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# Hydrometallurgical Recovery of Critical Metals From Hardface Alloy Grinding Waste: A Laboratory Study

By L. D. Redden, R. D. Groves, and D. C. Seidel



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# UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

BV	bed volume	min	minute
°C	degree Celsius	mL	milliliter
cm	centimeter	mL/min	milliliter per minute
g	gram	mol	mole
g/L	gram per lîter	mol/L	mole per liter
g/min	gram per minute	$\mu { m m}$	micrometer
(gal/h)/ft <sup>2</sup>	gallon per hour per square foot	mV	millivolt
h	hour	pct	percent
h in Hg	hour inch of mercury	pct rpm	percent revolution per minute
h in Hg kg	hour inch of mercury kilogram	pct rpm vol	percent revolution per minute volume
h in Hg kg L	hour inch of mercury kilogram liter	pct rpm vol vol pct	percent revolution per minute volume volume percent
h in Hg kg L Ib	hour inch of mercury kilogram liter pound	pct rpm vol vol pct	percent revolution per minute volume volume percent
h in Hg kg L lb	hour inch of mercury kilogram liter pound	pct rpm vol vol pct	percent revolution per minute volume volume percent

# HYDROMETALLURGICAL RECOVERY OF CRITICAL METALS FROM HARDFACE ALLOY GRINDING WASTE: A LABORATORY STUDY

By L. D. Redden,<sup>1</sup> R. D. Groves,<sup>2</sup> and D. C. Seidel<sup>3</sup>

# ABSTRACT

As part of the Bureau of Mines program to reduce U.S. reliance on foreign suppliers of strategic and critical metals, research was conducted to improve technology for the recovery of critical metals from hardface alloy grinding waste, a form of superalloy scrap. This report describes a hydrometallurgical process that demonstrated on a laboratory scale that 79 pct of the chromium, 97 pct of the cobalt, 99 pct of the manganese, 99 pct of the nickel, and 90 pct of the tungsten could be recovered in chemical form from hardface alloy grinding waste. The process involved deoiling the grinding waste, followed by chloride-based dissolution of the deoiled material. A high-grade calcium tungstate (CaWO<sub>4</sub>) product was recovered from the resultant leach residue by caustic leaching and precipitation. Iron, cobalt, manganese, and nickel chlorides were sequentially recovered from the leach liquor by solvent extraction. Amine extractants were used to extract the iron, cobalt, and manganese; decanal oxime was used to extract the nickel. Market-grade cobalt chloride (CoCl<sub>2</sub>), manganese chloride (MnCl<sub>2</sub>), and nickel chloride (NiCl<sub>2</sub>) products could be produced directly from the resultant strip liquors. The final raffinate was a relatively pure chromic chloride (CrCl<sub>3</sub>) solution that compared favorably with commercial solutions.

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A major goal of the Bureau of Mines  $(30)^4$  is to reduce U.S. reliance on imported strategic and critical minerals and metals. This goal can be achieved, in part, by developing technology to recover critical metals from domestic superalloy scrap. The Bureau has investigated hydrometallurgical procedures to recover chromium, cobalt, manganese, nickel, and tungsten from hardface alloy grinding waste, a form of superalloy scrap. This report describes a recovery process developed by the Bureau as a result of these investigations.

Each year, significant quantities of hardface alloy grinding waste are produced by various domestic industries. Approximately 3.5 million lb (25) of hardface alloys are annually converted through grinding operations to a finely divided waste material. In addition to containing significant quantities of nickel and chromium, these hardface alloy grindings contain over 1 million lb of cobalt, which is approximately 8 pct of the 1986 U.S. cobalt consumption (15).

The proportion of critical metals in the grindings is substantially less than that in the hardface alloys because of severe contamination from cutting oils, abraded grinding media, and grindings from iron-based alloys. Suitable reprocessing technology has not been available for such highly contaminated scrap, and most grinding wastes have been either stockpiled or transported to industrial waste disposal sites.

A considerable amount of research has been conducted and numerous processes have been proposed to recover critical metals from superalloy and related types of scrap; however, process complexity and adverse economics have prevented all but a few processes from being implemented commercially. A few plants, using proprietary processes, are currently recycling some scrap; unfortunately, little information is available on the type of scrap that is treated or on the technology being used.

Of the recycling investigations reported in the literature, one of the earliest and most wide ranging was conducted by Kenworthy (14) of the Bureau. Several modes of processing were investigated in this study, such as pyrometallurgical treatment, dissolution in acid by electrolytic corrosion, and oxidation by chemical or thermal treatments. In general, pyrometallurgical treatment lacked the selectivity to produce salable products. The oxides produced by chemical or thermal oxidation were dissolved by sulfation, acid leaching, or by fusion with alkali followed by water leaching. Liquors resulting from the various modes of dissolution were treated by troublesome chemical precipitation techniques to recover the critical metals. Since Kenworthy's work, the bulk of the recycling research can be divided into three basic areas: pyrometallurgical

processing, hydrometallurgical processing, and processes combining both pyrometallurgical and hydrometallurgical treatments. Pyrometallurgical treatment is the least selective of the three procedures. Consequently, this type of treatment is typically limited to moderately contaminated scrap. Currently, many secondary alloy producers smelt and selectively oxidize scrap to produce master alloys containing nickel, cobalt, iron, and chromium. Goto (10) has proposed oxidizing scrap until all iron and chromium are partitioned to the slag. Sulfur is then added to the melt to form a nickel-cobalt matte. The matte is treated by mineral processing techniques similar to those used in the primary nickel industry. Recently, Kusik (16) proposed a process wherein chromium is oxidized into a slag phase. After slag-metal separation, ferrochromium is produced from the chromium-rich slag by reduction with ferrosilicon. The chromium-depleted metal may be sold as a master alloy. Although these procedures may be suitable for some types of scrap, fine grindings are typically undesirable for pyrometallurgical treatment because of high contaminant levels.

Unlike pyrometallurgical treatment, hydrometallurgy can be very selective and provide an essentially complete elemental separation; however, there are many problems associated with the hydrometallurgical approach, such as difficult liquid-solid separations. Brooks (7) and Baggott (4) separately proposed similar hydrometallurgical processes wherein scrap was dissolved with hydrochloric acid (HCl), producing a chloride leach liquor containing the major scrap constituents nickel, cobalt, chromium, and iron. Liquors were then treated to separate and recover the metal values and produce chemical products. Cobalt was recovered by solvent extraction, and nickel was recovered by precipitation. The methods of chromium and iron recovery are of particular interest. Baggott coprecipitated iron and chromium from the leach liquor at a controlled pH, but the precipitate was very difficult to filter. Brooks introduced a novel modification wherein iron was extracted from the liquor with a secondary amine prior to cobalt extraction. Following cobalt extraction, chromium was precipitated as a basic chromium sulfate. Although this procedure provided a chromium-iron separation and improved the filtration characteristics of the precipitate, it was reagent- and energy-intensive and produced an impure chromium product.

Hall (11) proposed a sulfate-based process wherein scrap was dissolved with sulfuric acid ( $H_2SO_4$ ) sparged with sulfur dioxide ( $SO_2$ ). Pearson (21) incorporated into this process a densification technique that precipitated filterable iron and chromium hydroxides, after which cobalt was recovered from the filtrate by solvent extraction and electrowinning. Although the densification procedure provided a means for separating iron and chromium from the

<sup>&</sup>lt;sup>4</sup>Italic numbers in parentheses refer to items in the list of references preceding the appendix.

cobalt, it was slow and required extreme dilution of the liquor to minimize cobalt loss.

Because of the difficulties associated with chromium recovery in hydrometallurgical processes, several investigators have studied combined pyrometallurgical and hydrometallurgical treatments. Scrap is generally pretreated by pyrometallurgical means to make it amenable to chemical attack by increasing the scrap surface area or changing the composition so as to make the attack specific to certain elements. For example, Thomas (29) proposed sulfiding the scrap to produce a matte, which was fragmented and selectively leached with aqueous chlorine at a controlled redox potential (Eh). The bulk of the chromium remained in the leach residue, and the valuable metals were recovered from the leach liquor. A similar pyrometallurgical treatment was proposed by DeBarbadillo (9) to produce a fragmented matte that was treated by conventional mineral processing techniques to separate a chromium-free, nickelrich phase from a chromium-rich phase. The chromiumrich phase was treated by pyrometallurgical means to produce a chromium-nickel alloy, and the nickel-rich phase was treated by hydrometallurgical means to produce electrolytic nickel and cobalt. Rosof (28) proposed carburizing a melt to form insoluble carbides of the chromium and the other refractory components. The carburized metal was then treated by hydrometallurgical means to recover the cobalt and nickel.

Several processes have been proposed or are currently under investigation in which the pyrometallurgically treated scrap is cast into soluble anodes. The anodes are dissolved electrolytically to produce impure nickel-cobalt anolytes. Aue (3) proposed treating the anolyte by solvent extraction to produce purified cobalt and nickel strip liquors from which electrolytic cobalt and nickel would be produced. Hayashi (12) proposed purifying the anolyte by precipitation procedures followed by electrodeposition of a nickelcobalt alloy. Currently, Holman (13) is investigating a similar procedure in which a nickel-cobalt alloy is produced by controlled-potential electrolysis.

