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Influence of anticaking agents on the caking of sodium chloride at the powder and two-crystal scale

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ABSTRACT

The effectivity of the anticaking agents ferrocyanide, ferricyanide and iron(III) *meso*-tartrate on the caking of sodium chloride was studied at the powder scale and on a two-crystal scale. Using the integrated stirring energy as a measure of caking strength of the powders gives results that agree well with industrial experience with these anticaking agents. For two single crystals, the required separation force was used as a measure for the caking strength. In this case, higher dosages of anticaking agents are required to prevent caking. This is caused by an increase in the number of contact points between the crystals, as was concluded from the surface morphology of the sodium chloride crystals, which we studied using atomic force microscopy. This change of the surface morphology is in turn caused by the applied anticaking agents. This shows that it is not only the surface area, but also the number of contact points, and thus the particle size distribution, which are critical in determining the optimal dosage of anticaking agents on caking powders.

1. Introduction

Caking, or the agglomeration of a free-flowing powder into lumps, is a major problem when handling solid hygroscopic particulate materials, and has therefore been studied for a long time [1,2]. Many different mechanisms for caking exist. For (crystalline) hygroscopic materials caking is commonly caused by partial dissolution and subsequent recrystallisation of the solid during humidity variation of the environment. When handling small amounts of material, caking can be prevented by keeping the material dry, or by adding a drying agent. However, at large scale this is no longer possible, and anticaking agents are required.

Sodium chloride (NaCl) is a well-known example of caking material. When used as table salt, caking can easily be prevented by adding some rice to a salt shaker. However, most of the sodium chloride produced is used by the chemical industry for the production of chlorine gas (Cl_2) by electrolysis, for which many tonnes of salt are shipped. At this scale, caking must be prevented by an anticaking agent. For sodium chloride, many anticaking agents are known [3]. Anticaking agents are usually crystal growth inhibitors [4]: by inhibiting crystal growth the crystals agglomerate much less. Since the 1950s, (sodium or potassium) ferrocyanide ($[Fe(CN)_6]^{4-}$) has been the most common anticaking agent for sodium chloride globally, and its influence on the growth of this crystal was already studied in 1965 [5,6].

Even though ferrocyanide works very effectively as an anticaking agent, it has some drawbacks during electrolysis. The iron causes iron hydroxide ($Fe(OH)_3$) formation on the membrane and electrodes, and the nitrogen forms nitrogen trichloride (NCl_3), an explosive gas. Because of its stability and ionic nature, ferrocyanide is also difficult to remove prior to electrolysis. Therefore, a new anticaking agent, iron(III) *meso*-tartrate (Fe-mTA, a 1:1 molar mixture of $FeCl_3$ and *meso*-$C_4H_6O_6$, active at pH 4–5) was developed [7,8]. This anticaking agent is nearly as effective as ferrocyanide, but less stable and therefore the iron can more easily be removed prior to electrolysis by adding lye. Also, it does not contain nitrogen, so no nitrogen trichloride gas is formed should the compound enter the dialysis process. Recently, we showed how both agents inhibit the crystal growth of sodium chloride at the nanometre scale [9,10].

The translation from growth inhibition at the nanometre scale to the prevention of caking at a bulk scale is not trivial. The nanometre scale experiments were performed in idealized systems and on very smooth surfaces. It is also known that parameters like water adsorption, deliquescence and moisture migration [11–14], as well as the contact angle and the amount of contact points between particles are very important in caking [15]. Caking has been studied mainly at the powder scale, by measuring the flowability of a material [16,17].

While the process of solid bridge formation is the major caking mechanism in hygroscopic crystalline powders [18], only a few studies have been performed that looked at the actual contact points between

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individual, polycrystalline, particles and studied the solid bridge formation between those particles [19–22], Also the effect of anticaking agents on the caking of powders has been studied surprisingly little [23,24].

In this paper we investigate the process of caking and the influence of anticaking agents thereon at the powder and at the two-crystal scale, in order to show that growth inhibition on the crystal surface at the nanometre scale and anticaking of materials at the powder scale are essentially the same phenomena.

2. Experimental

Two different types of experiments were performed. Caking was studied at the powder scale using a rheometer test. At the two-crystal scale, we used cleaved sodium chloride crystals and measured the bond strength between them using a pulley and a balance. In both cases, the force needed to break the bonds between the caked crystals is measured. This force has been measured for untreated sodium chloride and for sodium chloride treated with increasing amounts of anticaking agent. Various anticaking agents and related compounds were tested.

2.1. Powder cake strength

A method using a rheometer (Powder Flow Analyzer type TA-XT21, Stable Micro Systems) was developed to compare the caking behaviour of sodium chloride samples. The rheometer measures the vertical component of the force required to turn a two-fold segmented, twisted blade through a (caked) powder while slowly moving downward, forcing the powder to flow in a reproducible manner. The forces required for the deformation and flow of the powder were recorded and plotted against the distance travelled by the blade through the sample. The integral of this curve is proportional to the dissipated energy, which is a measure for the cake strength.

