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THE EXTRACTION OF NICKEL WITH ALIPHATIC OXIMES

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ABSTRACT

U.S. Bureau of Mines researchers investigated the use of aliphatic oximes to extract nickel from acidic, nickelous-chromic-chloride solutions. Batch solvent extraction tests were conducted to characterize the nickel extraction and stripping properties of several oximes. Results indicated that the oximes selectively extracted nickel over chromium by an ion pair mechanism. Nickel was most effectively stripped from the loaded oxime extractants with dilute hydrochloric acid; however, these acidic strip solutions partially degraded the oximes to their parent aldehydes by hydrolysis. The oximes could, however, be regenerated by contacting the solvent phase with a neutralized hydroxylamine-hydrochloride solution. Decyl oxime was successfully used in a continuous counter-current solvent extraction circuit that incorporated loading, stripping, and regeneration stages. The decyl oxime degraded 12 pct per loading and stripping cycle, but was effectively regenerated prior to recycling to the head of the circuit.

INTRODUCTION

The Bureau of Mines investigated the use of aliphatic oximes to extract nickel from acidic chloride solutions as part of a more comprehensive investigation to recover cobalt, nickel, chromium, and other metals from hardface alloy grinding waste. The approach taken was to dissolve the grindings in a two-stage $HCl-Cl_2$ leach and then separate and recover the metals from the resulting acidic chloride solution (1). Sequential solvent extraction (SX) steps with amine extractants were used to recover iron, cobalt, and manganese. The principal components of the remaining solution were nickel and chromium. The purpose of the experimental work described herein was to develop a SX procedure to separate and recover nickel from this remaining solution.

One method for separating nickel and chromium in acidic chloride solutions is to raise the pH and precipitate chromic hydroxide (2). Dilution is required to prevent gelling. The precipitates are voluminous and filtration rates are impracticably slow. Brooks (3) proposed adding Na_2SO_4 to chloride liquors to precipitate a basic chromium sulfate and obtain a more filterable product. The precipitation procedure was complicated, but filtration rates were improved. However, the resulting filter cakes contained about 70 pct moisture and were difficult to wash.

In a study of cobalt and nickel SX from nitrate solutions with organophosphorus acids, Preston (4) found a synergistic effect with mixtures of di(2-ethylhexyl) phosphoric acid (DEHPA) and ethylhexanal oxime (EHO), an aliphatic, nonchelating oxime. The mixture extracted both metals at a lower pH than DEHPA without EHO. The synergism was greater for nickel extraction, and the selectivity of cobalt over nickel shown by DEHPA alone was reversed. In a subsequent study (5), the extraction characteristics of nickel in nitrate solutions with mixtures of DEHPA and several nonchelating oximes were investigated. The results showed that different degrees of synergism or enhancement of extraction at low pH values were produced with different oxime structures. The order of increasing synergism followed the decreasing order of steric hindrance about the oxime functional group. Octnyl oxime and EHO showed the greatest synergistic effect.

In the currently reported investigation, testing was initiated with EHO-DEHPA mixtures to extract nickel from acidic chloride solutions. As research progressed, EHO-DEHPA mixtures were found to be unsuitable for use in a continuous countercurrent solvent-extraction circuit. Mixtures with other extractants and other oximes were then investigated and decanal oxime (DOX) was determined to be the most suitable extractant for recovering nickel from grinding waste process solutions. However, much of the data reported herein to illustrate the nickel extraction characteristics of aliphatic oximes was obtained with EHO and EHO mixed with various accelerators.

EXPERIMENTAL

Oxime Preparation

The aliphatic oximes used in this investigation were not available from commercial sources and were prepared in the laboratory. The procedure utilized was for the preparation of heptyl oxime from heptyl aldehyde (6). The following equation represents the oxime preparation reaction:

$$2RHC{=}O + 2NH_2OH{\cdot}HCl + Na_2CO_3 = 2RHC{=}N\text{-}OH + 2NaCl + 3H_2O + CO_2 \qquad (1)$$

where $R = C_6H_{13}$.

Although the described procedure was for preparing heptyl oxime, it was also found to be satisfactory for preparing octyl oxime, EHO, and DOX from their respective aldehydes. The reported purities of the aldehydes used to prepare the various oximes were, in percent, decanal 98, heptanal 95, and octanal 99. The ethylhexanal was designated as practical grade and the $NH_2OH{\cdot}HCl$ was 99 pct pure.

The purity of the oxime products was not rigorously determined, but maximum nickel loadings and equation 2 stoichiometry indicates that oxime purity varied batchwise from about 85 to 90 pct. However, for reporting concentrations in this investigation, the oxime products were assumed to be 100 pct pure. The other reagents utilized in this investigation were tested as received from the suppliers. Reagent-grade chemicals were used to produce simulated grinding waste process solutions.

Feed Solution Composition

Nickel extraction research was started before the various steps of the hardface alloy leaching and metal recovery process were fully established. Consequently, the composition of feed for nickel solvent extraction was not known with certainty. Feed for the initial tests was compounded from chemical reagents to represent hardface alloy leach liquor after the iron and cobalt had been removed with amine extractants, and its composition was, in grams per liter, 30 Ni, 32 Cr, 8 Mn, and 140 Cl plus 0.8 mol/L H^+.

The simulated cobalt circuit raffinate was used to establish the general nickel extraction characteristics of aliphatic oximes. As research progressed on the other individual metal recovery steps of the process, it was found that the nickel solvent-extraction feed would be a manganese circuit raffinate containing, in grams per liter, 12 Ni, 84 Cr, and 200 Cl plus 0.4 mol/L H^+. Feed of this composition was used in the subsequent test work.

Solvent Extraction Procedure

Tests were conducted at room temperature, in separatory funnels agitated with a wrist-action shaker, unless otherwise specified. Separated aqueous and organic phases were analyzed for chromium, manganese, and nickel by atomic absorption spectroscopy, unless otherwise specified. Samples were analyzed for chloride by titrating with silver nitrate.