Although the combined pyrohydrometallurgical approach has several advantages, the practical difficulties associated with pyrometallurgically pretreating finely divided, oily grindings are considerable. To avoid pretreatment difficulties and to utilize the fine grindings' high-surface area, a chloride-based hydrometallurgical approach was selected for this investigation.

A major research objective was to develop technology to produce purified solutions from which marketable chemicals or high-grade metal products could be recovered. Except for the recovery of  $CaWO_4$ , the research did not go beyond the production of purified solutions, because technology is available for subsequent recovery operations.

# SAMPLE DESCRIPTION AND PRETREATMENT

A sample considered to be typical of hardface alloy grinding waste was obtained from a midwestern manufacturer. The grindings were contaminated with moisture, cutting oil, iron-based alloy grindings, and grinding media. Drying and solvent deoiling test results showed that the sample contained 2.4 pct water and 23.7 pct oil.

The high cutting oil content in the grinding waste was anticipated to interfere with subsequent solvent extraction operations; consequently, the as-received grinding waste was deoiled to provide a clean feed material for laboratory testing. The deoiling procedure consisted of slurrying grinding waste with perchloroethylene at 20 pct solids for 15 min at room temperature. The slurry was then filtered and the filter cake reslurried with clean perchloroethylene. Five cycles of slurrying and filtering were carried out with each sample. The final filter cake was washed on the filter with additional perchloroethylene until the filtrate was not discolored with oil, after which the cake was dried at 110° C to remove residual solvent. Used perchloroethylene was purified by distillation and recycled.

The effectiveness of the deoiling procedure was determined by refluxing a sample of cleaned grindings in a Soxhlet extractor. Weight loss measurements revealed that the cleaned grindings contained 0.54 pct oil. Thus, the deoiling procedure removed 98.3 pct of the contaminating oil.



95 µm

Figure 1.-Cleaned grinding waste (X 210).

The deoiled grindings were then screened on a 35-mesh sieve to break up clumps and remove large pieces of foreign material. A screen analysis of the minus 35-mesh fraction showed that 95.7 pct of the material was finer than 100 mesh, indicating that the grinding waste would be suitable for agitation leaching.

Microscopic examination (fig. 1) showed the cleaned grinding waste to be composed of fine metallic and nonmetallic particles. The majority of the particles, elongated shreds of metal, tended to interlock and entrap the nonmetallic particles. Because of this interlocking, physical separation techniques failed to reject the nonmetallics. Chemical analyses of the cleaned grinding waste are presented in table 1.

#### TABLE 1. - Analyses of cleaned grinding waste

	Analyses,
	pct
Element:	
Co	15.1
Cr	19.8
Fe	31
Mn	3.6
Μο	.20
Ni	11.5
W	5.1
Acid-insoluble <sup>1</sup>	13.1
Residual oil	.54

<sup>&</sup>lt;sup>1</sup>Principally Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and SiC.

# PROCESS DESCRIPTION

The recovery process included the following operations: Cleaned grindings were dissolved with chloride lixiviants, producing a residue and a chloride leach liquor. Tungsten, which precipitated as tungstic acid  $(H_2WO_4)$  during the leaching operation, was recovered from the leach residue as synthetic CaWO<sub>4</sub> by caustic leaching and precipitation with calcium chloride (CaCl<sub>2</sub>). Iron, cobalt, manganese, and nickel chlorides were sequentially recovered from the leach liquor by solvent extraction, producing high-purity strip liquors from which salable chemicals or high-grade metal products could be produced. The final raffinate was suitable for sale as a purified  $CrCl_3$  solution. A generalized process flowsheet is shown in figure 2. Tables A-1 through A-5, located in the appendix, give the composition of the various streams depicted in figure 2.

# GRINDING WASTE DISSOLUTION

Research was conducted to establish procedures and gather engineering data applicable to a batch leaching operation. Batch dissolution was selected for two reasons. First, because of the small quantities of material produced, a processing plant would require only a relatively small leaching operation, which could be accommodated by a batch system. Second, mechanical pumps used in continuous leaching systems on similar scrap had failed (7-8), owing to the highly corrosive and abrasive nature of the pulp. Slurry pumping could be eliminated by situating the batch leaching reactor directly above the filter and draining the pulp by gravity onto the filter.

Initial dissolution studies focused principally on upgrading the grindings by selectively leaching impurities such as iron. These attempts were only partially successful, and the research approach was changed to that of complete dissolution. Two requirements were then established. First, dissolution of metal values must be nearly complete, and second, the leach liquor produced must be amenable to subsequent recovery operations. Both chloride- and sulfate-based lixiviants were investigated.

Preliminary leaching tests indicated that dissolution kinetics were much faster with HCl or aqueous chlorine than with  $H_2SO_4$  or even  $H_2SO_4$  sparged with  $SO_2$ . In addition, the formation of metal chlorocomplex ions in solution enabled selective metals separations to be made

more readily in a chloride system than in a sulfate system (19). Based on these considerations, the two chloridebased lixiviants were selected for further testing.

#### **EXPERIMENTAL APPARATUS**

Equipment used in laboratory dissolution studies is shown in figure 3. The 10.5-cm-diam, 3-L baffled glass reactor can be disassembled at the reactor clamp for ease in cleaning and transferring leach pulp. The bottom portion of the reactor was placed in a heating mantle, which, along with the exothermic dissolution reactions, provided heat for leaching at elevated temperatures. Temperature was maintained with a proportional temperature controller. Agitation was provided with a Breda-type Teflon<sup>5</sup> fluorocarbon polymer agitator connected to a glass shaft. An additional agitator was positioned near the top of the reactor to dissipate foam. Chlorine, when used, was sparged into the pulp through a glass tube that introduced the gas directly below the lower agitator. A reflux condenser and a spiral gas absorber were used to treat offgases prior to venting in an exhaust hood.

<sup>&</sup>lt;sup>5</sup>Reference to specific products does not imply endorsement by the Bureau of Mines.



Figure 2.-Generalized process flowsheet.





Figure 3.-Leaching apparatus.

# FOAM CONTROL

When HCl was used for dissolution, either alone or with chlorine gas, a stable foam was generated by the rapid evolution of hydrogen from the leach pulp. The foam volume increased with increasing pulp temperature and reached a maximum of about three times the original pulp volume when the temperature exceeded 50° C. The foam typically persisted for about 20 min before subsiding.

Tests were conducted to determine the variables affecting the relative volume of foam produced during the initial stages of leaching. Test results indicated that decreasing the rate at which grinding waste was fed to the batch reactor at the beginning of a leach reduced the foam-to-pulp ratio. In addition, test results indicated that increasing the reactor diameter reduced the foam-to-pulp ratio. It is difficult to predict the grinding waste foaming characteristics in a commercial-scale reactor, but on the basis of laboratory tests, it appears that foaming would be greatly minimized because of the larger reactor diameters.

#### PRELIMINARY TESTING

Leaching tests were initially conducted with chlorine gas or HCl. Although satisfactory dissolution was observed with both lixiviants (25), third-phase problems resulted when the leach liquors were contacted with solvent extraction reagents. The third phase was caused by tungsten in the leach liquors, which reacted with the extractants to form a semisolid compound that was insoluble in both solvent and aqueous phases.

Because of the reducing conditions when leaching with HCl, 90 pct of the dissolved iron was in the ferrous state. After filtration, HCl liquors were sparged with chlorine to oxidize the iron so that it could subsequently be recovered with amine extractants. When chlorine oxidation was conducted at boiling temperatures, tungsten precipitated from the leach liquor as H<sub>2</sub>WO<sub>4</sub>, producing liquors containing 0.05 g/L WO<sub>3</sub>. Apparently, the combination of high oxidation potentials and high residual acid concentrations was necessary to precipitate the tungsten. Oxidized HCl liquor was contacted with various organic extractants, and thirdphase formation was not observed. Aqueous chlorine leach liquors also had high oxidation potentials; however, they did not have the residual acid concentrations of HCl leach liquors. Consequently, tungsten did not precipitate from these liquors. When aqueous chlorine leach liquor was contacted with various organic extractants, third phases were observed.

# TWO-STAGE HCI-CI, DISSOLUTION

The promising results obtained by oxidizing HCl leach liquors led to the development of a two-stage HCl-Cl<sub>2</sub> dissolution procedure. First, the grindings were leached with HCl. Then, before filtration, the leach pulp was sparged with chlorine gas to oxidize ferrous ions, improve dissolution, and precipitate tungsten.

The principal difference between two-stage dissolution and HCl leaching followed by chlorine oxidation is the number of filtration steps required to produce clarified leach liquors. In the case of HCl leaching, chlorine is sparged into the liquor after the leach residue has been removed by filtration. An additional filtration is then required to remove precipitated tungsten. With two-stage HCl-Cl<sub>2</sub> dissolution, chlorine is introduced into the leach pulp prior to filtration. Precipitated tungsten is then separated from the liquor along with the leach residue in a single filtration of the pulp.

#### **Theoretical Lixiviant Requirement**

The theoretical lixiviant requirement for two-stage dissolution was calculated on the basis of the total chloride, derived from HCl and chlorine gas, needed to dissolve and oxidize grinding waste metallics to these ions:  $Co^{2+}$ ,  $Cr^{3+}$ ,  $Fe^{3+}$ ,  $Mn^{2+}$ ,  $Mo^{6+}$ ,  $Ni^{2+}$ , and  $W^{6+}$ . The chloride requirement was determined to be 142.6 g per 100 g of grinding waste.

