



report

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Factors influencing crystallisation from mixed acid pickling baths for stainless steel

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Sammanfattning/Summary <p>During pickling of stainless steel metal fluorides are generated in the acid solution. If the concentration gets too high, precipitation and crystallisation can occur. Different factors that may influence the crystallisation in pickling bathes of mixed acid (HF/HNO₃) have been investigated in laboratory experiments and evaluated also with multivariate methods. The results are compared with some findings reported in literature.</p> <p>Some of the results are:</p> <p>In order to predict if crystallisation occurs it will be needed to know values of several parameters like retention time, temperature, concentration of nitric acid, hydrofluoric acid and iron. Single knowledge of e.g. the iron concentration is not sufficient. Higher concentrations of iron, hydrofluoric acid and nitric acid increase the probability for crystallisation.</p> <p>Time is an important factor for crystallisation. Pickling bathes from different companies showed some difference in the crystallisation behaviour. Presence of seed material, both metal fluoride crystals and iron oxide increases the crystal growth rate.</p> <p>Other parameters that were investigated are: Kinetic energy by shaking, the age of the test solution, increased pressure and aeration (intensified contact with air)</p>	
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1 Introduction

An important step during production of stainless steel is the surface treatment. One part of the surface treatment is pickling with acid. A common pickling process uses a mixture of nitric acid and hydrofluoric acid especially for higher grades of stainless steel. It is this mixture of acids that will be investigated in this report.

During the pickling process the acid dissolves metal from the treated surface. Metal fluorides are generated in the acid solution. Increasing metal concentrations influence the pickling process. If the concentration gets too high, precipitation and crystallisation can occur. Therefore it is important to keep a metal concentration that allows efficient pickling without risk for precipitation or crystallisation. Thus, metals have to be separated from the bath and acid concentrations have to be controlled.

Today there is only limited knowledge about the crystallisation of metal fluorides from pickling acid. Some investigations are reported in the literature, but are often not directly applicable due to different choice of parameters and different questions investigated.

In this report factors influencing the crystallisation will be investigated closer. Crystallisation causes problem in the pickling bath, but may be used outside the pickling bath for separation of metals.

1.1 Project partners

The following persons were involved actively in the project and are hereby grateful acknowledged for their contribution to the project:

- AvestaPolarit Nyby: Jan-Eric Nilsson, Magnus Petterson, Thorsten Schneiker
- AvestaPolarit R&D Centre: Maria Karlsson, Sven-Eric Lunner, Lars Nilsson, Anders Stenqvist
- Naturvårdsverket: Husamuddin Ahmadzai.
- Sandvik Steel AB: Sofia Åkesson

2 Factors influencing crystallisation

Crystallisation from solution can be described as a two-step process. The first step is the generation of crystals (nucleation) and the second step is the growth of crystals. Both steps are important for crystallisation processes. The amounts of crystals formed in the pickling baths after a certain time will be a combination of the equilibrium for the

crystallisation process and the kinetics with which the reaction proceeds. The most likely main reaction for formation of crystals is $\text{FeF}_3(\text{aq}) \rightarrow \text{FeF}_3(\text{s})$.

The nucleation can be divided in two different types, homogenous and heterogeneous. During homogenous nucleation clusters are built in solution. According to Chianese, the nucleus must have a radius greater than a certain size to be stable. This can be expressed by the equation for the free energy:

$$\Delta G = 4 \pi r^2 \gamma + (4/3) \pi r^3 \Delta G_v$$

γ = The surface tension

ΔG_v = The free energy for crystal formation

The nucleus is stable when $\Delta G < 0$. For a nucleus larger than the critical size, the energy gained from the formation of the crystal body is greater than the energy needed for formation of the crystal surface, as the volume included in the formation term increases with a factor r^3 and the surface area included in the surface term increases with a factor r^2 .

The degree of supersaturation is a crucial parameter for crystallisation. A solution is supersaturated when the actual concentration of a substance is higher than its concentration in solubility equilibrium. When solubility in a solution changes, e.g. with change in temperature, the degree of supersaturation changes. The nucleation rate rises with higher degree of supersaturation and in general with higher temperature. There is a range of supersaturation when the solution is metastable. If the degree of supersaturation rises above the metastable zone, crystallisation occurs spontaneously.

In technical applications heterogeneous nucleation occurs due to impurities, surface contact (e.g. crystalliser walls), stirrers, baffles. These factors imply that in general a lower supersaturation is needed than what would be the case for homogenous nucleation.

During secondary nucleation new crystals are formed from parent crystals. The secondary nucleation is complex. Three processes govern it:

- 1 generation of secondary nuclei on or near a solid phase
- 2 removal of clusters
- 3 growth to form a new solid phase.

Also for secondary nucleation supersaturation is the critical parameter. The role of temperature is not fully understood, but in several systems the nucleation rate decreases with increased temperature. Stirring should lead to a lower nucleation rate according to Myerson, but some cases show different results. Harder contact material seems often be better for nucleation. Teflon for example is often not working well.

As mentioned in Perry, industrial crystallisation is suggested to be the sum of homogenous and secondary nucleation due to contact with walls, impellers, and contacts between crystals.

Several mathematical models have been proposed to describe nucleation and growth. An empirical relation between overall growth rate and overall concentration driving force for a crystal system is according to Chianese:

$$R_G = k_g (c - c')^m$$

Where

R_G = mass growth rate, $\text{kg m}^{-2} \text{s}^{-1}$

k_g = growth rate constant

c = solute concentration

c' = equilibrium concentration

m = overall growth rate order

The growth rate constant depends on two steps; the diffusion step to the crystal surface and the integration of solute into the crystal lattice, called integration step.

The diffusion controlled mass transfer can be described by

$$R_G = k_d (c - c_i)$$

and the integration step by

$$R_G = k_i (c_i - c')^m$$

which is the mass transfer for the integration step. For both steps the coefficient can be expressed according to Arrhenius law,

$$k_d = k_{d0} e^{-(E_d/RT)}$$

$$k_i = k_{i0} e^{-(E_d/RT)}$$

with

c_i = concentration at the crystal/solution interface

k_{d0} = temperature independent diffusion growth rate constant

k_{i0} = temperature independent integration growth rate constant

E_d = Energy of activation, J mol^{-1}

R = Gas law constant, $\text{J mol}^{-1} \text{K}^{-1}$

T = Temperature, K

The change of both k_g and the degree of supersaturation ($c-c'$) with the temperature will decide whether an increase in temperature will increase the speed of the crystallisation or not. The equations are simplified relations of the crystallisation process.

Impurities have different effects. When lowering the surface tension the nucleation is improved. On the other hand blocking of surfaces has a negative effect on the nucleation. Additives may change the solubility, which in turn effects the nucleation. Nucleation is often inhibited by ions. In general larger charge shows larger effects (Cr>Fe>Ni>Na).

When using seed crystals, larger seed crystals work better according to Myerson.

The second step in crystallisation is crystal growth. The crystal growth is important for the final crystal size distribution (CSD). The crystal size distribution often plays a role in products produced by industrial crystallisation. According to Perry, crystal growth is a layer by layer process. In many cases crystals with the same geometry have the same growth rate. Crystal growth will not be discussed more in detail in this report.

3 Crystallisation of metal fluorides reported in literature

3.1 General findings

Different factors influencing the pickling have been reported by Wallén and Lagerberg. Lagerberg reports on factors influencing the pickling as well as a short general description of the pickling chemistry.

The primary goal of pickling is the removal of oxides and the upper layer containing less chromium. Mechanisms and reactions are not known in detail, but nitric acid is important for dissolving of oxides and the less-chromium layers. Fluorides are needed to bind metal ions and prevent generation of a new oxide layer.

- The **surface oxide properties** are determined by the pre-treatment. They influence the pickability of the steel. The surface layer varies in chemical composition and mechanical properties like tears. Tears facilitate pickling of the material. Pickling time can be reduced by mechanical and/or electrolytic pre-treatment of the surface layer.
- The **pickling bath composition** influences the pickling rate and solution of metals. Pickling at low (0.8M) nitric acid concentration was faster than at high (3.5M) nitric acid concentration as reported by Lagerberg. Increased hydrofluoric acid concentration increased the pickling rate.

- The **content of dissolved metals**, especially iron, chromium and nickel is also important for the pickling process. Some iron is reported to catalyse the pickling process, but laboratory experiments show a decreased pickling rate when metals are added, especially iron.
- **Circulation of the pickling bath** increases the pickling rate, because of the improved transport processes in the bath.
- **Bath temperature** is important for the pickling. If the temperature is increased with 10 to 15 °C the pickling rate is twice as high.

3.2 Solubility of iron in pickling solutions of different acid concentrations

In an investigation by Reddy, Wang and Chen the solution of iron from samples of iron and stainless steel (AISI 416 and 316) has been investigated. An increased nitric acid content increases the iron solubility.

At a higher hydrofluoric acid concentration the iron solubility increases up to a HF concentration of 6M. At higher concentrations, e.g. 8 M the solubility decreased again. Solubility values were dependent on the material applied for solution and on the nitric acid concentration. At higher hydrofluoric acid concentrations and high iron concentrations fluoride can be consumed by generation of different iron fluoride complexes. Nitric acid concentrations below 160 g/l influence this process positively. All numbers given in this article are total acid concentrations and not dissolved acid (nitrate or fluoride concentration, respectively).

The iron solubility was highest in experiments with metallic iron, lower in experiments with AISI 416 and lowest for AISI 316.

Investigations reported by Krepler show the influence of temperature and hydrofluoric acid concentration on the solubility of iron in mixed pickling acid. As shown in Figure 1 the solubility increases with temperature, i.e. at lower temperature less iron is soluble. A surplus of hydrofluoric acid decreases the solubility. Krepler found a delay in the formation of visible crystals. At iron concentrations of 100 g/l and more, the delay was half an hour or less, but at iron concentrations of 60 g/l the delay was more several hours. The higher concentrations correspond to a higher supersaturation. The acid concentrations were about 2.4M nitric acid and 1M hydrofluoric acid.

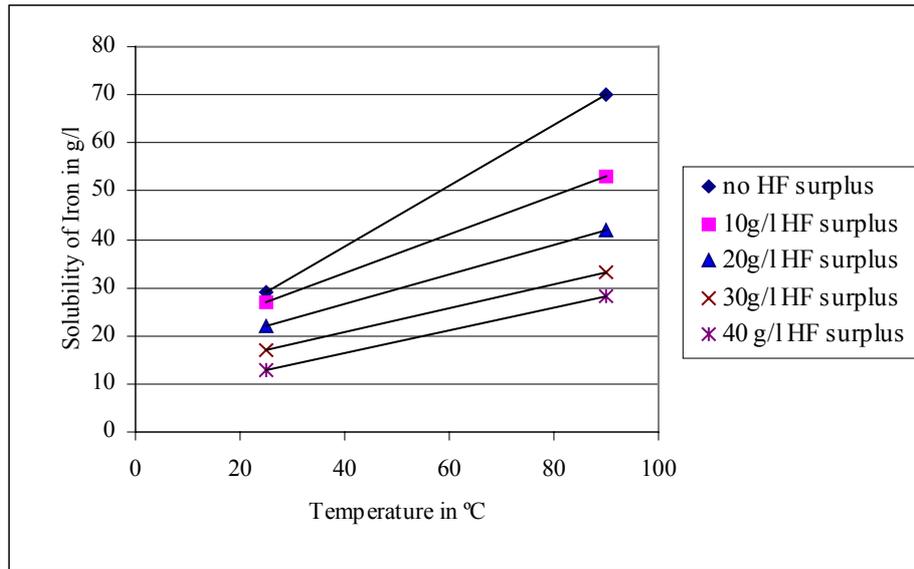


Figure 1. Solubility of iron in mixed acid containing 150g/l of nitric acid and different amounts of hydrofluoric acid in addition to the amount required for formation of FeF₃ (From: Krepler, A.)

