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Removal of iron fluorides from spent mixed acid pickling solutions by cooling precipitation at extreme temperatures

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ABSTRACT

The precipitation crystallisation behaviour of spent mixed acid pickling solutions (HF/HNO_3) for stainless steel surface finishing was investigated. The main target was to extent the knowledge about the temperature dependency of these metal containing pickling acids at temperatures below 0 °C to induce precipitation by a temperature change instead of a salt supersaturation in the liquid.

It was found, that ferric fluoride (FeF_3) precipitates at temperatures below −35 °C under the conditions investigated which provides new approaches for the regeneration of spent pickling solutions.

1. Introduction

Steel pickling processes require large amounts of acid and water. In order to keep the pickling efficiency constant a part of the pickling acid solution has to be discharged as waste and replaced by fresh solution or regenerated continuously. Spent pickling acid solutions contain not reacted acids (free acid) and metal salts (bound acid) [1]. Especially pickling acid solutions for stainless steel are highly hazardous because they consist of a mixture of hydrofluoric (HF) and nitric acid (HNO_3). In the metal finishing industry this acid mixture is commonly called "mixed acid". Thus, the expression "mixed acid" as a synonym for a HF/HNO_3 mixture will be applied in the following. In companies with very large pickling lines (>2000 L/h waste acid solution) total regeneration for regeneration of both free and bound acids (e.g. by pyrohydrolysis) is state-of-the-art [2,3]. However, innovative and economic processes for the recycling of these solutions are still of interest for metal working companies dealing with pickling steps in the production chain.

Previous investigations showed that the best way to crystallise metal fluorides from spent pickling acid solution is to pre-concentrate the solution. Pre-concentration is necessary since the metal salts - like any other solutions - precipitate only when the solutions are supersaturated. Depending on the concentration of the acids and the metals the precipitation process starts at temperatures significantly above 0 °C [4,5]. Different experiments were conducted at 20 °C and 4 °C with an iron content of 29 and 37 g/L, respectively, at various HF and HNO_3 concentrations for a period between few hours and 150 days. Thus, an amount of about 1 to 10 g/L salt crystals was gained. The experiments showed, that the higher the HF concentration and the longer the crystallisation time were the more crystals were formed. This result was anticipated since more fluoride for the formation of complexes is available at higher HF concentrations [4,5]. Furthermore, it is also possible to remove metal fluoride crystals from pre-concentrated solutions after heating and cooling them rapidly [6]. The sudden change of solubility causes a precipitation crystallisation.

The precipitation crystallisation processes mentioned above need supersaturated solutions with a concentration near the maximum solubility which can be achieved, e.g. by energy-intensive evaporation. The ferric-chloride-water-phase diagram indicates, that ferric chloride precipitates at temperatures below 0 °C [7], please ref. Fig. 1. The diagram shows that for different concentration conditions even significantly above 0 °C crystallites of either $FeCl_3{\cdot}6H_2O$ or $3.5H_2O$ are contained in the liquid. For low ferric chloride concentrations at temperatures below 0 °C considerably more crystallites can form. Due to this property ferric chloride can be precipitated from according solutions. Since this behaviour is typical for salt-containing solutions, for other ferric compounds a similar behaviour can be assumed. Thus, the target of the investigations discussed in the following was to examine the precipitation crystallisation behaviour of ferric fluorides at temperatures significantly below 0 °C. When it is possible to precipitate ferric fluorides at those temperatures a new processing approach for solutions containing fluorides may be developed.

