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Determination of iron and chromium fluorides solubility for the treatment of wastes from stainless steel mills

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Abstract

Stainless steel pickling waste bath is one of the most important environmental problems in stainless steel mills because of its high toxicity and economic losses due to conventional neutralization treatment of this waste. Nitric and hydrofluoric acids reclamation solves only a part of the problem while metals still are considered as a waste and the whole content of hydrofluoric acid is not recovered because fluoride forms very stable complexes with metals. In this work metal-fluoride complexes solubility is determined in order to design a process for metals recovery, consisting of separating iron and chromium, precipitated as $K_2FeF_5(s)$ and $CrF_3(s)$, from nickel that remains in solution. Iron and chromium would be further hydrolyzed for oxides recovery, while fluoride release to solution and is recycled to selective precipitation stage. Results are obtained by the application of a novel equilibrium model for spent pickling liquors (SPL) called in this work "UCM-Model". Its applicability is evaluated by comparison with other literature models and it is used in the determination of thermodynamic solubility products. Obtained values are K_s, $K_2FeF_5(s) = \exp(-4.1 \pm 0.5 - (1400 \pm 200)/T\,(K))$ and K_s, $CrF_3(s) = \exp(-7.8 \pm 1.0 - (5800 \pm 500)/T\,(K))$.

Keywords: Stainless steel; Spent pickling liquor; Solid fluorides; Solubility; Iron; Chromium

1. Introduction

Stainless steel pickling consists of removing oxides scale formed at metallic surface during its manufacturing. This is actually achieved by chemical descaling by immersion in HNO_3/HF baths. When metals concentration is higher than 5% of solution, metallic fluorides supersaturate and acid bath must be withdrawn due to pickling ability loss. Exhausted pickling baths are considered as hazardous wastes, mainly composed by nitrate: 150–180 $g\,L^{-1}$; fluoride: 60–80 $g\,L^{-1}$; iron(III): 30–45 $g\,L^{-1}$; chromium(III): 5–10 $g\,L^{-1}$; and nickel(II): 3–5 $g\,L^{-1}$. Its acidity is very high, with approximately 2 mol H^+ per litre (corresponding to free HNO_3) and 1–2 mol as non-dissociated hydrofluoric acid. Spent pickle liquor (SPL) is catalogued as hazardous waste K062, regulated under the Resource Conservation and Recovery Act in the United States, and 110105* in the European List of Wastes. Therefore, a treatment process is compulsory for steel mills [1]; classical spent pickle liquor, SPL, management consist of neutralization with lime, obtaining a filter cake composed mainly by metallic hydroxides and fluorides mixed with CaF_2 [2]. Nitrate remains in liquid effluent, so it has to be treated for disposal. This method generates large volume of wastes and provokes high acid consumption in steel pickling.

Free acid reclamation methods are based on acid retardation [3] units or diffusion dialysis [4], which recover only part of nitric acid and non-dissociated hydrofluoric acid, producing a residual stream composed by hydrofluoric acid and metallic complexes that has to be disposed off. Total acid reclamation methods are based on chemical reactions to displace complex formation equilibriums for hydrofluoric acid total recovery; these processes are evaporation with sulphuric acid [5,6], solvent extraction [7], pyrohydrolysis [8,9], electrohydrolysis [10] and precipitation [11–13]. Although acids recovery yield is high enough, high installation costs and doubtful metals recycling make necessary to develop new treatments.

Our research group has proposed a treatment process [14], shown in Fig. 1, based on selective precipitation to obtain recyclable metals.

Spent pickle liquor is fed to a precipitation stage with potassium hydroxide and potassium fluoride, where $K_2FeF_5 \cdot H_2O(s)$

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Nomenclature

a_i	activity in molar scale ($\mathrm{mol\,L^{-1}}$)
A	Debye–Hückel parameter
A', B'	parameters for temperature dependence of solubility (Eq. (12))
B	interaction parameter of Humer and Wu method
B_{ca}	Bromley's model interaction parameter
B'_{ca}	Bromley's model parameter
C	interaction parameter of Humer and Wu method
C_i	molar concentration of I ($\mathrm{mol\,L^{-1}}$)
D	interaction parameter of Humer and Wu method
E	interaction parameter of Humer and Wu method
F_i	Bromley's model parameter
I	ionic strength, molal scale ($\mathrm{mol\,kg^{-1}}$)
K_{s}	solubility product
$K_{\mathrm{s,2}}$	solubility product proposed in Ref. [17]
%KF	addition of free fluoride as percentage of alkali stream
m_i	molal concentration of I ($\mathrm{mol\,kg^{-1}}$)
R^2	squared correlation index
SPL	spent pickling liquor
z_i	ionic charge of component i
Z_{ca}	charge mean of cation–anion interaction

Greek letters

β	interaction parameter of Humer and Wu method
$\beta_{\mathrm{FeF_5}^{2-}}$	thermodynamic stability constant of $\mathrm{FeF_5}^{2-}$
ϕ_{MX}	osmotic coefficient of water in a MX solution
γ_i	activity coefficient of i
ν	stoichoimetric coefficient

and $CrF_3{\cdot}2H_2O(s)$ crystallize and are separated from Ni^{2+} that remains in solution and is precipitated as $Ni(OH)_2(s)$ with a purity of 85%. Iron and chromium fluorides are hydrolyzed in other stage, releasing fluoride to solution and obtaining a recyclable mixture of iron and chromium hydroxides. Precipitation mechanism of metallic fluorides is shown in Fig. 2.