Krepler also measured the progress of crystallisation at different temperatures and different starting iron concentrations. At 70 and 80 gram iron per litre the crystallisation was faster for 50 °C in the beginning than at 25°C, but the end point reached was somewhat lower for 25 °C. Starting iron concentrations of 90 and 100g/l were only tested at one temperature. The experiments showed clearly that the crystallisation process was faster for a higher starting iron concentration and that the stable iron concentration of dissolved iron was lower when starting at higher iron concentrations.

4 Experimental investigations on crystallisation

4.1 Material and methods

4.1.1 Pickling bath solutions

Two companies, AvestaPolarit and Sandvik supplied samples from their pickling baths. Samples have been taken from bathes that have been in operation; thus containing mixed acid (hydrofluoric and nitric acid) as well as metals, mainly iron, chromium and nickel. The original metal content of the Sandvik solution was 38 gram per litre; 33,5 gram per litre of total was iron. The original AvestaPolarit solution contained ca. 35 grams of metals per litre; 30 gram per litre of total was iron. The other metals were mainly chromium and nickel.

Table 1. Composition of original pickling bath samples before treatment

Solution	Metal content (g/l)	HNO ₃ (M)	free HF (M)
AvestaPolarit	35	1,7	1,4
Sandvik	38	2,5	1,75

Concentrated crystallisation solutions were produced from the original solutions by evaporation. By addition of acids and distilled water different test concentrations could be achieved. The concentrations of acids for the different crystallisation experiments were varied between 0,5 M and 4 M each. Iron concentrations were varied between 10 and 49 gram per litre. The volume of each test solution was 100 or 200 ml.

4.1.2 Factors investigated

Many factors may influence the crystallisation of metal fluorides in mixed acid solutions. Taking the conditions during industrial pickling processes into account, the following factors were chosen for the investigations:

- Hydrofluoric Acid (HF) concentration
- Nitric acid (HNO₃) concentration
- Iron (Fe) concentration
- Temperature
- Addition of seed crystals and their composition
- Kinetic energy
- Pressure
- Aeration
- Sample origin and age

Factorial design was applied to test all parameters except for pressure, aeration and sample origin and age. These parameters were only tested at specific test conditions.

The test solutions were produced from the original solutions by evaporation over one or two nights at 60°C in open beakers, between 2 and 10 litre at the same time. By dilution with water and addition of the acids (HF and HNO₃) the final desired acid concentrations were reached.

The test solutions were stored in plastic bottles of low (20 and 40 °C) or high-density polyethylene (60 °C). The temperature was maintained by storing of the bottles in heat bathes for 40 °C and 60 °C, and in room air for 20 °C and 4 °C (cooling room).

The seed crystals in most experiments were iron fluoride crystals from real pickling baths. The amount of 0,13 g of FeF₃ crystals, with approximately 50% water content,

was added to 100-ml solution. In some experimental the seed crystals have been of iron oxide delivered by AvestaPolarit.

When the effect of kinetic energy was investigated, a shaking apparatus for horizontal shaking was used at 100 –150 rpm.

The effect of pressure was investigated by introducing nitrogen gas at high pressure into a Teflon (resistant against these acids) vessel containing the investigated solution (within the plastic sample bottles). Supporting stainless steel surrounded this Teflon vessel.

A small aquarium pump and a small nozzle were used for testing of aeration.

4.1.3 Analysis

For the analysis of the acids and the metal content Scanacon SA 70 acid analysis equipment was used. This equipment works by measuring the density of the solution and by measuring the potential of H^+ and F^- with special developed ion selective electrodes. The relationship between the measured potentials and the concentration of free acids is a complex non-linear function. A computer is used to calculate these relations. Algorithms within the computer, using the density of the solution and the level of free acids could also estimate the content of metals.

The content of iron was measured by atomic absorption.

The crystallisation was followed by weight-measurements of the crystals in the sample bottles after decanting of the liquid. After measurement the liquid was filled into the sample bottle again.

4.1.4 Evaluation methods

Each parameter that has been tested was evaluated separately. Multivariate statistics were applied for evaluation of the influence of several factors at the same time. Modde and Simca-P were used for the multivariate evaluation.

Multivariate Data Analysis is the collective term for a group of mathematical methods to investigate the statistical properties of empirical data. In combination with appropriate experimental design, it becomes a powerful tool to construct predictive models such as PLS (Partial Least Squares) and DA (Discriminant Analysis). In PLS models the response parameter is predicted from a set of variables (factors) whose variations are known to influence the value of the response. The DA is useful as a methodology for characterising differences among groups with respect to a set of

variables, on the basis of the observations. DA can be used to develop decision criteria for the assignment of unknowns to one of the possible groups.

R2Y and Q2 are two statistical values the quality of a model. They can vary in the interval 0-1. These two statistical values reveal how much of the variance in the response parameter is covered by the model. A value of 0.7 means, that the model explains 70 per cent of the total variation in the data. The difference between R2Y and Q2 is that one of them, R2Y, is calculated for the model calibration data, i.e. the data with known values for the response that was used to fit the model. The other one, Q2, is the result of an iterative cross-validation procedure where each part of the data is left out of the calibration once. Therefor Q2 gives a measurement of how good the model is at predicting the response parameter for new data, not used in the model calibration.

4.2 Results and Discussion

4.2.1 Multivariate evaluation of crystallisation experiments

4.2.1.1 Results

Experiments have been performed according to factorial design in order to gain much information with a reasonable amount of experiments. Factors that have not been investigated and evaluated with multivariate statistical methods are: pressure, aeration, age and origin of original solution.

In a first set of experiments with test solution from AvestaPolarit, the following parameters have been varied:

- Hydrofluoric acid concentration
- Nitric acid concentration
- Iron concentration
- Temperature
- Addition of seed crystals
- Shaking of samples

The results from the first set of experiments suggested that shaking had no significant effect under the tested conditions. More details can be found later in this report. The effect of the addition of seed crystals was also investigated and is reported more in detail later in this report. Addition seemed to increase the amount of crystals.

For additional experiments it was decided to exclude the parameters shaking and addition of seed crystals. Therefore further experiments were performed without shaking and with addition of seed crystals. The experiments, all performed with pickling

bath from AvestaPolarit, were evaluated with multivariate methods taking the other four parameters into account. Figure 2 and Figure 3 show the results of this evaluation after 20 hours and 23 days of crystallisation. Larger columns illustrate the influence of different parameters on the crystallisation. A positive factor increases the crystallisation. The black lines at the columns show the statistically possible range in the 95 per cent confidence interval. Columns with more than one parameter mean a combined influence that needs both parameters, e.g. the presence of both HF and HNO₃.

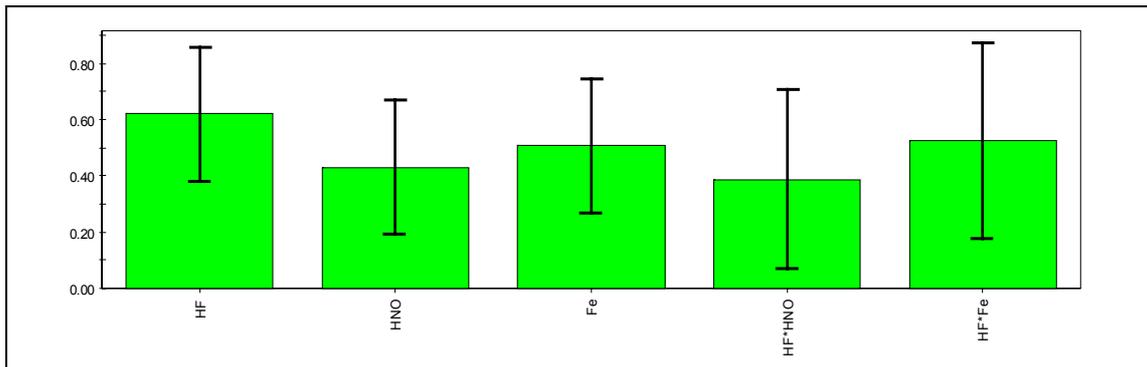


Figure 2. Multivariate evaluation (PLS) of 2 sets of crystallisation experiments (AvestaPolarit solution), main factors after 20 hours of crystallisation

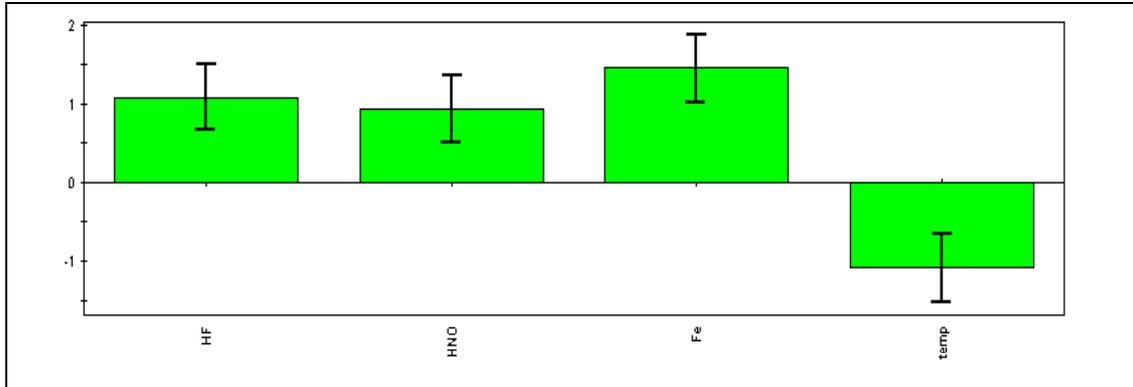


Figure 3. Multivariate evaluation (PLS) of 2 sets of crystallisation experiments (AvestaPolarit solution), main factors after 23 days of crystallisation

Initial measurements at 60° C were probably wrong after a time period of 1 week and longer due to diffusion through the sample bottle material. Due to the problems with the crystallisation results at 60 °C, some of these experiments were repeated with less permeable sample bottles. The used input data for the analyses are shown in appendix 1.

The quality parameters of the models are shown in Table 2. The statistical evaluation could explain the results between 65 and 88 per cent for the different evaluations. The models could explain about 80 per cent of the experimental values, but the quality to

predict crystallisation is lower, about 66 to 71 per cent. Figure 4 illustrates the quality of the model by plotting observed values versus predicted values. The closer values are to the diagonal line, the better the prediction.

