Fluoride Speciation in Stainless Steel Pickling Liquor

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Mixtures of hydrofluoric and nitric acids are used in the pickling of stainless steels, in order to remove oxide scale, generating pickling waste liquors with high HF concentration. Species appearing in this mixed acid solution are fluoride-metal complexes with high stabilization constants. This work discusses about the modelling of equilibrium reactions that could take place, like complexation of iron and chromium. As observed in the literature, 31 species could be present in pickling liquor with 25 equilibrium reactions. Activity coefficients are calculated using Bromley's methodology that depends on cation–anion interaction parameter B. New parameters at 25°C have been calculated, using Nelder and Mead Simplex Algorithm. The new model shows that FeF_3, CrF^{2+} and Ni^{2+} are the main metallic forms in the solution and undissociated hydrofluoric acid has a high relative concentration, while free fluoride practically does not exist in solution. In neutralization processes, free fluoride is released from undisocciated hydrofluoric acid. Therefore, high fluoride complexes are formed, which could precipitate instead of metal hydroxides.

KEY WORDS: stainless steel; pickling; fluoride complexes; equilibria modelling; iron; nitric acid, hydrofluoric acid.

1. Introduction

Pickling of stainless steel is actually achieved with aqueous mixtures of hydrofluoric and nitric acid in order to remove oxides scale formed in the steel surface. This treatment has more efficiency than other pickling methods, but generates high volume of dangerous and toxic wastes[1]. Nitric acid oxidizes and dissolves Fe(II)–oxides scale while hydrofluoric acid is used due to its great reactivity and stabilizing capacity of metals in solution due to complexes formation.[2] So, air pollutants (hydrogen fluoride and NO_x), solid wastes (metal fluorides with descaled chromium oxides) and exhausted pickling liquor are generated.

Pickling liquor composition is shown in **Table. 1**.[3] Total metals concentration is not higher than 5% because metals fluorides could precipitate. From 20 to 40% of total fluoride is forming HF while the remaining fluoride is forming metal complexes and free fluoride practically does not exist in solution[4].

Metal-fluoride complexes have high influence on the treatment of pickling liquor. For instance, neutralisation with alkali, like KOH or NaOH, is normally achieved with short residence time and high base concentration.[5] Then, metals are not able to release all the fluoride and high fluoride content solids are produced. Therefore, these solids are not recyclable to the electric arc furnace.

Moreover, free acid recovery processes have low efficiency for fluoride and recovered mixture is polluted with metals,[6] while total acid recovery needs to break complexes without fluoride losses.[7,8]

The aim of this paper is to develop an equilibrium model for predicting complexes concentrations when pickling liquor is produced and when metals precipitate from it. The equilibrium reactions among species shown in Table 1 are referred in the literature.[9,10] Thus, there could be 25 reactions in the pickling liquors, where 31 species could participate (**Table 2**). Since ionic strength in the pickling liquor is not kept constant, activity coefficients have to be calculated as a function of the ionic strength and total components concentration. The initial attempts to model HNO_3/HF pickling liquors were made by optimizing equilibrium constants in order to represent measurable values like complexed fluoride, hydrofluoric acid or nitric acid.[4] The range of application of these models is quite narrow, taking into account the high variability of acid baths concentrations. Bromley's Methodology[11] calculates activity coefficients

Table 1. Standard pickling liquor composition.

Component	Composition (g/L)
Free HNO_3	100-130
Total NO_3^-	120-160
Free HF	20-40
Total F^-	60-80
Fe(III)	35-45
Cr(III)	5-10
Ni(II)	3-6

Table 2. Equilibrium reactions and pickling liquor species.