As it is shown in Fig. 2, metal complexes react with fluoride, released from hydrofluoric acid dissociation, forming $CrF_3(aq)$ and $FeF_5{}^{2-}(aq)$. Total content of fluoride in SPL is not enough for total iron and chromium precipitation as fluorides, so other mechanisms could take place, like oxides and hydroxides precipitation, which make nickel to co-precipitate, decreasing $Ni(OH)_2(s)$ recovery rate. This problem is avoided if free fluoride is added, obtaining high yields of nickel separation. Selected cation for precipitation was potassium because of the high solubility of potassium fluoride and KOH effectiveness for displacing fluoride equilibriums. Recent studies [15] determined that optimal conditions for $K_2FeF_5(s)$ and $CrF_3(s)$ precipitation are 60–65 °C, pH 4–4.2 and KF addition of 14–15% of total alkali stream.

The aim of this work is to determine $K_2FeF_5(s)$ and $CrF_3(s)$ solubility in SPL neutralization processes with KOH using the UCM-Model for chemical equilibrium calculation, based on Bromley method [16–18]. Previously, this model is compared with SSPEC (Stainless Steel Pickle Equilibria Calculation) used in other works [19,20] for solubility calculation.

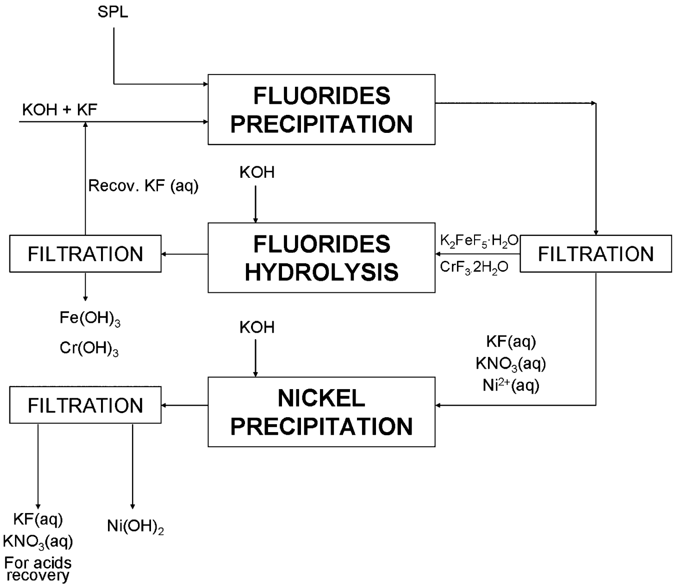

Fig. 1. Process diagram of SPL metals recovery.

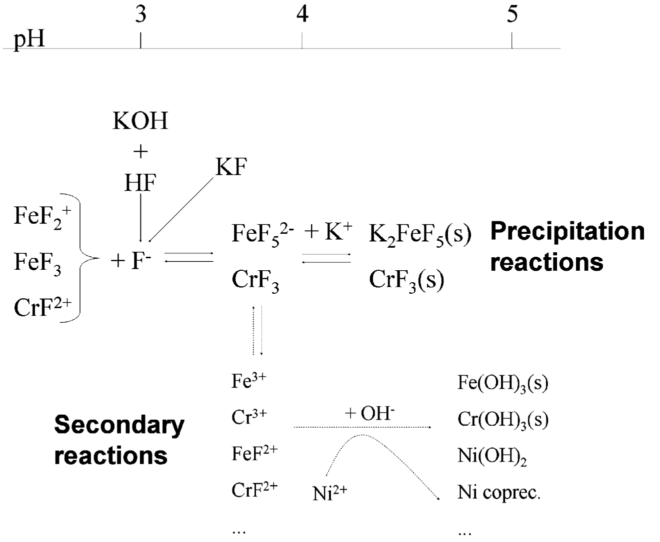

Fig. 2. Mechanism diagram of fluorides precipitation from SPL.

2. Reaction system modelling

Chemical reactions taking place in SPL systems are those involving iron and chromium fluoride complexes, acid–base equilibriums, cations hydrolysis and nitrate–iron complex [21]. This provides a system of 25 reactions with 31 species, which is solved by adding mass and charge balance.

For equilibrium concentration calculation, thermodynamic constants at 25 °C were considered, so activity coefficients must be evaluated at the same temperature. When higher temperatures are considered, logarithmic variation is considered as done in the literature [19]. Thermodynamic constants for the considered equilibriums are shown in Table 1.

Table 1
Chemical equilibrium reactions in stainless steel SPL

Equilibrium pattern	Reaction	log *K* (25 °C)
Acid–base	$HF \rightleftarrows H^- + F^-$	−3.2
	$HNO_3 \rightleftarrows H^+ + NO_3^-$	1.43
Complexation by fluoride	$HF + F^- \rightleftarrows HF_2^-$	0.7
	$Fe^{3+} + F^- \rightleftarrows FeF^{2+}$	5.5
	$Fe^{3+} + 2F^- \rightleftarrows FeF_2^+$	9.7
	$Fe^{3+} + 3F^- \rightleftarrows FeF_3$	12.7
	$Fe^{3+} + 4F^- \rightleftarrows FeF_4^-$	14.9
	$Fe^{3+} + 5F^- \rightleftarrows FeF_5^{2-}$	15.4
	$Fe^{3+} + 6F^- \rightleftarrows FeF_6^{3-}$	−0.6
	$Cr^{3+} + F^- \rightleftarrows CrF^{2+}$	4.4
	$Cr^{3+} + 2F^- \rightleftarrows CrF_2^+$	7.7
	$Cr^{3+} + 3F^- \rightleftarrows CrF_3$	10.2
	$Ni^{2+} + F^- \rightleftarrows NiF^+$	0.7
Complexation by nitrate	$Fe^{3+} + NO_3^- \rightleftarrows FeNO_3^{2+}$	1.0
Metallic cations hydrolysis	$Fe^{3+} + OH^- \rightleftarrows FeOH^{2+}$	11.6
	$Fe^{3+} + 2OH^- \rightleftarrows Fe(OH)_2^+$	20.9
	$2Fe^{3+} + 2OH^- \rightleftarrows Fe_2(OH)_2^{4+}$	25.1
	$Cr^{3+} + OH^- \rightleftarrows CrOH^{2+}$	10.2
	$Cr^{3+} + 2OH^- \rightleftarrows Cr(OH)_2^+$	18.0
	$Cr^{3+} + 4OH^- \rightleftarrows CrO_2^- + 2H_2O$	29.0
	$Cr^{3+} + 6OH^- \rightleftarrows CrO_3^{3-} + 3H_2O$	27.2
	$Ni^{2+} + OH^- \rightleftarrows NiOH^+$	4.7
	$Ni^{2+} + 2OH^- \rightleftarrows Ni(OH)_2$	8.0
	$Ni^{2+} + 3OH^- \rightleftarrows NiO_2H^- + H_2O$	11.6
Precipitation reactions	$FeF_3(s) \rightleftarrows Fe^{3+}(aq) + 3F^-(aq)$	Unknown
	$CrF_3(s) \rightleftarrows Cr^{3+}(aq) + 3F^-(aq)$	Unknown
	$K_2FeF_5(s) \rightleftarrows FeF_5^{2-}(aq) + 2K^+(aq)$	Unknown
	$Fe(OH)_3(s) \rightleftarrows Fe^{3+}(aq) + 3OH^-(aq)$	−37.4
	$Cr(OH)_3(s) \rightleftarrows Cr^{3+}(aq) + 3OH^-(aq)$	−31.8
	$Ni(OH)_2(s) \rightleftarrows Ni^{2+}(aq) + 2OH^-(aq)$	−15.8