Maximum nickel loading was found to be proportional to oxime concentration. The oxime concentration was determined using a procedure in which the maximum nickel loading of an unknown was compared to that of several standards. Solvent samples were loaded to capacity with nickel by contacting with cobalt or manganese circuit raffinate at an aqueous-to-organic (A:O) ratio of 5.0 for 60 min.

RESULTS AND DISCUSSION

Nickel Extraction with EHO

Initial exploratory tests were conducted with EHO-DEHPA mixtures. The feed was the previously described simulated cobalt raffinate with the pH adjusted to 2.0 by adding NaOH solution. Results from 20-min contacts at an A:O ratio of 1.0 showed that all solvents containing EHO had extracted some nickel. Analyses of the loaded solvent samples containing 0.5 M DEHPA, and 0, 0.25, 0.5, and 1.0 mol/L EHO indicated that the samples loaded to 0.02, 2.9, 4.9, and 8.1 g/L Ni, respectively. Thus, EHO extracted nickel from acidic chloride solutions at a pH of 2.0 in the presence of DEHPA; however, DEHPA alone extracted relatively little nickel.

The effect of EHO and DEHPA concentrations was determined with initial the feed solutions at their natural acidity, 0.8 mol/L HCl. In these tests, solvent EHO concentrations varied from 0.0 to 2.5 mol/L, and DEHPA concentrations varied from 0.0 to 1.0 mol/L. The solvents were then loaded to capacity with nickel.

Test results showed that without EHO, DEHPA alone did not extract significant amounts of nickel from the acidic chloride solutions; however, EHO without DEHPA did extract nickel, and nickel loading increased from 4.3 g/L with 0.5 mol/L EHO to 19.4 g/L with 2.5 mol/L EHO. Improved nickel extractions were obtained with EHO-DEHPA mixtures. For example, with 2.5 mol/L EHO and 0.15 mol/L DEHPA, the nickel loading was 32.8 g/L. Based upon the stoichiometry of equation 2 and a 90 pct oxime purity, the nominal loading limit for EHO is 33.0 g/L Ni.

A series of tests was conducted with a solvent containing 1.0 mol/L EHO and 0.5 mol/L DEHPA to determine the effect of pH on nickel extraction. Nickel concentration in each of the aqueous samples was 25 g/L, and the acidity varied from 0.8 mol/L to a pH of 2.2. Equal volumes of aqueous and solvent phases were contacted with a wrist-action shaker for 30 min. Results showed that aqueous phase acidity did not significantly effect the nickel extraction. The loaded solvent samples contained 13 to 14 g/L Ni. Chromium was not extracted, and manganese loading decreased from 0.22 g/L at an aqueous feed of pH 2.2 to 0.015 g/L at an acidity of 0.8 mol/L. Thus, the 1.0 mol/L EHO-0.5 mol/L DEHPA solvent was selective for nickel over chromium throughout the entire acidity range tested and was most selective over manganese at the highest acidity.

The loaded solvent samples obtained in the preceding and other tests were analyzed for chloride content. The analyses showed that all of the samples contained chloride, and that the chloride-to-nickel mole ratios ranged from 1.81 to 2.09. The mean value was 1.96, and the ratio did not vary with either the EHO or the DEHPA concentration. Thus, nickel appeared to be extracted as an ion pair or neutral complex with the stoichiometric composition of $NiCl_2$. Further, the high-chloride ion concentration in the cobalt circuit raffinate (140 g/L) favors the formation of the neutral hydrated nickel-chloride complex, $Ni(H_2O)_4Cl_2$ (7-8).

Extraction by ion pair transfer has been characterized by Bridges (9) as the reaction of the organic extractant with the hydrated metal-bearing ion pairs to displace the coordinated water from the ion pair and form a molecule that is preferentially dissolved in the solvent phase. The following equation reflects this concept and is proposed to represent ion pair transfer nickel extraction with EHO:

$$Ni(H_2O)_4Cl_2 + 4EHO \rightleftharpoons Ni(EHO)_4Cl_2 + 4H_2O \qquad (2)$$

Nickel extraction kinetics were determined by contacting 2 vol of simulated cobalt raffinate with 1 vol of organic extractant in a closed stirred reactor. At timed intervals, the aqueous-organic mixture was sampled and the phases separated and analyzed for nickel.

The effect of temperature on nickel extraction kinetics was determined for 3.0 mol/L EHO modified with 0.15 mol/L DEHPA. Batch tests were conducted at temperatures ranging from 20°to 50° C. Test results presented in Figure 1 indicate that increased temperature increased the nickel extraction rate and decreased the equilibrium nickel loadings due to decreased ion association in the solvent phase (10). Decreased nickel loading with increasing temperature is expected in an ion pair transfer system and is explained by Bjerrum's theory of ion association (11).

Figure 1 also shows that at 40° and 50° C nickel loadings steadily decreased with increasing contact time after the solvents reached maximum nickel loadings. This was the first experimental indication that the nonchelating oximes were unstable in acidic solutions,and testing at elevated temperatures was discontinued because of this apparent instability.

Comparative tests were conducted to determine the effect of DEHPA on the nickel extraction rate. Times to achieve equilibrium nickel loadings were determined for 3.0 mol/L EHO and for 3.0 mol/L EHO plus 0.5 mol/L DEHPA. The results of these tests are presented in Figure 2 and show that extraction kinetics without DEHPA were extremely slow. DEHPA greatly increased the extraction rate but did not affect the equilibrium loading. Thus, DEHPA acted as an accelerator for the nickel extraction reaction.