Equilibrium Pattern	Reaction	Species
Acid-base	$HF \rightleftharpoons H^+ + F^-$ $HNO_3 \rightleftharpoons H^+ + NO_3^-$	HF, H^+, F^-, HF_2^- NO_3^-, OH^-, HNO_3
Fe(III) complexes	$Fe^{3+} + nF^- \rightleftharpoons FeF_n^{3-n}$ $Fe^{3+} + NO_3^- \rightleftharpoons FeNO_3^{2+}$ $mFe^{3+} + nOH^- \rightleftharpoons FeOH_n^{3m-n}$	Fe^{3+}, FeF^{2+}, FeF_2^+, FeF_3, FeF_4^-, FeF_5^{2-}, FeF_6^{3-}, $Fe(OH)^{2+}$, $Fe(OH)_2^+$, $Fe_2(OH)_2^{4+}$, $FeNO_3^{2+}$
Cr(III) complexes	$Cr^{3+} + nF^- \rightleftharpoons CrF_n^{3-n}$ $mCr^{3+} + nOH^- \rightleftharpoons CrOH_n^{3m-n}$	Cr^{3+}, CrF^{3+}, CrF_2^+, CrF_3, $Cr(OH)^{2+}$, $Cr(OH)_2^+$, CrO_2^-, CrO_3^{3-}
Ni(II) complexes	$Ni^{2+} + F^- \rightleftharpoons NiF^+$ $Ni^{2+} + nOH^- \rightleftharpoons NiOH_n^{2-n}$	Ni^{2+}, NiF^+, $Ni(OH)^+$, $Ni(OH)_2$, NiO_2H^-

by the assumption that cation–anion are the most important interactions, neglecting those anion–anion or cation–cation ones. In addition, only one interaction parameter is needed to calculate activity coefficients. Its application range is up to 6 mol/kg of ionic strength, so activity coefficients for pickling liquors can be modelled by applying Bromley's methodology with the following expression:

$$\log \gamma_i = -\frac{A z_i^2 I^{0.5}}{1 + I^{0.5}} + F_i \quad ....(1)$$

For a cation "C", which interacts with all anions "a", and an anion "A", which interacts with all cations "c", the term F_i is calculated as:

$$F_A = \sum_c B'_{cA} Z_{cA}^2 m_c; \quad F_C = \sum_a B'_{Ca} Z_{Ca}^2 m_a \quad ....(2)$$

Parameters B_{ca}' and Z_{ca} in the summations for all cations and anions are:

$$B_{ca}' = \frac{(0.06 + 0.6 B_{ca}) |z_c z_a|}{\left(1 + \frac{1.5 I}{|z_c z_a|}\right)^2} + B_{ca} \quad ....(3)$$

$$Z_{ca} = \frac{z_c + |z_a|}{2} \quad ....(4)$$

Where z is ion charge and B_{ca} is the Bromley parameter for cation–anion interaction.

For equilibrium concentration calculation, thermodynamic constants at 25°C were considered, so activity coefficients must be evaluated at the same temperature. When pickling liquor is modelled, twenty-seven activity coefficients must be calculated if $\gamma_i = 1$ is assumed for neutral species. In this work, the model is developed in several stages: Initial programming, taking into account parameters referred in the literature and the unknown parameters are set equal to zero; comparison of predicted hydrofluoric and nitric acid concentration with the experimental values; and optimization of Bromley's parameters for the pickling liquor system. Also, behaviour of complexes as a function of pH or added free fluoride is studied.

2. Materials and Methods

2.1. Pickling Liquors

The HNO₃/HF spent liquors were prepared by pickling 304 stainless steel plates in acid solutions of different compositions, adding fresh acid in order to reach the mean composition shown in Table 1. Thirteen different pickling liquors were prepared with different acid and metals concentration and kept at 25°C during few days, and then the composition of the liquors was analyzed.

2.2. Analysis

Metals concentration was analyzed using a VARIAN SpectrAA 220 spectrophotometer while fluoride and nitrate content was analyzed with Ion Selective Electrode technique (ISE).