Calculation of activity coefficients were made by a new equilibrium model for SPL, developed by our research group. It is based on Bromley's Method [16–18] for electrolyte activity coefficients:

$$\log \gamma_i = -\frac{A z_i^2 I^{0.5}}{1 + I^{0.5}} + F_i \tag{1}$$

$$F_A = \sum_c B'_{cA} Z_{cA}^2 m_c; \qquad F_C = \sum_a B'_{Ca} Z_{Ca}^2 m_a \tag{2}$$

$$B'_{ca} = \frac{(0.06 + 0.6B_{ca})|z_c z_a|}{(1 + (1.5I/|z_c z_a|))^2} + B_{ca} \tag{3}$$

$$Z_{ca} = \frac{z_c + |z_a|}{2} \tag{4}$$

where γ_i is the activity coefficient of ion i, z the ion charge and B_{ca} is the Bromley parameter for cation–anion interaction, represented by C or c for cations and A or a for anions.

Water activity is calculated by Hamer and Wu [22] method:

$$\log a_{H_2O} = -0.007824 \nu m_{MX} \phi_{MX} \tag{5}$$

where ν is the stoichiometric coefficient for a MX electrolyte. Osmotic coefficient, ϕ_{MX} is calculated as:

$$\phi_{MX} = 1 - 2.302585 \left\{ \frac{|Z_M Z_X| A}{B^3 m} \left[(1 + Bm^{1/2}) - 4.60517 \log(1 + Bm^{1/2}) - \frac{1}{(1 + Bm^{1/2})} \right] - \frac{\beta m}{2} - \frac{2Cm^2}{3} - \frac{3Dm^3}{4} - \frac{4Em^4}{5} \right\} \tag{6}$$

where A is the Debye–Hückel parameter and B, β, C, D and E are Humer and Wu [22] interaction parameters.

As the considered system is a multi-electrolyte problem, water activity was calculated considering only HNO_3 dissociation in water at the same ionic strength of the solution (SPL or neutralizing media). This model, called UCM-Model and developed in previous work [16], provides good results fitting when calculated Bromley parameters, shown in Table 2, are used. Comparison of UCM-Model with other models, like SSPEC, developed by Ref. [20] and used by Ref. [19], revealed that new

Table 2
Bromley parameters for anion–cation interaction in SPL used in the UCM-Model

Interaction	H^+	Fe^{3+}	FeF^{2+}	$FeF_2{}^+$	Cr^{3+}	CrF^{2+}	$CrF_2{}^+$	Ni^{2+}
F^-	−0.0659	0.0956	−0.0094	−0.0133	−0.0214	−0.0184	−0.0114	−0.1630
$NO_3{}^-$	−0.0748	0.0113	0.1421	0.3678	0.1900	−0.0742	−0.1744	−0.0192

model shows higher accuracy for a wider concentration range in free acidity prediction. SPL chemical composition and species distribution are shown in Table 3 for optimized model. Ionic strength of a typical SPL solution is about 3–4 mol kg^{-1}.

Nitrate does not form any stable metal complex, except for iron, so free nitric acid in pickle liquor is near to total nitrate content. Fluoride forms very stable complexes with iron and chromium; protons concentration is high enough for keeping hydrofluoric acid associated. Then, free fluoride, F^-, is too low if compared with total fluoride concentration.

Iron forms FeF_3(aq), which would precipitate, mainly as β-FeF_3(s) [19]. This process is too slow, so it is not considered when modelling in normal conditions and SPL management.

New chemical equilibriums studied in this work are represented by the following reactions and solubility products:

$$FeF_3(s) \rightleftarrows Fe^{3+}(aq) + 3F^-(aq) \tag{7a}$$

$$K_{s,FeF_3} = \gamma_{Fe^{3+}} C_{Fe^{3+}} \gamma_{F^-}^3 C_{F^-}^3 \tag{7b}$$

$$CrF_3(s) \rightleftarrows Cr^{3+}(aq) + 3F^-(aq) \tag{8a}$$

$$K_{s,CrF_3} = \gamma_{Cr^{3+}} C_{Cr^{3+}} \gamma_{F^-}^3 C_{F^-}^3 \tag{8b}$$

$$K_2FeF_5(s) \rightleftarrows FeF_5{}^{2-}(aq) + 2K^+(aq) \tag{9a}$$

$$K_{s,K_2FeF_5} = \gamma_{FeF_5{}^{2-}} C_{FeF_5{}^{2-}} \gamma_{K^+}^2 C_{K^+}^2 \tag{9b}$$

Although reaction (7a) is too slow in SPL, achieving equilibrium composition in several weeks, its solubility product is calculated from Österdahl and Rasmuson reported data [19]. In this reference equilibrium concentration is calculated with SSPEC, using equilibrium constants fitted for specific ionic strength and temperatures. This work uses thermodynamic constants that simplify calculation, which is independent from ionic strength. Reactions (8a), (8b), (9a) and (9b) are introduced in this work because they appear when pickling liquor is neutralized with potassium hydroxide, as it is proposed in Figs. 1 and 2. Activity coefficients and concentrations are calculated for filtrates composition from precipitation tests.