#### Effect of Varying Chloride Amount

Tests were conducted to determine the effect of variations in chloride addition on metal dissolution, leach liquor tungsten concentration, iron oxidation, and pulp filtration rate. All tests were conducted for 6 h at boiling temperatures of 100° to 104° C. Previous work had shown that these conditions were adequate for good dissolution (25). The concentration of feed acid was varied from 20.4 to 25.9 pct HCl, which provided 95.1 to 130.9 g Cl<sup>-</sup> per 100 g of grinding waste, respectively. Pulp density ranged from 17 pct solids at 20.4 pct HCl to 15.9 pct solids at 25.9 pct HCl. Pulp density and acid concentration were varied in this way to provide equal amounts of water, 585 g, for each leach. As a result, leach liquor volumes were similar, and saturated or greatly diluted solutions were avoided.

Pulp volume, grinding waste feed rate, and agitation were used to control foaming. Foam was contained in the 10.5-cm, 3-L reactor if no more than 0.75 L of pulp was leached, the grinding waste feed rate was less than 15 g/min, and the agitators were operated at greater than 1,000 rpm.

During the later portion of each test, for periods ranging from 2.2 h at 25.9 pct HCl to 3.2 h at 20.4 pct HCl, chlorine gas was sparged into the pulp at a rate that was estimated to be slightly less than the chlorine adsorption rate. Leaching conditions for individual tests and the residual leach liquor acid concentrations are given in table 2.

TABLE 2. - Experimental conditions<sup>1</sup> for two-stage leaching

		HCI	Residual acid	Total CI,
Test	Solids,	concen-	concentration,	g per 100 g
~	μοτ	pct	g/L H	grinaings
Α	17.0	20.4	0.40	116.7
В	16.8	21.4	.84	124.5
С	16.7	22.4	.97	128.3
D	16.5	23.3	1.15	135.8
Ε	16.3	24.2	1.43	143.2
F	16.1	25.1	1.69	147.1
<u>G</u>	15.9	25.9	1.84	151.5

<sup>1</sup>6-h total with 2.2 to 3.2 h Cl<sub>2</sub> sparging at 100° to 104° C.

### Dissolution of Cobalt, Nickel, and Chromium

Figure 4 shows the relationship between nickel, cobalt, and chromium dissolution and chloride addition. In each case, dissolution increased with increasing amounts of chloride. Nickel dissolution increased from 96.3 pct at 116.7 g Cl per 100 g grinding waste to 99 pct at 143.2 g Cl per 100 g grinding waste. Higher chloride additions did not improve nickel dissolution. Iron and manganese dissolutions, not shown in figure 4, were similar to that of nickel.

Cobalt dissolution increased from 93.8 pct at 116.7 g Cl<sup>-</sup> per 100 g grinding waste to 96.6 pct at 143.2 g Cl<sup>-</sup> per 100 g grinding waste. Further increases in the chloride addition had little effect. At 151.5 g Cl<sup>-</sup> per 100 g grinding



Figure 4.--Effect of chloride addition on two-stage grinding waste dissolution. Test conditions: leaching time, 6 h; temperature, 100° to 104° C; pulp density, 15.9 to 17.0 pct solids.

waste, cobalt dissolution increased only an additional 0.2, to 96.8 pct.

Chromium dissolution also increased with increasing amounts of chloride but was significantly lower than that of nickel and cobalt. At 116.7 g Cl<sup>-</sup> per 100 g grinding waste, chromium dissolution was 76.5 pct, and it increased to 84.1 pct at 151.5 g Cl<sup>-</sup> per 100 g grinding waste. Only small increases in chromium dissolution were realized by extending the leaching time to 13 h.

### Tungsten Concentration

Two-stage leaching produced liquors ranging in residual acid concentrations from 0.40 to 1.84 g/L H<sup>+</sup>. Acid concentration was found to have a significant effect on the tungsten concentration of leach liquor, as illustrated in figure 5. Tungsten concentration decreased markedly with increasing concentrations of acid. At acid concentrations of 0.40 g/L H<sup>+</sup>, the tungsten concentration was 9.3 g/L WO<sub>3</sub>, and it decreased to 0.045 g/L WO<sub>3</sub> at an acid concentration of 1.84 g/L H<sup>+</sup>.

#### Iron Oxidation

Essentially all of the iron in the leach liquors produced by two-stage leaching was oxidized to the ferric state; the Eh of the liquors, determined with platinum and saturated calomel electrodes, was greater than 900 mV.



Figure 5.–Effect of residual acid on leach liquor  $WC_3$  concentration. Test conditions: leaching time, 6 h; temperature, 100° to 104° C; pulp density, 15.9 to 17.0 pct solids.

#### **Filtration Rate**

At the completion of each leaching test, hot pulps were filtered, and the filtration rate was determined. The pulps were filtered on a top-loading filter with a vacuum of 15 in Hg at a temperature of  $55^{\circ}$  to  $60^{\circ}$  C. Prior to filtering, solids in the pulp were allowed to settle, and the leach liquor was carefully decanted. The solids were used to precoat the filter, and filtration rates were then determined for filtering the decanted leach liquor through the precoated filter. Filter cake thicknesses were about 0.25 cm.

Pulp filtration rates varied greatly. Low filtration rates, less than 3 (gal/h)/ft<sup>2</sup>, were measured when the chloride addition was less than 128.3 g per 100 grinding waste. At chloride additions of 128.3 g per 100 g grinding waste or greater, the filtration rate markedly improved, ranging from 33 to 78 (gal/h)/ft<sup>2</sup>. The maximum filtration rate, 78 (gal/h)/ft<sup>2</sup>, was obtained with 143.2 g Cl<sup>-</sup> per 100 g of grinding waste.

#### **Optimum Chloride Addition**

Selection of the optimum chloride addition was based on maximum cobalt dissolution, acceptable pulp filtration rates, and minimum WO<sub>3</sub> concentrations in the product liquor. Maximum cobalt dissolutions were achieved at chloride additions of 143.2 g per 100 g grinding waste and greater. Acceptable filtration rates, greater than 30 (gal/h)/ft<sup>2</sup>, were achieved at all chloride additions investigated above 124.5 g per 100 g grinding waste. Leach liquor tungsten concentrations of less than 0.05 g/L WO<sub>3</sub> were achieved at chloride additions greater than 143.2 g per 100 g grinding waste. Therefore, a chloride addition of 147.1 g per 100 g grinding waste or greater satisfies the criteria of maximum cobalt dissolution, minimum WO<sub>3</sub> concentrations, and high pulp filtration rates. Test F (table 2), conducted with 147.1 g Cl per 100 g grinding waste, most nearly meets these conditions. This test was conducted for 6 h at 16.1 pct solids with 25.1 pct HCl. Chlorine was sparged into the pulp during the last 2.3 h of the leach. These conditions dissolved 96.7 pct of the cobalt and produced a leach liquor in which essentially all the iron was oxidized. The liquor filtered at a rate of 63 (gal/h)/ft<sup>2</sup> and contained only 0.045 g/L WO<sub>3</sub>. In addition, preliminary solvent extraction tests indicated that third-phase formation was minimal.

#### **Chlorine Gas Utilization**

Chlorine consumption for test F (table 2) was determined by carefully measuring the chlorine input and output. Input was determined by weighing the chlorine gas cylinder before and after the leach. Output was determined by scrubbing the reactor offgas with a potassium iodine solution and titrating this solution with potassium thiosulfate. Chlorine input was found to be 46 g, and chlorine output was 2.3 g; therefore, 43.7 g of chlorine were utilized in the leaching and oxidation of 100 g of grinding waste. This represents a chlorine utilization efficiency of 95 pct.

### Scaled-Up Two-Stage Leaching

After optimum leaching conditions were established in the 3-L reactor, a 28.6-cm-diam, 12-L spherical reactor was used to produce larger volumes of leach liquor for subsequent testing and to gather information for a material balance. The larger reactor was not baffled but incorporated all other features of the 3-L reactor. The 12-L reactor is shown in figure 6.

Leaching conditions for the 12-L reactor were the same as the optimum conditions established for the 3-L reactor, except that filter cake wash water was recycled to the succeeding leaching operation and used as makeup water. In general, grinding waste dissolution slightly increased with wash water recycling; grinding waste constituent dissolutions were, in percent, 98.0 Co, 79.8 Cr, 99.2 Fe, 98.9 Mn, 75.0 Mo, 99.3 Ni, and 0.7 WO<sub>3</sub>.

As with the 3-L reactor, pulp volume, grinding waste feed rate, and agitation were used to control foaming. Foam was contained in the 12-L reactor if no more than 6 L of pulp was leached, the feed rate was less than 25 g/min, and the agitators were operated at greater than 600 rpm. Typically, 1,200 g of grinding waste was leached, and 4.2 L of leach liquor was produced.

Chlorine utilization in the scaled-up reactor was much less efficient than that in the smaller, 3-L reactor because of geometrical differences. In the smaller reactor, the pulp height-to-diameter ratio was 1.4, whereas that in the 12-L reactor was 0.5. Consequently, in the large reactor there was a shorter contact time between a rising bubble of chlorine gas and the leach pulp. To efficiently utilize the chlorine gas, it appears that a reactor with a large height-todiameter ratio should be used.