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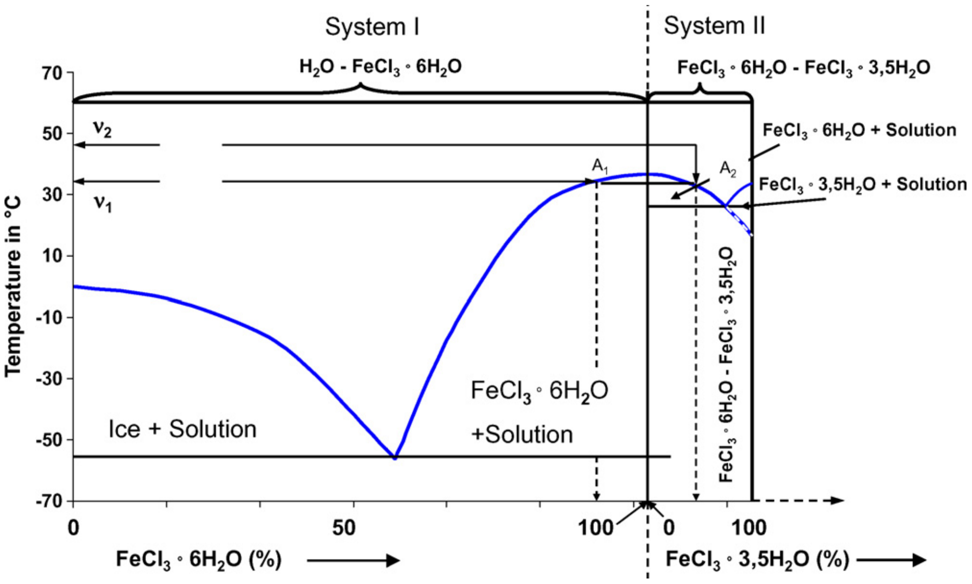

Fig. 1. Solubility of ferric chloride at different temperatures and for different concentrations according to [7].

The mixed acid solution used for stainless steel pickling consists of hydrofluoric acid as well as nitric acid. Both acids form different complexed salts with the dissolved metals. From literature the following equilibrium data for complexed iron are available [8,9]:

$$FeF_2{}^+ + F^- \Leftrightarrow FeF_3 \quad K_1 = \frac{\gamma_{FeF_3} \cdot c_{FeF_3}}{(\gamma_{FeF_2{}^+} \cdot c_{FeF_2{}^+}) \cdot (\gamma_{F^-} \cdot c_{F^-})} = 8 \times 10^2 \text{ L/mol}$$

$$FeF_3(aq) + F^- \Leftrightarrow FeF_4{}^- \quad K_2 = \frac{\gamma_{FeF_4{}^-} \cdot c_{FeF_4{}^-}}{(\gamma_{FeF_3} \cdot c_{FeF_3}) \cdot (\gamma_{F^-} \cdot c_{F^-})} = 1 \times 10^2 \text{ L/mol}$$

$$Fe^{3+} + NO_3{}^- \Leftrightarrow FeNO_3{}^{2+} \quad K_3 = \frac{\gamma_{FeNO_3{}^{2+}} \cdot c_{FeNO_3{}^{2+}}}{(\gamma_{Fe^{3+}} \cdot c_{Fe^{3+}}) \cdot (\gamma_{NO_3{}^-} \cdot c_{NO_3{}^-})} = 9.8 \text{ L/mol}$$

c_i [mol/L] is the concentration, K_i [L/mol] the solubility constant, and γ_i is the activity coefficient.

According to the solubility constants ferric fluoride will precipitate at lower concentrations than ferric nitrate. It is known, that FeF_3 precipitates at +25 °C and 5.5 wt% [7], but no data concerning the precipitation behaviour either at temperatures below 0 °C or in mixed acid solutions exists. The precipitation of ferric nitrate ($Fe(NO_3)_2$) occurs at temperatures between −28 and −12 °C at concentrations of 35.5 and 39.4 wt%, respectively [10].

The investigations described in the following are dealing with the crystallisation precipitation of ferric fluorides at temperatures of about −20 °C from solutions which were not pre-concentrated. Without a pre-concentration step for removing the ferric fluoride crystals from the spent pickling acid solution energy may be saved as the melting enthalpy of water (6 kJ/mol) is significantly lower than its evaporation enthalpy (40 kJ/mol) [11]. Thus, cooling the pickling acid solution from +60 °C to −45 °C requires about 3–4 times less energy than the evaporation of the liquid.

