Chapter 7

Summary

Anticaking agents are additives which prevent the agglomeration of a crystalline material into lumps, a process called caking. However, how they prevent caking is not known. In general, it is assumed that they inhibit crystal growth, thereby preventing solid bridge formation and thus caking. In this work, we investigate how anticaking agents work in more detail, using sodium chloride as a model system.

In chapter 2 surface X–ray diffraction is applied to show how the ferrocyanide ion adsorbs onto the surface of the sodium chloride crystal. It replaces a sodium ion and five surrounding chloride ions. We propose that because of the charge of the ferrocyanide ions adsorbed on the surface, the crystal can only continue growing by leaving a sodium vacancy, or by desorption of the ferrocyanide ion. As a consequence, the ferrocyanide ion blocks further growth of the crystals, thereby preventing caking.

In the third chapter, we show how the growth of sodium chloride crystals is inhibited by the anticaking agents ferrocyanide and iron(III) *meso*–tartaric acid. Using in–situ atomic force microscopy, it is shown how steps flow on clean crystals and how the step flow is inhibited by the anticaking agents. At sub–monolayer coverages, steps are temporarily pinned, while at higher coverages, no step movement is observed at all.

In chapter 4 the structure of the anticaking agent iron(III) *meso*–tartrate is discussed, as well as its interaction with the crystal surface. We derive its molecular structure using experimental techniques as well as molecular modelling. We show that the active complex is a binuclear iron(III) complex with two bridging *meso*–tartrate ligands. In solution, a water molecule coordinates to each iron atom. Probably this water molecule can be replaced when the complex adsorbs on the sodium chloride crystal surface. This adsorption results in step pinning, which in turn explains the anticaking activity of the iron(III) *meso*–tartrate complex.

Chapter 5 describes the effectivity of anticaking agents at a larger length scale compared to the preceding chapters. The anticaking agents ferrocyanide, ferricyanide and iron(III) *meso*–tartaric acid were studied at the powder scale and on a two–crystal scale. Results at the powder scale agree well with industrial experience with these anticaking agents, while at the two–crystal scale higher dosages of anticaking agents are required to prevent caking. This is caused by an increase in the number of contact points due to a change in surface morphology, which is in turn caused by the applied anticaking agents. Therefore 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.

The final chapter focuses on the caking of sodium chloride at low temperatures, which is caused by the formation of solid bridges of sodium chloride dihydrate in between the powder particles. Using the crystal structure, the morphology of the dihydrate crystals was determined. Also the growth rate of these crystals was determined, as well as the influence of anticaking agents on the growth rate. A likely candidate for the inhibition of dihydrate growth was found: iron(III) *L*–tartaric acid. In addition, the nucleation behaviour of dihydrate crystals was investigated. The nucleation rate was found to be extremely low and to increase with time. This is probably caused by the formation of a metastable prenucleation phase, which inhibits the nucleation of dihydrate crystals. The influence of the same additives on the nucleation rate was found to be limited.