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Nickel Extraction from Acidic Chloride Solutions with Aliphatic Oximes

R.D. GROVES and L.D. REDDEN

Salt Lake City Research Center, Bureau of Mines, U.S. Department of the Interior,
729 Arapeen Drive, Salt Lake City, UT 84108 (U.S.A.)

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ABSTRACT

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The U.S. Bureau of Mines investigated the use of aliphatic oximes to extract nickel from acidic nickelous-chromic chloride solutions. Batch solvent-extraction tests were conducted to characterize nickel extraction and stripping. The oximes tested, heptanal, octanal, 2-ethylhexanal, decanal and dodecanal, selectively extracted nickel over chromium by an ion pair transfer mechanism. Nickel was stripped from the loaded oxime extractants with dilute acid. When subjected to acidic processing conditions, the oximes partially degraded to their parent aldehydes by hydrolysis but were regenerated by contacting the solvent with a neutralized hydroxylamine-hydrochloride solution. Decanal oxime (DOX) was successfully used in a continuous countercurrent solvent-extraction circuit that incorporated three loading, six stripping and one regeneration stage. At steady state, the circuit produced raffinates, strip liquors and loaded solvents containing 0.002, 27.2 and 10.3 g/l Ni, respectively. The DOX degraded 12% per loading and stripping cycle but was effectively regenerated prior to recycling to the head of the circuit. Additional testing, in closed reactors, indicated that the stability of the DOX extractant could be improved by adding decyl aldehyde to the solvent and by stripping the solvent with a dilute solution of HCl and hydroxylamine hydrochloride; however, additional research is needed to determine long-term DOX stability in a process solvent-extraction circuit.

INTRODUCTION

The U.S. 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 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 solvent–extraction 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 solvent extraction 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. Octanal 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.

MATERIALS AND PROCEDURES

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 heptanal oxime from heptyl aldehyde [6]. The following equation represents the oxime preparation reaction.

$$2R\mathrm{HC{=}0} + 2\mathrm{HN_2OH \cdot HCl} + \mathrm{Na_2CO_3} \rightarrow 2R\mathrm{HC{=}N{-}OH} + 2\mathrm{NaCl} + 3\mathrm{H_2O} + \mathrm{CO_2} \tag{1}$$

where $R = C_6H_{13}$.

Although the described procedure was for preparing heptanal oxime, it was also found to be satisfactory for preparing octanal, EHO, DOX and dodecanal oxime from their respective aldehydes. The reported purities of the aldehydes used to prepare the various oximes were, in percent, decanal 98, dodecanal 96, heptanal 95 and octanal 99. The EHO was designated as practical grade and the $NH_2OH \cdot HCl$ was 99 pct pure. Based on product weights and the assumption that the recovered products were 100% oxime, yields greater than 95% were consistently achieved. The purity of the oxime products was not determined; however, for the purpose of reporting concentrations in this investigation, the oximes were assumed to be 100% pure.

Other reagents

The other reagents that were utilized in this investigation were used as received from the suppliers. Reagent-grade chemicals were used to produce simulated grinding waste process solutions. The diluents used with the oximes were either kerosene or Shell Cyclosol-63.[1]

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. This 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. Feed of this composition was used in the subsequent test work.

Experimental procedure

Solvent–extraction tests were conducted at room temperature, in separatory funnels agitated with a wrist-action shaker, unless otherwise specified. Prior

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[1] Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

to analyzing, aqueous samples were passed through cotton to remove any entrained solvent, and solvent samples were passed through Whatman 1PS phase separation paper to remove entrained aqueous solution. After the entrained phase was removed, samples 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.

EXPERIMENTAL RESULTS AND DISCUSSION

Nickel extraction with EHO

Initial exploratory tests were conducted with EHO-DEHPA mixtures containing 0.5 *M* DEHPA and 0, 0.25, 0.50 and 1.0 *M* EHO. 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, 0.25, 0.5 and 1.0 *M* 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 did not extract nickel.