2. Material and methods

The cooling precipitation experiments were performed in a vessel consisting of the Nickel-base alloy hastelloy (C22). Hastelloy is stable against the investigated acids and the applied temperatures. The vessel was insulated with layers of PU-foam, Styrodur and Neopren-foam. For cooling, a water-cooled cryostat (unistat 815W, Huber, Offenburg/Germany) was applied. The solution within the vessel was stirred by a mixer with variable rotational speed with a blade made of PTFE. Fig. 2 shows a picture of the hastelloy vessel and the insulation.

The temperature inside the cell was measured with three PT100 sensors enfolded with shrinkable tubing made of PTFE to avoid chemical reaction with the mixed acid solution. The mixer blade as well as the temperature sensors stuck through the top cover of the vessel. Two sensors were situated at the inner-radius of the vessel in two different levels and another sensor was arranged at the outer radius. Thus, it was possible to measure temperature profiles over the whole vessel geometry. The temperature was recorded by a computerised measuring (Dasylab with I-Net-box). In the schema in Fig. 3 it can be seen, that until the nucleation of ice the metered temperatures inside the vessel correlate well. The crystallisation points of the water-ice transformation as well as the metal salt precipitation were detected by the temperature increase due to the exothermic crystallisation energy [12,13]. Further, the ice formation or a high amount of salt crystals leads to a less uniform temperature gradient inside the vessel. With higher acceleration of the mixer it can be equalised. The accuracy of the temperature measurement inside the cooling vessel was measured by comparing the sensors. When the temperature inside the vessel is stable there is no difference between the sensors. Depending on the cooling velocity, ice nucleation and salt crystallisation the differences are less than 0.25–0.5 °C during the cooling process.

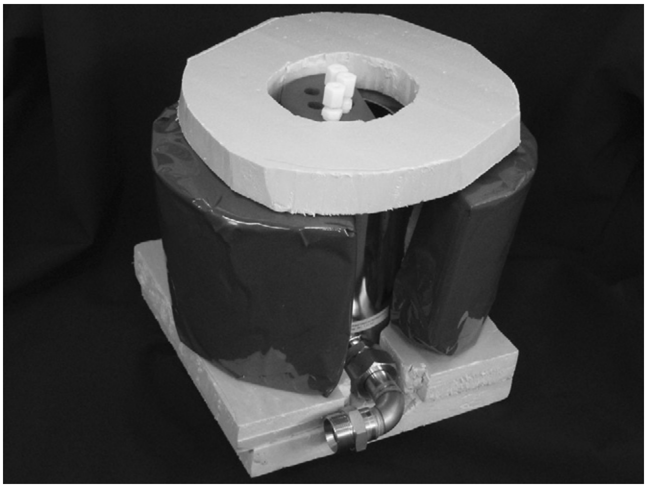

Fig. 2. Cooling vessel with top cover and insulation.

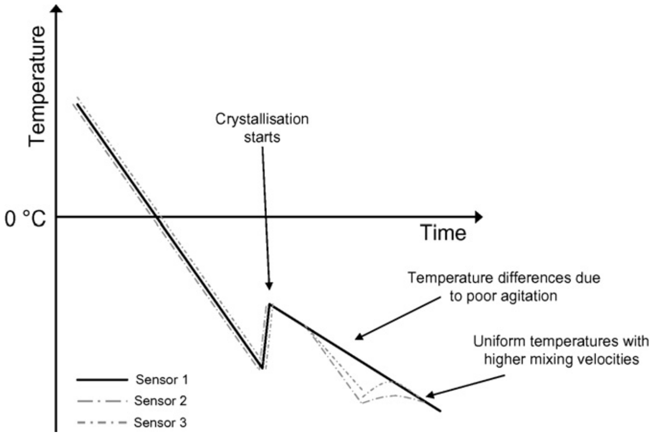

Fig. 3. Temperature profiles for cooling a solution.