Figure 6.-Twelve-liter leaching apparatus.

#### TABLE 3. - Analyses of grinding waste leach liquor

	<u>Analyses,</u> g/L		<u>Analyses,</u> <u>g/L</u>
Constituent		Constituent	
Ci Co Fe <sup>1</sup> Fe <sup>2+</sup>	348.0 35.3 37.8 73.4 <.03	H <sup>*</sup> Mn Mo Ni WO <sub>3</sub>	1.3 8.5 .33 27.3 .048

<sup>1</sup>Total Fe<sup>2+</sup> and Fe<sup>3+</sup>.

TABLE 4. - Analyses of composite grinding waste leach residue

	<u>Analyses,</u> pct		<u>Analyses,</u> pct
Constituent	`	Constituent	
Al <sub>2</sub> O <sub>3</sub>	37.8	Мо	0.20
C <sup>I</sup> Co Cr Fe	3.4 1.2 15.6 1	Ni SiC SiO <sub>2</sub> WO <sub>2</sub>	.31 2.5 10.9 25
Mn	.16		

<sup>1</sup>Organic.

Because of poor chlorine utilization in the 12-L reactor, the Eh of the leach liquor produced was relatively low, ranging from 250 to 400 mV as measured with platinum and saturated calomel electrodes. Consequently, tungsten precipitation and iron oxidation were incomplete. Filtered leach liquors assayed from 0.08 to 0.15 g/L WO<sub>3</sub> and from 0.05 to 1.0 g/L Fe<sup>2+</sup>, making these liquors unsuitable for subsequent processing. For the subsequent experiments, the leach liquor was further sparged with chlorine to completely oxidize the iron and then filtered to remove additional tungsten. The chemical analyses of the oxidized two-stage leach liquor are given in table 3.

# SEPARATION AND PURIFICATION OF VALUES

# TUNGSTEN RECOVERY FROM ACID LEACH RESIDUE

A composite sample of acid leach residue was prepared by combining the residues from several large-scale dissolutions. The dried, composite leach residue was screened through a 35-mesh sieve and blended to homogenize the sample. Partial chemical analyses are given in table 4. The  $Al_2O_3$ ,  $SiO_2$ , and SiC were present as grinding wheel debris; carbon was present as residual oil and metal carbides. Tungsten was present principally as  $H_2WO_4$ , which precipitated during leaching, and the remaining constituents were present as undissolved metal.

When the composite residue was leached in a caustic solution, a dark-brown liquor was produced. The brown color was caused by the dissolution of organics, probably residual cutting oil. High-grade synthetic  $CaWO_4$  was precipitated from the brown liquor with  $CaCl_2$ . Ammonium paratungstate (APT) was also considered as an end product; however, the stringent specifications for high-grade APT would require additional purification procedures that would be difficult to justify based on the size of the resource being considered.

#### Caustic Leaching

Caustic leaching of the composite residue was investigated to determine the optimum amount of sodium hydroxide (NaOH) required for tungsten dissolution. Tests were conducted at room temperature in an open, stirred reactor. The amount of NaOH used ranged from 2.33 to 18.64 g per 100 g residue. This range of caustic addition represented 27 to 216 pct of the theoretical caustic, 8.62 g per 100 g residue, required for complete tungsten dissolution based on the stoichiometry of the reaction represented by equation 1:

$$H_2WO_4 + 2NaOH \rightarrow Na_2WO_4 + 2H_2O.$$
(1)

In each test, 10.0 g of residue was leached with 30 mL of caustic solution for 1 h. The slurry was filtered, and the filter cake was washed with deionized water. Since  $SiO_2$  is somewhat soluble in caustic solutions, test results showing  $SiO_2$  dissolution are included along with those of WO<sub>3</sub> in figure 7.

These results show that 92 pct of the tungsten was recoverable by caustic leaching. Apparently, the

80 DISSOLUTION, pct 60 40 KEY WO3 20 Si02 0 5 10 15 20 NaOH ADDITION, g per 100 g residue Figure 7.—Effect of NaOH addition on the dissolution of  $WO_3$  and  $SiO_2$ . Test conditions: leaching time, 6 h; temperature, 25° C; caustic addition, 27 to 216 pct of theoretical.

100

unrecoverable 8 pct was present as undissolved metal or as tungsten carbide, which is insoluble in caustic solutions. At the optimum caustic addition, 116 pct of the theoretical requirement or 10.0 g NaOH per 100 g residue, 90 pct of the tungsten was recovered. At higher caustic additions, an additional 2 pct of the tungsten could be dissolved; however, significant quantities of SiO<sub>2</sub> were also solubilized.

#### Effect of Leaching Time on Dissolution

To determine the effect of leaching time on WO<sub>3</sub> and SiO<sub>2</sub> dissolution, tests were conducted at 11.65 g NaOH per 100 g residue, 135 pct of the theoretical caustic addition, in which the leaching time was varied from 5 to 90 min. The test results are presented in figure 8.

The results show that tungsten dissolution was rapid, as over 85 pct dissolved in 5 min. Dissolution further increased to 88.0 pct at 15 min and gradually increased to 91 pct in 90 min of leaching. SiO<sub>2</sub> dissolution was much slower, as less than 5 pct dissolved in 15 min, slowly increasing to nearly 31 pct in 90 min of leaching. Consequently, a short leaching time, 15 to 30 min, results in high tungsten dissolutions while minimizing the amount of SiO<sub>2</sub> solubilized.

# Scaled-Up Caustic Leaching

After leaching conditions had been established, the composite residue was leached on a larger scale to



KEY • W03

SiO2

Figure 8.-Effect of leaching time on WO3 and SIO2 dissolution. Test conditions: temperature, 25° C; caustic addition, 135 pct of theoretical.

produce sodium tungstate (Na<sub>2</sub>WO<sub>4</sub>) liquors for subsequent test work. Tests were conducted at room temperature in an open reactor. NaOH, 33.4 g, was added to 1.0 L of wash water recycled from the previous caustic leach. After the NaOH had dissolved, 334 g of composite residue was added to the solution. The resulting slurry was agitated for 15 min and then filtered.

The average amount of Na<sub>2</sub>WO<sub>4</sub> liquor produced was 0.75 L, and about 0.25 L of liquor was retained in the residue. The retained liquor was displaced by washing the filter cake with 1.2 L of deionized water The resulting wash liquor, about 0.95 L, was diluted to 1.0 L and recycled to the subsequent caustic leach. The procedure was repeated for five leaching cycles. At steady-state conditions, 90.0 pct of the tungsten was recovered in the caustic leach liquor. Partial chemical analyses of the steady-state caustic leach liquor are presented in table 5.

#### TABLE 5. - Analyses of caustic leach liquor

															<u>C</u>	c	n	s	ti	tu	e	n	t													<u>Analyses,</u> <u>g/L</u>
$C^{I}$								•		•			•	•		•		•			•														•	0.99
UI.										•	•							•	•	٠	,		•					•	•	•	•	•	•		•	3.1
Co										•		•	•				•		,	÷	2		•	•	•		3		•			÷	,			.002
Cr						ъ																												,		.002
Fe	÷						÷		,			•	•						5	•			,								•		•		•	.001
Mo						,																		•												.57
Na										•	•			•											,										,	22.5
Ni					•																,															.003
Si.		,																																		.95
WC	)3		•	,	•	,	,		ł		,	•	,		,	•	•	•	ł	•	•	,	,	•	1	•	•	•		•	,	ł	•	•		100.1

<sup>1</sup>Organic.

100

80

40

# Liquor Oxidation and Synthetic CaWO<sub>4</sub> Precipitation

Liquor oxidation was investigated because Altringer (1) reported that organic impurities hinder the precipitation of synthetic scheelite from  $Na_2WO_4$  liquors. Various oxidants were tested to treat the dark-brown caustic leach liquors.

The extent of oxidation was determined by the difference in chemical oxygen demand (COD) (2) between oxidized and untreated liquors. The COD provides a measure of the oxygen equivalent required to oxidize organic matter that is susceptible to oxidation by hot dichromic acid. Tests were conducted in which solutions of 260 g/L NaClO (sodium hypochlorite), chlorine gas, or 50 pct  $H_2O_2$ (hydrogen peroxide) were added or sparged into 80° C caustic leach liquor. The liquor was maintained at 80° C until the liquor's brown color changed to a pale yellow, indicating that oxidation was complete.

Test results showed that NaClO,  $Cl_2$ , and  $H_2O_2$  each oxidized approximately 70 pct of the organic at dosages of 60, 27, and 5.0 g per gram of carbon in the liquor, respectively. Higher dosages did not appreciably increase organic oxidation. Because of the large NaClO requirement and because chlorination adversely lowered the liquor pH,  $H_2O_2$  was selected for additional test work.