The effect of EHO and DEHPA concentrations was determined with the feed solutions at their natural acidity, 0.8 *M* HCl. In these tests, solvent EHO concentrations varied from 0.0 to 2.5 *M* and DEHPA concentrations varied from 0.0 to 1.0 *M*. The solvents were loaded to capacity with nickel by contacting with the aqueous feed solution at an A:O ratio of 1.0 for 30 min. After phase separation, the raffinate was withdrawn, another equal volume of fresh feed added, and the contact procedure repeated until each solvent sample had been contacted three times with fresh feed solution.

Test results showed that without EHO, DEHPA alone would not extract 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 *M* EHO to 19.4 g/l with 2.5 *M* EHO. Improved nickel extractions were obtained with EHO-DEHPA mixtures. For example, with 2.5 *M* EHO and 0.15 *M* DEHPA, the nickel loading was 32.8 g/l. Thus, EHO without DEHPA extracted nickel, but a small amount of DEHPA significantly improved nickel extraction.

Effect of pH

A series of tests was conducted with a solvent containing 1.0 *M* EHO and 0.5 *M* DEHPA to determine the effect of pH on nickel extraction. Feed for these tests was prepared by adding 5 ml of various concentrations of NaOH solution to 25 ml of the simulated cobalt raffinate. Nickel concentration in each of the diluted samples was 25 g/l and the acidity varied from 0.8 *M* 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 *M*. Thus, the 1.0 *M* EHO–0.5 *M* DEHPA solvent was selective for nickel over chromium throughout the entire acidity range tested and was most selective over manganese at the highest acidity.

Extraction mechanism

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 $NiCl_2$.

In an aqueous chloride system, the following nickel ions are known to exist; $Ni(H_2O)_6^{++}$, $Ni(H_2O)_5Cl^+$ and $Ni(H_2O)_4Cl_2$ [7,8]. A high-chloride ion concentration will favor the formation of the neutral hydrated complex. Apparently, the cobalt circuit raffinate chloride ion concentration (140 g/l) was sufficient for the formation of the hydrated nickel chloride ion pair.

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:

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

Extraction rates

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.

Effect of temperature

The effect of temperature on nickel extraction kinetics was determined for 3.0 *M* EHO modified with 0.15 *M* DEHPA. Tests were conducted at temperatures of 20°, 30°, 40° and 50°C. Temperatures were maintained by immersing the reactor in a water bath. Test results presented in Fig. 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 solvent–extraction system and is explained by Bejerrum'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 indication that nonchelating oximes may be unstable in acidic solutions. Testing at elevated temperatures was discontinued because of the apparent instability of the oximes.

Effect of DEHPA addition

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 *M* EHO and for 3.0 *M* EHO plus 0.5 *M* DEHPA. The results of these tests are presented in Fig. 2 and show that extraction kinetics without DEHPA were extremely slow. DEHPA greatly increased the extraction rate

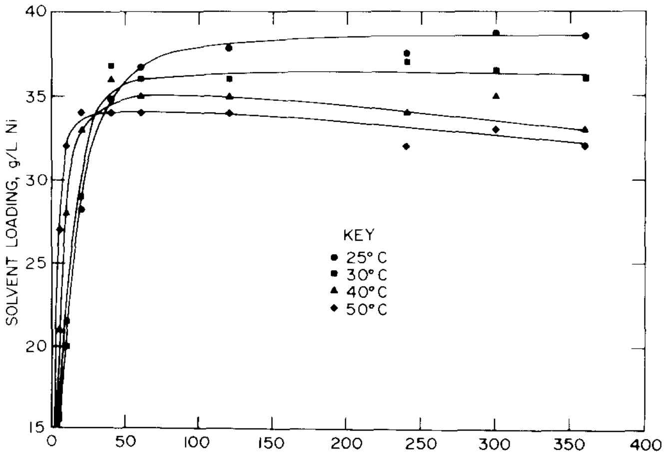

Fig. 1. Effect of temperature on nickel extraction rate with 3.0 *M* EHO and 0.15 *M* DEPHA.