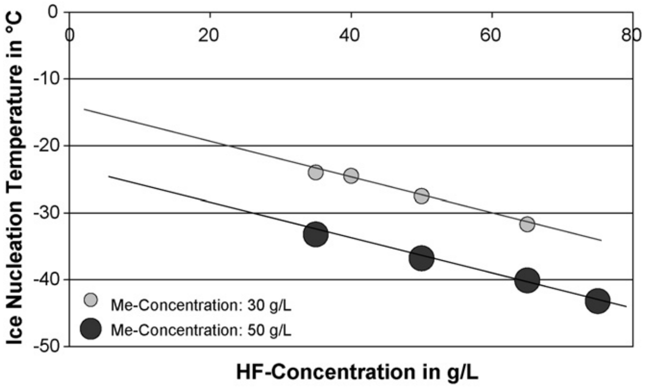

Fig. 4. Ice nucleation temperature of synthetic pickling acid solutions for cooling velocity $v = 0.25\ ^{\circ}\mathrm{C/min}$.

For the determination of the freezing temperature as a function of acid- and metal-salt-concentration different synthetic pickling acid solutions as well as spent pickling acid solutions from an industrial pickling line were frozen. The solutions were cooled down quickly to −5 °C and then slowly with different cooling velocities until the final temperature was reached. The reason for this procedure was to proceed to the target area where the freezing and crystallisation processes starts fast. To avoid any interactions during this first cooling step a temperature with a sufficient distance to the relevant temperature was chosen.

The chemical analysis of the samples (original acid solution, concentrate, melted ice) was done by acidimetric titration for free acid detection, lanthanum nitrate titration with a fluoride selective electrode for fluoride detection, photometry for nitrate detection and X-ray fluorescence analysis (XRF) for metal detection.

3. Results

Several synthetic pickling acid solutions were investigated prior to the research on the spent pickling acid solutions from the industrial plants. The different freezing temperatures as well as the formation of complexes and crystallisation of metal salts could be detected.

3.1. *Freezing of synthetic pickling acid solutions*

The concentrations of hydrofluoric acid and the metal content of the synthetic pickling acid solutions were varied to simulate the real conditions in pickling processes. Due to its high solubility nitric acid is not relevant for the salt crystallisation process and was not varied in these experiments. Table 1 shows the solutions investigated.

The cooling velocity was chosen in a way that the temperatures were as uniform as possible over the vessel. As expected, heat was released, when the nucleation of the ice started. The ice was distributed over the whole vessel, but mixed with mother liquid. A gravimetric separation of ice and mother liquid inside the vessel was not observed.

Table 1
Concentrations of acids and metals of the synthetic solutions investigated.

Solution no.	$c\,(\mathrm{NO_3}^-)$ [g/L]	$c\,(\mathrm{F}^-)$ [g/L]	Free acid [mol/L]	$c\,(\mathrm{Me})^{a}$ [g/L]
A	235	30	4	30
B	235	60	6	30
C	235	30	4	50
D	235	60	6	50

[a] The proportion of the metals is Fe:Ni:Cr = 36:5:9

By comparing all solutions, it became evident, that the ice formation was linearly dependent on acid and metal concentration. With rising HF-concentration the ice nucleation temperature falls (about 3.5 °C per 15 g/l rising HF-concentration). However, rising concentrations of the dissolved metals have a bigger influence on the ice formation temperature: The increase of the metal content of 20 g/l led to a decreasing of ice nucleation temperature of about 9 °C. The maximum difference between the ice nucleation temperatures are 16 °C, Fig. 4, which means that the process control will be difficult.

Fig. 5 shows a diagram with typical temperature profiles for cooling of a synthetic pickling acid solution (No. D with a cooling velocity of 0.25 °C/min). The first increase of temperature indicates the nucleation of ice crystals. When the fluoride concentration in the mother liquid rose above 65 g/L the formation of ferric fluoride complexes started. It has to be remarked, that this value is approximated based on the starting of the crystallite formation in different experiments. Because of the rapid crystallisation process it was not possible to detect the exact concentration of the fluoride at the beginning of the reaction.

In order to prove the independence of the velocity on the results, experiments were repeated with a lower cooling velocity. Comparing the nucleation temperature for ice formation of selected samples (Table 2) the main conclusion can be drawn that the nucleation temperature is slightly dependent of the cooling velocity. In contrast, the nucleation of the metal salts seems to be strongly dependent on the cooling velocity. This is caused by the higher concentration of the liquid and more and purer ice formed during the slower cooling.

