# Processing of Steel Rinse Waters through Coextraction and Selective Stripping

**M. A. Lobo-Recio, F. J. Alguacil, and A. López-Delgado**
Centro Nacional de Investigaciones Metalúrgicas (CSIC), Ciudad Universitaria, 28040 Madrid, Spain

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*Recovery of iron(III), $HNO_3$, and HF from stainless steel rinse waters by liquid–liquid extraction using Cyanex-923 extractant was studied. The influence of equilibration time, temperature, $V_{aq}/V_{org}$ phase ratios, and extractant concentrations on the extraction of iron(III) was investigated. Furthermore, the separate extraction of $HNO_3$ and HF by Cyanex-923 was also studied. Conditions for the coextraction of iron(III), $HNO_3$, and HF were established as: 30 min of contact, 20°C, $V_{aq}/V_{org}$ phase ratio of 1 and using undiluted Cyanex-923 (water presaturated) as extractant. Under the appropriate experimental conditions, water is effective for the selective stripping of the three extracted solutes.* © 2004 American Institute of Chemical Engineers *AIChE J,* 50: 1150–1155, 2004
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## Introduction

After pickling operations in steel works, the steel surface is rinsed with water to remove remainders of nitric and hydrofluoric acids used as pickling agents. Exhausted rinse waters from pickled stainless steel contain mainly $Fe^{3+}$, $Cr^{3+}$, and $Ni^{2+}$ ions and nitric and hydrofluoric acids, the average compositions of which were about 1 g/L $Fe^{3+}$, about 0.14 g/L $Cr^{3+}$, about 0.07 g/L $Ni^{2+}$, about 2 g/L $HNO_3$, and about 1 g/L HF (Frías et al., 2000). These rinse waters are usually neutralized with lime before their discharge, although no recovery of metals and/or acids is made. However, more stringent environmental legislation, especially in most industrialized countries, requires a decrease in the discharge of nitrates and other pollutant agents contained in industrial effluents (Directive 96/61/CE of the European Union Council). In this way, recent research lines that focus primarily on different technologies (liquid–liquid extraction, nanofiltration, electrodialysis, reverse osmosis, ion exchange, and so on) are being developed with the aim of recovering both metals and acids (Alguacil et al., 2002; Alonso et al., 1999; Haas and Vamos, 1995; Lunner, 2002; Navarro et al., 1996; Scott, 1997; Volesky, 2001).

Liquid–liquid extraction technology offers an attractive alternative for the treatment of such solutions because of its potential in managing great volumes of solutions (normally found in wastewaters) with a high-medium content in toxic solutes, which cannot be properly treated using other separation technologies (Rentish and Stevens, 2001). Moreover, liquid–liquid extraction can be selective in the separation of different solutes, although coextraction and selective stripping option are sometimes favored as being more economical because they requires fewer stages (Alguacil, 2002).

Kawasaki Steel Corporation is, to our knowledge, the only steelmaker that has developed and implemented a very complex extraction-based technology for recovering metals and acids from exhausted pickling liquors (Ohya et al., 1996), but it has not been applied to exhausted rinse water treatment.

The solvation reagent Cyanex-923 has proved its effectiveness in the separation of hazardous metals and mineral acids from various types of aqueous solutions (Alguacil and López, 1996; Alguacil and Martínez, 2001; Gupta et al., 2002; Regel et al., 2001; Rickelton, 1999; Saji et al., 1998; Wang et al., 2002), in which the stripping operation is more easily achieved than by the use of amine extractants (Regel et al., 2001; Wolters et al., 2002). Few data are available in the literature about considering liquid–liquid extraction in the treatment of stainless steel rinse waters, and thus the objective of this report is to study the factors that influence the extraction with Cyanex-923 of iron(III), $HNO_3$, and HF and to determine the best conditions of their coextraction and selective stripping, with

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Correspondence concerning this article should be addressed to A. López-Delgado at alopezdelgado@cenim.csic.es.

the aim of contributing to the body of research concerning extraction-based methods for recovering metals and acids from these wastewaters, with the consequent economic and environmental benefits.