Table 2 Quality parameters of the multivariate models after 20 hours and 23 days of crystallisation

Model	R2Y	Q2
20 hours	0.79	0.66
23 days	0.88	0.71

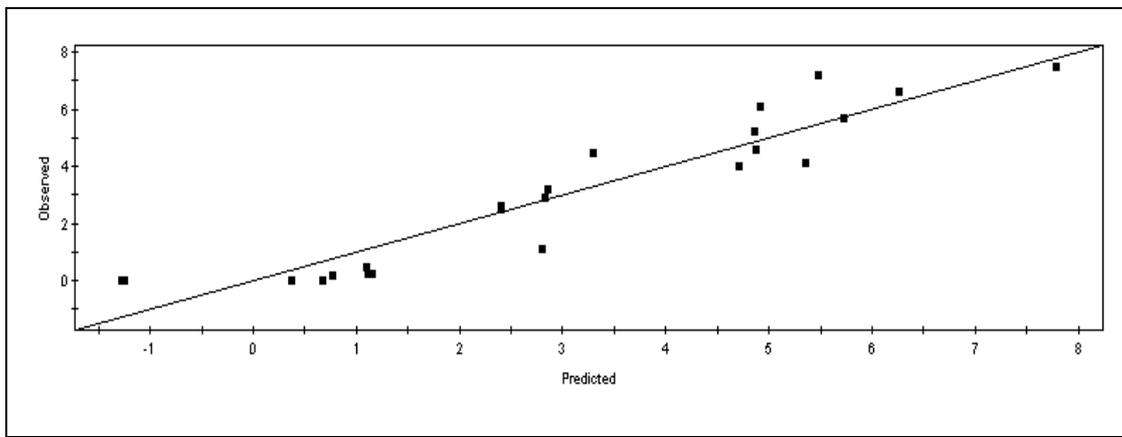


Figure 4. Predicted versus observed values for crystallisation after 23 days.

The equation for data after 23 days in the tested interval with the coefficients gained from the multivariate evaluation is:

$$Y = -7,35406 + 1.38726 * HF + 1.3762 * HNO_3 + 0.210301 * Fe - 0.0641189 * temp$$

Y= amount of crystals (mg/100ml)

HF, HNO₃: concentration in M

Fe: concentration in g/l

Temperature: in °C

Another evaluation with the values from the experiments after 23 days and some additional experiments at 20 °C was performed as discriminant analysis; i.e. it was tested for each combination of experimental conditions whether there was crystallisation or not. The evaluation was performed for crystallisation values after 14 days. The results are illustrated in Figure 5 for DA1 and Figure 6 for DA2. For each combination of parameters (i.e. acid concentrations, iron concentration and temperature) one x-value is generated and connected to the result “crystallisation occurs” (red triangle) or “no crystallisation” (blue triangle). The x-value does not have any physical explanation but

is a number generated by the model. Input data are shown in appendix 2. The coefficients for the different parameters are listed in Table 3.

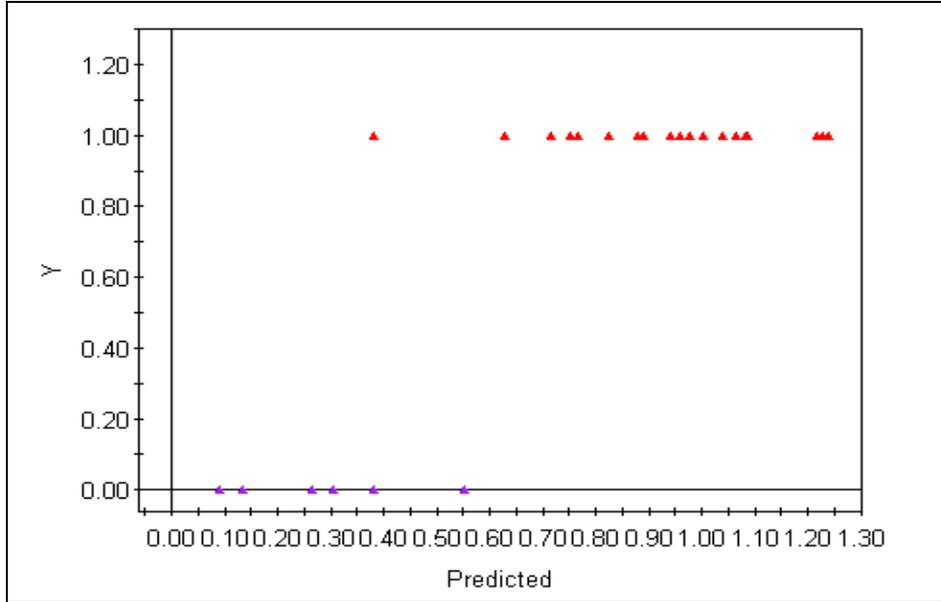


Figure 5. Discriminant analysis of crystallisation experiments, DA1 (red triangle=crystallisation, purple triangle=no crystallisation).

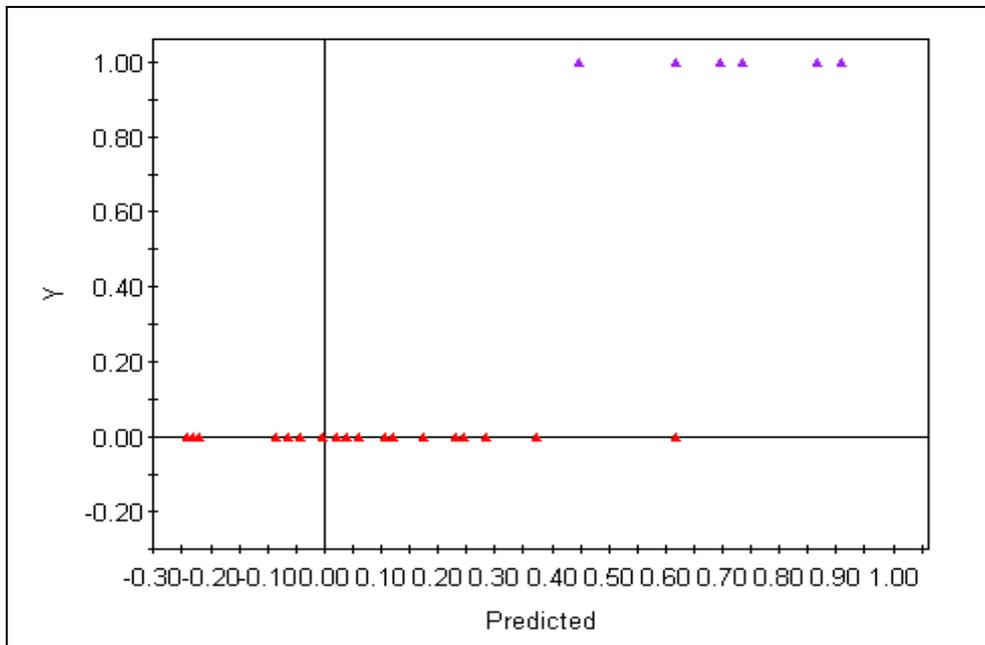


Figure 6. Discriminant analysis of crystallisation experiments, DA2 (red triangle=crystallisation, purple triangle=no crystallisation).

If the equation for DA1 is used, x values higher than 0.6 will lead to crystallisation, but values lower than 0.35 will not lead to crystallisation, which can be seen from Figure 5. Between 0.35 and 0.6 it is not possible to decide if crystallisation will occur. The corresponding values for DA2 are 0.4 and 0.65 as illustrated in Figure 6, i.e. if using the equation, values higher than 0.65 will **not** lead to crystallisation. The results for the experiments included in the evaluation are illustrated in Figure 5 and Figure 6. As the models are different for DA1 and DA2, the position of the red (crystallisation) and the purple (no crystallisation) is different in the two figures.

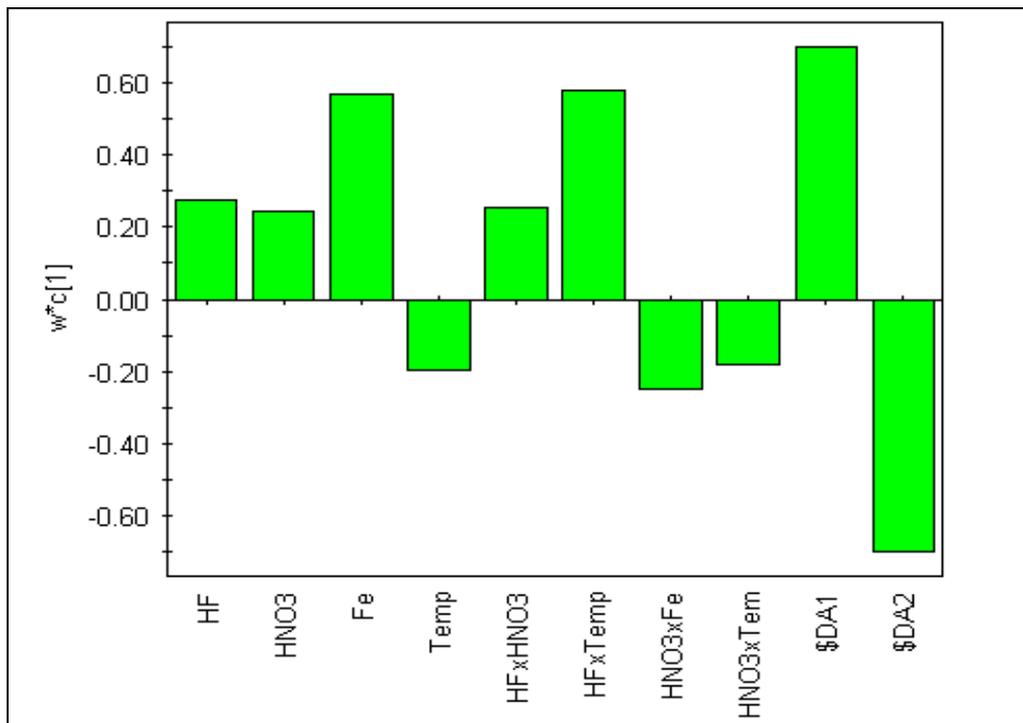


Figure 7. PLS of multivariate evaluation of dataset from crystallisation factorial experiments with 4 factors. Response parameter was amount of crystals after 14 days.

Figure 7 shows the importance of different parameters on the crystallisation according to the discriminant analysis. Parameters with a positive factor, e.g. HF concentration, increase the probability for crystallisation, parameters with a negative factor, e.g. temperature, decrease the probability for crystallisation. Larger factors mean a larger influence on crystallisation. The coefficients to use with not scaled data are also shown in Table 3, input data on which the model is based on can be found in Appendix 2.