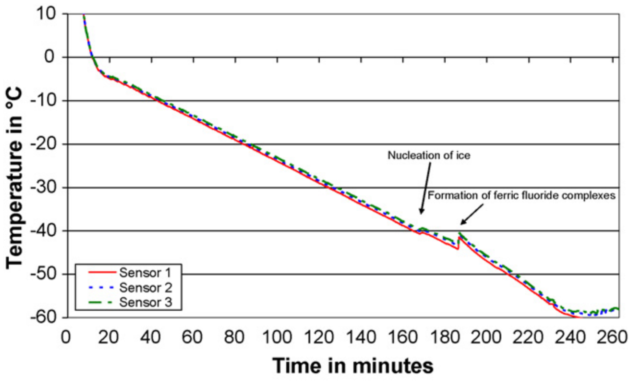

Fig. 5. Temperature profiles for cooling of synthetic pickling acid solution (No. D) with 0.25 °C/min with nucleation of ice and formation of ferric fluoride complexes.

Table 2
Nucleation temperatures in °C for ice and salt crystallisation of the synthetic pickling acid solutions for cooling velocities $\nu = 0.25$ °C/min and $\nu = 0.05$ °C/min.

Solution no.	Nucleation [°C] 0.25 °C/min		Nucleation [°C] 0.05 °C/min	
	Ice	Salt	Ice	Salt
A	−24	–	−24	–
B	−32	−45	−30	−40
C	−33	–	−31	–
D	−40	−43	−41	−36

Table 3
Concentration range of acids and metals of the spent pickling solutions investigated.

Solution no.	c (NO_3^-) [g/L]	c (F^-) [g/L]	Free acid [mol/L]	c (Me) [g/L]
Spent pickling acid	200–250	45–55	3–4	30–60

Table 4
Nucleation temperatures for ice and salt crystallisation of the spent pickling acid solution for cooling velocities $\nu = 0.25$ °C/min and $\nu = 0.05$ °C/min.

Solution no.	Nucleation [°C] 0.25 °C/min		Nucleation [°C] 0.05 °C/min	
	Ice	Salt	Ice	Salt
Spent pickling acid	−25	−45	−23	−33

3.2. Freezing of industrial spent pickling acid solutions

In order to check the comparability of the results from the synthetic pickling acid solutions spent pickling solutions from a stainless steel plant were investigated. The composition of the spent pickling acid solutions are presented in Table 3. The variation is due to the actual process situation.

The freezing behaviour of the spent pickling acid solution was investigated for a linear temperature profile and cooling velocities of both 0.25 and 0.05 °C/min. Table 4 shows the detected temperatures for nucleation and ice-formation. The ice nucleation point as well as the salt crystallisation point of the spent pickling acid solution were comparable to those found in the experiments with the synthetic solutions.

Table 5
Analytical results of the crystal composition after dissolving with 12.5% HCl.

Crystals	Fe in wt%	Cr in wt%	Ni in wt%	Fluoride in wt%	Nitrate in wt%
Average of synthetic solutions	28.4	0.65	0.03	29.9	n.d.
Average of spent pickling acids	29.7	1.0	<0.2	34.6	n.d.

Table 6
Calculation of the composition of the crystals formed in synthetic pickling acid solution No. D.

Element	Mol weight [g/mol]	Quantity of material [mol]	
		Syn. No. D	Spent acid
Fe	55.85	0.51	0.53
F	18.99	1.58	1.82
Cr	51.99	0.01	0.02
H_2O	18.01	2.23	1.93

3.3. Investigation of crystals formed

It was assumed, that during crystallisation ferric fluoride crystallites were formed. To verify this assumption, the particles formed in the concentrate of both the synthetic and the spent pickling acid solutions were separated by suction filtration and the composition was examined by a chemical pulping, followed by X-ray fluorescence analysis (XRF) and X-ray diffractrometry (XRD) to detect the crystal structure. The size of the particles contained in the liquid were measured with a Nanoparticle measuring system (NanoSight).

The particle measurement was applied as soon as the concentrates reached room temperature. Inside the concentrates particles were found with a mean diameter of about 180 nm; D_{10} was 122 nm and D_{90} was 486 nm.