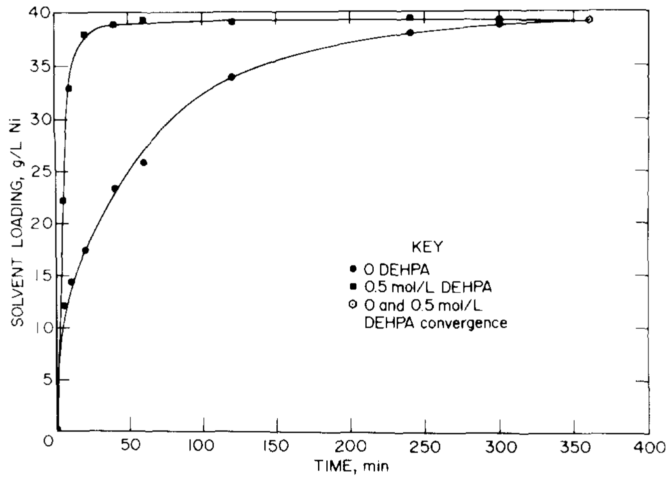

Fig. 2. Effect of DEHPA in 3.0 *M* EHO on nickel extraction rate.

but did not affect the equilibrium loading. Thus, DEHPA acted as an accelerator for the nickel extraction reaction.

Other accelerators

Testing continued with 3.0 *M* 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, (2) mono(2-ethylhexyl) phosphoric acid, (3) mono(2-ethylhexyl) benzyl phosphoric acid, (4) octylphenyl acid phosphate, (5) bis(2-ethylhexyl) pyrophosphoric acid, (6) sodium lauryl sulfate ($Na_2C_{12}H_{25}SO_4$), (7) dioctyl sulfosuccinate (Aerosol OT-100) and (8) di(tridecyl) sulfosuccinate (Aerosol TR-70). The concentrations of the various reagents tested were 0.15 *M* for the organophosphorus reagents, 6 g/l for the $Na_2C_{12}H_{25}SO_4$ 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 *M* 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 problems by producing stable emulsions. The organophosphorus reagents, however, produced rapid phase separations.

Extractant degradation

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. Both EHO solvents and EHO solvents containing accelerators partially degraded by hydrolysis reactions. The degradation products were identified as ethylhexyl aldehyde and hydroxylamine hydrochloride, the reactants from which the EHO had been synthesized. The following chemical equation represents this type of degradation:

$$RHC{=}N{-}OH + H_2O + HCl \rightleftarrows RHC{=}O + NH_2OH \cdot HCl \tag{3}$$

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 oximes tested were heptanal, octanal, decanal (DOX) and dodecanal. A 1.0-M solution of each oxime was contacted with an equal volume of feed for

TABLE 1

Nickel extraction by various nonchelating oximes

Oxime	Loaded solvent analyses (g/l)			
	Ni	Mn	Cr	Cl
Decanal	12.5	<0.001	<0.002	15.2
Dodecanal[a]	11.9	<0.001	<0.002	14.6
Heptanal	12.7	<0.001	<0.002	15.4
Octanal	12.6	<0.001	<0.002	15.8

[a] Test conducted at 40°C.

30 min in a stirred reactor and the nickel loadings determined. Heptanal and octanal oximes were diluted with kerosene to produce 1.0 *M* solvents. The DOX and dodecanal oxime were not sufficiently soluble in kerosene to produce 1.0 *M* solvents and Shell Cyclosol 63, an aromatic naphtha, was used as a diluent for these oximes. The dodecanal oxime was not sufficiently soluble in the Shell diluent at room temperature to produce a 1.0-*M* solution. Consequently, the dodecanal oxime was tested at 40 °C which increased the dodecanal oxime solubility such that a 1.0-*M* solution could be tested.