Free hydrofluoric and nitric acid concentrations were analysed by titration using an automatic titrator CRISON Compact D++. This method is based on two stages: first, pickling liquor is neutralized at pH 3.5–4.5, so total acid concentration can be calculated. The next stage consists of a previous reaction of pickling liquor with silica (SiO₂) that removes the whole HF content of the liquor. Thus, nitric acid concentration is determined by titration and HF is the difference between total acidity and nitric acid contents. Hydrofluoric acid measured with this technique is undissociated while nitric acid is dissociated.

3. Results and Discussion

3.1. Model Development

Equilibrium relationships between metals and anions in a pickling liquor have been found in the literature. So, taking into account material balance and activity coefficients, species concentration can be calculated from total metals and anion concentration shown in Table 1, using a modified Newton's method programmed in Matlab.[12] Initial approximation of Bromley's parameters was established on the referenced values, while unknown ones were set equal to zero.

3.2. Optimisation and Validation

The thirteen liquors were analysed, measuring the concentration of each component and determining free acidity by titration. This was compared with acid concentration calculated using the initial proposed model. Residual plots for hydrofluoric acid and nitric acid are shown in **Figs. 1**(a) and 1(b). This residual plots show a high tendency: when hydrofluoric acid concentration increases, predicted value is higher than experimental and when nitric acid increases in solution, the model predicts lower concentrations. This fact is probably due to the low real equilibrium constant, so undissociated hydrofluoric acid is overestimated by the model. The low dissociation of hydrofluoric acid then makes the values for calculated nitric acid concentration to be smaller than experimental due to the low protons transference. Then, interactions between H⁺ and fluoride or nitrate are not well estimated with references values, probably due to the high ionic strength of the liquor (from 2 to 3 mol/kg). New activity coefficients must be calculated for the correct dissociation prediction of both acids.

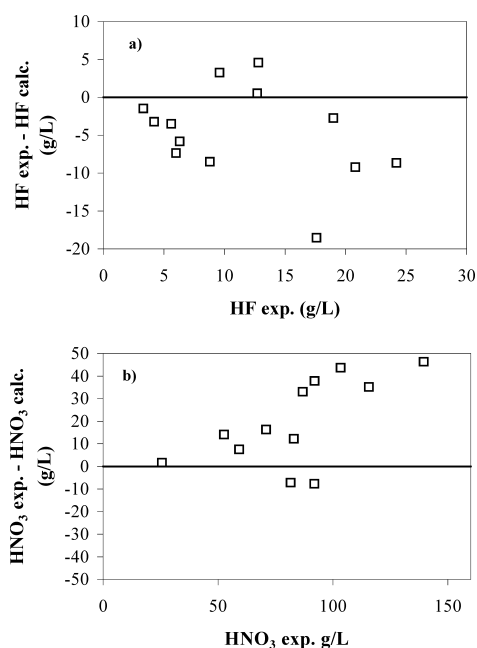Other important interactions are metallic compounds in

Fig. 1. Residual plots for hydrofluoic acid (a) and nitric acid (b) calculated from the initial model.
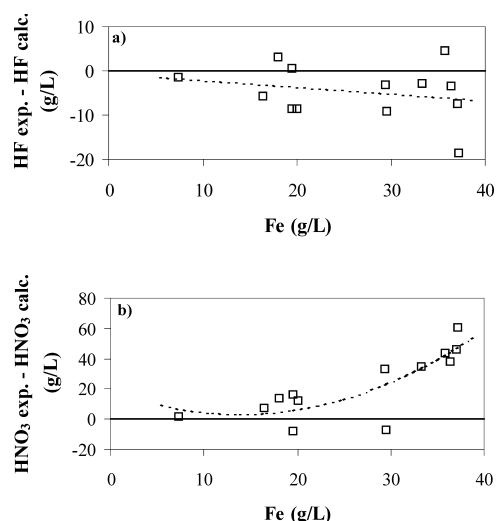

Fig. 2. Residual plots for hydrofluoric acid (a) and nitric acid (b) *vs.* total iron concentration.

Table 3. Initial and calculated Bromley's parameters at 25°C.