Batch tests were conducted to determine the effect of liquor oxidation and CaCl<sub>2</sub> addition on the precipitation of synthetic CaWO<sub>4</sub>. Fifty-percent-H<sub>2</sub>O<sub>2</sub> solution was used as the oxidant at additions of 0.0 to 10.0 g H<sub>2</sub>O<sub>2</sub> per liter of caustic liquor. Tests were conducted in a 100-mL reactor that contained 40.0 mL of Na<sub>2</sub>WO<sub>4</sub> liquor. H<sub>2</sub>O<sub>2</sub>, when used, was added to the liquor and allowed to react for about 10 min prior to heating of the liquor to 80° C for 1.0 h. A 100-g/L CaCl<sub>2</sub> solution was then added to the hot liquor. The CaCl<sub>2</sub> addition ranged from 100 to 177 pct of the theoretical requirement based on the stoichiometry of the reaction represented by equation 2:

$$Na_2WO_4 + CaCl_2 \rightarrow CaWO_4 + 2NaCl.$$
 (2)

After  $CaCl_2$  addition, the slurry was allowed to react for 1 h at 80° C and was then filtered. The CaWO<sub>4</sub> filter cake was then water washed.

Test results indicated that oxidation of the caustic leach liquor was not necessary based on tungsten recoveries, which were the same regardless of the oxidant amount used; however, the CaWO<sub>4</sub> produced from the untreated liquors was tan in color, whereas that produced from the oxidized liquors was white. It is not known if this difference in color is significant and would affect the salability of the product.

The range of CaCl<sub>2</sub> additions tested had only a slight effect on tungsten recovery. Theoretical CaCl<sub>2</sub> additions precipitated 99.7 pct of the tungsten, whereas additions ranging from 110 to 177 pct of the theoretical requirement precipitated essentially all the tungsten, producing filtrates containing only 0.002 g/L WO<sub>3</sub>. Table 6 gives the typical

TABLE	Synthetic CaWO <sub>4</sub> comparison
with	commercial specification

	Analyses, g/L										
Constituent	Synthetic CaWO₄	Commercial specificatior									
As	0.06	<0.2									
C	.3	NS									
Cu	<.01	<.4									
Μο	.14	<.4									
P.O.	.01	<.08									
S	.1	<.75									
Sn	.01	<1									
WO <sub>3</sub>	76	>65									

NS No specification.

composition of the synthetic  $CaWO_4$  produced at 110 pct theoretical CaCl and the commercial specification for tungsten ore concentrates (17). A comparison of the two indicates that the synthetic  $CaWO_4$  product is high grade and should be readily marketable.

# SOLVENT EXTRACTION OPERATIONS

Values in the acid leach liquor were separated and recovered by a series of solvent extraction operations. The formation of anionic chlorocomplexes was promoted by the high leach liquor chloride concentration, 348 g/L. The anionic chlorocomplexes are readily extracted by amines and quaternary ammonium halides. In general, the order of amine extraction (26) corresponds to the order of anionic chlorocomplex formation, which for the major cations in the grinding waste leach liquors is  $Fe^{3+} > Co^{2+}$ >  $Mn^{2+} > Ni^{2+}$  and  $Cr^{3+}$ . Nickel and chromium do not form aionic chlorocomplexes (20) to any extent at the chloride concentrations investigated and are, therefore, not extracted by amine extractants. Consequently, iron, cobalt, and manganese were sequentially extracted with amine reagents. Nickel was then extracted with decanal oxime, an experimental nickel extractant. The resulting raffinate was a purified CrCl<sub>3</sub> solution.

Unless otherwise specified, actual grinding waste solutions were used in the investigations. The exception is that a commercially marketed  $CrCl_3$  solution was used to make up the cobalt circuit scrub solution. The composition of commercial  $CrCl_3$  solution is given in table 7.

TABLE 7. - Comparison of evaporated nickel circuit raffinate with commercial CrCl<sub>3</sub> solution

																Ana	lyses, g/L
	Constituent												Evaporated raffinate	Commercially marketed solution			
$Cl^1$						,							,			340.0	260.0
Co																.004	.003
Cr														į,		160	156
Fe														,		.006	.005
Mn								,						į,		.006	.001
Ni				0											6i	 .004	.006

<sup>1</sup>The difference in CI concentration is due to a higher acidity in the raffinate.

#### Iron Solvent Extraction

Screening tests were conducted with primary, secondary, and tertiary amines and quaternary ammonium chlorides to determine which class of extractant would be best for removing ferric iron from the grinding waste leach liquor. The tertiary amines and the quaternary ammonium chlorides strongly extracted iron but were difficult to strip. Primary amines were found to be relatively poor iron extractants. Secondary amines, however, showed good extraction characteristics and were easily stripped with water. Consequently, a secondary amine, Amberlite LA-2, was selected for further investigation.

#### **Extraction Chemistry**

The high chloride concentration in the leach liquor, 348 g/L, promoted the formation of several ferric chloride complex ions (20). The anionic complex,  $FeCl_4^*$ , is most important to this investigation and is formed stepwise from  $FeCl_2^+$  and  $FeCl_3$  complexes. The overall equilibrium reaction may be represented by the following equation:

$$Fe^{3+} + 4Cl^{-} = FeCl_{4}^{-}.$$
 (3)

This anionic ferric chloride complex appears to be the species extracted by the chloride form of LA-2 amine. Test results have indicated that at maximum iron loading on the solvent, 1 mol of amine is associated with 1 mol of extracted iron. These findings were also reported by Brooks (7). The equilibrium reaction appears to be

$$FeCl_{4(aq)} + R_2NH_2Cl_{(org)}$$
$$\Rightarrow R_2NH_2FeCl_{4(org)} + Cl_{(aq)}, \qquad (4)$$

where the subscripts aq and org refer to the aqueous and organic or solvent phases of the species, respectively.

Stripping the loaded LA-2 amine is simply a matter of pushing reactions 3 and 4 to the left. This is most easily done by contacting the loaded solvent with water, which reduces the chloride concentration in the aqueous phase, thus repressing the formation of the extractable ferric chloride complex. Water stripping produces a ferric chloride (FeCl<sub>3</sub>) strip liquor and leaves the LA-2 amine extractant in the chloride form.

#### Extraction Concentration and Diluent Selection

A 0.5-mol/L concentration of LA-2 amine was selected based on solvent loading and viscosity considerations. Higher extractant concentrations substantially increased iron loading; however, the higher concentrations also increased solvent viscosity, which caused phase-separation problems. Shell Cyclo Sol 63, a high-flash-point aromatic naphtha, was selected to dilute the LA-2 amine because aliphatic diluents, such as kerosene, substantially depressed iron extraction. Modifiers were not used because phase separation was adequate, and the solvent remained homogeneous at all conditions investigated.

### **Iron Extraction**

An extraction isotherm was determined using a batch crosscurrent contacting procedure (6). The aqueous and solvent phases were contacted in separatory funnels on a wrist-action shaker for 30.0 min at room temperature. After phase separation, samples of the loaded solvent and the raffinate were analyzed for iron and cobait by radiochemical and atomic absorption spectrophotometric (AAS) techniques.

Test results in the form of an iron extraction isotherm (6) and a McCabe-Thiele analysis (27) are presented in figure 9. The figure indicates that three stages, operated at an aqueous-to-organic (A:O) ratio of 0.34, are required to extract the iron. Raffinates of less than 0.01 g/L Fe and loaded solvents containing 25 g/L Fe can be produced at these conditions.

In addition to iron, moderate amounts of cobalt were extracted from the leach liquor by LA-2 amine. The equilibrium relationship between iron and cobalt loading on



Figure 9.-McCabe-Thiele diagram for iron extraction. Test conditions: solvent, 0.5 mol/L LA-2 amine in Cyclo Sol 63 naphtha; aqueous phase, grinding waste leach liquor; contact time, 30 min; temperature, 25° C.



Figure 10.—Effect of iron loading on cobalt extraction. Test conditions: solvent, 0.5 mol/L LA-2 amine in Cyclo Sol 63 naphtha; aqueous phase, grinding waste leach liquor; contact time, 30 min; temperature, 25° C.

LA-2 amine, contacted with grinding waste leach liquor, is given in figure 10. Data in the figure indicate that cobalt coextraction was most pronounced at low iron loadings. As iron loading increased, coextracted cobalt was crowded out of the solvent phase by the preferentially extracted iron chloride complex. Cobalt coextraction could be minimized to 0.005 g/L by loading the solvent to capacity with iron. The high iron concentration in the grinding waste leach liquor, 73.4 g/L, provided sufficient iron to load the solvent to capacity and consequently minimize cobalt extraction. In addition to cobalt, trace quantities of tungsten and molybdenum were also extracted with the iron.

# Iron Stripping

A stripping isotherm was determined by contacting loaded solvent containing 25 g/L Fe with water, using a procedure similar to that outlined for the extraction isotherm. Test results in the form of a stripping isotherm and a McCabe-Thiele analysis are presented in figure 11. The figure indicates that three stripping stages, operated at an A:O ratio of 0.5, are required to recover the iron. Strip liquors containing 50 g/L Fe and stripped solvents containing less than 0.1 g/L Fe can be produced at these conditions.