Analyses of the resulting loaded solvents are presented in Table 1. All four of the oximes tested extracted nickel from acidic chloride solution and were selective for nickel over manganese and chromium. Maximum nickel loading were similar for the oxime, heptanal, octanal and DOX, whereas dodecanal oxime nickel loading was slightly depressed. Because of limited dodecanal oxime solubility, work with this extractant was terminated.

Cyclic loading and stripping

Cyclic loading and stripping tests were conducted with the oximes, heptanal, octanal and DOX to determine their stability. Loading tests consisted of contacting 1.0 *M* 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 heptanal 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 octanal 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. Actual liquor derived from grinding waste leaching and sequential solvent–

extraction operations was used for the final evaluation of the DOX extractant in a continuous countercurrent circuit.

Extraction and stripping rates

Nickel extraction and stripping kinetics were determined for 1.0 *M* DOX. Extraction kinetic tests were conducted by 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 Fig. 3. Loading test results indicate that the extraction rate rapidly decreased with time. The initial loading rate was relatively fast as over 90% 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% of equilibrium was achieved in 5 min. However, it required 40 min to reach 90% of equilibrium and 240 min to reach equilibrium nickel loadings of 0.6 g/l.

The slow loading and stripping 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.

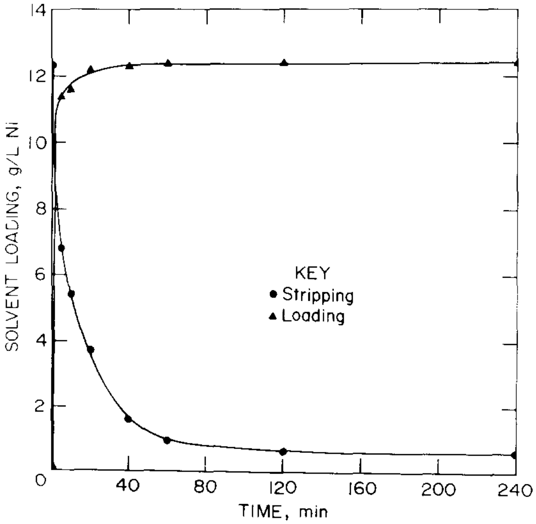

Fig. 3. 1.0 *M* DOX nickel loading and stripping kinetics.

Extraction and stripping isotherms

A nickel extraction isotherm was established by contacting the 1.0 *M* DOX extractant with simulated 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 Fig. 4. The figure indicates that a countercurrent solvent–

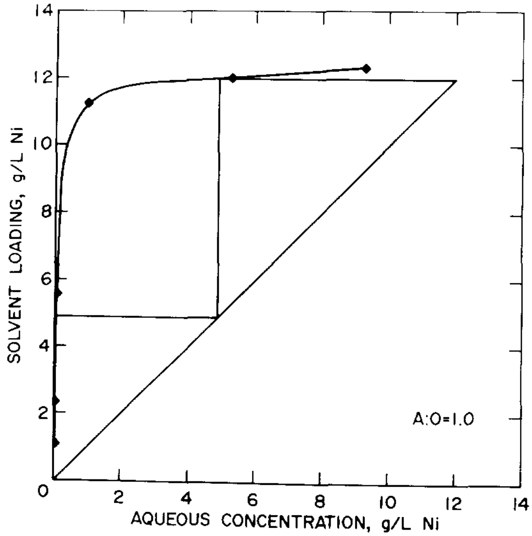

Fig. 4. McCabe-Thiele diagram for nickel extraction with 1.0 *M* DOX.