Interaction		Initial	Calculated	Interaction		Initial	Calculated
	H^+	0.0212	-0.0659		H^+	0.0903	-0.0748
	Fe^3	-0.0200	0.0956		Fe^3	0.0060	0.0113
	FeF^{2+}	Unknown	-0.0094		FeF^{2+}	Unknown	0.1421
	FeF_2^{+-}	Unknown	-0.0133		FeF_2^{+-}	Unknown	0.3678
F^-	Cr^3	-0.0440	-0.0214	NO_3^-	Cr^3	0.0815	0.1900
	CrF^{2+}	Unknown	-0.0184		CrF^{2+}	Unknown	-0.0742
	CrF_2^{+-}	Unknown	-0.0114		CrF_2^{+-}	Unknown	-0.1744
	Ni^{2+}	-0.1180	-0.1630		Ni^{2+}	0.0857	-0.0192

CrF^{2+}, CrF^{2+} and Ni^{2+}. This calculation was completed using the Nelder and Mead Simplex Optimization algorithm.[13] A multiresponse optimisation method has been prepared, because hydrofluoric acid and nitric acid concentration had to be optimised simultaneously. For this purpose, desirability function, ψ, has been defined for nitric and hydrofluoric acids residuals:

$$\Psi = \sqrt{\phi_{HF}\phi_{HNO_3}} \quad \dots\dots\dots\dots\dots(5)$$

where

$$\phi_{acid} = \begin{cases} 1 & F_{acid} = 0 \\ \dfrac{F_{acid\,max} - F_{acid}}{F_{acid\,max}} & 0 < F_{acid} < F_{acid\,max} \\ 0 & F_{acid} \geq F_{acid\,max} \end{cases} \dots\dots(6)$$

and

$$F_{acid} = \sqrt{\dfrac{\sum_1^n (\text{Exp. value} - \text{Calc. value})^2}{n-1}} \quad \dots\dots(7)$$

$F_{acid\,max}$ was set 30 g/L for HF and 50 g/L for HNO_3. Calculated Bromley's parameters are shown in **Table 3**. As it can be observed, literature and calculated values have high differences; this implies that these model parameters are valid only for pickling liquors because they have been calculated by fitting experimental values.

Optimal residual plots are shown in **Figs. 3**(a) and 3(b). It's observed that errors have little tendency for both acids as a function of acid concentration. For analysing new values of the parameters, statistics of the error distributions have been calculated (**Table 4**): a) confidence interval (95%) is determined for the error distribution and compared with the initial model responses and b) correlation index of the predicted values *vs.* experimental ones for both initial and optimised models.

Since mean error is less than the confidence interval for both acids in the optimised model, new parameters can be accepted for calculating provisional equilibrium concentrations in pickling liquors. The new model does not have any remarkable tendency between residuals and experimental concentrations. Thus, the optimised model fits experimental results in a reasonably well manner. This model has been compared with the data obtained in Ref. 4) by plotting calculated hydrofluoric acid *vs.* experimental values (**Fig. 4**).
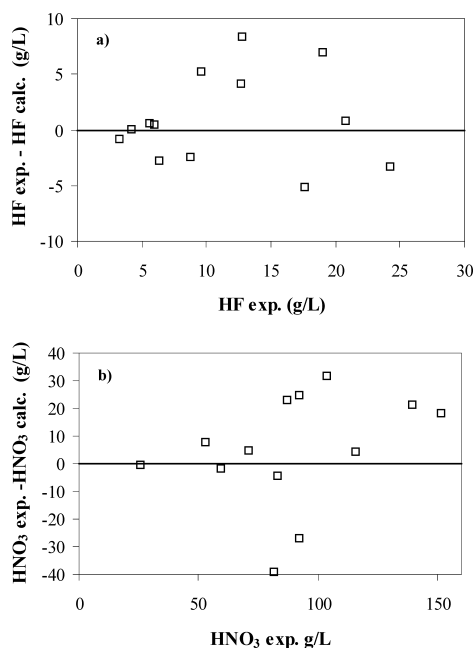
solution (free metals and metallic complexes). It's been observed a very important tendency of residuals *versus* iron concentration (**Figs. 2**(a) and 2(b)). When iron concentration increases, predicted values are higher than experimental for hydrofluoric acid. The behaviour of hydrofluoric acid, explained before, has a high influence on the complexation of metals because the fluoride released by dissociation is underestimated. Although this fact, interaction between iron and fluoride and the complexes formation has to be optimised, because interaction values for complex fluorides (FeF_n^{3-n}, CrF_n^{3-n}) with anions are unknown. For nitric acid, it's seen the opposite behaviour probably owing to free nitric acid increases from hydrofluoric acid dissociation and interaction parameters of cations and nitrate are unknown.