#### **Continuous Countercurrent Solvent Extraction**

#### **Circuit Design and Configuration**

A continuous countercurrent solvent extraction circuit was designed and constructed based on the McCabe-Thiele constructions in figures 9 and 11. A total of seven mixersettler-type contactors were used, four in the loading and three in the stripping sections of the circuit. One additional loading stage over the theoretical requirement



Figure 11.—McCabe-Thiele diagram for the stripping of iron. Test conditions: solvent, 0.5 mol/L LA-2 amine in Cyclo Sol 63 naphtha; aqueous phase, water; contact time, 30 min; temperature, 25°C.

was added to the circuit to compensate for expected inefficiencies in the mixer-settlers. Figure 12 shows the dimensions and configuration of the individual mixer-settler units used in the circuit. Agitation was provided with 2.5-cmdiam, flat, four-bladed, turbine-type impellers rotated at 800 rpm. The mixer-settler units were configured so that the solvent cascaded from higher to lower contacting units. The leach liquor and strip solution (water) were mechanically pumped countercurrent to the flow of the solvent. Figure 13 is a photograph of the circuit.

#### **Circuit Operation**

The iron solvent extraction circuit was operated intermittently for over 200 h with grinding waste leach liquor. The average flow rates for the solvent, feed liquor, and strip solution were 13.0, 5.0, and 7.6 mL/min, respectively. The concentration of extractant in the solvent ranged from 0.5 to 0.55 mol/L LA-2 amine because of diluent evaporation.

Average test results for 114.2 h of steady-state circuit operation are presented schematically in figure 14. The circuit extracted essentially all of the iron contained in the leach liquor, producing a raffinate containing, in grams per liter, 225 Cl, 38.6 Co, 41.6 Cr, 0.005 Fe, 9.4 Mn, 0.1 Mo, and 30.1 Ni.

After several hours of operation, a third phase was observed at the aqueous-solvent interface in the stripping settlers. The crud appeared to build up to a steady-state level that did not interfere with the stripping operation. The material was determined to be primarily an organometallic compound containing iron and traces of tungsten and molybdenum.



Figure 12.-Laboratory mixer-settler unit. Pyrex heat-resistant glass construction with Teflon fluorocarbon polymer baffle.







Figure 14.—Schematic of average iron circuit performance. Test conditions: solvent, 0.50 to 0.55 mol/L LA-2 amine in Cyclo Sol 63 naphtha; operating time, 114.2 h; temperature, 25° C.

## **Coextraction of Other Metals**

Initially, the circuit was operated with 0.5 mol/L LA-2 amine. At this condition, 0.5 pct of the cobalt reported to the FeCl<sub>3</sub> strip product solution. Cobalt coextraction increased to 1.5 pct as the concentration of LA-2 amine increased to 0.55 mol/L. The average cobalt loss over the 114.2 h of circuit operation was slightly less than 1.0 pct.

As the LA-2 amine concentration in the organic phase increased, the loading capacity of the solvent increased accordingly; however, the amount of extracted iron remained constant. Consequently, the actual iron loading decreased relative to the solvent iron-loading capacity. As the relative iron loading decreased, the cobalt crowding effect became less pronounced and cobalt coextraction increased. In addition to cobalt, some molybdenum and tungsten were coextracted by the LA-2 amine. The loaded solvent typically contained 0.1 g/L Mo and 0.004 g/L WO<sub>3</sub>. Strip liquors subsequently produced from the loaded solvent typically contained, in grams per liter, 92 Cl, 0.21 Co, 0.015 Cr, 47 Fe, 0.17 Mo, 0.015 Ni, and 0.01 WO<sub>3</sub>. Over 17

99 pct of the grinding waste iron was recovered in the  $FeCl_3$  strip liquor.

### **Cobalt Solvent Extraction**

Several commercially available amines, ranging in structure from primary to quaternary, were considered for recovering cobalt from the iron circuit raffinate. Tertiary amines have been suggested by several investigators (4, 7, 18, 26) to extract cobalt from chloride solutions; however, test work indicated that tertiary amines coextract significant amounts of manganese along with the cobalt.

All extractants tested, including secondary, tertiary, and quaternary amines, coextracted about the same amount of manganese; however, the tertiary amines extracted cobalt more efficiently and were more easily stripped than the others. Consequently, triisooctyl amine (TIOA), marketed by Henkel Corp. as Alamine 308, was selected for additional test work.

#### Extraction Chemistry

The high chloride concentration in the iron circuit raffinate, 225 g/L, promoted the formation of several complex cobalt chloride ions (20). The anionic cobalt tetrachloride complex ( $CoCl_4^2$ ) appears to be the species that is extracted by TIOA. The tetrachloride forms stepwise from  $CoCl^+$ ,  $CoCl_2$ , and  $CoCl_3^-$  complexes. The overall equilibrium reaction may be represented by the following equation:

$$\operatorname{Co}^{2^+} + 4\operatorname{Cl}^- = \operatorname{Co}\operatorname{Cl}_4^{2^-}.$$
 (5)

Brooks (7) and Monhemius (18) have shown that the chloride form of TIOA extracts the  $\text{CoCl}_4^2$  according to the following equilibrium:

$$\operatorname{CoCl}_{4(aq)}^{2} + 2R_{3}\operatorname{NHCl}_{(org)}$$
$$= (R_{3}\operatorname{NH})_{2}\operatorname{CoCl}_{4(org)} + 2\operatorname{Cl}_{(aq)}^{-}.$$
 (6)

In a manner similar to that for recovering iron from LA-2 amine, cobalt is recovered from TIOA by stripping with water or another solution void of chloride. This represses the formation of the  $\text{CoCl}_4^2$  ion in the aqueous phase and drives reactions 5 and 6 to the left.

#### **Diluent and Modifier Selection**

Kerosene and Cyclo Sol 63 naphtha were investigated as possible diluents for the TIOA. Batch screening tests were conducted to determine the effect of diluent on cobalt extraction. Test results indicated that both TIOAkerosene and TIOA-naphtha solvents were unstable and separated into two distinct phases when loaded with cobalt. The addition of modifiers such as isodecanol, 2-ethylhexanol, nonylphenol, and tributylphosphate (TBP), at concentrations greater than 10 vol pct, were required to homogenize the loaded TIOA-kerosene solvent; however, at these concentrations, the modifiers significantly depressed cobalt extraction.

Modifier concentrations of 2.5 vol pct homogenized the loaded TIOA-naphtha solvent; however, isodecanol, 2-ethylhexanol, and nonylphenol depressed the cobalt loading, whereas TBP slightly increased extraction. Because of the favorable results observed with the TIOA, naphtha, and 2.5 vol pct TBP solvent, this combination was selected for further research.

### **Extractant Concentration**

Batch tests were conducted to determine the TIOA concentration that would most efficiently extract cobalt from iron circuit raffinate. TIOA concentrations ranging from 0.2 to 0.6 mol/L were evaluated by determining cobalt extraction and stripping isotherms for the TIOAnaphtha-TBP solvents. McCabe-Thiele analyses of the isotherms indicated that increasing concentrations of TIOA decreased the number of contacting stages required to recover the cobalt, and the number of contacting stages was minimized with the 0.6 mol/L TIOA solvent. Extractant concentrations greater than 0.6 mol/L were not investigated because of the high viscosity of the loaded solvent; phase separations were too slow to be practical. Based on these considerations, a TIOA concentration of 0.6 mol/L was selected for additional study. McCabe-Thiele



Figure 15.-McCabe-Thiele diagram for cobalt extraction. Test conditions: solvent, 0.6 mol/L TIOA and 2.5 vol pct TBP in Cyclo Sol 63 naphtha; aqueous phase, iron circuit raffinate; contact time, 30 min; temperature, 25° C.

diagrams for cobalt loading and stripping with the selected solvent are given in figures 15 and 16, respectively.

# **Crowding Manganese From Loaded Solvent**

Batch test work indicated that only a marginal cobaltmanganese separation could be achieved by extracting cobalt from iron circuit raffinate because TIOA extracted both cobalt and manganese. As part of an investigation to improve the cobalt-manganese separation, additional tests were conducted to determine if coextracted manganese could be crowded from the loaded solvent by scrubbing with a CoCi<sub>2</sub>-CrCl<sub>3</sub> solution. CoCl<sub>2</sub> was used as a scrubbing agent to displace or crowd coextracted manganese from the loaded solvent. CrCl<sub>3</sub> was added to the scrub solution so that the chloride concentration could be varied independently of the cobalt concentration. CrCl<sub>3</sub> was selected because it would be available from downstream processing and does not form anionic chloride complexes; consequently, it is not extracted by the TIOA. Both the cobaltous and chromic ions are constituents of the grinding waste leach liquor and as such will not further complicate processing by introducing foreign cations.

Iron circuit raffinate that contained 38.6 g/L Co and 9.5 g/L Mn was spiked with <sup>60</sup>Co and <sup>54</sup>Mn radiotracers. The spiked raffinate was contacted with solvent at an A:O ratio of 8:1 for 15 min on a wrist-action shaker. Radiochemical analysis of the loaded solvent, which was verified by AAS techniques, indicated that the solvent contained 13.6 g/L Co and 0.23 g/L Mn.



Figure 16.—McCabe-Thiele diagram for cobalt stripping. Test conditions: solvent, 0.6 mol/L TIOA and 2.5 vol pct TBP in Cyclo Sol 63 naphtha; aqueous phase, water; contact time, 30 min; temperature, 25° C.

Samples of the loaded solvent were contacted for 15 min at an A:O ratio of 1:1 with several  $CoCl_2$ -CrCl<sub>3</sub> scrub solutions. The scrub solutions were made up from reagent-grade chemicals such that solution composition ranged from 0 to 16 g/L Co and from 100 to 260 g/L Cl. The scrubbed solvent and scrub product solution were analyzed for cobalt and manganese by radiochemical techniques. Chloride analyses were determined by chemical techniques.