3. Experimental

3.1. SPL preparation

Pickling liquor was prepared by solving AISI 304 stainless steel plates in HNO_3/HF mixtures (reagent grade) at 60 °C, adding fresh acid if necessary in order to reach standard composition of SPL. This solution was kept at 25 °C during few days.

3.2. Fluorides selective precipitation

An automatic CRISON D++ titrator was employed for SPL neutralization. Fifteen milliliters of liquor were fed to a 500 mL glass jacketed reactor with 150 mL of deionized water. Temperature was controlled by a thermostatic bath connected to reactor jacket and pH was measured with a pH probe and controlled by automatic titrator. When programmed temperature is reached, titrator starts neutralization to pH setpoint. For this purpose, aqueous mixture of KOH and KF is employed (reagent grade). The objective is to obtain a mixture of green crystals of $K_2FeF_5{\cdot}H_2O$(s) and $CrF_3{\cdot}2H_2O$(s) without oxides or hydroxides, so pH is set at 3.5–4.1 and alkali stream composition is 1.5 mol KOH L^{-1}and 3.6 mol KF L^{-1}. Stirring speed is 500 rpm and experimentation time was determined by titrator as a function of pH stability. Reaction system is considered to be equilibrated when pH is well stabilized (there is no alkali addition in a period higher than 1 h).

Precipitated solids were vacuum-filtrated and dried during 24 h at 105 °C and analyzed by X-ray diffraction (XRD) using a SIEMENS KRISTALLOFLEX 810 goniometer with Cu Kα radiation. Metals (Fe, Cr, Ni) concentration in the liquid effluent was determined by atomic absorption spectroscopy with a VARIAN SPECTRAA 220 spectrometer. Nitrate and fluoride concentration was measured with METTLER TOLEDO ion selective electrodes, with previous ionic strength adjustment.

3.3. Calculation methodology

Once a test has been carried out, data from final solution must be treated with the UCM-Model. A general

Table 3
SPL chemical composition and species distribution (percentage, mol/mol) with the UCM-Model

Nitrate (150 g L^{-1})		Fluoride (60 g L^{-1})		Iron (III) (40 g L^{-1})		Chromium (III) (10 g L^{-1})		Nickel (II) (5 g L^{-1})	
				Fe^{3+}	2.8%				
				FeF^{2+}	5.9%	Cr^{3+}	0.0%		
		HF	27.3%	$FeF_2{}^+$	10.5%	CrF^{2+}	79.4%		
$NO_3{}^-$	98.7%	$MeF_n{}^{3-n}$	72.0%	FeF_3	58.9%	$CrF_2{}^+$	19.6%	Ni^{2+}	99.9%
Others	1.3%	F^-	0.1%	$FeF_4{}^-$	19.6%	CrF_3	1.0%	Others	0.1%
		Others	0.6%	$FeF_5{}^{-2}$	0.5%	Others	0.0%		
				Others	1.8%				

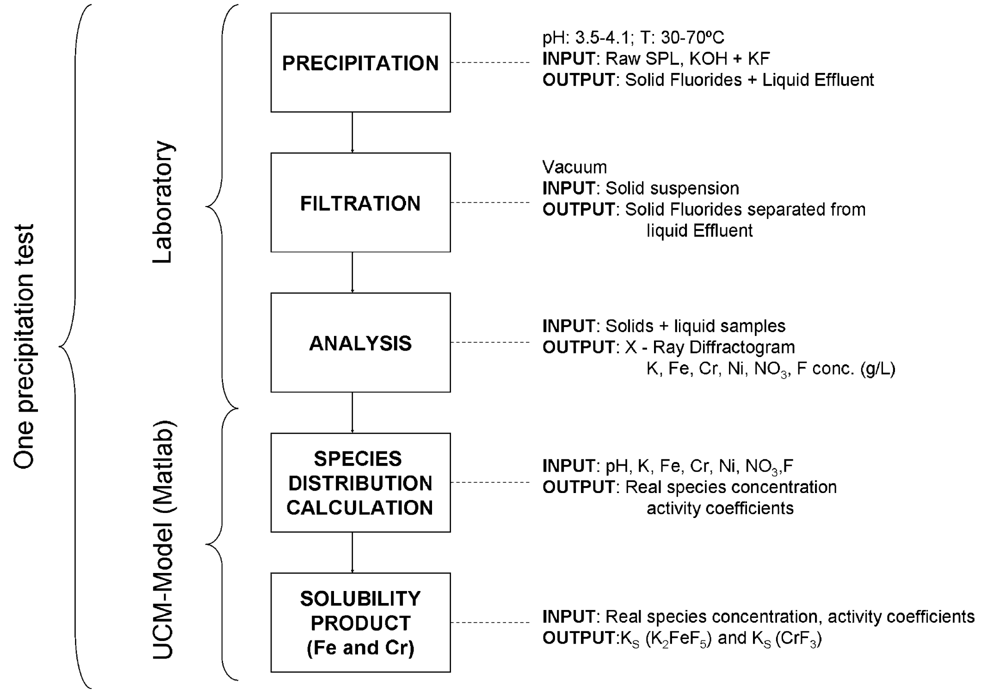

Fig. 3. General procedure for the calculation of solubility product.

scheme on experimental and calculation procedure is shown in Fig. 3.