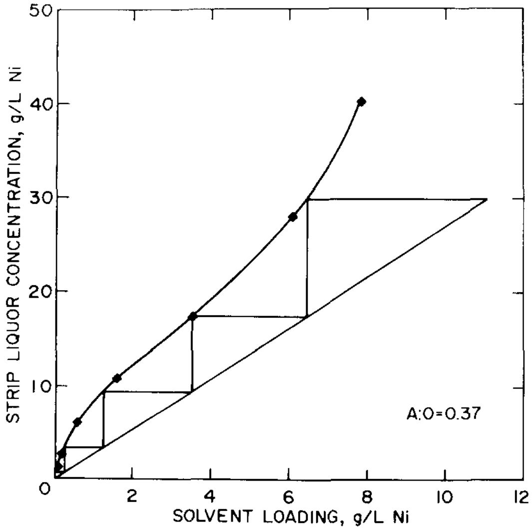

Fig. 5. McCabe-Thiele diagram for 1.0 *M* DOX stripping with 7.5 g/l HCl.

extraction circuit, containing two extraction stages and operating at an A:O 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 Fig. 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.

Countercurrent nickel extraction

A countercurrent mixer–settler solvent–extraction 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.

Initial circuit operation

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, as planned, and the stripping solution was 7.5 g/l HCl. The circuit was operated for 6 h during the day, shut down overnight and the procedure repeated the following day. The supply of 1.0 *M* DOX was sufficient to operate the circuit for two 6-h periods before returning the stripped solvent to the extraction circuit. Thus, 12 h of operation were required to subject the extractant to one complete cycle of loading and stripping.

The initial countercurrent nickel extraction campaign was for 96 h or eight complete cycles of solvent loading and stripping. After the third cycle of this campaign, the feed rate was decreased to 4.5 ml/min. Best results were obtained during the next three cycles of solvent through the circuit. The raffinate contained 0.002 g/l Ni and the strip liquor contained 32.2 g/l Ni. Thereafter, concentration of nickel in the raffinate gradually increased to 0.09 g/l in the eighth cycle. 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 available nickel.

Oxime regeneration

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 *M* 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% of the nickel compared with freshly prepared 1.0 *M* DOX. Thus, after eight complete cycles in the nickel solvent-extraction circuit, the extractant had degraded from 1.0 to 0.799 *M* DOX or had degraded at an average rate of 2.5% 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 Eq. 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 Eq. 1 [12], a sample of the degraded 0.799 *M* 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 h. This procedure increased the DOX concentration in the solvent from 0.799 to 0.979 *M* indicating that the DOX could be regenerated.

Circuit operation with extractant regeneration

After preliminary tests indicated that the degraded extractant could be regenerated with a $NH_2OH \cdot HCl\text{-}Na_2CO_3$ solution, the nickel extraction circuit was modified to include a stage for the 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 *M* and then additional DOX was added to attain a 1.0-*M* DOX extractant. The results from twelve 6-h periods of operation, or six complete cycles of the extractant through the system, are presented in Table 2.

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

TABLE 2

Daily product analyses for the countercurrent nickel extraction process with extractant regeneration

Nickel concentration (g/l)						DOX concentration (M)	
No.	Feed	Raffinate	Strip liquor	Loaded solvent	Stripped solvent	Before regeneration	After regeneration
1	12.7	0.002	34.1	9.6	0.11	0.815	0.822
2	12	0.002	31.6	9.7	0.13	0.918	0.927
3	12.3	0.002	29.7	9.5	0.052	0.887	0.987
4	12	0.002	27.7	10.2	0.015	0.856	1.02
5	12.1	0.002	28.9	9.9	0.024	0.882	1.04
6	12.3	0.001	29	10.6	0.034	0.900	1.02
7	12.2	0.001	28.8	10.3	0.020	0.916	1.03
8	11.2	0.001	27.2	10.4	0.010	0.890	1.03
9	12	0.003	24.9	10.2	0.011	0.910	1.05
10	12	0.001	26.9	10.4	0.024	0.910	1.03
11	12.1	0.004	26.5	10.2	0.019	0.950	1.05
12	12.4	0.004	29	10.5	0.041	0.930	1.04