Test results are presented in figures 17 and 18. Figure 17 shows the effect of varying concentrations of cobalt and chloride in the scrub solution on the percentage of manganese crowded from the solvent. The data in the figure indicate that both cobalt concentration and chloride concentration affect the amount of manganese crowded from the solvent. Over 88 pct of the manganese was crowded from the solvent using scrub solutions containing  $\geq 8 g/L$  Co. Solutions containing < 8 g/L Co were not as effective in crowding manganese from the solvent.

Figure 18 shows the effect of scrub solution chloride concentration on the distribution of cobalt between the scrub product solution and the scrubbed solvent. The dotted horizontal line in the figure at 13.6 g/L Co represents the cobalt loading of the unscrubbed solvent. The data indicate that cobalt concentration in the solvent increases with increasing chloride concentration as would be predicted by equations 5 and 6; however, only the scrub solution containing 260 g/L Cl produced a solvent that loaded higher than 13.6 g/L Co. The most desirable crowding effects were observed with scrub solutions



Figure 17.—Effect of cobalt and chloride concentrations on the crowding of manganese from loaded solvent. Test conditions: solvent, 0.6 mol/L TIOA and 2.5 vol pct TBP in Cyclo Sol 63 naphtha; aqueous phase, synthetic CoCl<sub>2</sub>-CrCl<sub>3</sub> solutions; contact time, 15 min; temperature, 25° C.

containing 260 g/L Cl and  $\ge 8$  g/L Co. Such solutions produced scrubbed solvents containing from 0.02 to 0.025 g/L Mn and from 15 to 16 g/L Co.

## **Continuous Countercurrent Solvent Extraction**

A continuous countercurrent solvent extraction circuit incorporating a scrubbing section was tested to determine if scrubbing the loaded solvent would improve the cobaltmanganese separation. A total of 12 mixer-settler-type contactors, identical to those used in the iron solvent extraction circuit, were used, 5 in the loading section, 2 in the scrubbing section, and 5 in the stripping section of the circuit.

## **Circuit Operation**

The circuit was operated intermittently for over 220 h with solvent, aqueous feed, scrub solution, and strip solution flow rates of 6.0, 4.0, 2.4, and 1.3 mL/min, respectively. The concentration of extractant in the solvent ranged from 0.60 to 0.64 mol/L TIOA because of diluent evaporation. Aqueous feed to the circuit was a blend of 41 vol pct iron circuit raffinate and 59 vol pct scrub liquor. The blended feed contained, in grams per liter, 248 Cl, 24.8 Co,



Figure 18.—Effect of scrub solution chloride concentration on cobalt distribution between aqueous and solvent phases. Test conditions: solvent, 0.6 mol/L TIOA and 2.5 vol pct TBP in Cyclo Sol 63 naphtha; aqueous phase, synthetic CoCl<sub>2</sub>-CrCl<sub>3</sub> solutions; contact time, 15 min; temperature, 25° C.

83.5 Cr, 4.1 Mn, and 12.2 Ni. The scrub solution was made up from reagent-grade chemicals and contained, in grams per liter, 265 Cl, 18.3 Co, 112 Cr, and 0.002 Mn. In actual practice, the scrub solution would be a blend of recycled cobalt strip liquor and nickel circuit raffinate (fig. 2). Water was used to strip the loaded solvent.

Average test results for the last 136 h of circuit operation are presented schematically in figure 19. The circuit extracted essentially all of the cobalt contained in the leach liquor, producing raffinates containing, in grams per liter, 217 Cl, 0.006 Co, 83.5 Cr, 0.003 Fe, 3.8 Mn, 0.001 Mo, and 12.2 Ni. The scrubbing section markedly improved the cobalt-manganese separation by reducing the manganese loading on the solvent from 0.17 to 0.003 g/L Mn. A strip liquor containing, in grams per liter, 99.1 Cl, 82.3 Co, 0.009 Mn, and 0.026 Mo was produced. Ninety-seven percent of the grinding waste cobalt was recovered in the CoCl<sub>2</sub> strip liquor.

During the first few hours of circuit operation, chemical analyses indicated that the strip liquor contained from 0.4 to 0.7 g/L Cr. It was subsequently determined that chromium was not extracted, but a small amount of scrub solution had been entrained in the solvent. As the loaded solvent flowed from the scrubbing to the stripping section of the circuit, the entrained scrub solution contaminated the strip liquor with chromium.

**Removal of Entrained Scrub Solution** 

A coalescing apparatus was designed and incorporated into the cobalt extraction circuit to remove entrained scrub solution from the loaded solvent. The coalescing apparatus was placed between the scrubbing and stripping sections of the circuit so that the scrubbed organic flowed through the coalescing apparatus prior to entering the stripping section. A schematic diagram of the coalescing unit is shown in figure 20. The scrubbed organic flowed into the coalescing unit and through a sheet of fabric prior to exiting the coalescer and flowing into the stripping section. The sheet of fabric provided a high-surface area on which the entrained aqueous droplets could grow and consequently separate from the solvent. Several types of fabrics, such as synthetics, cottons, and linens, were tested. Fabric performance was evaluated based on the resulting chromium concentration in the strip liquor.

Initially, cotton and linen fabrics produced strip liquors that contained less than 0.01 g/L Cr; however, after several hours of operation, the cotton and linen fabrics became saturated with the scrub solution, which restricted solvent flow. A tightly woven nylon fabric proved to be the most effective of the synthetic fabrics tested and produced strip solutions containing 0.15 g/L Cr over extended periods of operation.



Figure 19.-Schematic of average cobalt circuit performance. Test conditions: solvent, 0.60 to 0.64 mol/L TIOA and 2.5 vol pct TBP in Cyclo Sol 63 naphtha; operating time, 136 h; temperature, 25° C.



Figure 20.-Schematic of coalescing unit.

#### **Coextraction of Other Metals**

During the operation of the cobalt circuit, molybdenum was found to be completely coextracted with the cobalt. Only about 20 pct of the extracted molybdenum was stripped from the solvent, producing strip liquors containing 0.025 g/L Mo. The remaining 80 pct of the molybdenum remained on the solvent and was recycled within the circuit. After 220 h of operation, the solvent molybdenum concentration had built up to 0.05 g/L. This buildup of molybdenum in the solvent did not appear to affect circuit performance; however, continued buildup over an extended period would certainly be detrimental.



Figure 21.-Molybdenum extraction profile.

Tests were conducted to determine the feasibility of removing molybdenum from process solutions prior to cobalt solvent extraction. Two techniques of molybdenum removal were considered: (1) molybdenum solvent extraction with trioctylphosphate, as suggested by Brooks (7), and (2) carbon adsorption. Because of the low molybdenum concentrations in the solutions, carbon adsorption was investigated. Preliminary carbon adsorption tests were conducted to determine the feasibility of removing molybdenum from grinding waste leach liquor and iron circuit raffinate, which contained 0.35 and 0.1 g/L Mo, respectively. Test results indicated that molybdenum was more efficiently removed from the iron circuit raffinate than from the leach liquor. A continuous test was then conducted using a packed carbon column. Twenty-one liters of iron circuit raffinate were pumped at a rate of 5.4 mL/min through a 250-mL downflow column, which was packed with 12- by 20-mesh Darco lignite-based activated carbon. Test results, presented in figure 21, show the molybdenum extraction profile. The figure indicates that the first 16 BV or 3.9 L processed were essentially free of the molybdenum, containing 0.001 g/L Mo. The subsequent bed volumes of effluent markedly increased in molybdenum concentration such that after 28 BV, the molybdenum concentration exceeded 0.01 g/L. The molybdenum concentration continued to increase rapidly with subsequent bed volumes. The composite raffinate sample, 86.3 BV or 21 L, contained 0.025 g/L Mo, indicating that 75 pct of the molybdenum was removed by the activated carbon. Except for traces of tungsten and iron, no other elements were adsorbed by the carbon.

Molybdenum coextraction was not recognized to be a problem until the later stages of cobalt solvent extraction research. Consequently, a molybdenum removal step was not integrated into the process. However, it appears that molybdenum could be removed from the iron circuit raffifinate with two packed carbon columns connected in series. The first or lead column would extract the bulk of the molybdenum, and the second or scavenger column would remove any molybdenum remaining in the lead column effluent. Additional research is necessary to design such a system and assess carbon regeneration procedures.

#### Manganese Solvent Extraction

The cobalt solvent extraction research showed that TIOA had a strong affinity for manganese; consequently, the same solvent that was used to extract cobalt, 0.6 mol/L TIOA and 2.5 vol pct TBP in Cyclo Sol 63 naphtha, was selected to extract manganese from the cobalt circuit raffinate.

#### Extraction Chemistry

In a manner analogous to that of ferric and cobaltous ions, the manganous ion forms several chlorocomplexes in high-chloride solutions (20). The complex that appears to be extracted by TIOA is a manganese tetrachloride anion  $(MnCl_4^2)$ , which forms stepwise from cationic and neutral complexes. Results from batch tests have indicated that at a maximum theoretical loading, 2 mol of amine are associated with 1 mol of extracted manganese. Based on these findings, the chloride form of TIOA appears to extract the  $MnCl_4^2$  ion according to the equilibrium represented by the following equation:

$$MnCl_{4(aq)}^{2-} + 2R_3NHCl_{(org)}$$
$$= (R_3NH)_2MnCl_{4(org)} + 2Cl_{(aq)}^{-}.$$
(7)

As with iron and cobalt, manganese is recovered as a chloride salt from the loaded solvent by stripping with water or another solution void of chloride.