When each precipitation test is carried out and final suspension is filtrated, liquid effluent is analyzed by mentioned techniques. Input data for UCM-Model are test pH and concentration of main components. UCM-Model calculates the real species concentration in solution and their activity coefficient. Solubility products for K_2FeF_5(s) and CrF_3(s) are then calculated. Each experiment (T–pH) has been made at least three times in order to calculate statistic error.

4. Results and discussion

4.1. Model validation for solubility calculation

Before analysing experimental data, validation for solubility calculation of UCM-Model is achieved by comparing reported results from Refs. [19,20] and calculating solubility product of FeF_3(s) with other thermodynamic model used in Ref. [19].

4.1.1. Equilibrium model

UCM-Model, developed in Ref. [16], is used for calculation. This is the best model for equilibrium calculation in SPL and it is revealed by the comparison with SSPEC model developed in Ref. [20] and SSPEC constants proposed in Ref. [19]. In Fig. 4a and b free hydrofluoric acid concentration prediction (values from spent pickle liquors used in Ref. [16] for UCM model development) for the three models are shown.

As it can be observed in Fig. 4, UCM-Model fits experimental values better than SSPEC. This fact is due to the theoretical basis of UCM-Model: thermodynamic constants are used and activity coefficients are calculated, so it is no necessary

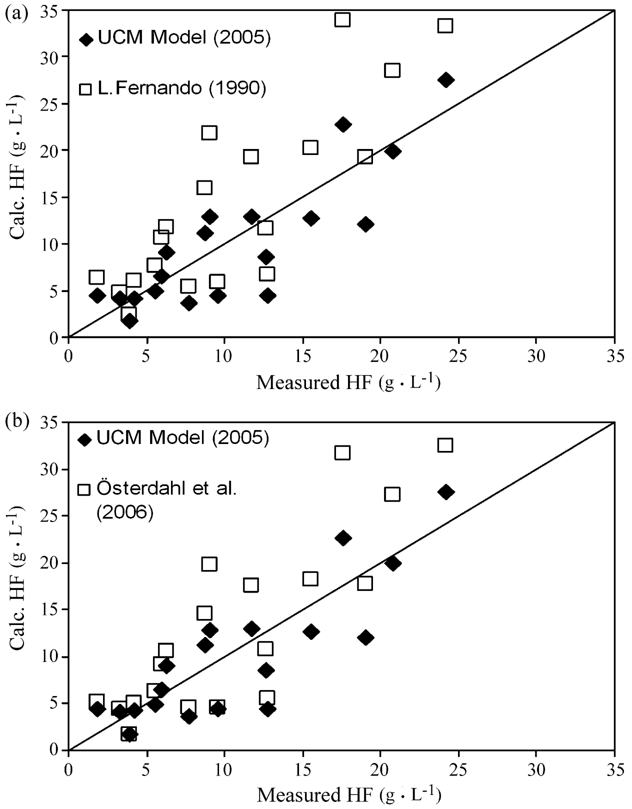

Fig. 4. Calculated HF concentration vs. measured for (a) UCM-Model and SSPEC with equilibrium constants from Ref. [20] and (b) UCM-Model and SSPEC with equilibrium constants from Ref. [19].

Table 4
Values of thermodynamic solubility product of $FeF_3(s)$ obtained from Ref. [19] data

Temperature (°C)	$-\log(K_s)$, FeF_3	Error (%)	R^2
30	13.5	3.4	0.976
40	13.1	2.4	0.980
50	12.6	3.3	0.981

to have equilibrium constants at any ionic strength, as in the case of Refs. [19,20]. Although acidity of SPL prediction is correct, proposed model applicability is restricted to liquors composition used in its optimization [16]: NO_3^-: 80–200 g L^{-1}; F^-: 60–120 g L^{-1}; Fe: 20–40 g L^{-1}; Cr: 4–12 g L^{-1} and Ni: 2–5 g L^{-1}.

4.1.2. $FeF_3(s)$ solubility

$FeF_3(s)$ precipitation is not included in the UCM-Model because iron fluoride precipitation is very slow in pickling liquors and tends to form micro-coagulates, which are hardly removable. The UCM-Model has been developed for its application in SPL treatment, where liquors life is not higher than 1 week. However, data reported by Östherdahl and Rasmuson [19] are used in this work for $FeF_3(s)$ solubility product calculation. Table 4 shows fitting results for 30, 40 and 50 °C. K_s is defined as Eq. (7b), error percentage is calculated as the ratio of K_s confidence interval (95% significance) and K_s value, and R^2 is the squared correlation index of model results and experimental results. Fig. 5 shows experimental data from Ref. [19] and new fitting curves from UCM-Model.

Iron(III) fluoride solubility product obtained is independent from ionic strength or pH and do not invalidate application of $K_{s,2}$ values of Österdahl and Rasmuson [19]. The values obtained in this work can be applied for calculating SPL composition only with the UCM-Model, as Österdahl and Rasmuson values must only be applied with the SSPEC program including equilibrium constants for each ionic strength and temperature. The improvement achieved by UCM-Model is the wide range of SPL composition, ionic strength and temperature in its use without changing equilibrium constant values.

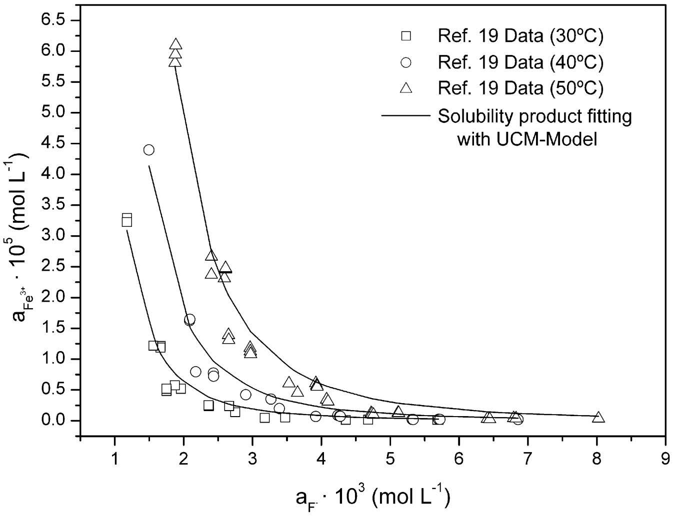

Fig. 5. Solubility curves for iron(III) fluoride.