## Experimental

Solutions with similar Fe(III), $HNO_3$, and HF contents to those of real rinse waters were prepared from $Fe(NO_3)_3{\cdot}9H_2O$, $HNO_3$, HF, and NaF chemicals (Merck, AR grade). The extractant Cyanex-923, used as supplied by the manufacturer (CYTEC Ind.), contains different phosphine oxides (Dziwinski and Szymanowski, 1998), and was diluted in Solvesso 100 (ExxonMobil Chem, Iberia, Spain), having >99% aromatic content or undiluted and water-presaturated, used to avoid volume changes in the extraction-stripping experiments.

Extraction experiments were carried out, under the corresponding experimental conditions, in thermostatic separatory funnels at the required temperature and mechanically shaken (700 rpm). Iron concentrations in the aqueous solutions were determined by atomic absorption spectroscopy (AAS) using a Perkin–Elmer 1100B spectrophotometer, whereas the corresponding metal concentrations in the loaded organic solutions were calculated by mass balance. Nitrate and fluoride concentrations in the aqueous phases were measured by ion chromatography (IC) using a Dionex DX-120 ion chromatograph; similarly to the above case, the corresponding organic phase concentrations were calculated accordingly to mass balance.

## Results and Discussion

To study the recovery of metals and acids from exhausted rinse waters, extraction-based experiments were carried out using Cyanex-923 as extractant agent. Previous experiments had shown that neither chromium(III) (Alguacil et al., 2000) nor nickel(II) are extracted by Cyanex-923; thus, synthetic solutions containing only $Fe^{3+}$, $HNO_3$, and HF in different concentrations were prepared.

### *Extraction of iron(III)*

A representative solution of a real rinse water, containing $Fe^{3+}$ (~1 g/L), $HNO_3$ (~2 g/L), and HF (~0.05 mol/L) was prepared and a study of the factors that influence the iron extraction (Cyanex-923 concentration, temperature, extraction time, and $V_{aq}/V_{org}$ phase ratio) was made (Figure 1). The best experimental conditions to promote maximum extraction were determined to be undiluted Cyanex-923 [Figure 1a], 20°C [Figure 1b], 30 min extraction time [Figure 1c], and $V_{aq}/V_{org}$ phase ratio of 1/1 [Figure 1d]. Under these conditions, the percentage of iron extraction (%E-Fe) was 90.6%.

The iron extraction by Cyanex-923 showed that the process was exothermic, as indicated by the decrease of %E-Fe as the temperature increased [Figure 1b]. $\Delta H°$ of the process was calculated from Eq. 1 (Alguacil et al., 1998), as follows

$$\log D_{\mathrm{Fe}} = -(\Delta H°/2.3RT) + C \tag{1}$$

where $D_{\mathrm{Fe}}$ is the corresponding iron distribution coefficient, defined as the ratio of the total iron(III) concentration in the organic and aqueous phases at equilibrium; and $C$ is a constant, with a resulting value of −19.5 kJ/mol.

To determine the number of stages required to extract completely the iron in a chosen volume phase ratio, an extraction isotherm was generated using the aqueous/organic continuous volume phase variation procedure. From Figure 2, it is shown that at a phase ratio of 1/1, two stages are needed to recover >95.5% $Fe^{3+}$ from the feed solution.

To evaluate the influence of nitric acid concentration on the iron extraction, solutions containing $Fe^{3+}$ (~1 g/L), HF (~0.05 mol/L) and $HNO_3$ (from 0 to 32 g/L) were prepared and %E-Fe was determined under the same above experimental conditions (Table 1, tests 1–4). The variation in the extraction percentages was not significant, and thus no influence in the iron(III) extraction from $HNO_3$ concentration could be deduced.