Table 3. Coefficients as result from statistical evaluation by discriminant analysis,

Coefficient	\$DA1	\$DA2
Const	-0,06232	1,06232
HF	-0,71984	0,719839
HNO3	0,510522	-0,51052
Fe	0,072806	-0,07281
Temp	-0,02417	0,024171
HF*HNO3	0,15494	-0,15494
HF*Temp	0,013316	-0,01332
HNO3*Fe	-0,02082	0,020816
HNO3*Temp	-0,00536	0,005359

4.2.1.2 Discussions

Figure 2 and Figure 3 from the first evaluation show a shift in the importance of different factors for 20 hours and 23 days. After 20 hours not only the acid and iron concentrations are important for the amount of crystals, but there are also combined effects of hydrofluoric acid with nitric acid and hydrofluoric acid with iron. Thus, the effect of higher iron or nitric acid concentration is higher if also hydrofluoric acid is present in the solution. After 23 days the situation is different. There are no combined terms with hydrofluoric acid and nitric acid or iron. The evaluation after 23 days shows a larger influence of the temperature. As mentioned before, some of the experiments at 60° C had to be repeated with other types of plastic bottles. During the first experiments brown iron marks could be recognised outside the bottles after some weeks of crystallisation, and all formed crystals disappeared after about 1 week. The most likely explanation is that diffusion occurred through the used material (low-density polyethylene) at the higher temperature, causing different conditions with time. The evaluation after 23 days was performed with the results from the repeated experiments.

The discriminant analysis in Figure 5 shows that there are two possible values for a specific range of x-values, i.e. the model is not suitable to explain all experiments well. The model gives a satisfying explanation only if the x-value generated is below about 0.3 corresponding to “no crystallisation” for DA1 and “crystallisation occurs” for DA 2. Values larger than about 0.7 correspond to “crystallisation occurs” for DA1 and “no crystallisation” for DA2. The model could be used to predict if crystallisation occurs only if the generated x value is below 0.3 or above 0.7 and if other parameters like crystallisation time and addition of seed crystals are kept like in the experiments.

As Figure 5 and Figure 6 show, the model is not able to predict when crystallisation will occur with high accuracy for all possible combination of parameters. In Figure 8 an example is given to compare values calculated by the model and the observed values.

The example shows the amount of crystals for high hydrofluoric acid concentration and low nitric acid concentration at different iron concentrations. The figure illustrates the problems for using the linear model for prediction of the amount of crystals, as the model uses a linear function, but the observed curve is not linear. A linear function was chosen as approach for the modelling. The model describes for the illustrated case well the iron concentration, at which crystallisation starts, but the prediction was of lower quality for other acid concentrations.

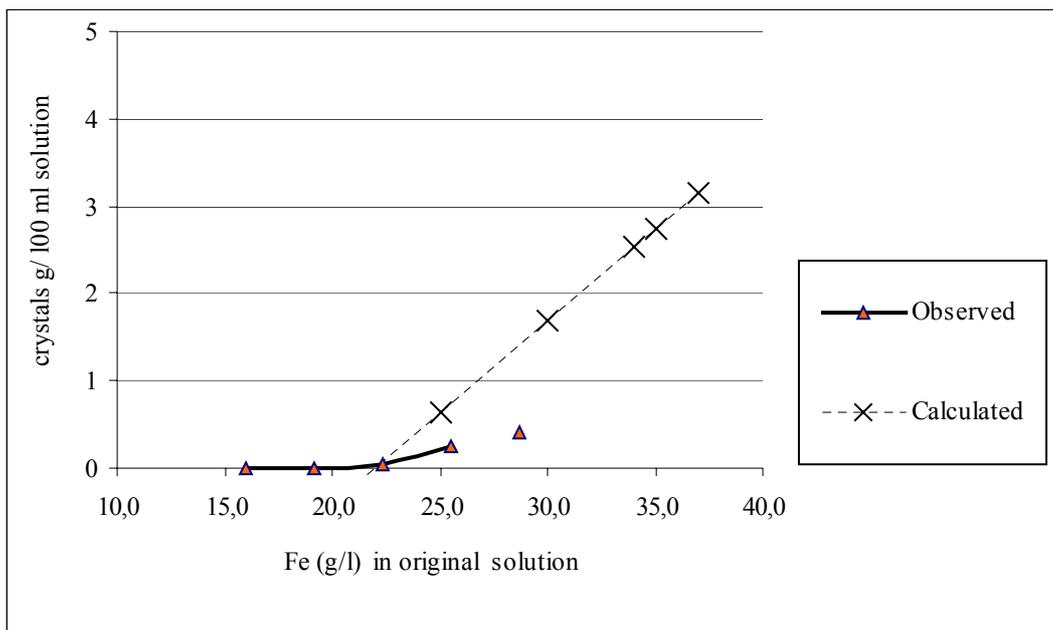


Figure 8. Comparison of calculated (from model) and observed amount of crystals for varying iron concentrations at a nitric acid concentration of 1.5 M and hydrofluoric acid concentration of 3.25 M after 23 days

According to the model several single and combined factors like e.g. hydrofluoric acid concentration and temperature influence the crystallisation like illustrated in Figure 7. Not regarding the uncertainty of the model the evaluation suggests the crystallisation to be controlled by a complex combination of different parameters. The model suggests for example an increased probability for crystallisation with higher nitric acid concentration alone and in combination with a higher hydrofluoric acid concentration, but a reduced crystallisation of a higher nitric acid concentration in combination with a higher temperature and in combination with a higher iron concentration. Due to the complexity of the system, it is worthwhile to look at the effect of single parameters as well. This will be done more in detail in the following text.

The multivariate model could be improved in several ways. More factors that influence the crystallisation results could be included in the model or its variation should be

prevented. For example, the age of the test solution has an influence on the test results as shown later in this report, but the factor was not included in the model. Testing different models besides the linear one could make another improvement.

4.2.2 Pickling bath composition (HF, HNO₃, Fe concentration)

4.2.2.1 Results

Many experiments with different pickling bath composition have been performed. It will not be possible to present all results in detail, but several interesting results will be shown in order to illustrate effects of different parameters. Experiments at different conditions have been performed to study the influence of the pickling bath concentration. Figure 9 illustrates the effect of different hydrofluoric and nitric acid concentrations at a starting iron concentration of 29 g/l. The experiment was performed with a pickling bath from AvestaPolarit, modified to get different concentrations.

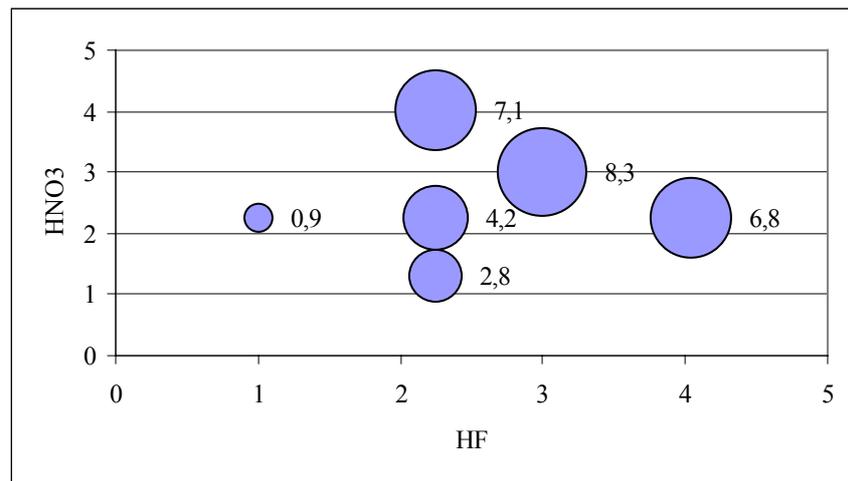


Figure 9. Amounts of crystals per 100ml solution after 4 months of crystallisation at room temperature (20-23 °C) with an iron content of 29g/l at the beginning of the experiment at various HF and HNO₃ concentrations (M), larger bubbles correspond to larger amount of crystals

The values shown in the diagram are the amounts of crystals in 100ml solution after 4 months of crystallisation. Larger bubbles correspond to larger amounts of crystals. Higher concentrations of each acid result in larger amounts of crystals. There is some crystallisation also at the lowest acid concentration level.

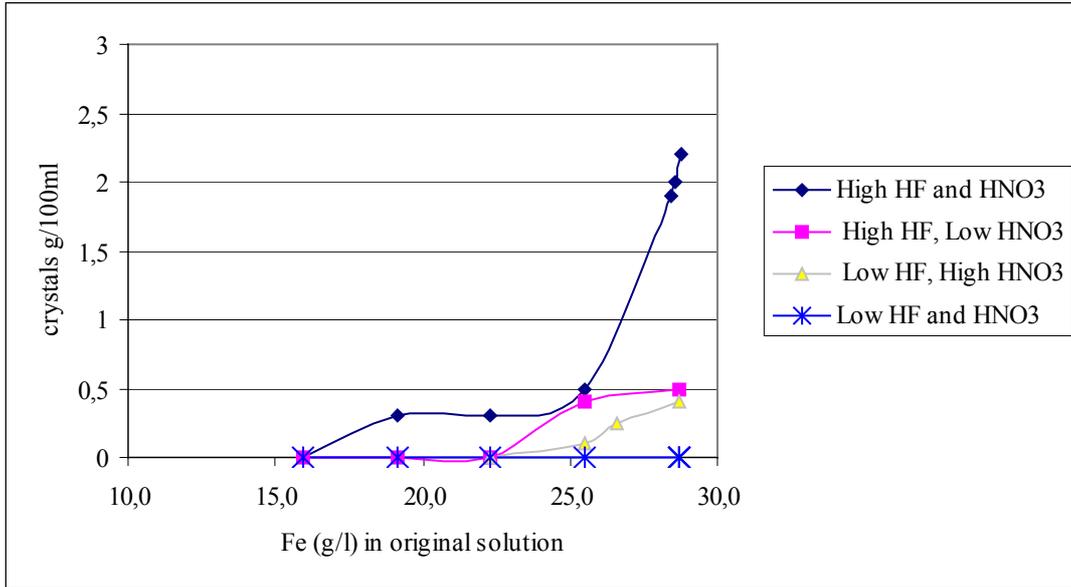


Figure 10. Amounts of crystals per 100 ml at different iron concentrations after 7 days at concentrations of 1.5M (low) to 3.3 M (high) of each acid.

The influence of the iron concentration on the crystallisation after 7 days is shown in Figure 10. In the experiment a pickling bath solution from AvestaPolarit was modified to reach different pickling bath compositions. The results are shown for two levels of nitric acid concentration and two levels of hydrofluoric acid concentration.

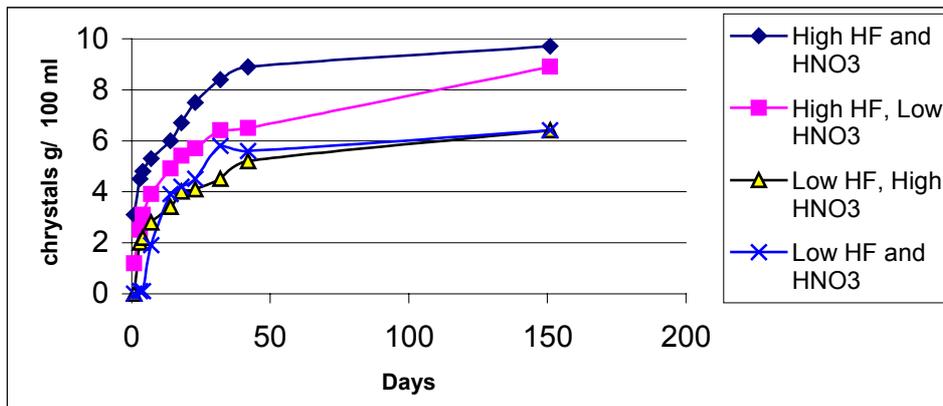


Figure 11. Amounts of crystals at room temperature per 100 ml with an iron concentration of 37 g/l at room temperature as function of time at concentrations of 1.5M (low) to 3.3 M (high) of each acid.