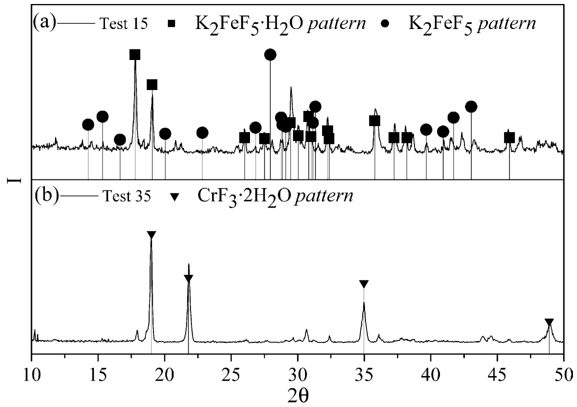

Fig. 6. X-Ray diffractograms of solid samples from test 15 (a) and test 35 (b).

4.2. $K_2FeF_5(s)$ and $CrF_3(s)$ solubility determination

Four sets of experiments were carried out, varying initial pickling liquor composition, pH and temperature. Liquid effluent analysis of the filtrate after precipitation was carried out. Results are provided in Table 5.

For the analysis of a real SPL, with iron, chromium and nickel, three samples with different concentration were considered (tests from 1 to 30). The specific case for chromium was analyzed in a simulated SPL solution with no iron or nickel, keeping free acidity of this sample equal to a standard pickling liquor solution.

Fluorides precipitation, shown in Fig. 1, is a process for separating nickel in the liquid effluent; other possibility, as hydroxides precipitation of iron and chromium, provokes nickel coprecipitation and reduce its recovery yield. So, fluorides solubility measurement is an extremely important task for maximizing metallic recovery.

Presence of $K_2FeF_5 \cdot H_2O(s)$ and $CrF_3 \cdot 2H_2O(s)$ mixtures are observed by XRD analysis, as it is shown in Fig. 6a. Crystallinity of solid mixture is near 99%. Fig. 6b shows also chromium fluoride precipitated from experiments without iron and nickel, where high crystallinity of $CrF_3 \cdot 2H_2O(s)$ is also observed.

As it is explained in the experimental section, K_s is calculated from real species distribution in the final effluent. Fitting equations, deduced for each compound, are defined as follows:

$$-\log a_{Fe^{3+}} = -\log K_{s,K_2FeF_5} + \log \beta_{FeF_5{}^{2-}} - [-\log(a_{F^-}^5 a_{K^+}^2)] \quad (10)$$

$$-\log a_{Cr^{3+}} = -\log K_{s,CrF_3} - 3(-\log a_{F^-}^3) \quad (11)$$

Figs. 7 and 8 shows solubility product fitting for both iron and chromium fluorides.

Table 5
Filtrate composition after precipitation tests

Test	SPL composition		T (°C)	pH	F ($g\,L^{-1}$)	NO_3^- ($g\,L^{-1}$)	Fe ($g\,L^{-1}$)	Cr ($g\,L^{-1}$)	Ni ($g\,L^{-1}$)
	Component	$g\,L^{-1}$							
1	F^-	54	30	3.5	7.4	12.1	2.9	0.8	0.4
2			40	3.5	7.8	11.7	3.1	0.9	0.4
3	NO_3^-	145	50	3.5	7.9	11.8	3.3	1.0	0.4
4			60	3.5	8.2	11.6	3.3	1.0	0.4
5	Fe(III)	38	70	3.5	8.3	14.5	3.4	1.1	0.4
6			30	4.1	7.0	13.6	2.1	1.0	0.4
7	Cr(III)	10	40	4.1	8.4	14.1	2.2	0.9	0.4
8			50	4.1	7.5	13.9	2.3	0.9	0.4
9	Ni(II)	4.8	60	4.1	7.9	15.3	2.3	0.9	0.4
10			70	4.1	7.1	16.1	2.3	0.6	0.4
11	F^-	45	30	3.5	6.5	15.5	2.8	1.0	0.4
12			40	3.5	6.8	15.7	2.9	1.0	0.4
13	NO_3^-	159	50	3.5	7.5	18.0	2.9	1.0	0.4
14			60	3.5	6.6	21.6	3.0	1.1	0.4
15	Fe(III)	37	70	3.5	7.1	27.8	3.2	1.2	0.5
16			30	4.1	5.7	11.3	1.5	0.9	0.4
17	Cr(III)	10.7	40	4.1	5.8	12.1	1.6	0.9	0.4
18			50	4.1	5.4	12.5	1.7	0.8	0.4
19	Ni(II)	4.6	60	4.1	5.6	14.0	1.8	0.8	0.4
20			70	4.1	5.0	16.1	1.9	0.5	0.4
21	F^-	47	30	3.5	6.8	18.3	3.2	1.0	0.4
22			40	3.5	7.4	19.0	3.1	1.2	0.4
23	NO_3^-	179	50	3.5	7.2	21.5	3.2	1.1	0.4
24			60	3.5	6.2	27.3	3.3	1.1	0.4
25	Fe(III)	34	70	3.5	5.8	34.5	3.4	1.1	0.5
26			30	4.1	5.5	14.4	1.2	1.0	0.4
27	Cr(III)	10.6	40	4.1	5.8	14.9	1.2	0.9	0.4
28			50	4.1	5.9	16.1	1.2	0.9	0.4
29	Ni(II)	4.6	60	4.1	5.5	18.6	1.2	0.8	0.4
30			70	4.1	5.1	19.4	1.3	0.6	0.4
31	F^-	32	30	3.5	2.9	6.9	–	1.0	–
32			40	3.5	3.2	7.8	–	1.0	–
33	NO_3^-	122	50	3.5	3.0	8.4	–	1.1	–
34			60	3.5	2.8	10.6	–	1.0	–
35	Fe(III)	–	70	3.5	2.4	12.5	–	1.0	–
36			30	4.1	4.1	6.3	–	1.1	–
37	Cr(III)	10.1	40	4.1	4.1	6.6	–	1.1	–
38			50	4.1	4.2	7.1	–	1.0	–
39	Ni(II)	–	60	4.1	3.5	7.4	–	0.9	–
40			70	4.1	3.7	10.3	–	1.0	–