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 M DOX was achieved. Regeneration to concentrations greater than 1.0 M was probably due to exceeding the 1.0 M 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 and the averages were, in grams per liter of nickel, feed 12.1, raffinate 0.002, loaded solvent 10.3, strip liquor 27.2 and stripped solvent 0.018. The average extractant concentration before regeneration was 0.92 M, and after regeneration it was 1.04 M. The difference of 0.12 M shows that the DOX extractant was degrading at a rate of about 12% per cycle. This degradation rate was considerably greater than the 2.5% per cycle estimated from the previous 96 h 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 of use was attributed to the buildup of aldehyde in the solvent. Apparently, an equilibrium was achieved between the aldehyde and the oxime, which according to Eq. 3, should decrease the DOX degradation rate.

DOX stability

Long-term batch tests were conducted to determine if an equilibrium would develop, as indicated by Eq. 3, between the DOX and its degradation products. Tests were conducted in closed stirred reactors in which 1.0 *M* decyl oxime was contacted for 432 h with solutions simulating those used in the nickel solvent–extraction 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 *M* DOX during the initial 200 h of testing and then maintained this concentration over the remaining 232 h 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 h 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 design strategy [13]. The initial DOX concentration was fixed at 0.8 *M* 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 *M* and HCl concentrations ranged from 0.0 (pH = 7.0) to 0.4 *M*.

Individual tests were conducted in closed, stirred, round-bottom flasks at an A:O ratio of 1:1 for 240 h. 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 Fig. 6 which graphically depicts the factor space that was investi-

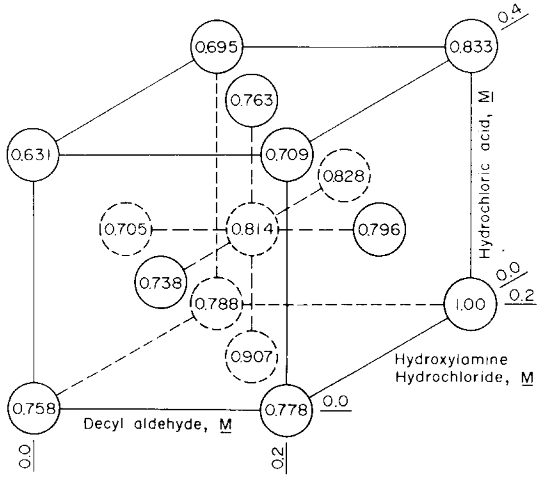

Fig. 6. Experimental factor space showing final DOX molarity of individual tests.

gated. 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 h 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 Eq. 4.

$$Y = M_{(\text{final})} - 0.8)/0.8) * 100 \qquad (4)$$

where $M_{(\text{final})}$ is the final DOX molarity.

Individual test conditions, final DOX molarity and the percentage change in DOX molarity, *Y*, are presented in Table 3. 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% at a 95% confidence level [14].

TABLE 3

DOX stability, test conditions and results

Initial conditions, molarity				Test results	
Test No.	Decyl aldehyde	Hydroxylamine hydrochloride	Hydrochloride acid	Final DOX molarity	Percentage change (*Y*)
1	0.20	0.20	0.40	0.833	4.12
2	0.00	0.20	0.00	0.788	−1.50
3[a]	0.10	0.10	0.20	0.810	1.25
4	0.00	0.00	0.40	0.631	−21.13
5[a]	0.10	0.10	0.20	0.823	2.88
6	0.20	0.00	0.00	0.778	−2.75
7	0.00	0.00	0.00	0.758	−5.25
8[a]	0.10	0.10	0.20	0.816	2.00
9	0.20	0.20	0.00	1.000	25.00
10	0.20	0.00	0.40	0.709	−11.38
11	0.00	0.20	0.40	0.695	−13.13
12	0.00	0.10	0.20	0.705	−11.88
13[a]	0.10	0.10	0.20	0.805	0.63
14	0.20	0.10	0.20	0.796	−0.50
15	0.10	0.20	0.20	0.828	3.50
16	0.10	0.00	0.20	0.738	−7.75
17	0.10	0.10	0.40	0.763	−4.63
18	0.10	0.10	0.00	0.907	13.38

