

Our purpose is to study the crystal growth kinetics of sodium and potassium nitrates and the morphology change due to the presence of foreign atoms into the crystallizing solution. Moreover, we also investigate the different growth rate as a function of those 'impurity' atoms. We also study the theoretical equilibrium morphology and the possible epitaxy between nitrates that can conduct to a change in morphology.

As a first step of the work we designed and built a special device to study growth kinetics either in pure systems or with impurities addition mainly of other nitrates.

The unit consists in four main bodies: an observing cell, a peristaltic pump, 2 thermostat baths with heat exchangers and a reservoir. The solution (of known concentration) leaves the reservoir at a temperature somewhat higher than the target temperature with the aim of the pump. It goes through a heat exchanger directly to the observing cell, where a crystal is glued and can be observed in a microscope. Immediately after leaving the cell its temperature is raised again with another heat exchanger that conducts to the reservoir. A 1 liter reservoir of solution is enough to have a constant concentration throughout all experiment. True growth temperature can be recorded continuously; there are two sensors into the solution at less than 5mm from the crystal.

With this unit we are able to control the main parameters that have an influence in the crystal growth which are: flow rate and growth temperature i.e. the supersaturation ratio.

It was found that NaNO_3 is very temperature sensitive. The metastable region is quite narrow, for a given concentration the gap between crystallization and dissolution can be less than 1°C [1]. Therefore we have to work in a very accurate way in order to control its behavior. Thus, all precaution cited above are self-explained to monitor experiments.

As in the literature found there is not an agreement in the NaNO_3 solubility curve we first re-determined it by the method proposed by Beckmann, W., Boistelle, R., and Sato, K. [2]. It consists in observing a crystal looking for a temperature in which it neither dissolves nor grows. This allows us to work at known supersaturation in the following experiments.

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The effect of foreign particles on the interface shape during solidification of crystals

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The shape of a solidifying interface is generally affected when it encounters foreign inert particles. The degree of deformation depends on the morphology and physical properties of the particles [1-4]. The overall effect also affects the pushing and captures process, when pushing is present.

In the present report the interaction between particle and interface is analyzed by means of a mathematical model employing the finite element method. The effect on the interface of different particle shapes and relative thermal conductivities between particle and melt was studied.

The results shown that for an isolating particle with respect to the melt the interface is convex in a degree that changes depending on the

particle shape and separation distance from the interface. The particle geometries considered for simplicity were spherical, cylindrical, conical and semi-spherical. For a conducting particle the interface changes to concave.

From the observation of the present results the trapping of the particles by the solid starts in different places; for a conducting particle the first points touching the solids are the corners while for an isolating particle this occurs at the particles center.

The analyses of these observations indicate that the probability of pore formation could be higher when isolating particle are present in the melt.

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Nucleation of gypsum at low supersaturations

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Crystallization from solution in natural environments mostly occurs at low to very low supersaturation. An example of this are the giant gypsum crystals of Naica (Mexico), where nucleation occurred at supersaturations very close to solution equilibrium [1]. Although nucleation is a well studied process in the laboratory, the majority of investigations focus on a high to medium supersaturation range. To attain a meaningful extrapolation from kinetic data obtained in the laboratory to natural conditions information on nucleation kinetics from low to very low supersaturated solutions are necessary. Therefore in this work, a method for studying the nucleation process at low supersaturations is proposed and this approach is applied to the case of crystallization of giant gypsum crystals at Naica.

Nucleation of gypsum was studied within low supersaturation ranges at 20 and 55 °C. Experiments were carried out in 0,2 ml batch reactors with no stirring, using a temperature controlled chamber at 20 °C, and a peltier based thermostatic multi-well set up, coupled to an inverted microscope (Nikon Eclipse TE2000-S) for the experiments at 55 °C [2]. All experiments were covered by a layer of mineral oil and sealed hermetically in order to avoid evaporation. The induction period (the time necessary for nucleation to take place) was measured by single microscope observation in all experiments.

As predicted by classical nucleation theory, an inverse relation in the induction period with temperature and supersaturation was found. Estimating the value of interfacial tension from the experimental data, we have compared the calculated values with values reported in literature obtained for homogeneous nucleation experiments [3,4,5]. Applying the kinetic model proposed by Liu [6,7] we found that gypsum has a very large susceptibility for heterogeneous nucleation (which also corresponds with our observations), and values of interfacial tension found in literature should be higher than reported. From these data we were able to extrapolate induction times for very low supersaturations (similar to those found in the waters of Naica, Mexico [1]). Thus, studying nucleation kinetics at low supersaturations allows us to access information on geological time scale crystallization processes occurring in Nature through laboratory experiments.