Testing continued with 3.0 mol/L EHO to identify other reagents that would accelerate nickel extraction. Twenty-five different reagents were tested; eight reagents, not counting DEHPA, showed promise for improving the nickel extraction rate and were evaluated further. They were (1) di(2-ethylhexyl) acid phosphate (mixed mono and dihydrogen phosphate esters), (2)

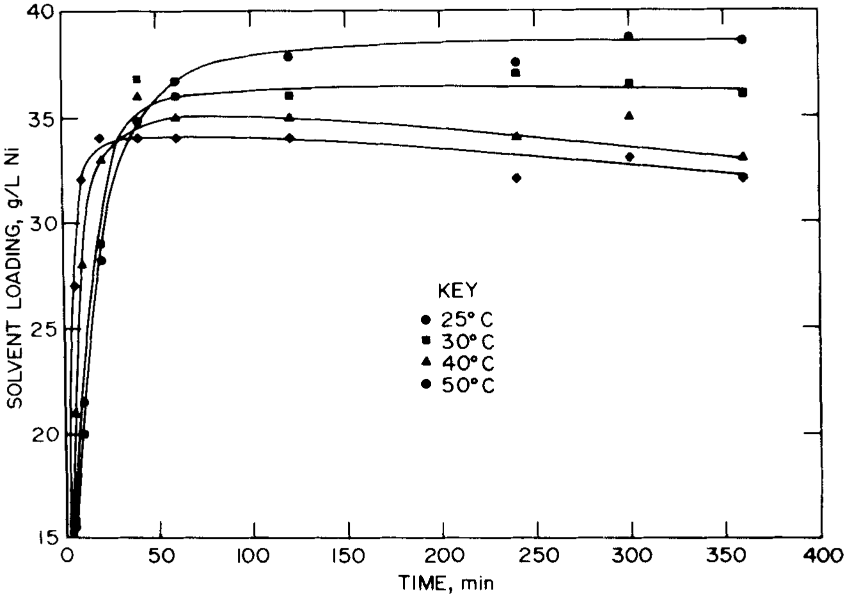

FIGURE 1. Effect of temperature on extraction rate with 3.0 mol/L EHO and 0.15 mol/L DEHPA.

mono(2-ethylhexyl) phosphoric acid, (3) mono(2-ethylhexyl) benzyl phosphonic acid, (4) octylphenyl acid phosphate (mixed mono and dihydrogen phosphate esters), (5) bis(2-ethylhexyl) pyrophosphoric acid, (6) sodium lauryl sulfate ($NaC_{12}H_{25}SO_4$), (7) dioctyl sulfosuccinate (Aerosol OT-100), and (8) di(tridecyl) sulfosuccinate (Aerosol TR-70). The concentrations of the various reagents tested were 0.15 mol/L for the organophosphorus reagents, 6 g/L for the $NaC_{12}H_{25}SO_4$, and 10 g/L for the two aerosol products.

Test results indicated that each of the reagents improved nickel extraction rates, and the improvements were essentially the same as were obtained with 0.5 mol/L DEHPA. Equilibrium extraction times ranged from 60 to 80 min, and nickel loadings ranged from 36 to 38 g/L. Although the $NaC_{12}H_{25}SO_4$ and the Aerosol products increased the reaction rate, they caused phase separation

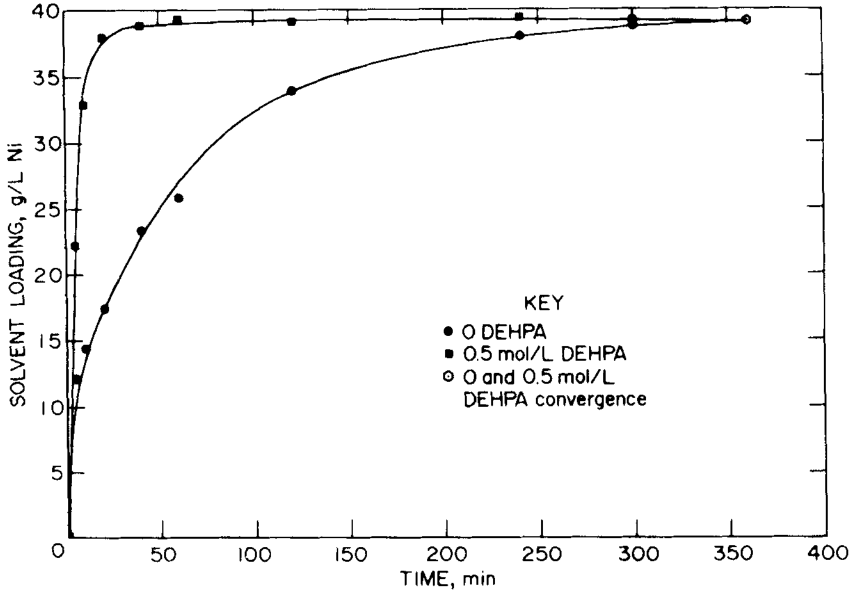

FIGURE 2. Effect of DEHPA in 3.0 mol/L EHO on extraction rate.

problems by producing stable emulsions. The organophosphorus reagents, however, produced rapid phase separations.

Inspection of loaded solvent samples that had aged for 2 to 3 weeks revealed that the samples containing DEHPA or one of the other organophosphorus accelerators had changed color from turquoise to green, and small, colorless acicular crystals had precipitated. The samples that did not contain organophosphorus compounds had not changed color and did not contain the crystalline precipitate. Similar precipitates were observed in aged, unused solvents that contained both EHO and organophosphorus modifiers. X-ray analysis identified the acicular crystals as a mixture of NH_4Cl and $NH_4H_2PO_4$. Apparently the EHO-organophosphorus mixtures were unstable, and EHO, the only source of nitrogen in the system, degraded to form ammonium ions; the resulting ammonium salts were insoluble in the solvent phases and precipitated.