In each experiment, the blade rotated at 0.2 rad/s while moving down at a rate of 0.43 mm/s, until it reached a depth of 10 mm into the powder. The vertical component of the force was recorded continuously. The integral of this force versus travelling depth was calculated from 4 to 8 mm into the sample, ignoring the surface of the sample, since the surface is often strongly, but irreproducibly caked. This integral, which represents the energy required to break the caked powder, was taken as a measure for the cake strength of the sample.

Samples were prepared by filling a sealable plastic bag with 49 ± 0.1 g of sodium chloride of high purity. An identical particle size distribution for all samples was obtained by "splitting" a larger sample. The average edge length of the cubic crystals was 300 ± 20 μm as was verified by optical microscopy for many crystals of this batch. This corresponds to $D[3,2] = 300$ μm. To this bag one gramme of demineralised water was added, in which the anticaking agent had been dissolved. This corresponds to 2.0% water content, which is comparable to salt production conditions. The bag was closed and the salt and water were mixed for about 5 min, until a visually homogeneous mixture was obtained. Then, the salt was transferred to an aeration cylinder (see Fig. 1).

In the cylinder the sample surface was smoothened and the sample was compressed using the rheometer. A pestle was placed on top of the sample and pressure was applied by the rheometer up to 1 kg, while rotating the pestle at 0.4 rad/s. After compressing, the pestle was removed and the sample was dried by dry air, which was introduced through a gauze at the bottom of the cylinder, at 1.5 l per minute for at least 80 min. During this period caking takes place by crystallization of salt from the brine between adjacent crystallites. In order to ensure that the water had completely been evaporated, the sample was weighed before and after drying.

After drying, the cylinder was transferred to the rheometer and the cake energy was measured. To check the reproducibility of the data, each sample condition was measured at least 4 times. The average caking energies were compared with the caking energy for clean sodium chloride, resulting in Relative Caking Energies (RCE), which were used for the evaluation of the results.

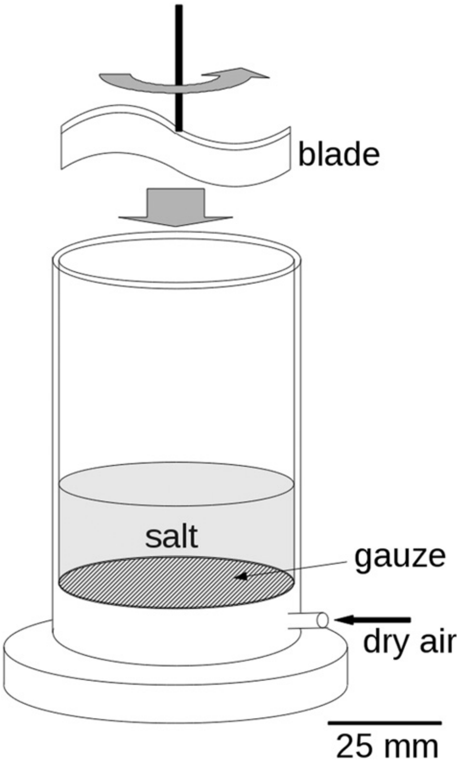

Fig. 1. The used aeration cylinders. The sample was placed in the cylinder on top of the gauze, compressed and afterwards dried by the dry air flow from the bottom.

All measurements include a very small, free flowing shear component. However, this component is negligibly small as was verified by measuring fresh, free flowing, non-caked NaCl powder in the same set-up. In addition, measurements for the different anticaking agents were always compared to measurements of caked clean salt (i.e. without additives). See e.g. left most column of Fig. 3.

RCE values were measured for several anticaking agents at several concentrations, given in parts per million (ppm). In the powder cake experiments, ppm was defined as mol active substance per 10^6 mol solid sodium chloride. For potassium ferrocyanide the concentrations were 0.8, 1.1 and 2.0 ppm and for potassium ferricyanide the concentrations were 0.07, 0.14, 0.3 and 0.6 ppm. Further concentrations were measured, but using a different batch of NaCl. Even though each set of data is internally consistent, it is not possible to compare data between batches, because differences in the particle size distribution and particle roughness lead to systematic differences. For the analysis, we used the most complete data set, all based on the same batch of NaCl crystals to compare the anticaking agents.

Since tartaric acid has two identical chiral centres, it has three stereoisomers: the optically active L and D isomers, and the optically inactive *meso* isomer. A racemic mixture of the L and D isomers is referred to as *LD*-tartaric acid [25]. Since *L*- and *D*-tartaric acids are each other's mirror images, they cannot have a different effect on an achiral crystal like NaCl, which has mirror symmetry planes in its crystallographic structure. Therefore, we only studied the pure *L*-isomer. The racemic mixture *LD*-tartaric acid can form mixed complexes with iron and therefore can have different properties than the *L*-isomer has. Analogous to the definition of Fe-mTA, iron(III) *L*-tartrate is defined as Fe-LTA and iron(III) *LD*-tartrate as Fe-LDTA.

Fe-mTA and its stereoisomerically related compounds Fe-LTA and Fe-LDTA were studied at pH 2 and pH 4.5. At pH 2, Fe-mTA, Fe-LTA