It is well known that fluoride anions form complexes with $Fe^{3+}$ cations (Ohya et al., 1996). This phenomenon makes difficult the recovery of HF and iron from exhausted pickling liquors and rinse waters (Filipsson and Ekengren, 1999; Stone, 1996; and references therein). To evaluate the influence of the fluoride concentration in the iron extraction, four experiments, in which fluoride concentrations were gradually increased in each of them, were carried out:

- Experiment I: $Fe^{3+}$ (~1 g/L) + $HNO_3$ (~2 g/L) + HF
- Experiment II: $Fe^{3+}$ (~1 g/L) + $HNO_3$ (~2 g/L) + NaF
- Experiment III: $Fe^{3+}$ (~1 g/L) + HF
- Experiment IV: $Fe^{3+}$ (~1 g/L) + NaF

Solutions initially containing NaF (experiments II and IV) were studied for comparative effects with respect to those initially containing HF (experiments I and III). The extraction results, as a function of fluoride concentration, are shown in Figure 3. In the experiments with NaF (experiments II and IV), sodium fluoride concentrations > 0.1 mol/L promoted the precipitation of a solid that was characterized as $Na_3[FeF_6]$ by X-ray diffraction. The highest extraction percentages (>99.5%) occurred in the absence of fluoride, and in the four experiments %E-Fe decreased when the fluoride concentration was increased. These facts indicate, as expected, that the fluoride anion makes the extraction of iron more difficult, which is attributed to the previously mentioned formation of Fe–$F_x$ complexes. Nevertheless, at moderate fluoride concentration (≤ 0.01 mol/L), %E-Fe was very high. In the four experiments, %E-Fe values were analogous up to 0.05 mol/L. For fluoride concentration > 0.05 mol/L, %E-Fe was higher in the experiments with HF (experiments I and III), thus indicating a less-favorable iron extraction when fluoride was furnished as NaF. This phenomenon can be attributed to the strong and weak electrolyte character of NaF and HF ($K_a = 6.94 \times 10^{-4}$), respectively. Thus at equal concentrations of NaF and HF, the free (dissociated) fluoride concentration is lower in the HF case, with the consequent relative increase in the iron extraction. The presence of 2 g/L $HNO_3$ does not seem to have any influence on the iron extraction, as determined earlier (Table 1) because %E-Fe values in experiments I and III (HF in the presence and absence of $HNO_3$, respectively) were very similar, and the same occurred when experiments II and IV (NaF in the presence and absence of $HNO_3$, respectively) were compared.

### *Extraction of acid*

A complementary study of acid extraction on solutions containing only $HNO_3$ (~2 g/L) and HF (~0.05 mol/L) or $HNO_3$ (~2 g/L) and NaF (~0.05 mol/L) was carried out to further evaluate the influence of the presence of iron(III) in the extrac-