Values of K_s for $K_2FeF_5(s)$ and $CrF_3(s)$ with errors, defined as K_s-confidence interval ratio, and squared correlation index for Eqs. (10) and (11) are shown in Tables 6 and 7. Calculated error values are below 5% so negligible pH influence on thermodynamic K_s is proved.

Solubility product relationship with temperature is correlated by expression:

$$\ln K_s = A' + \frac{B'}{T} \qquad (12)$$

Fitting results for Eq. (12) are shown in Table 8.

Table 6
$K_2FeF_5(s)$ solubility product and calculated errors

Temperature (°C)	$-\log(K_s)$, K_2FeF_5	Relative error (%)	Correlation index
30	3.72	1.6	0.977
40	3.64	1.9	0.985
50	3.57	2.2	0.968
60	3.56	3.3	0.940
70	3.48	1.1	0.988

Table 7
$CrF_3(s)$ solubility product and calculated errors

Temperature (°C)	$-\log(K_s)$, CrF_3	Relative error (%)	Correlation index
30	11.8	0.3	0.998
40	11.5	0.3	0.998
50	11.2	0.3	0.998
60	11.0	0.4	0.998
70	10.8	0.3	0.984

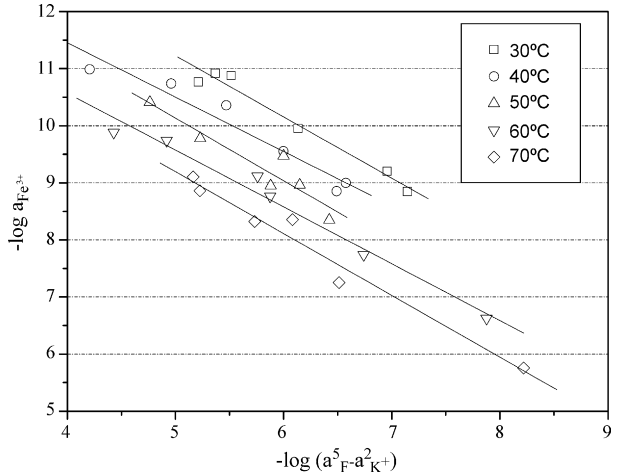

Fig. 7. Estimated activities for $K_2FeF_5(s)$ solubility product calculation.

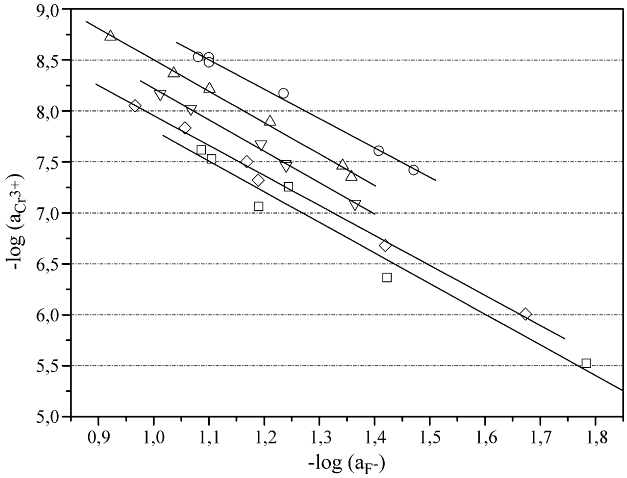

Fig. 8. Estimated activities for $CrF_3(s)$ solubility product calculation.

Expected behavior is observed, increasing solubility with temperature for both compounds. Obtained results show less variation with temperature of $K_2FeF_5(s)$ solubility product than $CrF_3(s)$. However, previous work [15] has shown that temperature can increase the quantity of chromium precipitated as fluoride, which is the opposite behavior of solubility product variation. This is due to a simple equilibrium adjustment because $CrF_3(aq)$ is a stable substance in solution due to complex formation. This fact can be explained when $CrF_3(aq)$ concentration is calculated with the UCM-Model in saturation conditions, as it is observed in Fig. 9.

As it is shown, $CrF_3(aq)$ concentration decrease with temperature because its stability constant decrease. Global effect is total chromium concentration decrease with temperature increase, although it depends on experimental conditions, like pH or SPL composition. $CrF_3(s)$ precipitation is induced by temperature increase, while $K_2FeF_5(s)$ is more soluble, producing opposite effects. In Ref. [15] is shown that optimal temperature range is 60–65 °C. Although fluorides crystallization by undercooling has been proposed for SPL treatment [23], it is shown that relatively high temperature (the same as in the pickling line) precipitation process is optimal for nickel separation from iron and chromium.

Table 8
Calculated parameters for Eq. (12) for solubility products of iron and chromium fluorides

	A'	B' (K)	R^2
$K_2FeF_5(s)$	−4.1 ± 0.5	−1400 ± 200	0.982
$CrF_3(s)$	−7.8 ± 1.0	−5800 ± 500	0.967

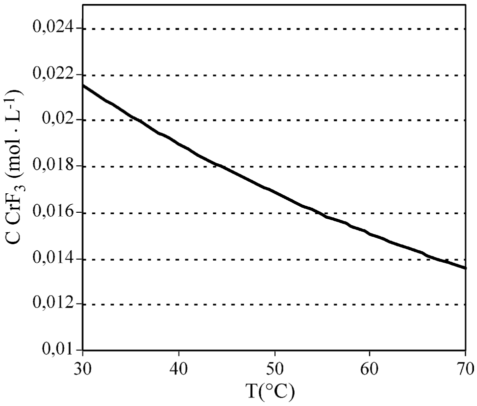

Fig. 9. $CrF_3(aq)$ equilibrium concentration variation with temperature.

