cleavage planes. However, evidence for this assumption was not presented.

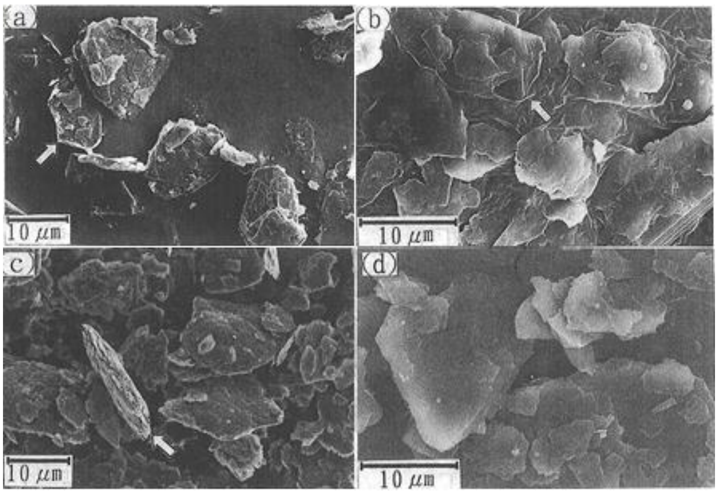

Figure 14: Shape of graphite particles after processing with different grinding aids; a: raw material, b: grinding without additive, c: grinding with tri-sec-butylaluminate and d: grinding with octofluoropentanol (pictures taken from [105]).

Moreover, Hasegawa et al. [55] observed dependences of the particle crystallinity on the grinding aid for the ultrafine grinding of limestone. As already mentioned above, further effects were reported in the field of co-milling, where the applied additives did not only result in an improved powder flowability of the micronized pharmaceuticals, but also in a beneficial dissolution behavior of these compounds [48-50].

6. Conclusion

Even though the benefits of grinding aids have already been shown in various experimental studies and industrial applications, the selection of appropriate chemicals and concentration is still mostly based on empirical knowledge. As shown in this review article, it is still hardly possible to derive a comprehensive understanding regarding the additive impacts on the grinding performance, even though more than 100 papers on this topic can be found in the literature.

On the one hand, there is a lack of understanding towards how the additive molecules interact with the solid surface. In particular, it is not yet understood how the molecular structure of the additive influences the adhesion forces between the particles, and thus, the particle and bulk behavior of the product. It is also hardly known why many grinding aids act solid-specific and which particular chemical parameters are relevant for this relation. On the other hand, it is also only partly known how the changes of the particle and bulk behavior may affect the micro- and macro-processes inside the mill as well as the whole grinding plant operation. This may especially be critical when transferring findings on grinding aids to other processes, as the impact of grinding aids may be completely different depending on the technical equipment or process mode. Altogether, common rules for selecting appropriate grinding aids do not exist. The high difficulty in the selection and the efficient application of grinding aids gets also clear by considering a further aspect: The variety of applied chemicals, ground materials and target finenesses, available mill types and process designs, mill and process parameters as well as analysis methods complicate the development of a comprehensive understanding based on the present studies.

This review article reveals that further extensive scientific work has to be done to develop such a comprehensive understanding. In a first instance, more investigations on the “particle-scale” need to be carried out to understand the specific interactions between the applied chemical and the solid product surface. It needs to be determined which physical-chemical properties of both, the additive as well as the solid surface, determine the mode of action of the grinding aid; especially regarding the adsorption strength, the reduction of the surface energy, the adsorption geometry or further steric stabilization effects. In a second step, a more comprehensive understanding is needed to which degree these aspects change the adhesions forces between the particles, and thus, properties like the agglomeration behavior of the particles, their dispersability, flow and fluidization properties or the compaction behavior of the powder. Finally, these findings are fundamental to estimate how the product reacts to the stressing conditions inside the mill, how the material is transported and how its behavior within air streams is changed or whether important product qualities of the powder are affected by the additives. Only if these very complex relations are understood, an efficient predictive selection of grinding aid additives will be possible for industrial processes in the future.