After 50 days of further growing the crystals were filtered out of the liquid and rinsed with de-ionised water. With chemical pulping with a 12.5% hydrochloric acid the crystals were prepared for the analysis. In the following Table 5 the analytical results of the crystals formed in the synthetic pickling acid solution No. D and the spent pickling acid solution are presented.

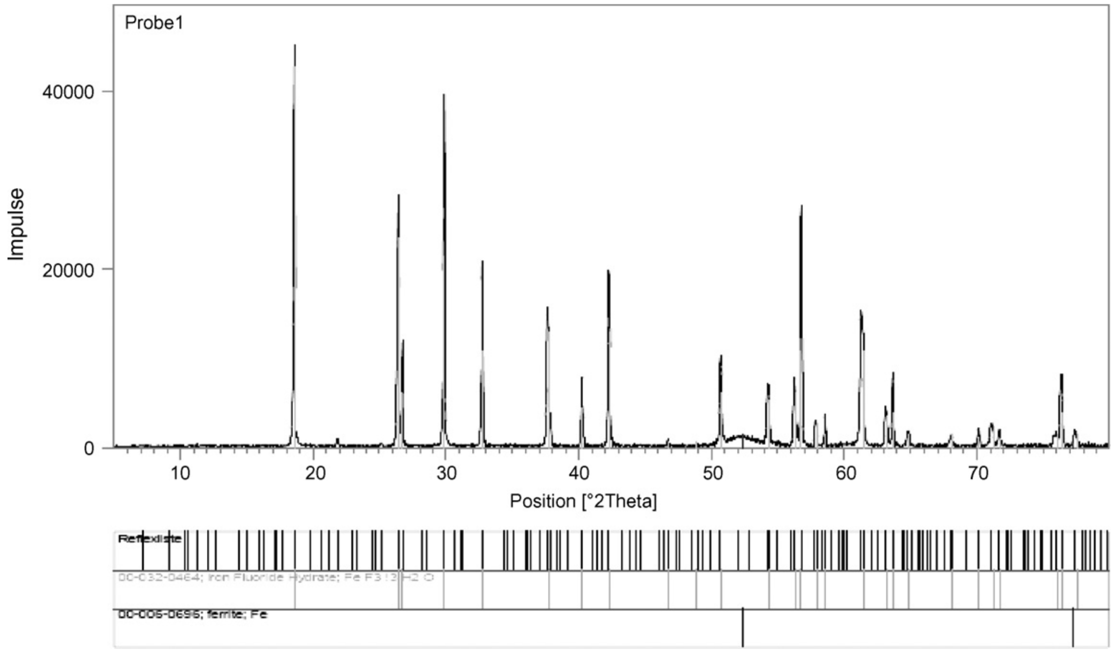

Fig. 6. XRD-analysis of the ferric fluoride hydrate (synthetic pickling acid solution).