[a] Center point replicates

The data in Table 3 was reduced using multiple linear regression techniques to produce the following polynomial model of the factor space:

$$\begin{aligned} Y^* = &-6.618692 + 157.1146(\mathrm{DAL}) + 82.18452(\mathrm{AMINE}) \\ &-73.61025(\mathrm{HCl}) + 393.75(\mathrm{DAL})(\mathrm{AMINE}) - 12.500(\mathrm{DAL})(\mathrm{HCl}) \\ &-50.00001(\mathrm{AMINE})(\mathrm{HCl}) + \\ &-633.0478(\mathrm{DAL})^2 - 226.5476(\mathrm{AMINE})^2 + 105.8632(\mathrm{HCl})^2 \end{aligned} \tag{5}$$

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.

Four response surfaces were generated at fixed HCl molarities from equation 5 and are presented in Fig. 7. Actual experimental results, presented in response surfaces A, C and D of Fig. 7, indicate that the model fits the experimental data reasonably well. The shaded areas in the response surface represent regions where the initial DOX concentration changed by less than ±2%.

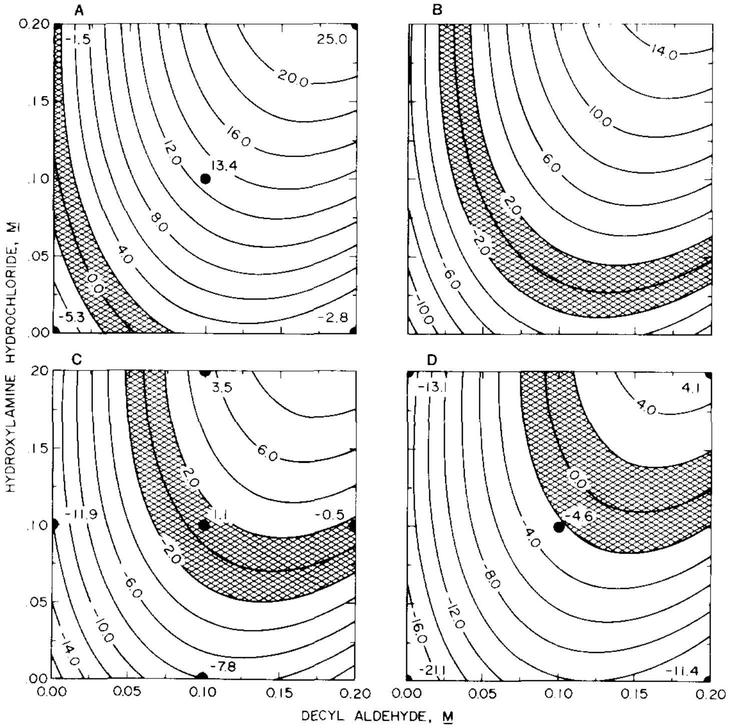

Fig. 7. Effect of HCl concentration on the percentage change in DOX molarity, A: HCl = 0.0 *M*; B: HCl = 0.1 *M*; C: HCl = 0.2 *M*; and D: HCl = 0.4 *M*. Shaded areas represent regions of DOX stability.