Then, the selected parameters to be calculated are those corresponding to the interaction between two anions, F^- and NO^{3-}, and eight cations, H^+, Fe^{3+}, FeF^{2+}, FeF^{2+}, Cr^{3+},

Fig. 3. Residual plots for hydrofluoric acid (a) and nitric acid (b) calculated from the optimised model.

Table 4. Statistics of error distribution for initial and optimised models.

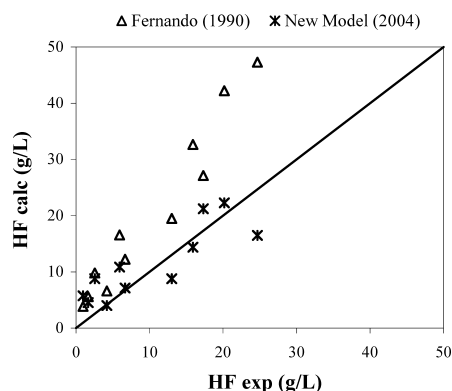| Statistic	Initial		Optimised	
	HF dist.	HNO$_3$ dist.	HF dist.	HNO$_3$ dist.
Mean Error (g/L)	-4.7	22.6	0.9	4.9
Standard deviation (g/L)	6.1	21.7	2.1	20.4
Conf. Interval $_{95\%}$ (g/L)	3.8	13.6	2.6	12.8
Correlation Index (r^2) Calc. Vs. Exp.	0.84	0.78	0.85	0.82
Absolute Mean Error (g/L)	6.0	25.0	3.2	16.0
Absolute Relative Error (%)	59	25	27	17

Fig. 4. Calculated *vs.* experimental plot for HF concentration. (Data from L.A. Fernando, 1990).

New model predicts experimental values with higher accuracy than model from reference, which shows a great tendency of residuals.

Table 5. Speciation of a standard pickling liquor.

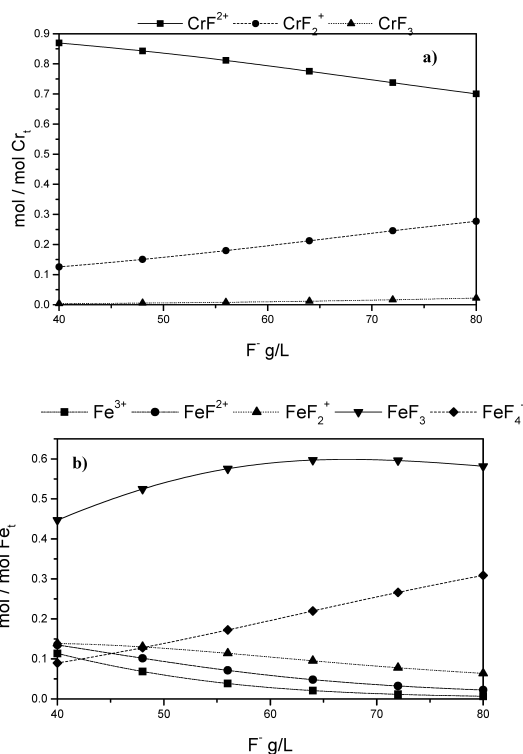| Nitrate 150 g/L (%)	Fluoride 60 g/L (%)		Iron (III) 40 g/L (%)		Chromium (III) 10 g/L (%)		Nickel (II) 5 g/L (%)	
			Fe^{3+}	2.8				
			FeF^{2+}	5.9	Cr^{3+}	0.0		
	HF	27.3	FeF$_2^+$	10.5	CrF^{2+}	79.4		
NO$_3^-$	98.7	MeF$_n^{3-n}$	72.0	FeF$_3$	58.9	CrF$_2^+$	19.6	Ni^{2+}	99.9
Others	1.3	F$^-$	0.1	FeF$_4^-$	19.6	CrF$_3$	1.0	Others	0.1
	Others	0.6	FeF$_5^{2-}$	0.5	Others	0.0		
			Others	1.8				