7. Appendix

Table 2: Examples of applied chemicals that showed positive impacts on dry grinding in different mill types (TBM = tumbling ball mill, BBM = box ball mill, VBM = vibration ball mill, VDM = vibration disc mill, VRoM = vibration rod mill, PBM = planetary ball mill, SMM = stirred media mill, VRM = vertical roller mill) in the case of various ground materials, including ultrafine grinding (UF) to the submicron range. Grinding success is characterized by the fineness factor (*fineness factor calculation based on sieve residue or mean particle size instead of specific surface area).

	Ground material	Grinding aid	Mill type	Fineness factor [%]	Related conc. [wt.%]	Ref.
Liquid / dissolved	Cement and cement clinker	Water	n/a	1.17	n/a	[31]
			TBM	1.20*	1.0	[76]
		Hexane	n/a	1.14	n/a	[31]
		Paraffin oil	n/a	1.18	n/a	[31]
		Mixture of aromatics	n/a	1.18	n/a	[31]
		Rape seed oil	n/a	1.20	n/a	[31]
		Dioxan	n/a	1.21	n/a	[31]
		Acetone	n/a	1.20	n/a	[31]
		Ethyl acetate	n/a	1.23	n/a	[31]
		Isopropanol	n/a	1.28	n/a	[31]
		Ethylene glycol	TBM	1.21	0.05	[59]
		Water + ethylene glycol (50/50)	TBM	1.10	0.04	[67]
		Diethylene glycol	n/a	1.27	n/a	[31]
		Water + diethylene glycol (50/50)	TBM	1.07	0.04	[67]
		Propylene glycol	TBM	1.24	0.05	[59]
		Polypropylene glycol	TBM	1.18	0.05	[59]
		Lignin-based	TBM	1.12	0.03	[11]
		Mixture of fatty acids	TBM	1.07*	0.3	[76]
		Polyethylene glycol 6000	TBM	1.03*	0.5	[76]
		Fatty acid salts	TBM	1.23*	0.5	[76]
		Base of titanate + phosphite	TBM	1.40*	0.75	[76]
		Butylacrylate	TBM	1.07*	0.5	[76]
		2-Ethylhexylacrylate	TBM	1.07*	0.5	[76]
		Acetate	TBM	1.07*	0.5	[76]
		Triethanolamine	TBM	1.18	0.0175	[27]
			TBM	1.08	0.06	[80]
			VDM	1.16	0.06	[80]
			TBM	1.03	0.03	[106]
			TBM	1.7*	0.1	[76]
			TBM	1.1	0.1	[60]
		Modified triethanolmine	TBM	1.06	0.03	[106]
		Water + triethanolmine (50/50)	TBM	1.06	0.04	[67]
		Water + triethanolmine (60/40)	TBM	1.40	0.10	[73]
		Water + polycarboxylate ether (60/40)	TBM	1.26	0.10	[73]
		Water + dodecylbenzene sulphonic acid (50/50)	TBM	1.07	0.04	[67]
		Water + sulphite waste liquor (70/30)	TBM	1.03	0.065	[67]
		Phenyl polyglycol ether	TBM	1.25	0.0175	[27]
		Heptanoic phosphonic acid	TBM	1.21	0.0175	[27]
		Decanol	TBM	1.14	0.0175	[27]