TABLE 4

Stability test conditions and results, molarity

Test no.	Decyl aldehyde	Hydroxylamine hydrochloride	Hydrochloric acid	Final DOX molarity	Molarity change, %
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

Based on the reproducibility of the experimental procedure, a change in the predicted DOX concentration of ±2% is statistically insignificant. Consequently, the shaded areas in Fig. 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 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 Eq. 5, to determine the minimum acid concentration that will yield good phase separation. Test conditions and results are given in Table 4. Tests conducted at HCl concentrations of 0.0 and 0.025 *M* resulted in poor phase separations; however, at acid concentrations of 0.050 *M* and above, good phase separations were observed. Test 21 indicated that 0.8 *M* DOX could be stabilized by adding 0.05 *M* decyl aldehyde and by stripping with a solution of 0.05 *M* hydroxylamine hydrochloride and 0.05 *M* HCl.

Although the results from these closed-vessel tests indicate that the DOX can be stabilized, it is not clear that closed-vessel equilibrium are representative of conditions in open solvent-extraction circuits. Aliphatic oximes are known to be reactive compounds and in addition to degradation to an aldehyde, there is a possibility of degradation to an amide and a nitrile. It should also be noted that the aldehyde may not be a stable end product and may further degrade via auto-oxidation to a carboxylic acid. Additional research is needed to determine long-term DOX stability in a process solvent–extraction circuit.

SUMMARY AND CONCLUSIONS

An investigation was conducted to develop a solvent–extraction process to recover nickel from acidic chloride solutions. Based on the work of Preston

[4,5], DEHPA modified with EHO was tested to recover nickel from acidic chloride solutions. Test results indicated that EHO alone would extract nickel; however, the extraction rate was inordinately slow. DEHPA alone did not extract nickel; however, DEHPA acted as an accelerator and markedly increased the nickel extraction kinetics of EHO.

Additional testing indicated that EHO–DEHPA solvents were unstable. In the presence of DEHPA or other organophosphorus reagents, EHO degraded to form ammonium ions which were unstable and precipitated as a mixture of acicular NH_4Cl and $NH_4H_2PO_4$ crystals. Other non-organophosphorus reagents tested as accelerators were not compatible with continuous countercurrent operation. Various unmodified, 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 that of EHO combined with an accelerator.

The acidic chloride solutions caused the straight chain aliphatic oximes to partially degrade to an aldehyde and a hydroxylamine hydrochloride. The aldehydes formed by oxime degradation were aqueous insoluble and remained in the solvent phase. Additional testing showed that the degraded oxime solvents could be regenerated by contacting the solvent with a dilute hydroxylamine hydrochloride solution. Based on minimizing extractant degradation, DOX was selected as the most satisfactory nickel extractant.

The DOX extractant was successfully used in a countercurrent nickel solvent–extraction circuit which consisted of three extraction, six stripping and one regeneration stage. The regeneration stage restored the solvent to 1.0 *M* DOX prior to recycling it to the head of the extraction section in a 6-cycle test run. The feed was derived from processing hardface alloy grindings and contained, in grams per liter, 12 Ni, 84 Cr and 200 Cl. The extractant was 1.0 *M* DOX diluted with Shell Cyclosol-63 and the stripping agent was 7.5 g/l HCl. After steady-state conditions were established in the circuit, average nickel analyses were, in grams per liter, feed 12.1, raffinate 0.002, strip liquor 27.2, loaded solvent 10.3 and stripped solvent 0.018. The DOX extractant degraded by 12 pct as it passed through the circuit, but was effectively regenerated before returning to the head of the extraction section.

Additional batch testing, in closed reactors, indicated that the stability of the DOX extractant could be improved by adding decyl aldehyde to the solvent and by stripping the solvent with a dilute solution of HCl and hydroxylamine hydrochloride. Although this was not verified in a continuous countercurrent solvent–extraction circuit, the addition of decyl aldehyde and hydroxylamine hydrochloride appears to stabilize the DOX extractant.

DOX, modified with decyl aldehyde, shows promise for separating nickel from acidic nickel-chromium solutions; however, the slow extraction and stripping kinetics indicate that a commercial operation might have high capital and solvent inventory costs. Additional research is needed to determine long-term DOX stability in a process solvent–extraction circuit.

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