# 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.


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## 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 $\left(\mathrm{Cl}_{2}\right)$ 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 $\left(\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{4-}\right.$ ) has been the most common anticaking agent

[^0]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 $\left(\mathrm{Fe}(\mathrm{OH})_{3}\right)$ formation on the membrane and electrodes, and the nitrogen forms nitrogen trichloride $\left(\mathrm{NCl}_{3}\right)$, 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 $\mathrm{FeCl}_{3}$ and meso- $\mathrm{C}_{4} \mathrm{H}_{6} \mathrm{O}_{6}$, active at $\mathrm{pH} 4-5$ ) 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
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 $0.2 \mathrm{rad} / \mathrm{s}$ while moving down at a rate of $0.43 \mathrm{~mm} / \mathrm{s}$, 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 $49 \pm$ 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 $300 \pm 20 \mu \mathrm{~m}$ as was verified by optical microscopy for many crystals of this batch. This corresponds to $\mathrm{D}[3,2]=300 \mu \mathrm{~m}$. 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 $0.4 \mathrm{rad} / \mathrm{s}$. 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,


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.
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.

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 $10^{6} \mathrm{~mol}$ 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 $L D$-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 $L D$-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) $L D$-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
and Fe-LDTA were studied at 3.15 and 6.3 ppm . At pH 4.5 , Fe-mTA was studied at 2.1, 4.2, 6.3 and 8.4 ppm , while Fe-LTA and Fe-LDTA were studied at 12.6 ppm .

### 2.2. Two-crystal cake strength

In addition to the experiments on powders, experiments were performed on two individual crystals to investigate the caking bond strength and the influence of the anticaking agents on this bond strength. In these experiments, caking was simulated by first placing the crystals in a humid environment for one hour, and afterwards drying them using a dry nitrogen flow. Cubic, \{100\}-facetted crystals were used, cleaved from melt grown sodium chloride crystals, which were purchased from Ted Pella, Inc. (Redding, Ca, USA).

The crystals had an approximate size of $3 \times 3 \times 4 \mathrm{~mm}$, and the contact surfaces were polished using a polishing cloth, in order to make them equally rough. The bottom crystal was glued onto a small weight, and an aqueous solution ( $12.5 \mu \mathrm{l}$ ) containing the anticaking agent was applied to the top face of this crystal. After the droplet had almost completely evaporated, the upper crystal, on top of which a small hook was glued, was placed on top of the bottom crystal. The top crystal was rotated by $45^{\circ}$ in order to avoid epitaxial matching, since this would greatly increase the cake bond strength and will rarely occur in a bulk sample.

After preparation, the stack of crystals was placed in a desiccator at a relative humidity (RH) of $75 \%$, to simulate caking at high humidity. This humidity was maintained by a saturated sodium chloride solution at the bottom of the desiccator. The desiccator was slightly warmed up by placing it on a hot plate set at $50^{\circ} \mathrm{C}$ for one hour in order to speed up evaporation. The temperature in the desiccator increased only a few degrees, which did not influence the experiments since both the solubility and deliquescence humidity of sodium chloride are almost independent of the temperature. Under these conditions, the crystals attract water and will slightly dissolve.

Afterwards, the crystals were removed from the desiccator, and placed in a different one in which the crystals were dried by a constant dry nitrogen flow for at least one hour. In this period, the attracted water is evaporated and the dissolved sodium chloride will recrystallise, forming a solid bridge between the two crystals. After drying, the stack was removed from the dry environment and subsequently placed on a balance in order to measure the cake bond strength (see Fig. 2).

The cake bond strength was measured by attaching the hook at the top crystal to a home-built lifting device and attaching a second, heavier


Fig. 2. Sketch of the set-up used to investigate the caking bond strength between individual crystals. The crystals are not in epitaxial contact, but the contacting \{100\} faces are rotated $45^{\circ}$ with respect to each other.
weight to increase the maximum pulling force. This crystal stack-weight assembly is weighed by the balance during pulling. The lifting device pulls at a very slow, but constant rate, avoiding breaking of the caking bond by an initial shock. The hook and the pulling direction were centred exactly to prevent tilting of the crystals and thereby introducing a torsion force to the system. The reading of the balance is recorded at the moment the bond breaks. Like the powder caking experiments, we report the cake bond strength relative to the value for the clean crystals, as a relative caking force (RCF).

To compare the results of the two-crystal experiments with the powder caking experiments, a method is required to compare the applied concentrations of the anticaking agents, because the surface to volume ratio is very different in both experiments, and anticaking agents are surface active substances. Therefore, the concentrations were rescaled to the surface of the powder particles. For cubic particles with an average edge length of $300 \mu \mathrm{~m}, 1 \mathrm{~mol}$ of NaCl represents an area of $0.54 \mathrm{~m}^{2}$. Therefore, 1 ppm of anticaking agent is equivalent to a coverage of $1.85 \times 10^{-6} \mathrm{~mol} / \mathrm{m}^{2}$. This coverage is defined as 1 ppm in the two-crystal (and surface morphology) experiments.