In is the amount of formed crystals at different levels of acid shown as function of time, at an iron concentration of 37 gram per litre.

4.2.2.2 Discussion

The experiments show clearly that the pickling bath composition has an important influence on the crystallisation from pickling acid. Both the concentrations of nitric acid, hydrofluoric acid and iron have an influence on the crystallisation. Therefore it is not sufficient to know one of the concentrations, e.g. the iron concentration, in order to predict if crystallisation occurs. There is also a time effect. Even at low concentrations (1 M HF, 2.25 M HNO₃, 29 g/l Fe) some crystallisation occurs after a period of 4 months as shown in Figure 9. After a shorter period, 7 days, no crystallisation could be observed for low acid concentrations even at higher iron concentrations.

In order to predict if crystallisation occurs it will be needed to know several parameters like retention time, concentration of nitric acid, hydrofluoric acid and iron.

The effects of hydrofluoric acid concentration and iron concentration are expected as fluoride and iron are needed for generation of iron fluoride crystals. Higher concentrations increase the supersaturation, which in turn increases the probability for crystallisation. The influence of hydrofluoric acid corresponds well with Kreplers findings as illustrated in Figure 1.

The influence of nitric acid is more difficult to understand. The experiments show clearly a higher amount of crystals for higher nitric acid concentrations. This effect seems to be smaller at a higher iron content of 37 g/l (Figure 11), than at a lower content of 29 g/l (Figure 9). The combined effect of nitric acid and iron was also detected in the PLS evaluation after 20 hours experimental time shown in Figure 7, which gave a negative term for the combination of HNO₃ and Fe, i.e. decreasing the probability for crystallisation.

The nitric acid concentration might play a role in the effective iron concentration. In the experiments only the total iron content was measured. If some iron is not dissolved, it might be dissolved at a higher nitric acid concentration. The HNO₃ seems also to speed up the kinetics of the crystallisation as shown in Figure 11. The equilibrium value is reached faster at the higher HNO₃ concentration.

4.2.3 Temperature

4.2.3.1 Results

The temperature was one of the parameters that have been varied in the experiments. Figure 12 shows the influence at different iron concentrations after 2 hours of experiments. At 60 °C there is more crystallisation and crystallisation occurs at lower iron concentrations.

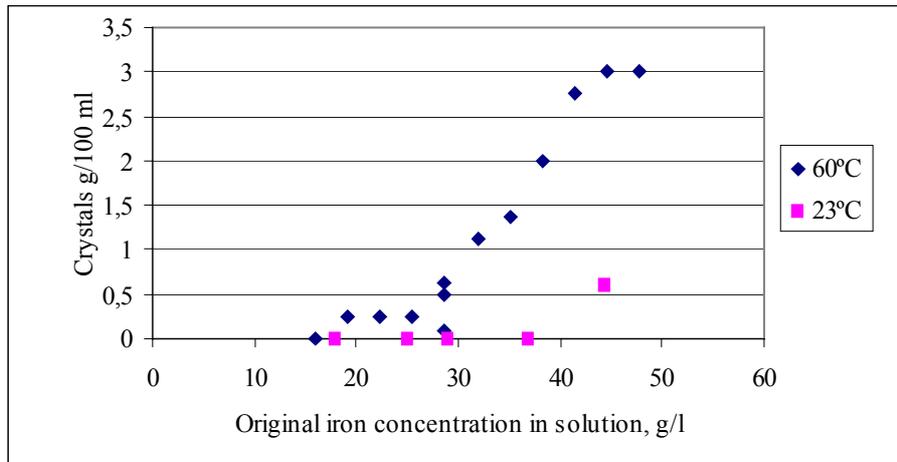


Figure 12. Crystallisation from AvestaPolarit pickling solution at different iron concentrations after 2 hours, acid concentrations are 3M HF and 3M HNO₃

Temperature effects after longer experimental times are illustrated in Figure 13. The amount of crystals was measured after 3 days, 7 days and 14 days. Experiments were performed at 4, 40 and 60 °C under the same conditions. At 40 °C three identical experiments were performed resulting only in small differences in the amount of crystals. The results show that the highest amount of crystals could be found at 40 °C after 3 days and 7 days. After 14 days the highest amount of crystals was found at 4°C, i.e. the amount of crystals was decreasing with increasing temperature.

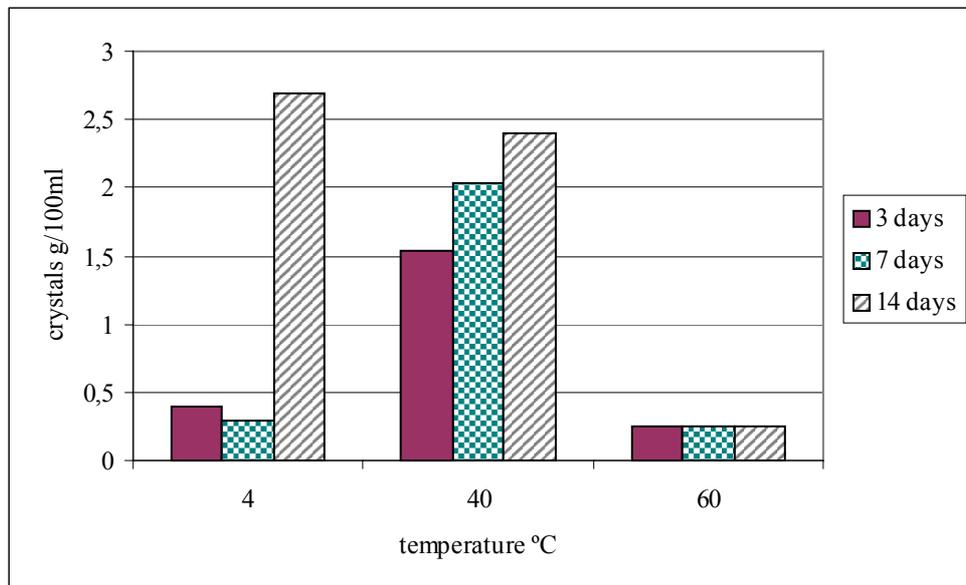


Figure 13. Crystallisation at different temperatures from AvestaPolarit pickling bath solution with 2.25 M HF, 2.25 M HNO₃, 29 g/l Fe, average values of 3 experiments at 40 °C

4.2.3.2 Discussion

The results of the experiments show clearly the influence of the temperature on the crystallisation from pickling acid solution. In order to understand the results it is important to distinguish between kinetic effects and equilibrium. The results suggest that crystallisation is accelerated at higher temperatures, but that the equilibrium amount of crystals is lower at higher temperature at least for medium iron concentration (29 g/l). As it will be shown later, crystals formed at higher temperatures contain more solvent, i.e. even if the crystal growth rate is higher the decrease of the iron concentration in the solution will not follow the same pattern.

Theoretically the temperature will influence the crystallisation by the heat balance of the crystallisation reaction and by solubility changes. No data for the heat balance could be found, though.

The decreased amount of crystals at higher temperature fits well to the results reported by Krepler, reporting increased iron solubility at higher temperature.

In the pickling bath the temperature is kept at about 60 °C. This high temperature increases the risk for crystallisation after a short retention time of the pickling acid according to the results of the experiments. For control of crystallisation outside the pickling bath for separation purposes, a high temperature is favourable for short retention times, but a lower temperature will result in larger amounts of crystals at a longer retention time.

4.2.4 Pressure

4.2.4.1 Results

Two samples with different iron content were tested at different pressure for 19 hours. Figure 14 shows the amounts of crystals that were measured at the end of the experiment.

The results show opposite effects of the pressure at different iron contents. At lower iron content a higher pressure increases the crystallisation, at higher iron content a higher pressure decreases the amount of crystals.

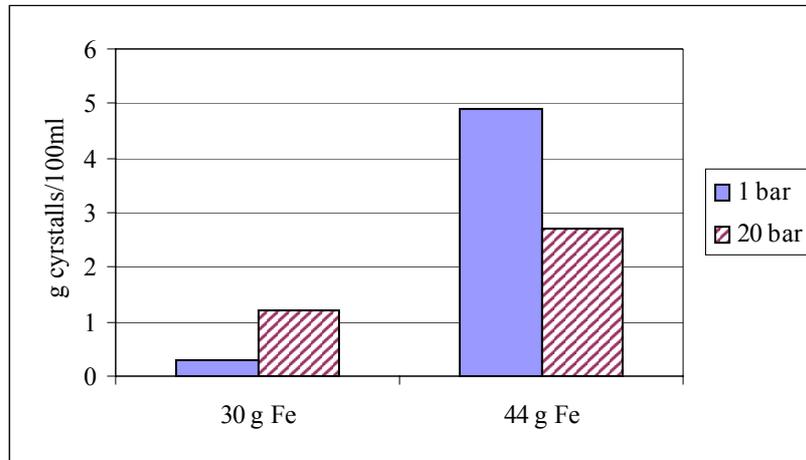


Figure 14. Amount of crystals per 100-ml solution. Crystallisation at different pressure. HF= 3M and HNO₃=2,35 M. Result after 19 hours, 0,12 g FeF₃ was added initially.

4.2.4.2 Discussion

The amount of crystals generated is different in the experiments at ambient pressure and under higher pressure. The results show an opposite influence of the pressure at two different iron contents. It is not possible to explain the results with only with at pressure effect.

A possible explanation might be a varying size and composition of the crystals, which where not investigated for the pressure experiments. A variation of the water content within the crystals could be observed in other experiments, though. Different pressure might cause differences in the crystal composition, giving an explanation for the variation at 44 gram Fe /litre. The increased pressure could result in crystals with less water content resulting in a smaller amount of crystals although about the same amount of iron fluoride crystallises. There is no explanation why the effect only should occur at higher iron concentrations. The variations at 30 grams could be an effect of variation overall within the experiments.

More experiments will be needed to clarify the pressure influence. In a pickling bath the pressure varies especially due to pumping of the pickling acid.

4.2.5 Aeration

4.2.5.1 Results

Two experiments with aeration and two corresponding experiments without aeration were performed. The effect of initial shaking when introducing the seed crystals was investigated simultaneously. Figure 15 shows the results from the experiments. Both

straight lines are experiments that could be compared for the effect of aeration, and both dashed lines, respectively.