		Potassium ethyl xanthate	TBM	1.13	0.0175	[27]
		Lignosulfonate	TBM	1.11	0.0175	[27]
		Dipotassium phosphate	TBM	1.07	0.0175	[27]
		Organophosphate	TBM	1.06	0.0175	[27]
		Methyl silicon oil	TBM	1.04	0.0175	[27]
		Oleic acid	BBM	1.05	0.025	[107]
			TBM	1.06	0.1	[98]
		Sunflower oil	BBM	1.04	0.1	[107]
		Amine-based	TBM	1.19	0.096	[108]
			TBM	1.51	0.08	[77]
		Glycol-based	TBM	1.07	0.128	[108]
			TBM	1.29	0.08	[77]
		Acid-based	TBM	1.03	0.042	[108]
		Polymer-based	TBM	1.1	0.1	[60]
	Cement raw meal	Soapstock (sunflower oil)	TBM	1.46	0.5	[66]
		Soapstock (corn oil)	TBM	1.38*	1.0	[66]
		Triethanolamine	TBM	1.24*	1.5	[66]
	Limestone	Water	SMM	1.1	0.25	[104]
		Triethanolamine	SMM	1.3	0.25	[104]
			TBM	1.15	0.03	[61]
			TBM	1.13	0.1	[67]
			VBM	1.44	0.1	[32]
		Triisopropanolamine	VBM	1.48	0.1	[32]
		Ethylene glycol	SMM	1.3	0.25	[104]
			TBM	1.09	0.1	[67]
			VRoM	2.0^{uf}	3.6	[55]
		Diethylene glycol	VBM	1.34	0.1	[32]
		Triethylene glycol	VBM	1.26	0.1	[32]
		Propylene glycol	VRoM	2.1^{uf}	3.4	[55]
		Methanol	VRoM	2.7^{uf}	4.2	[55]
		Ethanol	VRoM	2.5^{uf}	4.2	[55]
			VBM	1.48	0.1	[32]
		1-Propanol	VRoM	2.0^{uf}	4.3	[55]
		1-Hexanol	VBM	1.43	0.1	[32]
		1-Decanol	VBM	1.24	0.1	[32]
		1-Heptanoic acid	VBM	1.48	0.1	[32]
		1-Undecanoic acid	VBM	1.51	0.1	[32]
		Oleic acid	TBM	1.11	0.005	[67]
		Poly-acrylic-acid-based	SMM	1.3	0.2	[109]
		Water + sulfite waste liquor (70/30)	TBM	1.02	0.05	[67]
	Quartz	Water	VRoM	1.1^{uf}	5.6	[78]
			TBM	1.05	0.025	[67]
		Methanol	VRoM	1.9^{uf}	4.6	[78]
		Ethanol	VRoM	2.0^{uf}	4.6	[78]
		2-Propanol	VRoM	1.8^{uf}	4.5	[78]
		1-Butanol	VRoM	1.6^{uf}	2.8	[78]
		1-Hexanol	VRoM	1.7^{uf}	4.3	[78]
		Cyclohexanol	VRoM	1.7^{uf}	5	[78]
		Ethylene glycol	VRoM	1.8^{uf}	6	[78]
			TBM	1.06*	0.0175	[27]
			TBM	1.02	0.05	[67]
		Propylene glycol	VRoM	2.0^{uf}	6	[78]
		Glycerol	VRoM	1.8^{uf}	6.8	[78]
		Benzene	VRoM	1.2^{uf}	3.1	[78]

		Hydroxamic acid	TBM	1.08*	0.0175	[27]
		Sodium stearate	TBM	1.08*	0.0175	[27]
		Heptanoic phosphonic acid	TBM	1.07*	0.0175	[27]
		Methyl silicon oil	TBM	1.07*	0.0175	[27]
		Triethanolamine	TBM	1.06*	0.0175	[27]
			TBM	1.03	0.05	[67]
		Cetyl sulfate	TBM	1.05*	0.0175	[27]
		Tributyl phosphate	TBM	1.05*	0.0175	[27]
		Sodium cetyl sulfate	TBM	1.03*	0.0175	[27]
		Dipotassium phosphate	TBM	1.01*	0.0175	[27]
		Lignosulfonate	TBM	1.02*	0.0175	[27]
		Potassium ethyl xanthate	TBM	1.06*	0.0175	[27]
	Feldspar	Water	VRoM	1.2^{uf}	4.8	[62]
		Methanol	VRoM	2.1^{uf}	6.2	[62]
		Ethanol	VRoM	2.5^{uf}	6.2	[62]
		2-Propanol	VRoM	2.1^{uf}	6.2	[62]
		1-Butanol	VRoM	2.8^{uf}	6.	[62]
		1-Octanol	VRoM	1.7^{uf}	3.9	[62]
		Cyclohexanol	VRoM	2.4^{uf}	7.3	[62]
		Tetraethoxysilane	VRoM	2.5^{uf}	7.1	[62]
		Various commercial blends	SMM	1.33*	0.2	[110]
	Blast Furnace Slag	Mix of water/PCE/TIPA	TBM	1.14	0.2	[71]
		Mix of water/PCE/TEA	TBM	1.09	0.2	[71]
		Mix of water/PCE/DEG	TBM	1.08	0.2	[71]
	Fly ash	Triethanolamine + ethylene glycol (1:1)	TBM	1.14	0.05	[111]
	Alumina	Methanol	VRoM	15.6^{uf}	4.6	[112]
		Ethanol	VRoM	12.2^{uf}	2.9	[112]
		2-Propanol	VRoM	13.9^{uf}	2.9	[112]
		Ethylene glycol	VRoM	12.2^{uf}	6.3	[112]
	Calcined black talc		PBM	1.17	n/a	[113]
	Silicon carbide pigment	Polyethylene glycol ether	VBM	2.0^{uf}	1.0	[75]
	Silicon carbide	Polyethylene glycol ether	VBM	2.3^{uf}	1.0	[75]
	Silicon nitride	Polyethylene glycol ether	VBM	1.18	0.5	[75]
	Iron oxide pigment	Polyethylene glycol ether	VBM	1.1^{uf}	1.0	[75]
	Graphite	Tri-sec-butylaluminate	n/a	2.7	1.6 mole/kg	[105]
		Octafluoropentanol	n/a	3.0	1.6 mole/kg	[105]
		1-pentanol	n/a	2.0	1.6 mole/kg	[105]
	Chitosan powder	Polyethylene glycol	PBM	1.75*	10.0	[38]
		Lauryl alcohol	PBM	2.07*	10.0	[38]
Solid	Cement and cement clinker	Carbon black		1.49	1.28	[43]
		Stearic acid	TBM	1.07	0.025	[35]
			BBM	1.09	0.025	[107]
		Lauric acid	BBM	1.06	0.025	[107]
		Myristic acid	BBM	1.07	0.1	[107]
		Sodium stearate	TBM	1.17	0.0175	[27]