The two-crystal caking experiments were performed with three different anticaking agents: ferrocyanide, ferricyanide and $\mathrm{Fe}-\mathrm{mTA}$. Ferrocyanide was studied at $0.7,14,17.5,21,24.5,28,35$ and 70 ppm , ferricyanide at $7,14,17.5$ and 35 ppm and $\mathrm{Fe}-\mathrm{mTA}$ at 5,53 and 182 ppm . The anticaking agents were applied using a small $12.5 \mu \mathrm{l}$ water droplet in order to minimise surface roughening.

### 2.3. Surface roughening

The crystal surface roughening was studied using atomic force microscopy (AFM). Anticaking agents ( 14 ppm ) were applied to cleaved single crystal surfaces and then treated according to the procedure followed for the two-crystal experiments, except for the stacking of the crystals. The resulting surface morphology was mapped using a Dimension 3100 AFM in contact mode, with commercial silicon nitride tips.

## 3. Results

### 3.1. Powder cake strength

Fig. 3 shows the results of the rheometer experiments on powder caking. The method using the integrated energy gives relatively small


Fig. 3. RCE values for all studied anticaking agents: ferro- and ferricyanide, iron(III) tartrates at pH 4.5 and at pH 2 . Both ferro- and ferricyanide are effective anticaking agents. At pH 2 , none of the iron tartrates are effective anticaking agents, while at $\mathrm{pH} 4.5 \mathrm{Fe}-\mathrm{mTA}$ is effective. The other tartrates are much less active even at higher dosages. For Fe-mTA and ferricyanide we found that reducing the concentration reduces the effectivity, although the effectivity of ferrocyanide is not improved further at dosages above 0.8 ppm .
experimental variation, $2-18 \%$, at 4 experiments per condition. Such errors are small compared to other test methods, especially in the case of heavily caked powders [16]. The results are in agreement with industrial experience, since 1.4 and 5 ppm are used for ferrocyanide and Fe-mTA respectively. In Fig. 3 it can be seen that ferrocyanide is a very good anticaking agent at a dosage of 0.8 ppm . Raising the dosage further does not result in significantly better anticaking. Fig. 3 also shows that ferricyanide is approximately just as effective as ferrocyanide: at a dosage of 0.6 ppm , it is nearly as good as ferrocyanide at 0.8 ppm . Lowering the dosage of ferricyanide shows a reduction in anticaking effectivity. We were not able to compare the data to the low concentrations of ferrocyanide, since these were obtained on another batch of NaCl . However, it is very probable that the anticaking effectivity for ferrocyanide also decreases at lower concentrations, as this is also known from industrial practice.

From Fig. 3 it can be seen that Fe-mTA is a good anticaking agent at pH 4.5 , with an increasing effectivity for increasing dosage. Even though the dosages of $\mathrm{Fe}-\mathrm{LTA}$ and Fe -LDTA at pH 4.5 are relatively high, their anticaking effect is still limited. It can be seen that none of the iron(III) tartrates are good anticaking agents at pH 2 . The caking strength is reduced by only $20-30 \%$ as compared to clean NaCl , which is insufficient to prevent caking.

### 3.2. Two-crystal cake strength

The results from the two-crystal caking experiments are shown in Fig. 4. This method results in larger experimental variation than the rheometer method. Therefore more experiments (10-20) were performed per condition. The results were tested for significance using the Mann-Whitney U-test [26], the significance criterion used was 5\%. The experimental variation becomes especially large at the concentration where the anticaking agents start working, since at these concentrations about half the samples were nearly uncaked, while the other half of the samples were strongly caked.

The larger spread of the results in the two-crystal experiments might partly be due to a not completely uniform distribution of the anticaking agent on the crystal surface, although great care was taken to realize such an even distribution.

Fig. 4 as well as statistical analysis clearly shows that ferrocyanide and ferricyanide both reduce the caking bond strength, while Fig. 4 also shows that Fe-mTA is not effective. Ferrocyanide reduces the cake


Fig. 4. RCF values for crystals treated with various amounts of ferrocyanide, ferricyanide and $\mathrm{Fe}-\mathrm{mTA}$ at pH 4.5 . No significant decrease of caking is found for $\mathrm{Fe}-\mathrm{mTA}$, whereas ferrocyanide and ferricyanide strongly reduce caking. However, both ferro- and ferricyanide require a much higher dosage than required to reduce powder caking (see Fig. 3).
strength significantly at 8.75 ppm and higher. Ferricyanide also reduces the cake strength significantly, at 7 ppm and higher. Fe-mTA does not reduce cake strength at the applied concentrations and even seems to enhance it. However, this enhancement is not statistically significant. Since $\mathrm{Fe}-\mathrm{mTA}$ did not reduce caking in the two-crystal experiments, the inactive Fe-LTA and Fe-LDTA compounds were not studied using this method.

### 3.3. Surface roughening

Fig. 5 shows the surface morphology of NaCl , clean and after treatment with anticaking agents and after exposure to humid ( $\mathrm{RH}=75 \%$ ) air. As expected, dissolution in the adsorbed water layer and subsequent recrystallisation of the surface layer, causes some roughening, even on the clean crystals. For clean surfaces, some spikes are formed 100500 nm in height. In between these, the surface is relatively smooth, with macrosteps of $5-10 \mathrm{~nm}$ height.