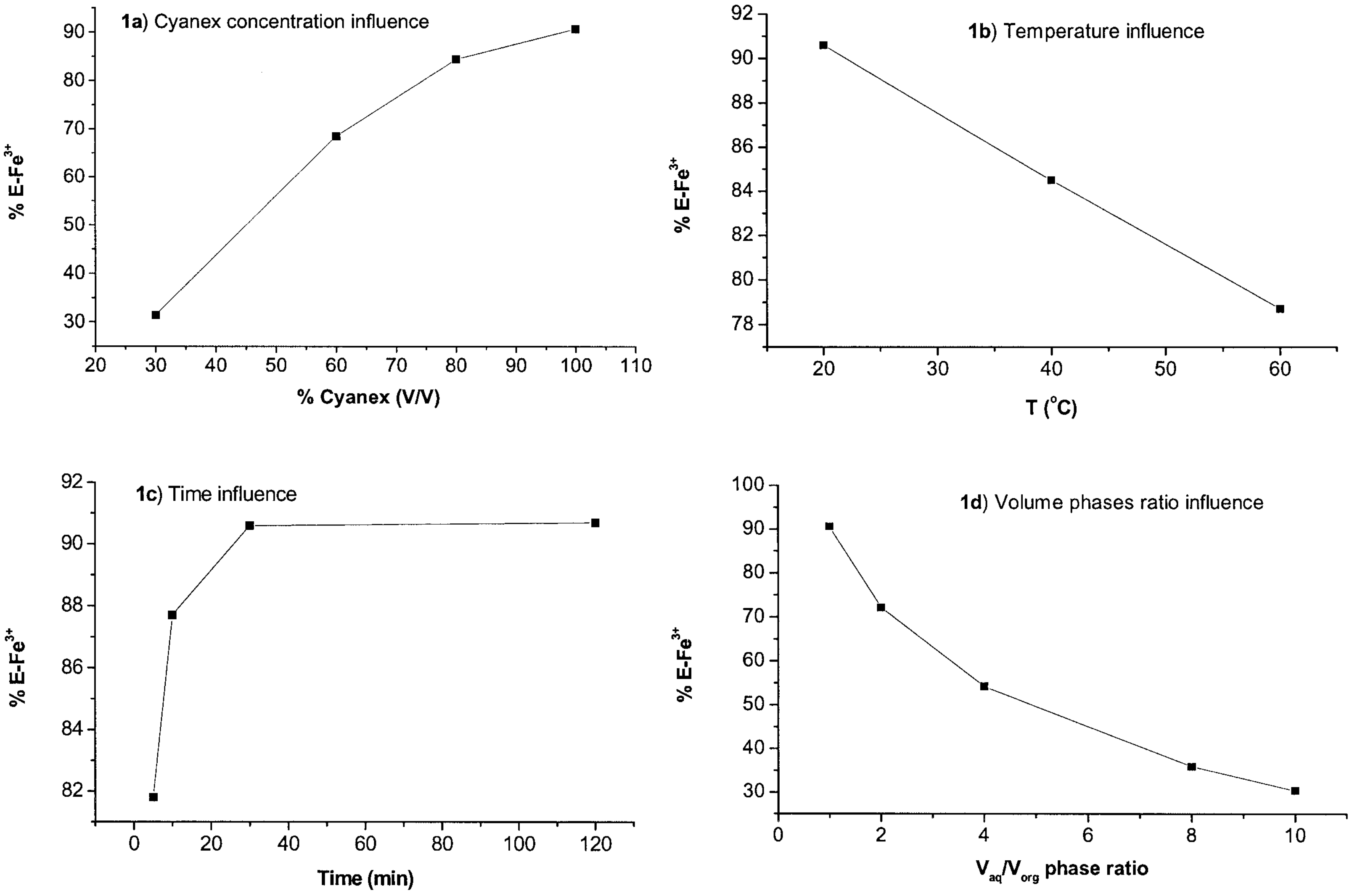


**Figure 1. Extraction of iron(III) by Cyanex-923 under various experimental conditions.**

(a) Temperature 20°C, equilibration time 30 min, $V_{aq}/V_{org}$ phase ratio of 1; (b) undiluted Cyanex-923, 30 min of contact time, $V_{aq}/V_{org}$ phase ratio of 1; (c) undiluted Cyanex-923, temperature 20°C, $V_{aq}/V_{org}$ phase ratio of 1; (d) undiluted Cyanex-923, temperature 20°C, equilibration time 30 min.

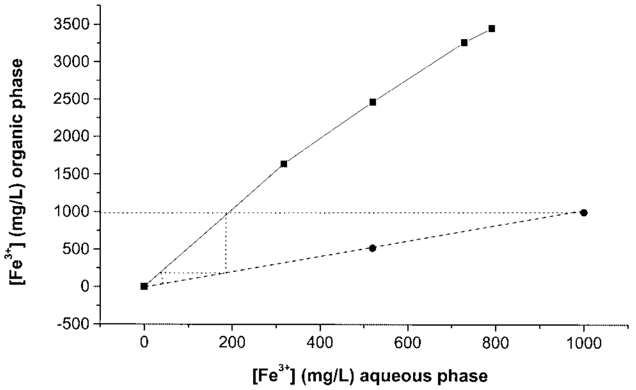


**Figure 2. Iron(III) extraction isotherm.**

Organic phase: undiluted Cyanex-923. Temperature 20°C. Contact time 30 min.