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The growth morphology of gypsum crystals: an experimental study

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Gypsum (calcium sulfate dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is the most abundant sulfate mineral throughout natural earth systems and is also present in a wide range of industrial processes (e.g. construction material, fertilizer) where the morphology and size of the crystals determines the final characteristics of the product. But despite its importance in natural and artificial processes neither the growth nor equilibrium morphology of gypsum crystals are properly understood [1]. A series of crystallization experiments were conducted to identify the key parameters that control the growth morphology of gypsum crystals.

When gypsum precipitates from a supersaturated CaSO_4 solution, single crystals, twins and spherulites are formed. All of them present the same trend in growth morphology as a function of temperature and supersaturation. At low temperatures ($\approx 4^\circ\text{C}$) mainly plate like crystals are formed and morphology varies little with supersaturation. At higher temperatures ($\geq 20^\circ\text{C}$) crystals with needle habits are dominant, becoming more elongated as supersaturation increases. When supersaturation surpasses a critical value crystal size starts to decrease. The influence of temperature and supersaturation on the growth morphology can be, roughly, explained in terms of changing growth kinetics with varying temperature [2] and increased nucleation at higher supersaturation. Although it should be mentioned that crystals grown under the same experimental conditions always present a large variation in growth morphology (except at 4°C). Transmission Electron Microscopy was used to observe the growth morphology of crystals at the early stages of crystallization and this large variation in morphology was also observed (Figure 1). These results indicate that the nucleation stage and/or the early stages of growth have a large influence on the growth morphology of gypsum.

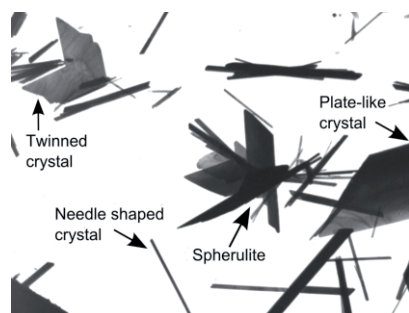


Figure 1. TEM image of gypsum crystals grown at room temperature (Saturation Index $\text{gypsum} = 0.73$). Chemical reaction stopped after 4 minutes since reagents are in contact.

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Crystallization of acetaminophen on a polymer surface

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Polymorphic control has long been desired. One of the ways to achieve this control is by heterogeneous nucleation. Recently the use of polymers as heteronuclei has been investigated and the results suggest that the polymers to some extent are able to facilitate selective growth of polymorphs [1]. Furthermore heterogeneous nucleation can be a way to obtain polymorphs, which have not been produced before because of a large kinetic barrier in the aggregation step.

In this study the mechanisms behind heterogeneous nucleation on a noncrystalline polymer surface are investigated. An important factor in the initial aggregation of molecules on a surface could be the roughness of the surface. In addition to the roughness the polarity of the surface is too suspected to contribute to the selective growth.

The roughness of spin-coated polymer surfaces is determined by AFM, and the polymorphic form and orientation of acetaminophen crystallized on the surface is determined by powder X-ray diffraction.

In addition to the experimental work a theoretical approach is also taken. Because of the substantial size of acetaminophen interaction with the surface, it is not feasible to treat the whole system quantum mechanically. The system is therefore treated with quantum mechanics/molecular mechanics. This implies that the system is divided into a smaller part treated by quantum mechanics and a part treated by molecular mechanics.

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In situ study of temperature effects on protein crystallization

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Despite the number of protein structures solved by X-ray diffraction increases exponentially, the quality of the single crystal samples obtained from standard crystallization procedures still limit structural studies and results obtained. The classical theory for crystallization some nuclei may become crystals when they exceed the free energy barrier and the critical size. Physical-chemical parameters such as temperature, pH and concentration alter the height of the free energy barrier and consequently the critical nuclei size and the growth rate. Indeed the physical-chemical changes in the protein solutions during the crystallization process are complex and far from well understood [1].

According to Marseille Protein Crystallization Database crystallization essays have been performed in two preferential temperatures: 277K or 293K [2]. Results presented in the literature