Surfaces treated with $\mathrm{Fe}-\mathrm{mTA}$ look quite similar to the clean surface. Similar spikes are formed, though more than on the clean surface. They are somewhat lower, $100-250 \mathrm{~nm}$. In between, the surface is also relatively smooth, with features of 5-10 nm height.

Ferrocyanide and ferricyanide cause a very different surface morphology. The surfaces look very rough, with macrosteps and hillocks of 100-500 nm high. The surface treated with ferrocyanide has less macrosteps than the surface treated with ferricyanide, and it has large, smooth terraces in between the macrosteps, on which the steps are $2-5 \mathrm{~nm}$ high. The surface treated with ferricyanide does not have these terraces, and consists of many more hillocks.

## 4. Discussion

At the powder scale, the anticaking agents behave more or less as expected. The dosage required for good anticaking corresponds well to the industrial experience. For ferricyanide and Fe-mTA (at pH 4.5), the anticaking effect is found to decrease at lower dosage. For ferrocyanide and $\mathrm{Fe}-\mathrm{mTA}$, we found that increasing the dosage above the industrially applied amount ( 1 ppm and 5 ppm respectively) does not improve the anticaking effectivity significantly. Also ferricyanide is found to be a good anticaking agent, only slightly weaker than ferrocyanide.

The fact that Fe-mTA is not effective at pH 2 is probably caused by a difference in the complexation, since the colour of the solution changes from yellow ( pH 2 ) to green ( $\mathrm{pH} 4-5$ ). The colour of the Fe-LTA and Fe-LDTA also changes, namely from yellow ( pH 2 ) to red ( $\mathrm{pH} 4-5$ ), but both complexes are almost inactive as an anticaking agent at each pH condition. The relation between the complexation of the iron tartrates and their anticaking activity will be elaborated elsewhere [27].

At the two-crystal scale, the results deviate from those at the powder scale. Ferro- and ferricyanide do reduce the caking bond strength, but they require a much higher concentration than in the powder scale experiments: 10-20 ppm versus 1 ppm at the powder scale. Fe-mTA does not seem to work at all. This difference can be explained from the surface roughness, since it increases the number of contact points between the crystals. The more contact points, the stronger the crystals will cake [28]. At the powder scale, the number of contact points/lines will be approximately one per side face, as the crystals are expected to form mainly vertex/edge-surface contacts. This also explains that the particle size distribution is very important in preventing caking, since small particles will have the same amount of contact point per particle, but more contact points per unit of mass.

In the two-crystal experiments, the crystal surfaces are in nearperfect contact and therefore will have much more contact points, depending on the surface roughness. The surfaces roughened by the anticaking agents ferro- and ferricyanide will have contact points at


Clean



Ferrocyanide



Fe-mTA


Ferricyanide

Fig. 5. Surface morphology and cross-sections of the clean NaCl surface and after application of anticaking agents ( 14 ppm ), both after exposure to $75 \% \mathrm{RH}$. Top left: clean surface; top right: Fe-mTA; bottom left: ferrocyanide; bottom right: ferricyanide.
each local maximum. As an increased number of contact points increases caking, a higher concentration of anticaking agent is required than at the powder scale.

The smoother surfaces formed by Fe-mTA will have even more contact points, since there are relatively few spikes of only 100250 nm : almost every hillock will be in contact with the other crystal.

Therefore, even more contact points are present than in the case of ferro- and ferricyanide, requiring an even higher concentration of Fe-mTA. Unfortunately, this amount is above the solubility of Fe-mTA in water at pH 4.5 , so we were not able to apply Fe-mTA in this amount.

## 5. Summary and conclusions

It is shown that both caking strength and the influence of anticaking agents on caking can be studied quantitatively and reproducibly at the powder scale and on the two-crystal scale. The experimental variation is very small at the powder scale, compared to other testing methods, and therefore the integrated energy method is recommended for caking strength measurements. The caking strengths are very reproducible within a batch, but comparison between different batches is not possible owing to variations in particle size and roughness.

The effectivity of the anticaking agents at the powder scale is in good agreement with industrial experience. For $\mathrm{Fe}-\mathrm{mTA}$, the pH of the solution is critical for its anticaking effectivity. Furthermore, ferricyanide is nearly as effective as an anticaking agent as ferrocyanide.

Even though the same trends in anticaking effectivity can be detected at the two-crystal scale as on the powder scale, a higher amount of anticaking agent is required at the two-crystal scale. This is caused by the larger number of contact points between the crystals and therefore by the surface roughness. This increases caking and therefore a higher concentration of anticaking agent is needed. However, from a qualitative point of view, no essential differences were found between the micro- and macroscopic scales. The observed differences are due to differences in surface morphology. Thus growth inhibition induced by the anticaking agents as observed in situ by AFM in the idealised microscopic systems [10] is the mechanism by which anticaking agents work at the bulk scale.

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