tion of acids. The experimental conditions were undiluted Cyanex-923, $V_{aq}/V_{org}$ phase ratio of 1/1, 20°C, and extraction time varying from 1 to 30 min. Nitrate and fluoride concentrations in the aqueous phase before and after extraction were measured by IC. The results of extraction are shown in Figure 4. One observes the very fast and effective extraction of both acids in the $HNO_3$ + HF sample. Thus, after 1 min of extraction, %E-$NO_3^-$ [Figure 4a] and %E-$F^-$ [Figure 4(b)] were 72.3 and 90.0%, respectively, values that remained practically constant over time. In contrast, when $F^-$ was supplied as NaF, both a dramatic decrease in %E-$NO_3^-$ (with a maximum percentage of 9.3% after 5 min) [Figure 4a] and a notable decrease in %E-$F^-$ [Figure 4b] with respect to that $HNO_3$ + HF sample were observed. These phenomena can be explained on the basis of the relatively basic character of fluoride anion, which could promote the following equilibrium in the aqueous phase before the extraction (Eq. 2)

$$NO_3^- + H^+ + Na^+ + F^- \leftrightarrow NO_3^- + Na^+ + HF \qquad K_{eq} = 1/K_a = 1440.92 \quad (2)$$

| | $NO_3^-$ | $H^+$ | $Na^+$ | $F^-$ | HF |
|---|---|---|---|---|---|
| Initial concentration (mol/L) | 0.03 | 0.03 | 0.05 | 0.05 | 0.00 |
| Equilibrium concentration (mol/L) | 0.03 | 0.001 | 0.05 | 0.021 | 0.029 |

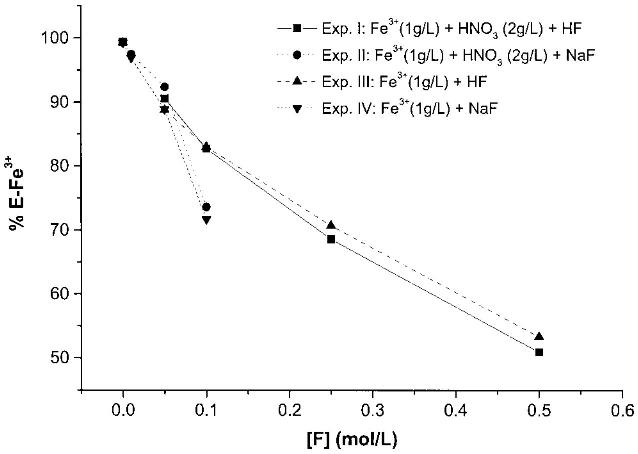


**Figure 3. Fluoride concentration influence on iron(III) extraction. Experimental conditions as in Table 1.**

Thus, most of the protons initially furnished by the nitric acid could be bonded to the fluoride anions in the aqueous solution to form hydrofluoric acid. Consequently, $NO_3^-$ would be practically not extracted because the dissociated $H^+$ concentration would be very low in the earlier extraction aqueous phase, and only the fluoride as HF would be extracted.

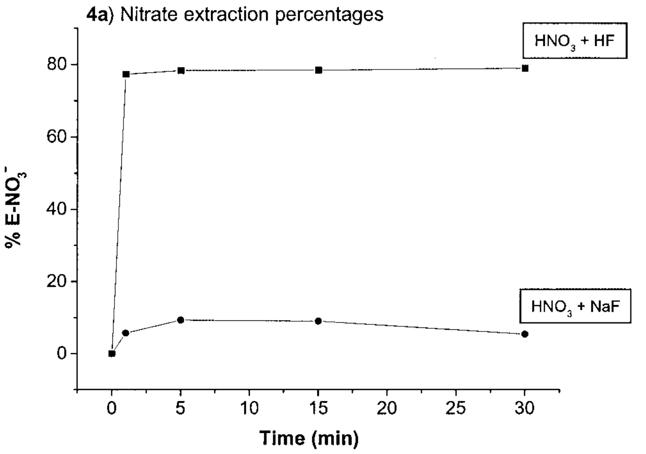
Extraction of acids by Cyanex-923 on solutions containing iron(III) were analyzed in the same solutions used for iron(III) determinations. Table 1 shows some representative examples of the total iron(III), nitrate, and fluoride concentrations determined, as well as the corresponding extraction percentages. $HNO_3$ concentrations were calculated from the difference between total nitrate and nitrate from $Fe(NO_3)_3$ in aqueous phases both before and after extraction and, consequently, the calculated %E-$HNO_3$ values in Table 1 correspond to the minimum extraction percentages. Importantly, in all cases in which fluoride was supplied as HF, %E-$F^-$ values were slightly lower that those obtained in the absence of iron(III) for 30 min extraction time [89.9%; Figure 4(b)], indicating that iron(III) does not favor HF extraction by Cyanex-923 attributed to the above-mentioned formation of Fe–$F_x$ complexes, which cannot be extracted.

