SOLUBILITY OF Ni IN SPENT PICKLING SOLUTIONS

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ABSTRACT

Nickel solubilities in spent pickling solutions (i.e. $HF-HNO_3-H_2O$ solutions) were measured as a function of HF and HNO_3 acid concentrations. The chemical analysis of the industrial pickling solutions and sludges were made. The stable phases observed in the sludges are $FeF_3 \cdot 3H_2O$ and (FeCr) $F_3 \cdot 3H_2O$. Pure Ni, and stainless steel type 316 were used in this study. The results showed that the solubility of Ni increased with increase in concentrations of HF in pickling solution at a fixed concentration of HNO_3. An excellent agreement between the experimental solubility data and the theoretical data was obtained. X-ray diffraction analysis showed that the solid solubility product formed is mainly $NiF_2 \cdot 4H_2O$ compound.

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1. INTRODUCTION:

Production of stainless steels requires pickling in aqueous solutions to obtain the desired surface properties. Mixed-acid pickling solutions of two or more acids are used for cleaning the oxide covered stainless steels, which are formed during the annealing process. The most common pickling solutions contain nitric and hydrofluoric acids. In practice, the stainless steels may be left in the pickling solution longer than necessary, causing excessive dissolution of the bulk steel, resulting in losses of several thousand tons of nickel annually(1).The dissolved metals also increase the use of acids in the pickling bath by complexing of precipitating acid salts(2-5). The high cost of waste acid disposal and loss of the valuable metals they contain are important considerations. A study, therefore, was undertaken to investigate the solubility of nickel in $HF-HNO_3-H_2O$ solutions.

2. EXPERIMENTAL

2.1 Composition of industrial pickle solutions

In stainless steel industrial pickling processes, composition and temperatures of pickling solutions, varies significantly from one industry to another. Chemical analysis of 10 samples from the representative companies are shown in Table 1. As can be seen from the table, the composition range for the samples analyzed are within the reported range of industrial pickling solutions, compositions 10-40 weight percent HNO_3 and 2 to 16 weight percent HF(6). Temperatures of pickling solutions are reported to vary from 298-350K. As expected, the concentration of chromium and nickel in solution, as shown in Table 1, increases with an increase in total concentration of acids in the pickling solutions. Figure 1 shows the SEM-EDAX micrograph of the crystalline phases in pickling sludges. The chemical analysis of the phases identified are shown in Table 2. The phases observed are FeF_3 $3H_2O$ and $(FeCr)F_3 \cdot 3H_2O$. these observations are in agreement with the analysis of fluorides based on standard Gibbs free energy change. FeF_3 and CrF_3 are more stable (larger negative free energy) compared to NiF_2, FeF_2 and CrF_2.

Table 1. Chemical analysis of industrial pickling solutions

Industry Sample #	Chemical composition wt. pct.				
	Fe	Cr	Ni	NO_3^-	F^-
1	1.353	0.070	0.300	11.740	1.127
2	8.907	0.627	0.620	10.510	3.119
3	2.667	0.680	0.560	13.690	2.949
4	2.880	0.340	0.780	11.460	3.102
5	4.960	0.786	0.620	13.500	5.080
6	4.710	0.850	0.500	16.000	5.800
7	1.440	0.140	0.260	16.300	1.120
8	3.130	0.440	0.770	12.900	3.440
9	2.710	0.522	0.411	8.250	5.910
10	2.430	0.496	0.291	14.110	4.670
Range	1.35-8.9	0.07-0.85	0.26-0.78	8.25-16.30	1.12-5.91

Table 2. Chemical analysis of industrial pickling sludges

Industry Sample#	Chemical Composition wt. pct.			Comments
	Fe	Cr	Ni	
1	31.0	0.78	0.038	X-ray diffraction and SEM-EDAX analysis. Phases: $FeF_3 \cdot 3H_2O$ and $(FeCr)F_3 \cdot 3H_2O$
2	30.5	0.73	0.041	
3	28.0	1.50	0.057	

2.2 Materials

Stock solutions of 71∓1 wt. pct. HNO_3 and 49∓1 wt. pct. HF certified by ACS specifications are used with no further additions. The alloy (stainless steel type 316) and pure Ni metal are used in the present study.