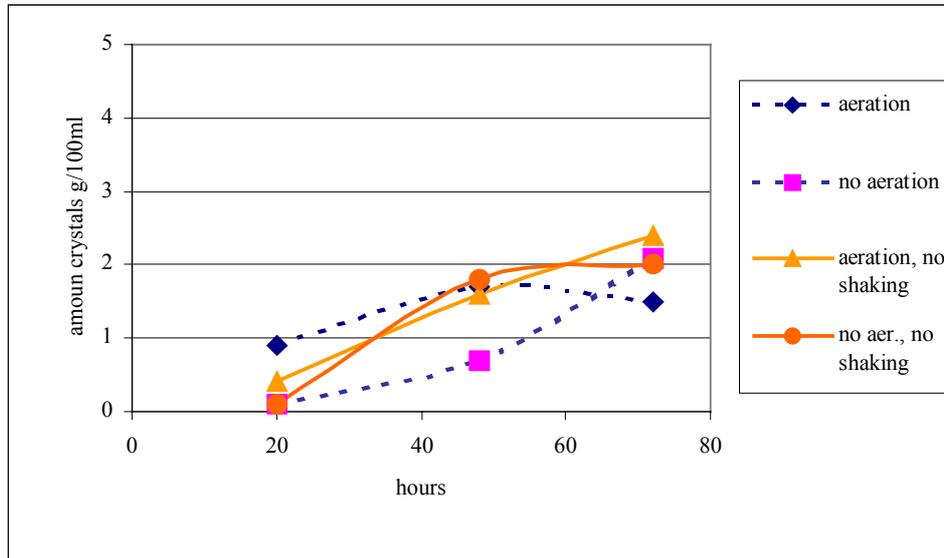


Figure 15. Crystallisation with and without aeration, 25 g Iron per litre and HF = HNO₃ 3M.

4.2.5.2 Discussion

The results suggest that there is no large effect of aeration as long as the evaporated liquid is compensated by addition of water, which was done in these experiments. Without compensation a change in crystallisation can be expected, as the composition of the liquid is different, which in turn influences the degree of supersaturation.

However, one effect of aeration could be observed. The crystals formed were denser in aerated samples.

The aeration was tested to simulate contact of the pickling acid with air, as it can happen when pumping the acid over an open sieve for separation of large particles. At the sieve evaporation of pickling acid can change the crystallisation conditions as well as the sieve surface may serve facilitate crystallisation. Therefore pumping of supersaturated pickling acid over an open sieve will increase the risk for crystallisation at the sieve.

4.2.6 Age of the solution

4.2.6.1 Results

Test solutions were prepared for experiments at different times from the same mother solution. To check the influence of ageing of the solution, experiments with identical parameters were performed with 3 weeks between the start dates. Figure 16 and Figure 17 show the results from the experiments.

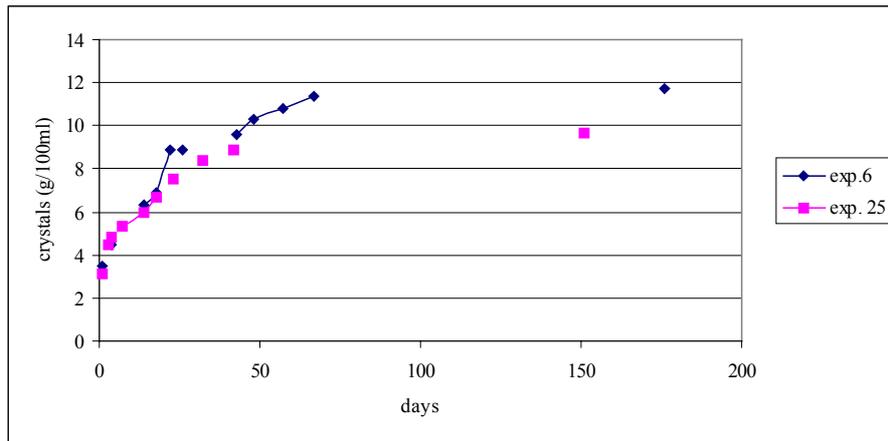


Figure 16. Crystallisation of two pickling acid mixtures with the same iron (37g/l), HF (3,25M) and HNO₃ (3M) prepared from the same mother liquid at different times (3 weeks between the first experiment no. 6 and the second no. 25)

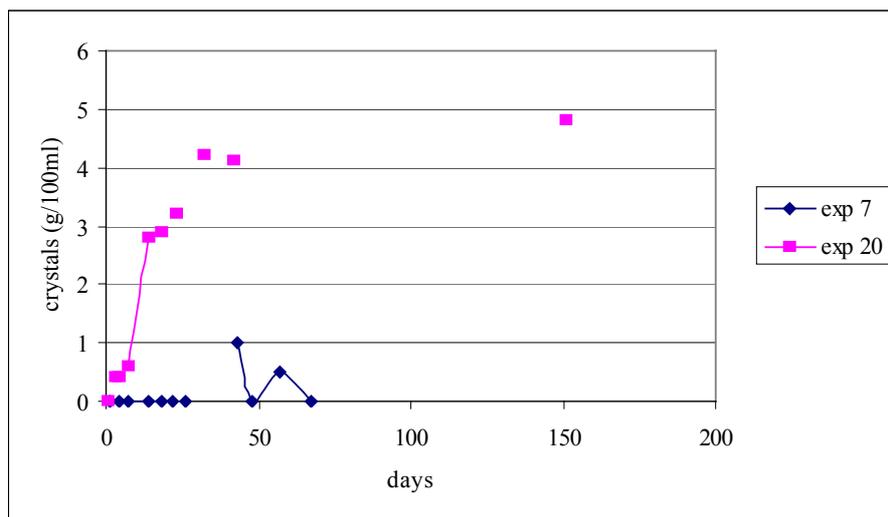


Figure 17. Crystallisation of two pickling acid mixtures with the same iron (25g/l), HF (3,25M) and HNO₃ (1,5M) content, prepared from the same mother liquid at different times (3 weeks between the first experiment no. 7 and the experiment with the aged sample no. 20)

4.2.6.2 Discussion

At a higher concentration of nitric acid and iron there is no significant difference between the results from the two experiments during the first 50 days of experiment. Only the last values show a larger difference. There is no clear explanation for this difference, as samples with the same composition should reach the same equilibrium when exposed to the same conditions. If the composition of sample had changed during 3 weeks storing, differences in crystallisation should have occurred already in early stages of the experiment. The result might be caused by statistical variation in the samples.

In the experiments with lower iron and nitric acid content there is a remarkable difference in the results showing a more crystallisation in the later experiments with older solutions. Between 40 and 60 days the crystallisation decreased and increased 2 times. There is no obvious explanation to the results, there might be one or two wrong values.

When the iron concentration was lower, 25 g/l, and the concentrations of both acids high, there was a slow crystallisation rate for the sample which was not aged. The results indicate an effect of using mother liquids with different ages at least for lower iron and nitric acid content, as all other conditions are equal. In the tests with low iron content, the mother liquid has been diluted more from the mother liquid.

One possible explanation for an ageing effect is that some of the iron is not fully dissolved at the earlier starting point for the experiments. Analysis with Scanacon and also with atomic absorption does not show if the measured metals are dissolved or present as small colloids. It could be impossible for this metals to dissolve at weaker HNO₃ acid concentration; this might explain the absence of crystals at the lower HNO₃ concentration (Figure 17).

Another explanation might be that during the ageing process small colloid nuclei are formed. These could speed up the crystallisation process.

The ageing effect does also effect the multivariate evaluation, as it is not possible with the data available to compensate for the effect before evaluation.

4.2.7 Crystal composition

4.2.7.1 Results

An analysis of the difference between the metal content in the pickling liquid before and after the crystallisation was made for crystallisation experiments at different temperatures, 20 and 60 °C, and at different original iron content.

Assuming that all iron that disappeared from the pickling acid formed iron fluoride crystals, the amount of formed iron fluoride (FeF_3) within the crystals was calculated from the analyses. The solvent fraction in the crystals was determined as the difference between the calculated and the observed amounts of crystals. In Figure 18 and Figure 19 the solvent content in per cent is shown for different original iron concentrations at 20 and 60 °C.

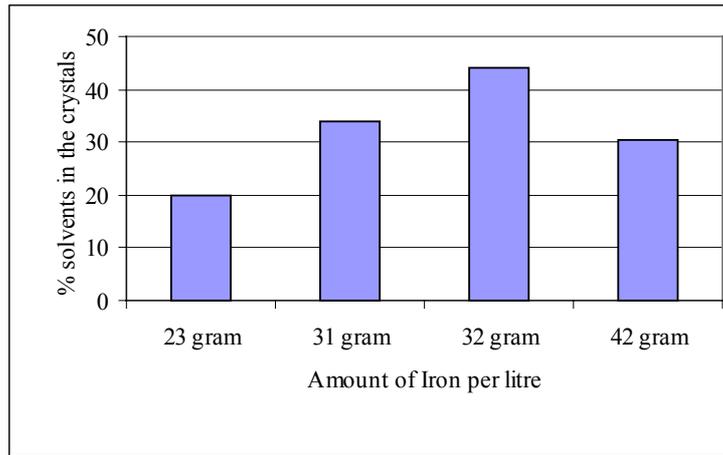


Figure 18. Percentage of solvent in crystals formed at 20°C at different iron concentrations

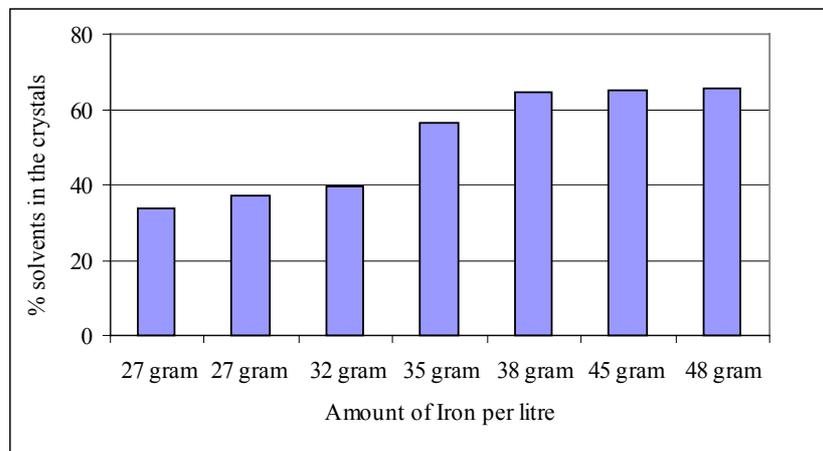


Figure 19. Percentage of solvent in crystals formed at 60°C at different iron concentrations.

4.2.7.2 Discussion

The calculated results show that the content of solvent in the crystals varies with different iron concentrations and different temperatures. At lower temperature and lower iron concentration, the solvent content in the crystals is lower. The amount of solvent increases with increasing iron concentration, except for one value at 20 °C.

The differences in the crystal composition can be due to the crystallisation rate. At higher temperature a higher crystallisation rate was observed. It is possible that more liquid is included in the crystals when the crystallisation process is faster.