Tests 1–4, with $Fe^{3+}$ (~1 g/L), HF (~0.05 mol/L), and $HNO_3$ concentrations varying from 0.0 to 32 g/L, seem to indicate that the increase of $HNO_3$ concentration has no influence on HF extraction. There was a clear increase in %E-$HNO_3$, when in solutions with a constant $HNO_3$ concentration

**Table 1. Ion Concentrations (g/L) in the Aqueous Phase Before ($[X]_0$) and After ($[X]_f$) Extraction and Extraction Percentages***

| Test | $[Fe]_0$ | $[Fe]_f$ | %E-Fe | $[NO_3^-]_0$ | $[NO_3^-]_f$ | %E-$NO_3^-$ | %E-$HNO_3$ | $[F^-]_0$ | $[F^-]_f$ | %E-$F^-$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1: Fe (~1 g/L) + HF (~0.05 mol/L) | 1.09 | 0.12 | 88.9 | 3.67 | 0.53 | 85.5 | — | 1.00 | 0.18 | 82.0 |
| 2: Fe (~1 g/L) + $HNO_3$ (~2 g/L) + HF (~0.05 mol/L) | 1.18 | 0.11 | 90.6 | 5.91 | 0.76 | 87.1 | 80.3 | 1.05 | 0.15 | 85.7 |
| 3: Fe (~1 g/L) + $HNO_3$ (~16 g/L) + HF (~0.05 mol/L) | 1.25 | 0.07 | 94.4 | 20.05 | 2.65 | 86.7 | 84.7 | 1.10 | 0.18 | 83.6 |
| 4: Fe (~1 g/L) + $HNO_3$ (~32 g/L) + HF (~0.05 mol/L) | 1.28 | 0.10 | 92.2 | 34.49 | 5.44 | 84.2 | 83.1 | 0.97 | 0.20 | 79.4 |
| 5: Fe (~1 g/L) + $HNO_3$ (~2 g/L) | 1.03 | 0.01 | 99.1 | 5.35 | 0.85 | 84.1 | 57.3 | — | — | — |
| 6: Fe (~1 g/L) + $HNO_3$ (~2 g/L) + HF (~0.25 mol/L) | 1.03 | 0.32 | 68.9 | 5.28 | 0.89 | 83.1 | >100 | 3.96 | 1.10 | 72.2 |
| 7: Fe (~1 g/L) + $HNO_3$ (~2 g/L) + NaF (~0.05 mol/L) | 0.97 | 0.07 | 92.7 | 4.75 | 3.24 | 31.8 | 0.0 | 0.87 | 0.26 | 70.1 |
| 8: Fe (~1 g/L) | 1.25 | 0.01 | 99.2 | 41.6 | 0.45 | 98.9 | — | — | — | — |
| 9: Fe (~1 g/L) + HF (~0.25 mol/L) | 1.10 | 0.32 | 70.9 | 38.05 | 0.89 | 97.7 | — | 4.92 | 1.12 | 77.2 |
| 10: Fe (~1 g/L) + NaF (~0.01 mol/L) | 1.04 | 0.03 | 97.1 | 3.91 | 1.14 | 70.8 | — | 0.23 | 0.08 | 65.2 |
| 11: Fe (~1 g/L) + $HNO_3$ (~2 g/L) + HF (~0.05 mol/L) $V_{aq}/V_{org}$ phase ratio: 2/1 | 1.14 | 0.32 | 71.9 | 6.28 | 2.3 | 63.4 | 50.4 | 1.02 | 0.52 | 49.0 |

*Organic phase: undiluted Cyanex-923. Temperature: 20°C; contact time: 30 min; $V_{aq}/V_{org}$ phase ratio of 1/1 (except test 11).