2.3 PROCEDURE:

Solubility of nickel in HNO_3-HF-H_2O solutions was determined at a temperature of 298K. All experiments were carried out with a minimum equilibration period of 7 days. The experimental method used was described in detail elsewhere (7) and a brief description is given here. A known amount of metal was added to the 500 ml teflon bottles containing a known concentration of HNO_3 and HF acids. The concentration of HNO_3 and HF used were in the range of 1 to 8 molality. After equilibration, the solution samples were analyzed for Ni^{++}, NO_3^-, F^- using AA and IC. The crystalline phases were analyzed using SEM and X-ray diffraction.

3. RESULTS AND DISCUSSION:

3.1 Pure Nickel:

The solubility of nickel in solutions was determined as a function of concentration of HF and HNO_3. The results are shown in Figure 2. As seen from the figure, at a fixed concentration of HF, the solubility of nickel increased with increase in concentration of HNO_3 in solution. For example, at a fixed concentration of HF (2 molality), the solubility of nickel increased from 3.7 to 16.5 weight percent as the concentration of HNO_3 in solution increased from 1 to 8 molality respectively. For a given fixed HNO_3 concentration, no significant increase in solubility of nickel in solution was observed with increase in HF concentration from 1 to 8 molality.

3.2 Alloy

The solubility of nickel from 316 stainless steel in HNO_3-HF-H_2O solutions is shown in Figure 3. The chemical composition of 316 SS in wt. pct is: 16-18 Cr, 10-14 Ni, 2.0 Mn, 1.0 Si, 0.08 C, 0.045 P, 0.03 S and the balance is Fe. As seen from the figure, the solubility of Ni in solution increased with increase in concentration of HF and also increased with increase in HNO_3. For a fixed concentration of 4 molality of HNO_3, the solubility of nickel increased from 0.18 to 0.55 weight percent as the concentration of HF in solution increased from 1 to 8 molality. This is in very good agreement with the solubility of Ni observed in the industrial pickling solutions. As expected, the solubility of pure nickel in solutions as compared to 316 stainless steel, is about an order of magnitude higher. It is clear that the solubility of nickel is dependant on the elements such as Fe, Cr which are present in the alloy. The solubility data are compared in Figure 4. The data indicates that the presence of elements Fe, Cr and other cations reduce the solubility of nickel.

3.3 Theoretical consideration

X-ray diffraction analysis of the solid substance formed at higher acid concentrations in solutions are determined to be metallic fluorides. These metallic fluorides are mainly hydrated nickel fluoride crystals of $NiF_2\ 4H_2O$. The solubility of nickel fluoride at a specific temperature and pH can be calculated using solubility product or standard Gibbs free energies of formation. The solubility of solid in equilibrium with solution containing appropriate ions can be written in the general form as:

$$AB_{z\,(solid)} + zH^{+}{}_{(aq)} = A^{Z+}{}_{(aq)} + zHB_{(aq)} \qquad (1)$$

The standard Gibbs free energy of reaction (1) can be written in terms of equilibrium constant as:

$$\Delta G_f^o = -RT \ln K \qquad (2)$$

and equilibrium constant (K) is given as:

$$K = [HB]^z [A^{Z+}] / [AB_z] [H^+]^Z = \exp (-\Delta G_f^o / RT) \qquad (3)$$

When the system is in equilibrium (i.e. several solids and ions coexist), and if the standard Gibbs free energies of all the species are known, the solubility relationship can be deduced from the mass balance of the system containing nickel ions, the probable fluoride complexes reaction sequence can be written as follows:

$$HF = H^+ + F^- \quad (4)$$
$$HF + F^- = HF_2^- \quad (5)$$
$$Ni^{2+} + 2F^- = 2NiF^+ \quad (6)$$
$$NiF^+ + F^- = NiF_2 \quad (7)$$

and the probable nitrate complexes are

$$HNO_3 = H^+ + NO_3^- \quad (8)$$
$$Ni^{2+} + NO_3^- = NiNO_3^+ \quad (9)$$

The thermodynamics data for these species are presented in Table 4. The species considered are mainly aqueous fluoride complexes. The solubility of nickel in solutions was estimated using Pitzer's (8,9) equation along with the interaction parameters for complex species of fluoride reported by Fernando (5) and Wilson and Taube (10). The material and mass balance equations were established and solved by an iterative method to yield the equilibrium concentration of the species. The calculated concentrations of nickel ions for pure nickel and 316 SS alloys along with the experimental data at a fixed 4 molality of HNO_3 are presented in Table 4 and also in Figure 4. As can be seen, an excellent agreement between the calculated and the experimentally

Table 3. Thermodynamic data at 298K

Species	ΔG_f^0 (K cal/mol)	Reference
F^-	-66.64	(11)
HF	-70.95	(11)
HF_2^-	-138.18	(11)
Ni^{+2}	-10.9	(11)
NiF_2	-142.9	(11)
NO_3^-	-26.61	(11)
HNO_3	-26.61	(12)

Table 4. Calculated and Measured Solubility of Nickel at 298K

					Ni (wt%)	
Species	pH	Ni^{2+}	NiF^{-}	NiF_2	cal.	Expt.
316	1.90	0.2400	0.0000	$1.7x10^{-8}$	0.24	0.25
316	1.60	0.3400	0.0000	$2.8x10^{-8}$	0.34	0.33
316	1.49	0.5000	0.0000	$5.7x10^{-8}$	0.50	0.51
316	1.45	0.5500	0.0000	$7.6x10^{-8}$	0.55	0.55
Nickel	5.40	10.0000	0.0001	0.0005	10.00	10.00
Nickel	5.35	11.0000	0.0001	0.0006	11.00	11.10
Nickel	3.80	10.8000	0.0001	0.0007	10.80	11.00
Nickel	3.65	10.4000	0.0001	0.0008	10.40	10.60

measured solubility data is obtained. The solubility of nickel, as seen from the figure increased with an increase in concentration of HF. The calculated results confirm that at higher concentrations of HF, nickel fluoride crystals are precipitated. The measured experimental data, however , showed that the precipitates are formed at 4 molality of HF for 316 SS and at 6 molality for pure nickel in pickling solutions.

4. CONCLUSIONS:

The solubilities of nickel in pickling solutions (i.e. HNO_3-HF-H_2O solutions) were measured as a function of concentration of HNO_3 and HF. The solubility experiments were carried out at a concentration of HNO_3 and HF in the range of 1 to 8 molality at 298K. From the present study the following conclusions can be made:

1. The solubility of nickel increased with an increase in concentration of HNO_3 and also with an increase in concentration of HF in the concentration range of 1 to 8 molality of each HNO_3 or HF acids.

2. SEM and X-ray diffraction analysis showed that the solid solubility product formed is mainly NiF_2 $4H_2O$ compound in the case of nickel. The stable crystalline phases observed in the industrial stainless steel sludges are $FeF_3 \cdot 3H_2O$ and $(FeCr)F_3 \cdot 3H_2O$.

3. An excellent agreement between the experimentally measured solubility of nickel data and the calculated data is obtained.