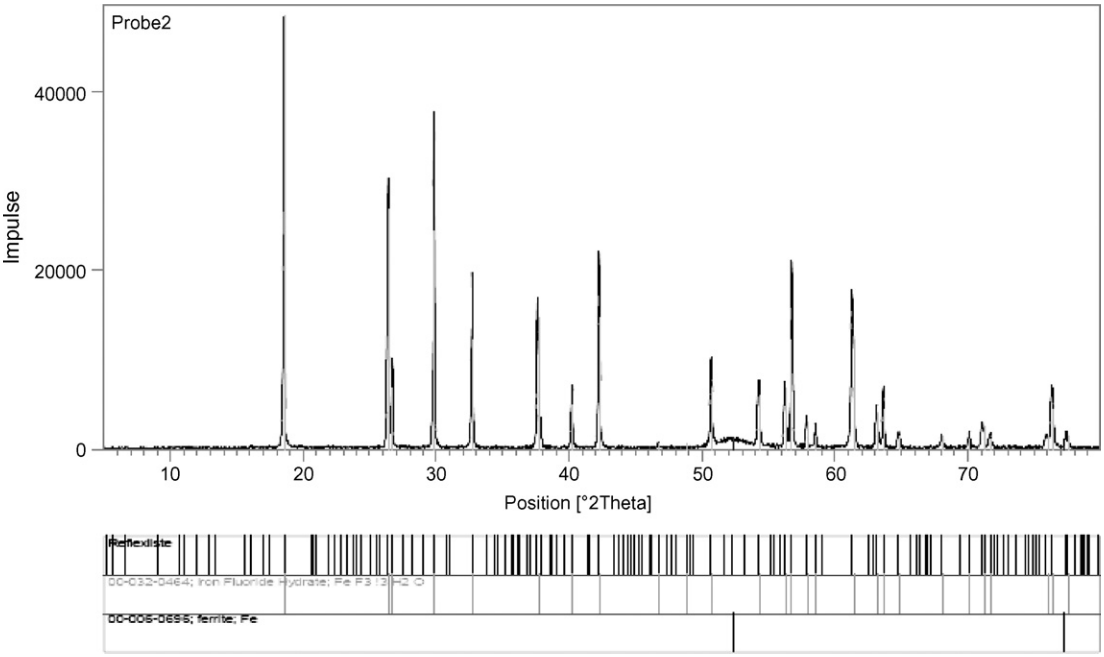

Fig. 7. XRD-analysis of the ferric fluoride hydrate (spent pickling acid solution).

Considering the molecular weight of the elements it is possible to calculate the composition of a given mass of crystals, please ref. Table 6.

It can be concluded, that FeF_3-complexes crystallised in the synthetic pickling acid solution. Chemical analysis and subsequent calculation proved, that the crystals formed in the spent pickling acid solutions might be FeF_3. But in this case a little more fluoride than stoichiometrically necessary was found. Since it is not possible that charged FeF_4^- complexes exist as a solid crystal component, free fluoride ions or even FeF_4^- ions are supposed to be dissolved in the water inclusions inside the crystal.

To investigate the structure of the complex crystals in detail, XRD was applied. This analysis showed for both samples, that ferric fluoride hydrate was formed. Fig. 6 shows the results for the synthetic pickling acid solution, Fig. 7 shows the results of the spent pickling acid solution. In detail, it is a $FeF_3 \cdot 3H_2O$-complex. Thus, the chemical analysis and stoichiometric calculations are confirmed by XRD measurement. As in both crystal samples a little more fluoride and water was found, it is obvious now, that parts of this are adhesive water.

4. Discussion

The solubility of ferric fluorides for temperatures above 0 °C are known from literature [1–8]. Based on these temperatures the removal of ferric fluorides from spent pickling solutions by precipitation crystallisation is only possible after enrichment of the acids and metals with e.g. evaporation [1,5]. However, this is an energy-intensive process. If hydrofluoric acid and water are evaporated in the same proportion as their concentrations in the original solutions were, a precipitation of metal is unlikely because hydrofluoric acid is removed from the solution due to its high partial pressure. Thus, one reaction partner for the crystallisation of ferric fluoride would be missing.

On the other hand a cooling process for concentration of a liquid through ice formation needs less energy and the precipitation of metal fluorides will be possible since the fluoride remains inside the solution forming solid metal fluorides. It is possible to precipitate ferric fluorides from the original diluted solutions because of their low solubility at temperatures considerably below 0 °C.

5. Conclusions

The investigations concerning the solubility of the ferric fluorides at very low temperatures have shown, that precipitation crystallisation is feasible. Because of this alternative precipitation process further investigations have to be conducted concerning the treatment of the mixed acid solutions from steel pickling processes. It seems to be possible to crystallise ferric fluoride without pre-concentration and without adding any chemicals. Since the crystals are not contaminated by other chemicals they can be recycled. It has to be proved whether it is possible to recycle the pickling solution to the process after metal salt crystallisation. The growth of bigger crystals from the initially formed ones is a very slow process. The acceleration of crystal growth for easy and fast separation is the subject of further investigations. The knowledge about the crystallisation of ferric fluorides at temperatures below 0 °C will lead to an improved processing of the mixed acid solutions from pickling processes, higher sustainability and resource efficiency.

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