Additional test work identified a second type of degradation that was caused by the acidic processing conditions that the solvents were subjected to. It was hypothesized that both EHO solvents and EHO solvents containing accelerators partially degraded by a well known hydrolysis reaction to ethylhexyl aldehyde and hydroxylamine hydrochloride (12). Infrared analysis identified a C=O band in the spectrums of the used solvents indicating the presence of an aldehyde or ketone. The following chemical equation represents the proposed degradation reaction:

$$RHC{=}N\text{-}OH + H_2O + HCl = RHC{=}O + NH_2OH{\cdot}HCl \quad (3)$$

where R = $CH_3(CH_2)_3CH(C_2H_5)$.

Selecting an Alternative Nickel Extractant

The kinetics of nickel extraction with EHO could be greatly improved with the addition of various accelerators such as organophosphorus compounds, $NaC_{12}H_{25}SO_4$ and Aerosol products; however, the organophosphorus accelerators promoted oxime degradation, and the Aerosol products caused phase separation problems. Consequently, tests were conducted with other nonchelating oximes to identify a more suitable extractant for recovering nickel from the grinding waste process solutions.

The reagents tested were heptyl, octyl, and decyl oxime (DOX). A 1.0 mol/L solution of each oxime was contacted with an equal volume of feed for 30 min in a stirred reactor and the nickel loadings determined. Heptyl and octyl oximes were diluted with kerosene to produce 1.0 mol/L solvents. DOX was not sufficiently soluble in kerosene to produce a 1.0 mol/L solvent and Shell Cyclosol 63, an aromatic naphtha was used as a diluent.

All three of the oximes tested extracted nickel from the acidic cobalt circuit raffinate and were selective for nickel over manganese and chromium. Maximum nickel loadings were similar indicating that reagent carbon chain length had no effect on extraction.

Cyclic loading and stripping tests were conducted with heptyl oxime, octyl oxime, and DOX to determine their stability in process solutions. Loading tests consisted of contacting 1.0 mol/L oxime extractant with an equal volume of simulated cobalt raffinate for 30 min. The loaded solvent was separated and then twice stripped for 30 min with 7.5 g/L HCl solutions. Previous test work with EHO had shown dilute HCl solutions to be a more effective stripping agent than water. Loading and stripping was then repeated until 15 cycles had been completed.

Test results showed that the nickel concentration of loaded heptyl oxime was 12.9 g/L in the first cycle, and there was a constant rate of decrease to 5.4 g/L in the 15th loading. The nickel loading of octyl oxime decreased from 11.3 to 9.1 g/L and the DOX from 10.7 to 10.3 g/L during the 15 loading and stripping cycles. All three oxime extractants showed some instability in the acidic chloride environment; however, extractant stability did increase with increased oxime carbon chain length. Because of the relative stability of DOX, it was selected as the most suitable nickel extractant and was used exclusively in subsequent test work.

Nickel Extraction with DOX

Research developments in processing the hardface alloy grinding waste leach liquor indicated that feed for the nickel extraction circuit would not be the cobalt circuit raffinate, as previously anticipated, but a manganese circuit raffinate. The composition of this manganese circuit raffinate was, in grams per liter, 12 Ni, 84 Cr, and 200 Cl. Feed of this composition, compounded from chemical reagents, was used for batch test work with the DOX extractant. For the final evaluation of the DOX-nickel extraction process in a countercurrent circuit, liquor derived from grinding waste leaching and sequential SX operations was used.

Nickel extraction and stripping kinetics were determined for 1.0 mol/L DOX. Extraction kinetic tests were conducted by

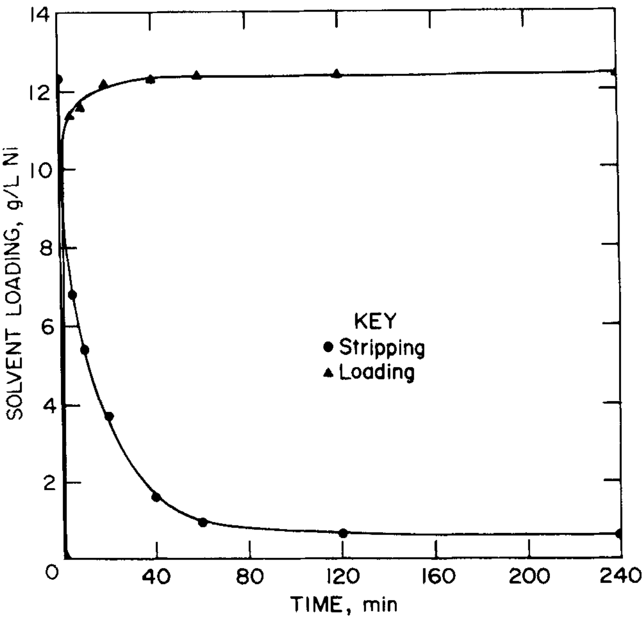

FIGURE 3. 1.0 mol/L DOX extraction and stripping kinetics.

contacting simulated manganese circuit raffinate with the DOX solvent in a stirred reactor at an A:O ratio of 2.0. Samples were taken at timed intervals. Stripping kinetic tests were conducted using a similar procedure except that the DOX solvent was loaded to 12.2 g/L Ni prior to contacting with a 7.5-g/L HCl strip solution.