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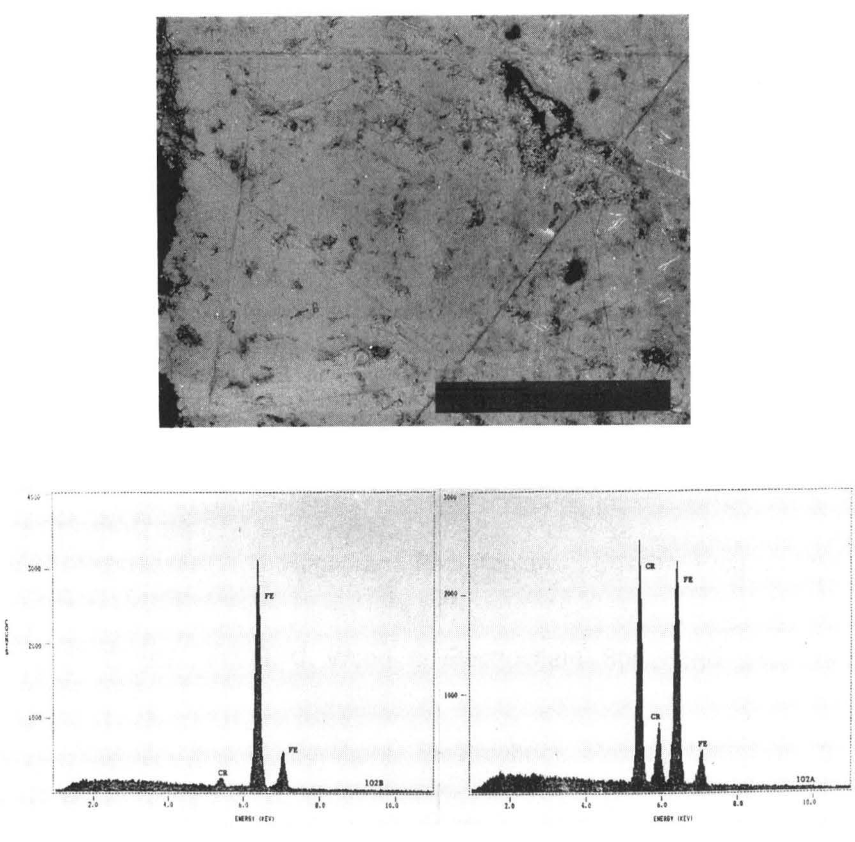

Figure 1. SEM-EDAX diffraction patterns and micrograph of industrial pickling sludges.