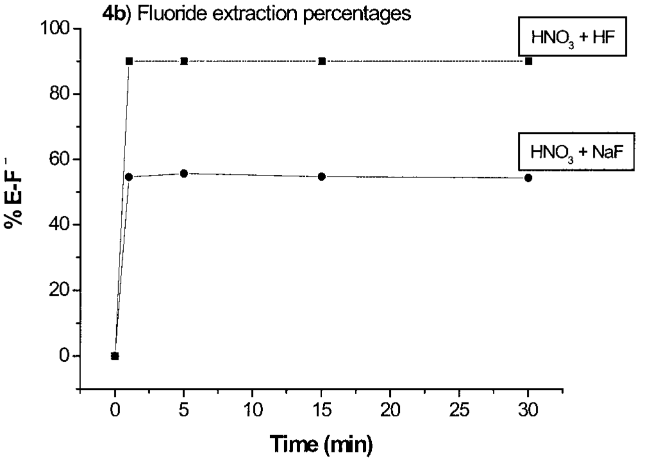


**Figure 4. Plot of acids extraction percentages versus extraction time.**

Undiluted Cyanex-923, temperature 20°C, $V_{aq}/V_{org}$ phase ratio of 1.

(~2 g/L), in that the HF concentration increased (tests 5, 2, and 6). In particular, in test 6, the %E-HNO$_3$ > 100% could suggest that a certain part of the nitrate, initially supplied as Fe(NO$_3$)$_3$, was extracted as HNO$_3$ because of the formation of Fe–F$_x$ complexes. The relatively low values of %E-HF and %E-Fe seem to confirm it. Consequently, it can be suggested that the presence of HF, although it does not seem to influence the total nitrate extraction, favors the extraction of HNO$_3$.

In contrast, when fluoride was provided as NaF (test 7), both a dramatic decrease of total nitrate extraction and a null HNO$_3$ extraction were observed, in which fluoride was extracted, probably as HF, in accordance with results from HNO$_3$ + NaF extraction experiments (Figure 4). In addition, it can also be concluded that when F$^-$ is supplied as NaF, only the nitrate as a counterion of Fe$^{3+}$ can be extracted. On the other hand, in the absence of HNO$_3$, the influence in the nitrate and fluoride extractions, derived from an increase in the HF concentration from zero to 0.25 mol/L (tests 8, 1, and 9), was studied. Thus, the presence of a low HF concentration (test 1) promoted a decrease in %E-NO$_3^-$, although a high concentration promoted both an increase in %E-NO$_3^-$ and a decrease in %E-F$^-$.

These phenomena can be explained on the basis of the formation of Fe–F$_x$ complexes, which could disfavor both iron and fluoride extractions and could favor nitrate extraction, possibly as HNO$_3$. The presence of only 0.01 mol/L NaF (test 10) caused a decrease of 28% in the nitrate extraction from Fe(NO$_3$)$_3$ (test 8). Finally, when tests 2 and 11 were compared, an extensive decrease in the acids extraction was observed for a $V_{aq}/V_{org}$ phase ratio of 2/1.

### *Selective stripping of iron(III), HNO$_3$, and HF*

In view of the good results obtained for the iron(III) and coextraction of acids from the type solution representative of exhausted rinse waters (Table 1, test 2), selective stripping of iron(III) and acids was tested using water as an acid-stripping agent from the organic phase resulting from the coextraction of the rinse water. Ion concentrations of this loaded Cyanex-923 phase were 1.14 g/L Fe$^{3+}$, 5.67 g/L NO$_3^-$, and 0.90 g/L F$^-$. Influences of stripping time, aqueous/organic volume phase ratio, and temperature on the selective stripping were studied, some representative results of which are shown in Table 2. In general, stripping of acids was more effective and required less time than that of iron(III). Recovery of acids was low at 20°C and $V_{aq}/V_{org}$ phase ratio of 1/1, but a strong increase was investigated at greater $V_{aq}/V_{org}$ ratios [i.e., 4/1 (tests 3–5)]. Under this condition the percentage of HNO$_3$ stripping (%S-HNO$_3$) was very high, suggesting that a certain portion of nitrate as Fe$^{3+}$ counterion in the organic phase was stripped as HNO$_3$. The best percentage of HF stripping occurred at 60°C and 30 min contact time (test 5). However, at this temperature the highest percentage of iron(III) stripping also occurs. This phenomenon suggested that the best conditions for the selective stripping of iron(III) and acids were $V_{aq}/V_{org}$ phase ratio of 4/1, 20°C, and 10 min equilibration time (test 3). Under these conditions the Fe$^{3+}$ content of the aqueous solution is very low; the HNO$_3$ recovery is total; and the HF recovery, always affected by the iron(III) presence, is in the range usually accepted for hydrofluoric acid recovery from exhausted pickling liquors or rinse waters from pickled stainless steels (Frías et al., 2000; Stone, 1996).