Test results are presented in Figure 3. Loading test results indicate that the extraction rate rapidly decreased with time. The initial loading rate was relatively fast as over 90 pct of the equilibrium nickel loading was achieved in 5 min; however, it required 60 min to reach equilibrium nickel loadings of 12.4 g/L. Stripping test results indicate that like the loading rate, the stripping rate markedly decreased with time. The initial stripping rate was relatively fast as 50 pct of equilibrium was

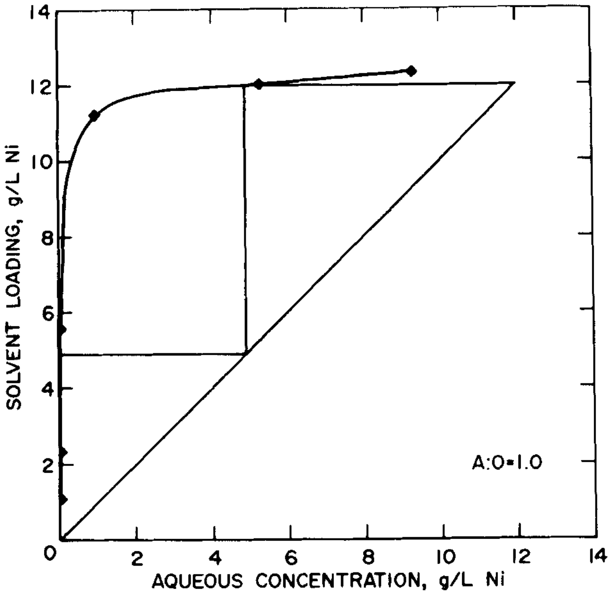

FIGURE 4. McCabe-Thiele diagram for 1.0 mol/L DOX extraction.

achieved in 5 min. However, it required 40 min to reach 90 pct of equilibrium and 240 min to reach equilibrium nickel loadings of 0.6 g/L.

The slow kinetics of DOX severely limit its potential as a commercial nickel extractant. Preliminary tests indicate that the kinetics of aliphatic oxime nickel extraction and stripping are increased at higher temperatures; however, the oximes were less stable at the increased temperatures. Additional research is needed in this area.

A nickel extraction isotherm was established by contacting the 1.0 mol/L DOX extractant with synthetic manganese raffinate at various A:O ratios in a stirred reactor for 60 min. The extraction isotherm and a McCabe-Thiele construction are presented in Figure 4. The figure indicates that a countercurrent SX circuit, containing two extraction stages and operating at an A:O

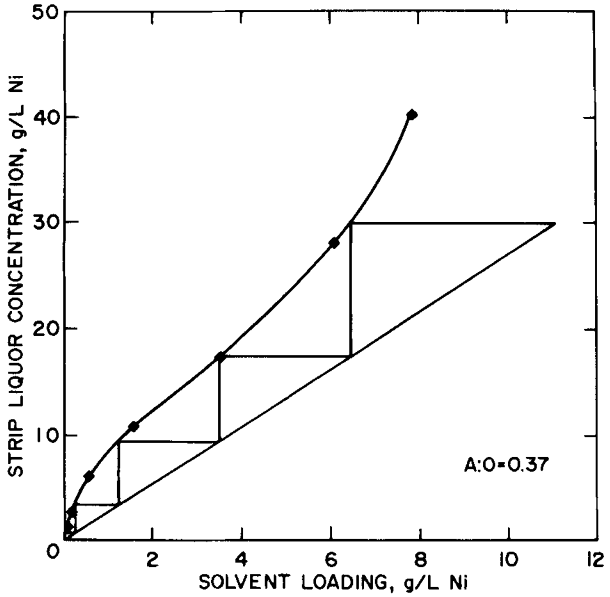

FIGURE 5. McCabe-Thiele diagram for 1.0 mol/L DOX stripping with 7.5 g/L HCl.

flow ratio of 1.0, would produce a loaded solvent containing 11.7 g/L Ni and a raffinate essentially free of nickel.

A nickel stripping isotherm was established by contacting samples of loaded solvent containing 11.1 g/L Ni with 7.5 g/L HCl solution at various A:O ratios in a stirred reactor for 60 min. The stripping isotherm and a McCabe-Thiele construction are presented in Figure 5. These results show that with an A:O flow ratio of 0.37, stripping will require five countercurrent stages. The strip liquor is projected to contain 30 g/L Ni and the stripped solvent only traces of nickel.

A countercurrent, mixer-settler type SX circuit was assembled to extract nickel from manganese circuit raffinate and to test the stability of the DOX extractant. Although the McCabe-Thiele diagrams indicated that two stages would be adequate for extraction and five stages for stripping, the assembled circuit contained three extraction and six stripping stages. The extra stages were added to compensate for the expected inefficiencies of the mixer-settler units.

The mixer-settler unit used for nickel extraction was designed to be compatible with the slow extraction rates and the rapid phase separation rates exhibited by the DOX extractants. The mixer-settler had a 430-mL mixing volume and a 108-mL settling volume. A loading mixing compartment had a 43-min retention time at an aqueous feed rate of 5.0 mL/min and an A:O ratio of 1.0. Similarly, a stripping mixing compartment had a 63-min retention time at a strip solution flow rate of 1.85 mL/min and an A:O ratio of 0.37. With these flows, the retention times in the extraction and stripping settlers were 11 and 15 min, respectively.

The circuit was initially operated with an aqueous feed rate of 5 mL/min and an A:O ratio of 1.0 in the extraction section. In the stripping section, the A:O flow ratio was 0.37, and the stripping solution was 7.5 g/L HCl. The circuit was operated for 6 hr during the day, shut down overnight, and the procedure repeated the following day. The supply of 1.0 mol/L DOX was sufficient to operate the circuit for two 6-hr periods before recycling the stripped solvent. Thus, 12 hr of operation were required to subject the extractant to one complete cycle of loading and stripping.

The initial countercurrent extraction campaign was for 96 hr or eight complete cycles of solvent loading and stripping. After the third cycle, the feed rate was decreased to 4.5 mL/min. Best results were obtained during the next three cycles. The raffinate contained 0.002 g/L Ni, and the strip liquor contained 32.2 g/L Ni. Thereafter, the nickel concentration in the raffinate gradually increased to 0.09 g/L. Apparently the DOX extractant was slowly degrading with each cycle of use, producing a condition in which there was insufficient oxime to extract all the nickel.