Fig. 5. Influence of fluoride content in the speciation of Cr (a) and Fe (b).

3.3. Speciation of HNO$_3$/HF Pickling Liquors

Species concentrations can be calculated from the new set of parameters shown in Table 3. These results are shown in Table 5 from a standard concentration of pickling liquor (NO$_3^-$ 150 g/L, F$^-$ 60 g/L, Fe 40 g/L, Cr 10 g/L and Ni 5 g/L). Nitrate and nickel exist as ionic species (NO$_3^-$, Ni^{2+}) and the amount of free fluoride, iron or chromium is very low compared to complexes concentration.

Iron is mainly forming FeF$_2^+$, FeF$_3$ and FeF$_4^-$ and chromium is forming CrF^{2+}. This implies that recovery processes have to break these complexes in order to release fluoride and metals, being the fluoride chemistry a very important factor for the treatment of pickling liquors.

In **Figs. 5**(a) and 5(b) it is shown the influence of fluoride content on chromium and iron species in a standard pickling liquor composition. High fluoride content complexes of both metals are formed when F$^-$ increases, as it is deduced from equilibrium expressions. However, iron is more reactive to fluoride than chromium because the fluoride

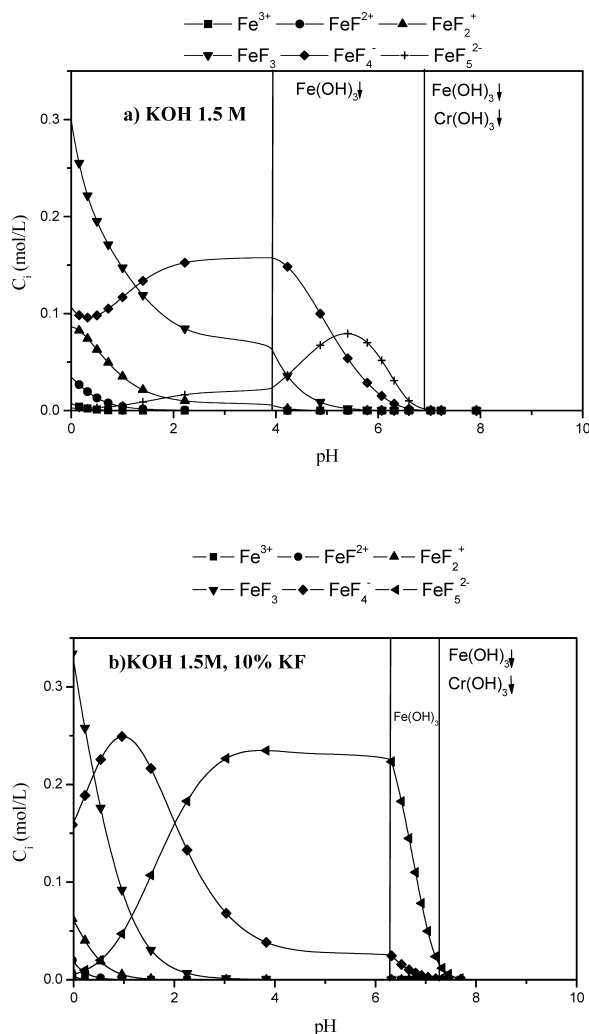Fig. 7. Iron complexes phases diagram as a function of pH and %KF added to KOH 1.5 M.