4.2.8 Time

4.2.8.1 Results

The crystallisation experiments were performed during a time period of several weeks. Some experiments lasted up to 4 months. During the experimental period the amount of crystals was registered at specific times. The following three figures show the amount of crystals at different times for different iron concentrations and different temperatures.

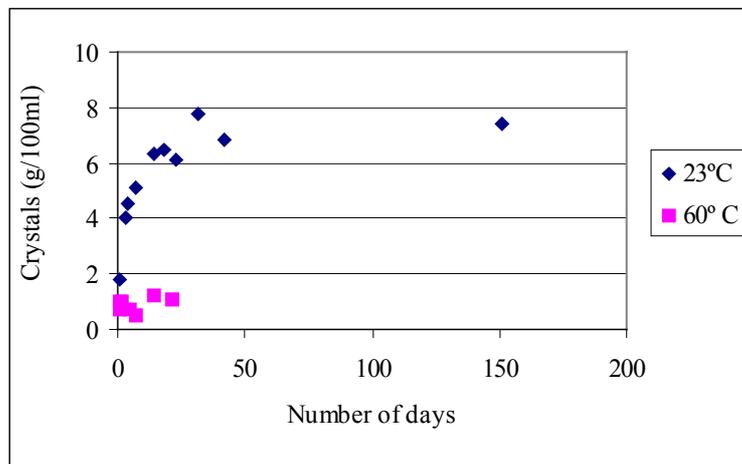


Figure 20. Crystallisation at different times and temperatures from AvestaPolarit solution with 25 g/l iron, 3M nitric acid and 3.25 M hydrofluoric acid

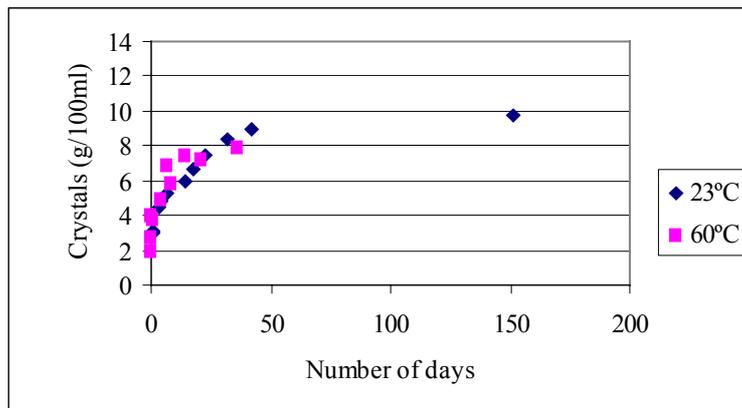


Figure 21. Crystallisation at different times and temperatures from AvestaPolarit solution with 37-38 g/l iron, 3M nitric acid and 3.25 M hydrofluoric acid

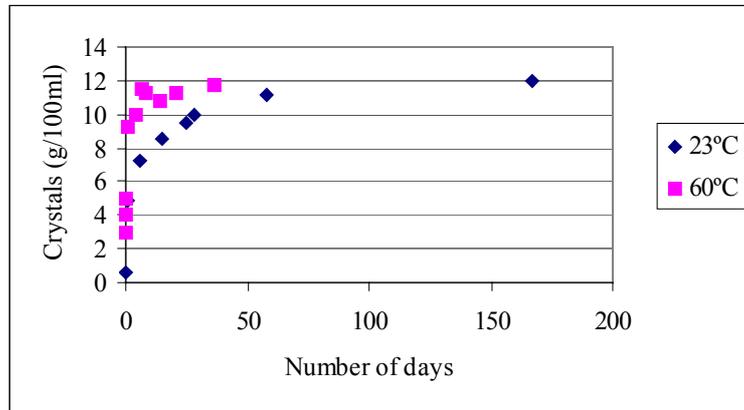


Figure 22. Crystallisation at different times and temperatures from AvestaPolarit solution with 44 g/l iron, 3M nitric acid and 3.25 M hydrofluoric acid

4.2.8.2 Discussion

The influence of time on crystallisation has two components. At shorter time intervals kinetic effects are important. At longer time intervals it is important when equilibrium is reached.

The results reveal the crystallisation from mixed pickling solution as a rather slow process. It takes up to several months for the solutions to reach a stable crystal concentration. There is also a delay in crystallisation. In several experiments were crystallisation occurred, no additional crystals were observed after one day of crystallisation, although seed crystals had been added.

The pickling bath composition and temperature influence the kinetics of crystallisation. At a lower iron concentration, there is almost no crystallisation at 60°C, but the stable levels are reached after some days. At 23 °C it takes more than one month to reach stable conditions at a higher level than at 60 °C. At 44 g/l iron higher crystal concentrations are reached during the first day of crystallisation. The crystallisation rate is higher at 60 °C than at 23 °C, but it should be noticed that the higher crystallisation rate might be explained partly by the higher solvent content in crystals formed at higher temperature.

The observed behaviour is important for the operation of pickling bathes. Pickling bathes can have a retention time of several months. At higher iron concentrations there will be a significant amount of crystals in the pickling bath already after some days. By choosing a lower iron concentration, fewer amounts of crystals will be formed.

If crystallisation is used as a separation process for separation of iron from pickling baths the results indicate that a temperature of 60°C can be used for an increased crystallisation rate at higher iron concentrations.

4.2.9 Addition of seed crystals

4.2.9.1 Results

Addition of seed crystals from former crystallisation experiments was performed in different quantities. Also addition of iron oxide as “seed crystals” was tested, because iron oxide is present in pickling baths from the previous steel treatment steps.

Figure 23 shows the crystallisation as function of time for a solution without and solution with addition of crystals. MeF_3 crystal was added and also iron oxide powder of the type that occurs in real pickling solutions. The metal fluoride crystals were smaller than 0.5 mm in diameter, estimated about 0.1 mm. Iron oxide particles were of varying size up to 1 mm, but mostly smaller than 0.5 mm.

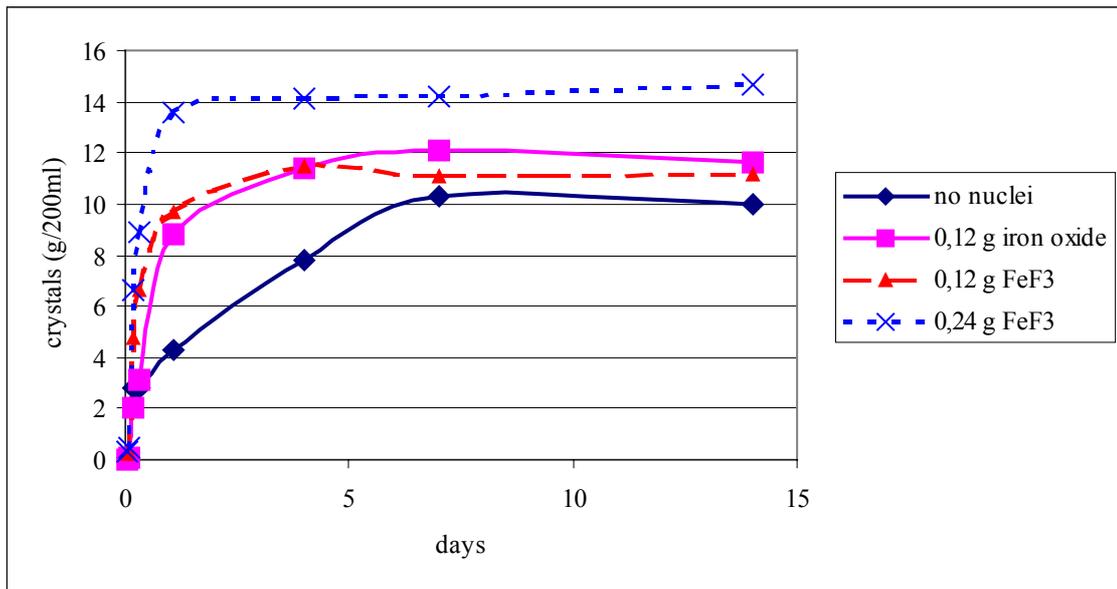


Figure 23. Crystallisation for a solution with 38 gram per litre iron, $\text{HF}=3,25 \text{ M}$ and $\text{HNO}_3=3 \text{ M}$

The figure shows that the highest amount of added nuclei results in the highest reaction rate.

Figure 24 illustrates the reaction with and without addition shown at a lower iron concentration. After a certain time the amount of formed crystals are similar for the two solutions when the equilibrium of the crystallisation almost is reached.

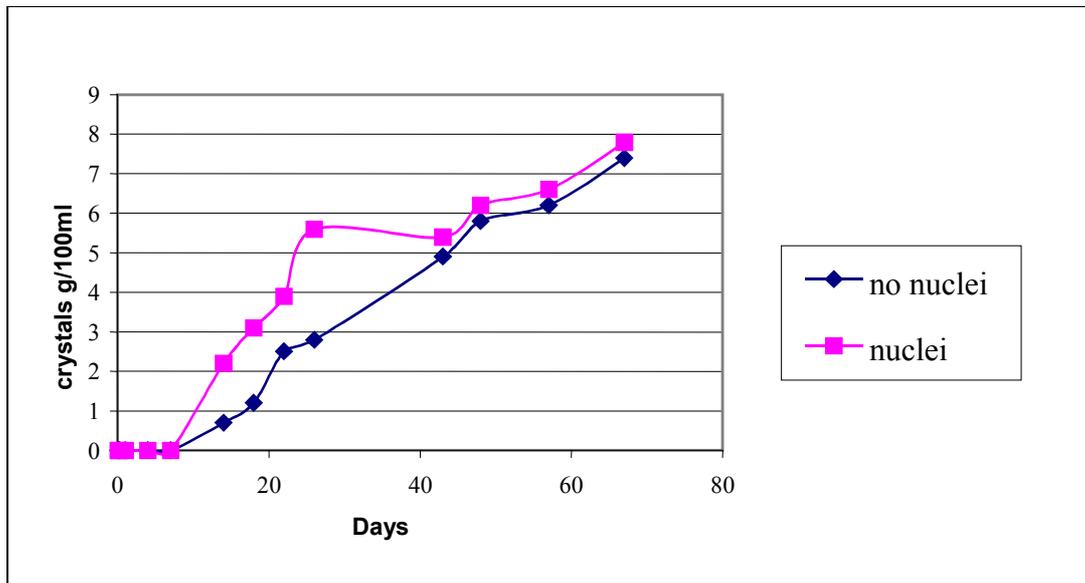


Figure 24. Crystallisation kinetics with and without addition of nucleus for a solution with 29 g/l iron, HF and HNO₃ = 3M

In these experiment 0,12 mg of a metal fluoride crystal was added to one of the solutions (total of 100 ml).

4.2.9.2 Discussion

As a certain size is needed for crystals to be stable, addition of seed crystals larger than the critical size may effect the crystallisation. The results of the experiments indicate that addition of seed crystals increases the crystallisation rate, but has less influence on the final amount of crystals as the results of Figure 24 show.

Both iron oxide and iron fluoride crystals can be used as seed crystals with similar results. Addition of a higher amount of crystals increased the crystallisation rate and the final amount of crystals. It might be that the addition of more crystals allows a steady state concentration nearer to the solubility than with addition of fewer crystals.