The extent of oxime degradation was determined by comparing the nickel-loading capacity of used solvent from the countercurrent circuit with the nickel-loading capacity of freshly prepared 1.0 mol/L DOX. The manganese circuit raffinate was spiked with ^{63}Ni isotope, and relative nickel loadings were determined by radiochemical techniques. Results from the loading tests showed that the used solvent from the circuit would load only 79.9 pct of the nickel compared with freshly prepared 1.0 mol/L DOX. Thus, after eight complete cycles in the nickel solvent-extraction circuit, the extractant had degraded from 1.0 to 0.799 mol/L DOX or had degraded at an average rate of 2.5 pct per cycle.

The degradation was due to hydrolysis of the oxime promoted by the acidic conditions in the nickel extraction circuit. The hydrolysis of the DOX was similar to that given for EHO in equation 3. The aldehyde degradation product was water insoluble and remained in the solvent phase. Because aldehydes react with hydroxylamine salts in neutral solutions to form oximes by equation 1 (13), a sample of the degraded 0.799 mol/L DOX solvent was contacted with a solution containing 17.5 g/L $NH_2OH \cdot HCl$ and 13.3 g/L Na_2CO_3 at an A:O ratio of 1.0 for 1 hr. This procedure increased the DOX concentration in the solvent from 0.799 to 0.979 mol/L indicating that the DOX could be regenerated.

After preliminary tests indicated that the degraded extractant could be regenerated with a $NH_2OH \cdot HCl\text{-}NaCO_3$ solution, the nickel extraction circuit was modified to include a stage for regeneration. The regeneration stage consisted of a single mixer-settler unit in which the stripped solvent was contacted with a $NH_2OH \cdot HCl\text{-}Na_2CO_3$ solution. The A:O flow ratio to the mixer was 1.0, and the concentration of reagents was varied to achieve maximum oxime regeneration. The retention time in the mixer was about 40 min. Except for the regeneration, the countercurrent circuit operating procedure was the same as previously described. However, before startup, all degraded solvent was removed from the circuit and regenerated to 0.979 mol/L, and then additional DOX was added to attain a 1.0 mol/L DOX extractant. The results from

TABLE 1. - DAILY PRODUCT AND SOLVENT ANALYSES

	Nickel Concentration, g/L					Dox Concentration, mo/l	
No.	Feed	Raffinate	Strip Liquor	Loaded Solvent	Stripped Solvent	Stripped Solvent	Regenerated Solvent
1	12.7	0.002	34.1	9.6	0.11	0.815	0.822
2	12	.002	31.6	9.7	.13	.918	.927
3	12.3	.002	29.7	9.5	.052	.887	.987
4	12	.002	27.7	10.2	.015	.856	1.02
5	12.1	.002	28.9	9.9	.024	.882	1.04
6	12.3	.001	29	10.6	.034	.900	1.02
7	12.2	.001	28.8	10.3	.020	.916	1.03
8	11.2	.001	27.2	10.4	.010	.890	1.03
9	12	.003	24.9	10.2	.011	.910	1.05
10	12	.001	26.9	10.4	.024	.910	1.03
11	12.1	.004	26.5	10.2	.019	.950	1.05
12	12.4	.004	29	10.5	.041	.930	1.04

twelve 6-hr periods of operation, or six complete cycles of the extractant through the system, are presented in Table 1.

Test results indicated that nickel was successfully extracted from manganese circuit raffinate for six complete cycles of solvent through the circuit. During the first 3 days (1.5 cycles), the regeneration solution contained 3.8 g/L $NH_2OH \cdot HCl$ and 2.9 g/L Na_2CO_3, which was not sufficient to completely regenerate the DOX. Thereafter, a regeneration solution containing 14.0 g/L $NH_2OH \cdot HCl$ and 10.7 g/L Na_2CO_3 was used, and a resulting extractant concentration range of 1.02 to 1.05 mol/L DOX was achieved. Regeneration to concentrations greater than 1.0 mol/L was probably due to exceeding the 1.0 mol/L target when adjusting the extractant concentration and/or diluent evaporation during the intermittent operation of the circuit.

During the first 6 days (3 cycles) of operation, the circuit was approaching steady state, and analyses of the products were variable; however, during the final 6 days (3 cycles), product analyses were relatively consistent. Average extractant concentration before regeneration was 0.92 mol/L, and after regeneration it was 1.04 mol/L. The difference of 0.12 mol/L shows that the DOX extractant was degrading at a rate of about 12 pct per cycle. This degradation rate was considerably greater than the 2.5 pct per cycle estimated from the previous 96 hr of operation. Thus, the degradation rate must have been great during the first cycle of use, and when the extractant was recycled without regeneration, the degradation rate was materially decreased. The decrease in degradation after the first cycle was attributed to the buildup of aldehyde in the solvent. Apparently, an equilibrium was achieved between the aldehyde and the oxime, which according to equation 3 should decrease DOX degradation.

Long-term batch tests were conducted to determine if an equilibrium would develop, as indicated by equation 3, between the DOX and its degradation products. Tests were conducted in closed stirred reactors in which 1.0 mol/L decyl oxime was contacted for 432 hr with solutions simulating those used in the nickel SX circuit. Test results indicated that the bulk of the degradation occurred when the solvent was contacted with the strip solutions. Solvent contacted with 7.5 g/L HCl solution degraded to 0.9 mol/L DOX during the initial 200 hr of testing and then maintained this concentration over the remaining 232 hr indicating that an equilibrium had been reached between DOX and its degradation products. Solvents that were contacted with aqueous feed solutions such that the oxime was loaded to capacity with nickel did not degrade in over 432 hr of testing. Apparently, DOX is stabilized when complexed with nickel.