4.3. Influence of pH and added KF

Solubility product of precipitating fluorides is a useful tool for calculating SPL behavior in neutralization with potassium hydroxide and excess free fluoride. Evolution of SPL composition with pH and free fluoride added to alkali solution, composed by KOH 1.5 M, is studied in Figs. 10 (with 0% of KF added to alkali) and 11 (with 10% KF), where ideal neutralization is supposed, with no dilution water as in solubility assays.

It is observed that fluorides tend to precipitate at lower pH when more free fluoride is added. Iron hydroxide appears at pH 3.6 if no free fluoride is added. Complex distribution does not change below pH 1, but higher pH provokes the formation of

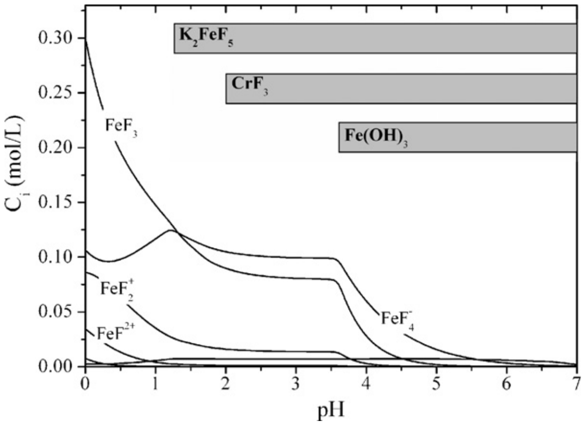

Fig. 10. Fluoride–iron complexes concentration in neutralization with KOH 1.5 M without potassium fluoride addition.

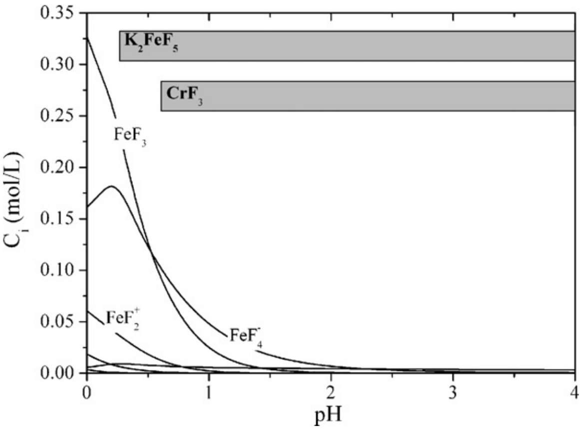

Fig. 11. Fluoride–iron complexes concentration in neutralization with KOH 1.5 M and 10% potassium fluoride addition.

high-fluoride content complexes, which can be controlled by %KF addition.

In Fig. 12 precipitating phases are shown as a function of fluoride addition and neutralization pH.

Addition of free fluoride increases K_2FeF_5(s) precipitation pH range and increase hydroxide precipitation pH. Total precipitation of iron is achieved if high amounts of fluoride are added (higher than 8% in alkali stream) while chromium total precipitation is achieved if hydroxide is obtained. As Fig. 1 indicates, chromium must be obtained as CrF_3(s) with a precipitation yield from 80% to 90%, while 99% of iron is precipitated. Remaining Cr can be recovered in nickel hydroxide precipitation reducing its purity.

K_2FeF_5(s) and CrF_3(s) are stable at values of pH higher than 6 if great amounts of KF are added. However, solubility product determination experiments had been made below pH 4.5 in order to avoid hydroxide precipitation. This is due to the dilution of 15 mL of SPL in 150 mL of deionized water that makes Fe^{3+} (and probably Cr^{3+}) concentration to be higher, while phase diagram has been calculated with no dilution.

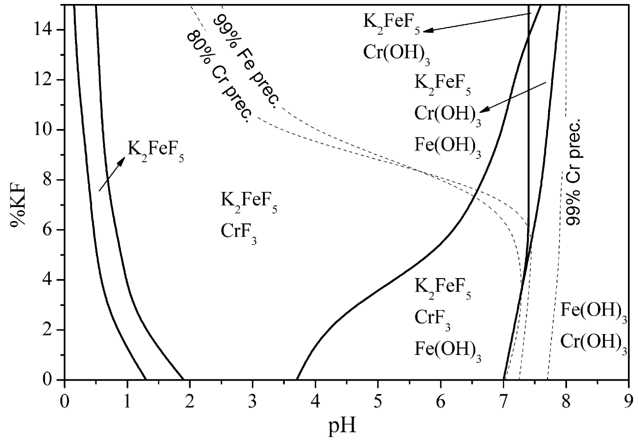

Fig. 12. Precipitating phases as a function of neutralization conditions (30 °C). Dash lines represent contour curves for several percentages of precipitated iron and chromium.

5. Conclusions

In this work the applicability of UCM-Model for SPL equilibrium calculation and solubility measurement has been proved. This tool will be a very important model for determining kinetics and designing of process stages for pickling liquor treatment.

The UCM-Model can be used to predict solubility curves for FeF_3, which appears in pickling baths by oversaturation, and other species as K_2FeF_5 and CrF_3 that can be precipitated during the neutralization of SPL or other treatment processes. Also, the solubility is correlated to temperature.

In comparison to other models, that proposed in this paper is valid for wider concentration ranges of SPL and it is not affected by ionic strength or free acidity, since it calculates these factors, as well as equilibrium concentrations, by using Bromley's methodology for the estimation of activity coefficients.

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