**Table 2. Ion Concentrations (g/L) in Water after Selective Stripping and Stripping Percentages**

| | Test | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $V_{aq}/V_{org}$ | $T$ (°C) | $t$ (min) | [Fe] | %S-Fe | [NO$_3^-$] | %S-NO$_3^-$ | %S-HNO$_3$ | [F$^-$] | %S-F$^-$ |
| 1 | 1/1 | 20 | 10 | 0.11 | 9.6 | 0.97 | 17.1 | 32.1 | 0.19 | 21.1 |
| 2 | 1/1 | 20 | 30 | 0.12 | 10.5 | 1.04 | 18.3 | 34.2 | 0.18 | 20.0 |
| 3 | 4/1 | 20 | 10 | 0.04 | 14.0 | 0.71 | 50.1 | >100 | 0.14 | 62.2 |
| 4 | 4/1 | 40 | 10 | 0.07 | 24.5 | 1.30 | 91.7 | >100 | 0.14 | 62.2 |
| 5 | 4/1 | 60 | 30 | 0.09 | 31.6 | 0.83 | 58.5 | >100 | 0.15 | 66.7 |

## Conclusions

Coextraction and selective stripping of iron(III), $HNO_3$, and HF from analogous solutions to the exhausted rinse waters from pickled stainless steels have been studied in this work.

From the study of the influent factors in the coextraction of iron(III) and acids with Cyanex-923, it was deduced that the best coextraction conditions are undiluted Cyanex-923 as organic phase, 20°C temperature, 30 min extraction time, and a $V_{aq}/V_{org}$ phase ratio of 1/1. Under these conditions coextraction occurred with good yields (%E-$Fe^{3+}$, 90.6; %E-$HNO_3$, 80.3; %E-HF, 85.7). Iron extraction resulted in an exothermic process and it was determined that two stages could be necessary for extracting >99.5% $Fe^{3+}$ from the solution under the above conditions. When $HNO_3$ concentration was increased, no influence on the extraction percentages was observed. In contrast, a decrease in %E-$Fe^{3+}$ was found as the fluoride concentration was increased, attributed to the formation of Fe–$F_x$ complexes, which disfavor iron(III) extraction. A different behavior with respect to the acid extraction depending on the fluoride supplying species was observed. It is thus worth noting the high %E-$HNO_3$ values when $F^-$ was furnished by HF, indicating that the nitrate initially supplied as $Fe(NO_3)_3$ was partially extracted as $HNO_3$ because of the formation of Fe–$F_x$ complexes. However, high concentrations of fluoride, supplied as NaF, promoted the precipitation of the complex $Na_3[FeF_6]$, and lower concentrations promoted a dramatic decrease in %E-$NO_3^-$ and no $HNO_3$ extraction.

The selective stripping of iron(III) and acids was carried out using water as an acid-stripping agent. The effects of temperature, stripping time, and $V_{aq}/V_{org}$ phase ratio on selective stripping were studied: the best conditions found were 20°C, 10 min, and 4/1, respectively. Under these conditions the %HF recovered is acceptable for this type of solutions, the $HNO_3$ recovery is quantitative, and the iron contents are within acceptable limits for the reuse of these acidic streams. Subsequent concentration of these acid solutions could make possible their reuse in new pickling processes, diminishing the nitrate and fluoride discharge to the environment. On the other hand, the iron contents in the recovered rinse waters are within the limits allowed for their discharge. In conclusion, coextraction and selective stripping technology, using undiluted Cyanex-923 as reagent, has proved to be a good method to recover acids from exhausted pickled stainless steel rinse waters.

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