Additional batch tests were conducted to empirically determine the equilibrium relationships between DOX, decyl aldehyde, hydroxylamine hydrochloride, and HCl. Eighteen batch tests were conducted using a three factor, face-centered cubic

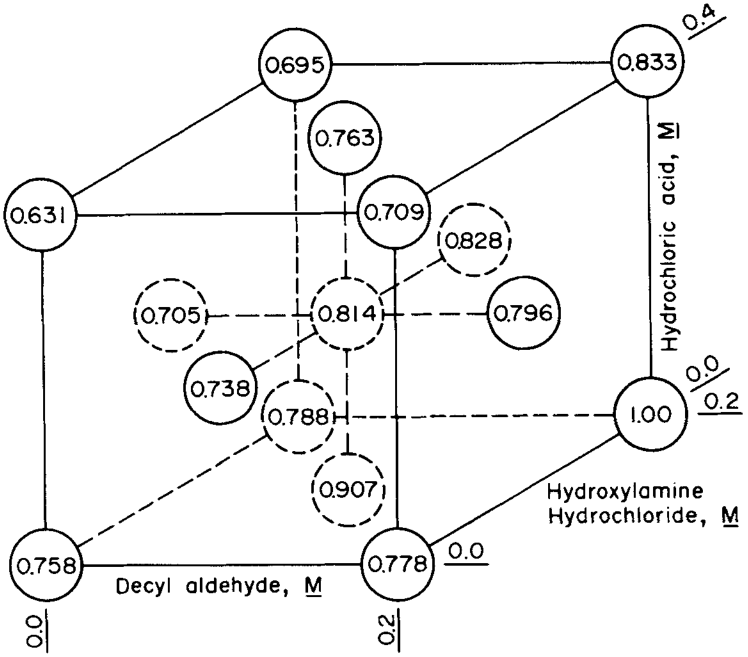

FIGURE 6. Experimental factor space showing final DOX molarity of individual tests.

design strategy (14). The initial DOX concentration was fixed at 0.8 mol/L for all tests to avoid the possibility of producing solvents that were saturated with DOX. The decyl aldehyde concentration in the solvent phase, and the hydroxylamine hydrochloride and the HCl concentrations in the aqueous phase were selected as the independent variables. Decyl aldehyde and hydroxylamine hydrochloride concentrations ranged from 0.0 to 0.2 mol/L and HCl concentrations ranged from 0.0 (pH = 7.0) to 0.4 mol/L.

Individual tests were conducted in closed, stirred, round-bottom flasks at an A:O ratio of 1:1 for 240 hr. A closed reactor was selected to minimize evaporation. Samples of solvent were periodically taken, and the oxime concentration was determined using the maximum nickel loading procedure. Test results are given in Figure 6 which graphically depicts the factor space that was investigated. The circle location within the factor space indicates the conditions at which individual tests were conducted, and the values within the circles represent the final DOX molarity after 240 hr of agitation with the appropriate aqueous phase.

Two general trends can be observed from the data. First, DOX degradation is promoted by increasing HCl concentrations, and second, in the absence of HCl, decyl aldehyde and hydroxylamine hydrochloride react to produce DOX in stoichiometric quantities.

Test data was fit to an empirical model using the percentage change in DOX molarity as the objective function, Y, which is defined by equation 4.

$$Y = ((\underline{M}_{(final)} - 0.8) / 0.8) * 100 \qquad (4)$$

where $\underline{M}_{(final)}$ is the final DOX molarity.

Individual test conditions, final DOX molarity, and the percentage change in DOX molarity, Y, are presented in Table 2. Tests 3, 5, 8, and 13 were replicates conducted at the center of the factor space to provide a measure of experimental error. Results from these four replicates indicate that the procedure was reproducible within about ±2 pct at a 95-pct confidence level (15).

The data in Table 2 was reduced using multiple linear regression techniques to produce the following polynomial model of the factor space:

$$Y^* = -6.62 + 157.12(DAL) + 82.19(AMINE) - 73.61(HCl) + 393.75(DAL)(AMINE) - 12.50(DAL)(HCl) - 50.00(AMINE)(HCl) - 633.05(DAL)^2 - 226.55(AMINE)^2 + 105.86(HCl)^2 \qquad (5)$$

where Y^* is the predicted percentage change in DOX molarity, (DAL) is decyl aldehyde molarity, (AMINE) is hydroxylamine hydrochloride molarity, and (HCl) is HCl molarity. Predicted Y^* values from

TABLE 2. - DOX STABILITY, TEST CONDITIONS AND RESULTS

Initial Conditions, Molarity				Test Results		Predicted Response
Test No.	$C_{10}H_{21}HC{=}O$	$NH_2OH \cdot HCl$	HCl	Final DOX Molarity	Pct Change, Y	Pct Change, Y^*
1	0.20	0.20	0.40	0.833	4.12	5.10
2	.00	.20	.00	.788	-1.50	.76
3	.10	.10	.20	.810	1.25	.91
4	.00	.00	.40	.631	-21.13	-19.13
5	.10	.10	.20	.823	2.88	.91
6	.20	.00	.00	.778	-2.75	-.52
7	.00	.00	.00	.758	-5.25	-6.62
8	.10	.10	.20	.816	2.00	.91
9	.20	.20	.00	1.000	25.00	22.61
10	.20	.00	.40	.709	-11.38	-14.02
11	.00	.20	.40	.695	-13.13	-15.75
12	.00	.10	.20	.705	-11.88	-12.15
13	.10	.10	.20	.805	.63	.91
14	.20	.10	.20	.796	-.50	1.32
15	.10	.20	.20	.828	3.50	5.27
16	.10	.00	.20	.738	-7.75	-7.98
17	.10	.10	.40	.763	-4.63	-2.35
18	.10	.10	.00	.907	13.38	12.65

equation 5 are included in Table 2. A comparison between experimental and predicted values indicates that the model fits the experimental data reasonably well.