		Sodium hydroxamic acid salts	TBM	1.16	0.0175	[27]
	Limestone	Calcium stearate	TBM	1.22*	0.4	[54]
			VBM	1.03	0.05	[63]
		Magnesium stearate	VBM	1.15	0.05	[63]
		Palmitic acid	VBM	1.08	0.10	[63]
		Stearic acid	VBM	1.13	0.10	[63]
	Soda glass	Lithium nitrate	VBM	47.4^{uf}	15.0	[41]
	Sericite	Lithium nitrate	VBM	2.8^{uf}	33.3	[42]
		Sodium nitrate	VBM	3.0^{uf}	33.3	[42]
		Potassium nitrate	VBM	4.2^{uf}	33.3	[42]
		Rubidium nitrate	VBM	4.7^{uf}	33.3	[42]
	Aluminum	Stearic acid	VBM	n/a	2.2-3.1	[36]
		Oleic acid	VBM	n/a	3.2-4.6	[36]
		Aluminum stearate	VBM	n/a	6.4-9.0	[36]
	Brass powder	Stearic acid	TBM	n/a	0.1-0.4	[37]
		Paraffin wax	TBM	n/a	0.1-0.4	[37]
		Oleic acid	TBM	n/a	0.1-0.4	[37]
	Zinc oxide	Sodium chloride	PBM	3.58^{uf}	n/a	[39]
	Nickel oxide	Amorphous carbon	VBM	1.36^{uf}	1.5	[114]
	Zirconia	Sodium chloride	PBM	3.75^{uf}	20.0	[40]
	Alumina	Sodium chloride	PBM	1.42^{uf}	20.0	[40]
	Iron oxide pigment	Nano-disperse silicon oxide	VBM	1.16^{uf}	1.5	[75]
		Nano-disperse alumina	VBM	1.57^{uf}	1.5	[75]
	Chitosan powder	Citric acid	PBM	1.12*	10.0	[38]
		Cholesterol	PBM	2.07*	10.0	[38]
		Lauric acid	PBM	2.43*	10.0	[38]
		Lauryl amine	PBM	2.80*	10.0	[38]
		Sodium lauryl sulfate	PBM	2.55*	10.0	[38]
		Capric acid	PBM	2.33*	10.0	[38]
		Myristic acid	PBM	2.95*	10.0	[38]
		Palmitic acid	PBM	2.95*	10.0	[38]
		Stearic acid	PBM	3.11*	10.0	[38]

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