Fig. 6. Influence of pH in the speciation of iron when pickling liquor is neutralized with KOH 1.5 M (a) and KOH 1.5 M, 10% KF (b).

content of chromium complexes is lower than the one for iron, forming FeF_4^- while chromium main component is CrF_3.

3.4. Speciation as a Function of pH

When liquor is neutralised with an alkali solution, the concentration of complexes varies as a function of pH. In **Fig. 6**(a), high fluoride content complexes concentration increases when alkali is added. This is due to the neutralization of hydrofluoric acid that releases free fluoride to the solution. Iron and chromium are well stabilized by fluoride in solution, since theoretical precipitation of hydroxides would occur at higher pH than in the absence of this anion. Concentration of FeF_4^- and FeF_5^{2-} increases if KF is added to the solution, as seen in Fig. 6(b). This is due to displacement of equilibria due to high F^- concentration.

In previous works,[14] it has been shown that K_2FeF_5 and CrF_3 precipitate when KOH is used as alkali and KF as an additive. For total iron and chromium precipitation, the optimal experimental conditions were pH 4.1–4.3, temperature from 58 to 65°C and potassium fluoride added to the alkali has to be higher than 14%. If these conditions are analysed with the equilibrium model for standard pickling liquor, FeF_5^{2-} is the predominant specie (**Fig. 7**). Then, pre-
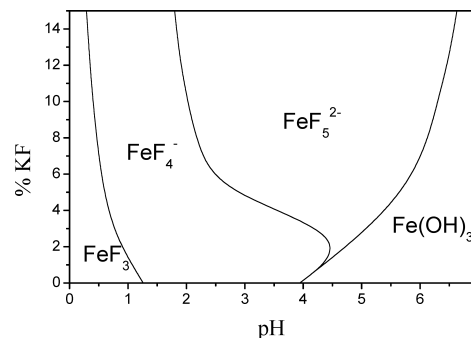
cipitation equilibrium is established between potassium and iron fluorides, while chromium is supersaturated as CrF_3.

It has also been demonstrated that nickel co-precipitates with mixtures of iron and chromium hydroxides, but not with mixed fluorides. Then, iron and chromium must be precipitated as fluorides in order to achieve an effective separation method among nickel and other metals in the pickling liquor. Solubilities of K_2FeF_5 and CrF_3 have to be calculated in order to determine the precipitation diagram of pickling liquors. Then, this model can be applied to the correct prediction of complexes concentration or determining the volume of alkali necessary for the neutralization of pickling liquor as well as total iron and chromium concentration as a function of pH.

4. Conclusions

Pickling liquors can be modelled by Bromley's methodology for electrolytes in solution. New parameters have been proposed, with high relative accuracy on predicting free acid concentration. Activity coefficient calculation provides better results than models with fitted equilibrium constants. The model predicts that the main species for metals are FeF_3, CrF^{2+} and Ni^{2+} while for anions are NO_3^- and HF, although fluoride forms several stable complexes with metals. When pickle liquor is neutralised, high fluoride complexes are formed, before hydroxides precipitation. These complexes precipitate when free fluoride is added to the medium, achieving an effective separation of nickel from iron and chromium. Solid fluorides can be treated with potassium hydroxide, releasing the fluoride content to solution; this implies a reduction of the environmental risk of wasted pickling baths.

Nomenclature

A: Constant of Bromley's Model, 0.5303
B_{ca}: Bromley's parameter for anion a and cation c
m_i: Molality of component i (mol/kg)
n: Number of analysed pickling liquors
I: Ionic Strength (mol/kg)
z_i: Charge of ion i

γ_i: Activity coefficient of component i

ν_i: Stoichmetric coefficient of component i

ψ_i: Desirability function

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