At the higher iron content (38 g/l) the amount of crystals is almost stable after 15 days, but at the lower iron content the process takes much longer time and no stable amount of crystals is reached after 60 days.

The results seem to be independent of how the crystal nuclei are introduced into the solution as there was no effect of initial shaking after the addition of crystal nucleus (results not shown for that parameter).

In the pickling bath it can be assumed that there will be crystals present, e.g. not dissolved iron oxide from the surface that is treated. Surfaces of walls and pipes may

also work as ground for crystallisation. Small particles like tested in the laboratory tests may dissolve in real pickling bathes instead of increasing the pickling rate, depending on the bath conditions. On the other hand larger particles especially of iron oxide may occur under real bath conditions.

For separation purposes the addition of further crystals will be useful to reduce the time needed for crystallisation.

4.2.10 Kinetic energy

4.2.10.1 Results

Kinetic energy is added to the mixed acid in pickling bathes, mainly by pumps. In industrial crystallisation processes kinetic energy is added to the slurry by stirring. Therefore it is interesting to investigate if addition of kinetic energy increases the crystallisation of metal fluorides.

The continuously shaking of the bottles did not show any noticeable effect for the kinetic of the crystallisation. To illustrate the effect of shaking, the total amount of eight experiments with and 8 experiments without shaking are compared in Figure 25. There is a slight difference between the amount of crystals with and without shaking.

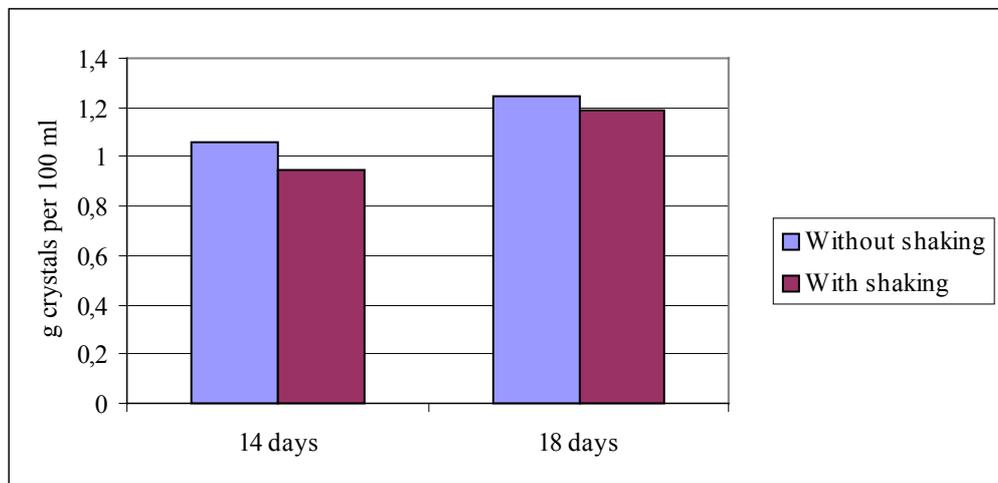


Figure 25. Summarised amount of crystals from 8 experiments each with and without shaking

4.2.10.2 Discussion

The comparison of experiments performed with and without shaking show a slightly higher amount of crystals gained in experiments without shaking, but the difference is not significant. The experiments were performed under certain conditions for shaking

with a shaking apparatus for horizontal shaking used at 100 –150 rpm. Even if there is now significant effect on crystallisation under the tested conditions, it is possible that addition of kinetic energy can influence crystallisation.

Increased kinetic energy, e.g. by shaking, stirring or pumping increases the mass transfer, which can have a positive influence on crystallisation. On the other hand may nuclei be destroyed if the kinetic energy is too high, which will reduce the crystallisation rate when nuclei are reduced below or prevented from growing to the critical size.

4.2.11 Origin of the solution

4.2.11.1 Results

To investigate if the origin of the solution did not change the equilibrium, equilibrium data for different iron concentrations were compared, see Figure 26, for Sandvik and AvestaPolarit solutions. The amount of crystals from the Sandvik solutions was lower than from the AvestaPolarit solutions.

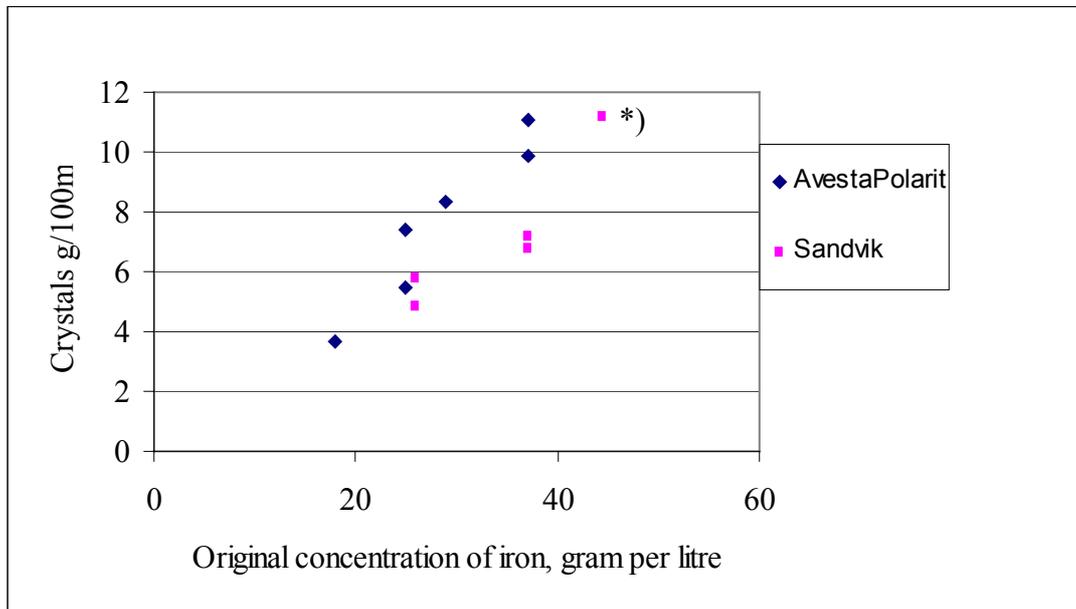


Figure 26. Comparison between pickling bath solutions from AvestaPolarit and Sandvik, nitric acid 3 (except for point marked “*”): nitric acid 3,5M), hydrofluoric acid 3M

4.2.11.2 Discussion

The equilibrium results do not differ significantly between experiments performed with solutions from different origin. The differences, i.e. a smaller amount of crystals from

Sandvik solutions, may be caused by different composition of parameters not measured like the concentration of non-iron metals. The total amount of chromium and nickel in both solutions is between 10 and 20 per cent. It is also possible that the composition of crystals varies, as only the total amount of crystals was measured, but not the composition.

5 Conclusions

From the experiments and results reported in literature, several conclusions can be drawn:

- There is no simple correlation between single **pickling bath parameters** like e.g. HF concentration and the crystallisation in the bath. In order to **predict if crystallisation occurs** it will be needed to know values of several parameters like retention time, temperature, concentration of nitric acid, hydrofluoric acid and iron.
- The **multivariate models** gained from the experiments can be used in some interval in order to predict if crystallisation occurs.
- Higher concentrations of iron, hydrofluoric acid and nitric acid increase the likelihood for crystallisation
- **Time** is an important factor for crystallisation. After an experimental time of several months crystallisation occurs also at lower hydrofluoric acid concentrations. In several cases the crystallisation could be observed only after more than one day of experimental time. Results indicate that addition of seed crystals and high temperature increase the crystallisation rate. At higher iron concentrations a stable amount of crystals was reached faster.
- Pickling bathes **from different companies** showed some difference in the crystallisation behaviour at the same conditions (acid concentration, iron concentration etc.), probably due to different bath composition.
- Presence of **seed material**, both metal fluoride crystals and iron oxide increases the crystal growth rate. Metal fluoride crystals and iron oxide showed the same effect. By addition of a larger amount of seed crystals the crystallisation rate was enhanced.
- **Shaking** at the tested intensity did not effect crystallisation significantly
- **The age of the test solutions** had an influenced the test results, which influenced the evaluation of other parameters.

- The results from the experiments indicate that **aeration** did not have a significant influence under the tested condition. Under some real conditions like an open sieve and intensive contact with air there might be an effect due to concentration changes and surfaces suitable for crystallisation.
- **High pressure** has been tested in experiments with contradictory results. More investigations would be needed to prove if pressure has a significant influence on crystallisation.

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Appendix 1

Data for PLS-model, response parameter was crystallisation after 20 h

HF	HNO3	Fe	Temp	kri20h (g/100ml)
2,25	2,25	29	40	0
2,25	2,25	29	40	0
2,25	2,25	29	40	0
2,25	2,25	29	4	0
1,5	1,5	25	20	0
1,5	3	25	20	0
3,25	1,5	25	20	0
3,25	3	25	20	1,8
1,5	1,5	37	20	0
1,5	3	37	20	0
3,25	1,5	37	20	1,2
3,25	3	37	20	3,1
2,25	2,25	11,665	40	0
1	2,25	29	40	0
2,25	1,3	29	40	0,4
2,25	4,0335	29	40	2,4
4,0335	2,25	29	40	2,4
2,25	2,25	47,335	40	2,4
1,5	1,5	25	60	0
1,5	3	25	60	0
3,25	1,5	25	60	0
3,25	3	25	60	0
1,5	1,5	37	60	0
1,5	3	37	60	0,4
3,25	1,5	37	60	1,2
3,25	3	37	60	3,8
2,25	2,25	29	60	0,2

Appendix 2

Data for discriminant analysis

HF	HNO3	Fe	Temp	kinetic	seed	14 d
2,25	2,25	29	4	0	10	2,7
3,25	1,5	18	20	0	10	0
1,5	1,5	25	20	0	10	0,2
1,5	3	25	20	0	10	2,2
3,25	1,5	25	20	0	10	0
3,25	1,5	25	20	0	10	2,8
3,25	3	25	20	0	10	6,3
3,25	3	29	20	0	10	2,2
1,5	1,7	37	20	0	10	3,9
1,5	3	37	20	0	10	3,4
3,25	1,5	37	20	0	10	4,9
3,25	3	37	20	0	10	6,3
3,25	3	37	20	0	10	6
2,25	2,25	11,7	40	0	10	0
1	2,25	29	40	0	10	0
2,25	1,3	29	40	0	10	0,5
2,25	2,25	29	40	0	10	2,2
2,25	2,25	29	40	0	10	2,6
2,25	2,25	29	40	0	10	2,4
2,25	4,03	29	40	0	10	4,2
4,03	2,25	29	40	0	10	4,4
2,25	2,25	47,3	40	0	10	5,4
1,5	1,8	25,5	60	0	10	0
1,5	3	25,5	60	0	10	0
3,25	1,8	25,5	60	0	10	0,25
3,25	3	25,5	60	0	10	1,2
2,25	2,25	29	60	0	10	0,25
3,25	3	38,25	60	0	10	7,5



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