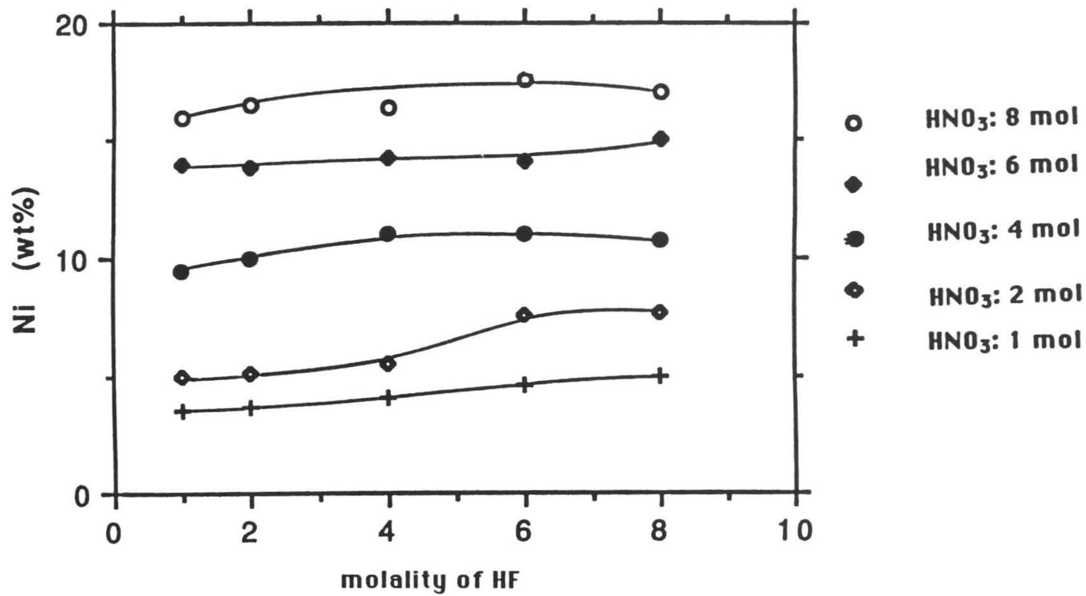

Figure 2: Solubility of pure Ni in HNO_3-HF-H_2O solutions at 298K

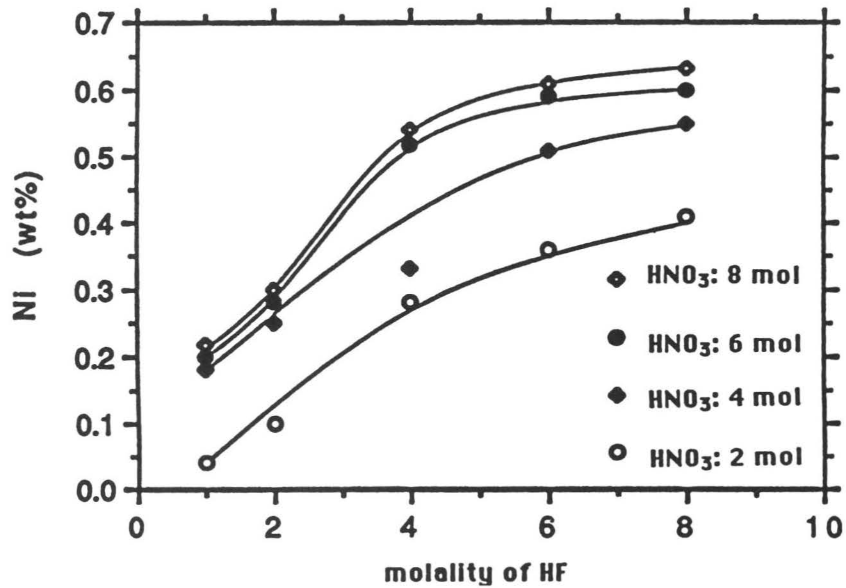

Figure 3: Solubility of 316 ss in HNO_3-HF-H_2O solutions at 298K

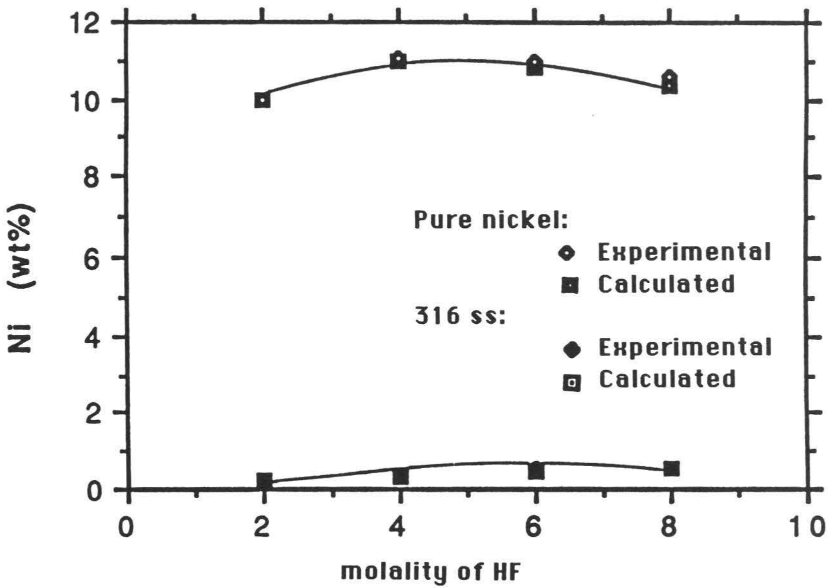

Figure 4: Calculated and measured solubility of Nickel in HNO_3-HF-H_2O solutions at 298K and molality of HNO_3=4 mol.

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