Four response surfaces were generated at fixed HCl molarities from equation 5 and are presented in Figure 7. The cross hatched areas in the response surfaces represent regions where the initial DOX concentration changed by less than ±2 pct. Based on the

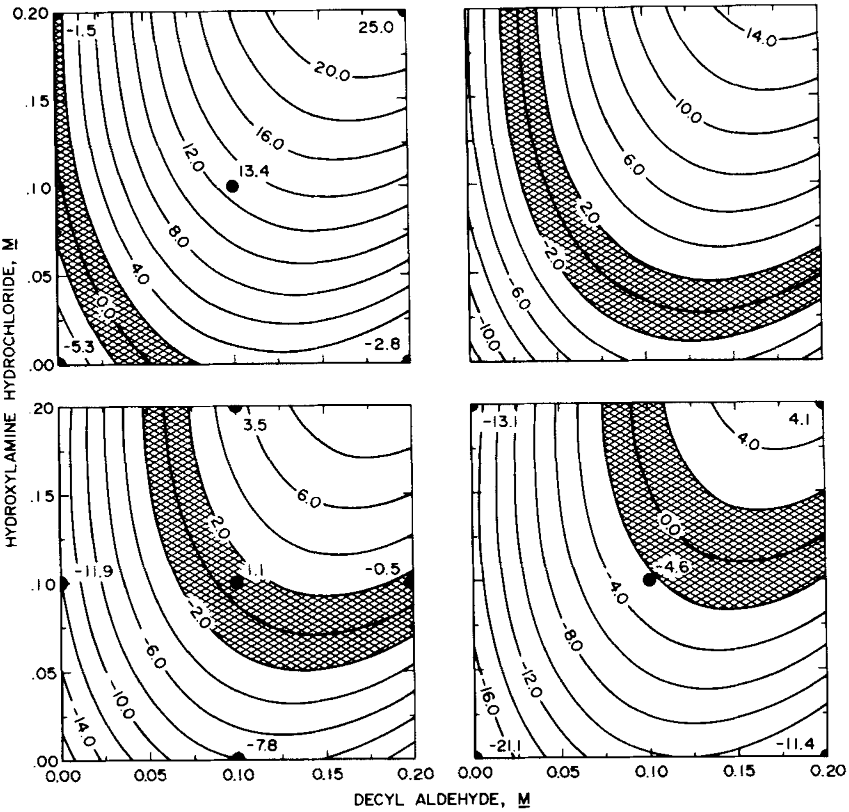

FIGURE 7. Effect of HCl concentration on the percentage change in DOX molarity, A: HCl=0.0 mol/L; B: HCl=0.1 mol/L; C: HCl=0.2 mol/L; and D: HCl=0.4 mol/L. Cross hatched areas represent predicted regions of DOX stability. Shaded dots represent actual experimental results.

reproducibility of the experimental procedure, a change in the predicted DOX concentration of ±2 pct is statistically insignificant. Consequently, the cross hatched areas in Figure 7 indicate conditions at which the DOX extractant is predicted to be stable.

A comparison of the response surfaces shows that with increasing acid concentrations, increasing concentrations of decyl

TABLE 3. - STABILITY TEST CONDITIONS AND RESULTS, MOLARITY

Test No.	$C_{10}H_{21}HC{=}O$	$NH_2OH{\cdot}HCl$	HCl	Final DOX Concentration	Pct Change, Y
19	0.025	0.025	0.000	0.818	2.25
20	0.040	0.040	0.025	0.805	0.63
21	0.050	0.050	0.050	0.790	-1.25
22	0.100	0.010	0.050	0.766	-4.25
23	0.065	0.065	0.100	0.772	-3.50
24	0.100	0.100	0.200	0.764	-4.50

aldehyde and hydroxylamine hydrochloride are required to stabilize the DOX. Minimum concentrations of aldehyde and hydroxylamine hydrochloride would be economically preferable; however, phase separation was poor without some HCl in the aqueous phase. It appears that the most satisfactory conditions at which the oxime is stable are with just enough acid to allow good phase separation.

Six additional tests were conducted, at stable solvent conditions as predicted by equation 5, to determine the minimum acid concentration that will yield good phase separation. Test conditions and results are given in Table 3. Tests conducted at HCl concentrations of 0.0 and 0.025 mol/L resulted in poor phase separations; however, at acid concentrations of 0.050 mol/L and above, good phase separations were observed. Test 21 indicated that 0.8 mol/L DOX could be stabilized by adding 0.05 mol/L decyl aldehyde and by stripping with a solution of 0.05 mol/L hydroxylamine hydrochloride and 0.05 mol/L HCl.

CONCLUSIONS

- EHO extracts nickel from acidic chloride solutions by an ion pair mechanism; however, the extraction rate is inordinately slow.

- Organophosphorus reagents, such as DEHPA, did not extract significant amounts of nickel; but acted as accelerators when combined with EHO.
- EHO-organophosphorus mixtures were unstable and degraded to form ammonium ions and phosphate ions that precipitated as a mixture of acicular NH_4Cl and $NH_4H_2PO_4$ crystals.
- Several straight-chain aliphatic oximes were tested and found to extract nickel from acidic chloride solutions. The extraction kinetics of the straight-chain oximes were similar to those of EHO combined with an accelerator.
- The acidic chloride solutions caused the aliphatic oximes to partially degrade to an aldehyde and hydroxylamine hydrochloride by a hydrolysis reaction; however, the degraded oxime solvents are easily regenerated by contact with a dilute hydroxylamine hydrochloride solution.
- Based on stability considerations, DOX proved to be the most satisfactory reagent for extracting nickel from acidic chloride solutions. The DOX extractant was successfully used in a countercurrent nickel SX circuit which consisted of three extraction, six stripping and one regeneration stage.
- Batch testing in closed reactors indicated that the stability of the DOX could be improved by adding decyl aldehyde to the solvent and by stripping the solvent with a dilute solution of HCl and hydroxylamine hydrochloride, thus eliminating the need for a regeneration stage.

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