# **Manganese Extraction**

An extraction isotherm was determined using a batch cross current procedure by contacting the solvent with cobalt circuit raffinate at a fixed A:O ratio of 1.0 and a contact time of 30 min. After phase separation, samples of the loaded solvent were analyzed for manganese by radiochemical and AAS techniques. Test results in the form of a manganese extraction isotherm and a McCabe-Thiele analysis are presented in figure 22. The figure indicates that two stages, operated at an A:O ratio of 0.77, are required to extract the manganese from the cobalt circuit raffinate. Loaded solvents containing 2.7 g/L Mn and raffinates containing less than 0.1 g/L Mn can be produced at these conditions.

# **Manganese Stripping**

A stripping isotherm was determined by contacting loaded solvent, containing 2.7 g/L Mn, with water, using a



Figure 22.--McCabe-Thiele diagram for manganese extraction with TIOA. Test conditions: solvent, 0.6 mol/L TIOA and 2.5 vol pct TBP in Cyclo Sol 63 naphtha; aqueous phase, cobalt circuit raffinate; contact time, 30 min; temperature, 25° C.

crosscurrent technique. Test results in the form of a stripping isotherm and a McCabe-Thiele analysis are presented in figure 23. The figure indicates that manganese can be stripped from the loaded solvent in one theoretical stage at an A:O ratio of 0.27. Strip liquors containing 10 g/L Mn and stripped solvents containing less than 0.01 g/L Mn can theoretically be produced at these conditions.

#### Continuous Countercurrent Extraction

#### **Circuit Design and Configuration**

A continuous countercurrent solvent extraction circuit was designed and configured based on the results of the McCabe-Thiele constructions in figures 22 and 23. A total of five mixer-settler-type contactors, identical to those used in the iron solvent extraction circuit, were used, three in the loading and two in the stripping sections of the circuit. One additional loading and one additional stripping mixersettler were added over what was theoretically required to compensate for inefficiencies inherent to mixer-settler-type contactors.

# **Circuit Operation**

The circuit was operated intermittently for 97.6 h with solvent, aqueous feed, and strip solution flow rates of 8.0, 6.0, and 2.0 mL/min, respectively. The concentration of TIOA in the solvent ranged from 0.6 to 0.63 mol/L TIOA because of diluent evaporation. Aqueous feed to the



Figure 23.-McCabe-Thiele diagram for the stripping of manganese. Test conditions: solvent, 0.6 mol/L TIOA and 2.5 vol pct TBP in Cyclo Sol 63 naphtha; aqueous phase, water; contact time, 30 min; temperature, 25° C.

circuit was cobalt circuit raffinate, which contained, in grams per liter, 217 Cl, 83.5 Cr, 3.8 Mn, and 12.2 Ni. Water was used to strip the loaded solvent.

Initial test results indicated that spent solvent was not completely stripped and contained an average of 0.02 g/L Mn. When this solvent was recycled, the manganese concentration in the raffinate increased from 0.002 to 0.05 g/L. The number of mixer-settlers in the stripping section was increased from two to three to reduce the concentration of manganese in the stripped organic and consequently reduce the manganese concentration in the raffinate. The additional mixer-settler improved the stripping operation such that stripped solvents containing 0.002 g/L Mn were produced.

Average test results for the last 45 h of circuit operation with three stripping stages are presented schematically in figure 24. The circuit extracted essentially all of the manganese in the aqueous feed, producing a raffinate containing, in grams per liter, 200 Cl, 0.002 Co, 83.5 Cr, 0.003 Fe, 0.003 Mn, and 12.2 Ni.

#### **Removal of Entrained Aqueous**

A coalescing apparatus like the one used in the cobalt solvent extraction circuit was incorporated into the manganese solvent extraction circuit to remove entrained aqueous solution from the loaded solvent. The apparatus was



Figure 24.—Schematic of average manganese circuit performance. Test conditions: solvent, 0.60 to 0.63 mol/L TIOA and 2.5 vol pct TBP in Cyclo Sol 63 naphtha; operating time, 45 h; temperature, 25° C.

placed between the loading and stripping sections of the circuit and was tested with a nylon fabric. The circuit was operated for over 22 h with the coalescing apparatus in place. The resultant strip liquors contained on the average, in grams per liter, 0.012 Co, 0.09 Cr, 10.6 Mn, and 0.03 Ni. Prior to using the coalescing apparatus, strip liquors containing 0.2 g/L Cr and 0.05 g/L Ni were produced. Therefore, the coalescing apparatus reduced the levels of chromium and nickel in the strip liquors by 55 and 40 pct, respectively.

# **Coextraction of Other Metals**

An analysis of the loaded solvent indicated that in addition to manganese, traces of cobalt, chromium, and nickel were extracted by the TIOA. Prior to assaying, samples of loaded solvent were filtered through Whatman 1PS silicone-treated phase-separation paper to remove any entrained aqueous solution. The filtered solvent was analyzed for nickel and chromium by AAS techniques. Analytical results indicated that the loaded solvent contained -0.004 g/L Co, 0.009 g/L Cr, and 0.002 g/L Ni.

#### Nickel Solvent Extraction

Nickel was recovered from manganese circuit raffinate with an experimental nonchelating oxime extractant because no commercial extractant was available to recover either nickel or chromium from the acidic solution. Nonchelating oximes have not previously been used to extract nickel from acidic chloride solutions but have been studied by other investigators (22-24) either as solvent modifiers to improve phase separation or in mixtures with organic phosphate extractants. Preliminary tests indicated that nonchelating oximes had potential for recovering nickel from acidic chloride solutions.

The nonchelating oximes studied in this investigation were not available from commercial sources; consequently, it was necessary to prepare them in the laboratory. The procedure used was for the preparation of heptanal oxime from heptanal (5). The aldehyde was reacted with an aqueous solution of hydroxylamine hydrochloride (NH<sub>2</sub>OH ·HCl), and the mixture was neutralized with sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>). An impure heptanal oxime reported as a separate phase on top of the aqueous reaction mixture and was readily separated. A reduced-pressure distillation described for oxime purification was found to be unnecessary when the oxime was used as a nickel extractant. Consequently, the impure oxime product was used for test work.

Although the preparation procedure was for heptanal oxime, it was found to be satisfactory for other oximes, such as octanal, ethylhexanal, decanal, and dodecanal. Based on product weights and the assumption that the recovered products were 100 pct oxime, yields greater than 90 pct were consistently achieved.

# **Preliminary Testing**

#### **Screening Tests**

Screening tests were conducted with each of the oximes to determine the best extractant for extracting nickel from acidic chloride solutions. Although the purity of the prepared oximes was not known, it was assumed to be 100 pct, and one formula weight per liter was taken to be a 1.0-mol/L solution. The heptanal, octanal, and ethylhexanal oximes were diluted with kerosene. Decanal oxime was not sufficiently soluble in kerosene at room temperature for a 1.0-mol/L solution, and Cyclo Sol 63 naphtha was used as the diluent. However, 1.0 mol/L was near the room-temperature solubility of decanal oxime. Dodecanal oxime was not sufficiently soluble in either kerosene or Cyclo Sol 63 naphtha at room temperature for a 1.0-mol/L solution and was eliminated from consideration for a nickel extractant.

Nickel extraction tests were conducted with a 1.0-mol/L solution of the remaining oximes. Test results indicated that, at equilibrium, each of the oximes loaded nearly 0.25 mol Ni per mole of oxime. The straight-chain oximes, heptanal, octanal, and decanal, reached equilibrium within 30 min of contacting; however, the branched chain, ethylhexanal oxime (EHO), required 4 h to reach equilibrium. Because of slow kinetics, EHO was eliminated from consideration as a nickel extractant.

# **Stripping Tests**

Concurrent with the extraction tests, preliminary stripping tests were conducted. Results from tests with loaded 1.0-mol/L EHO showed that water, dilute HCl, and dilute  $H_2SO_4$  were effective stripping solutions. Solutions containing chloride salts retarded stripping. Water proved to be unsatisfactory for stripping some of the other oxime extractants because emulsions were formed, and phase separations were slow. Stripping with dilute  $H_2SO_4$  was not advantageous when compared with dilute HCl stripping, and to avoid adding another anion to the system, dilute HCl was chosen as the stripping solution. Further testing showed that maximum stripping was achieved with a 7.5-g/L-HCl solution.

## **Degradation Tests**

Cyclic loading and stripping tests were conducted with 1.0-mol/L concentrations of the remaining oximes to determine the stability of the extractants. Fifteen cycles of loading and stripping were completed with each extractant. The results showed that nickel loadings decreased with each extractant as the number of loading and stripping cycles increased from 1 to 15. The decrease in nickel loading was probably a reflection of extractant degradation. The degradation rates for heptanal, octanal, and decanal oximes were 3.9, 1.3, and 0.25 pct per cycle, respectively. Based on minimizing oxime degradation, decanal oxime appeared to be the best nickel extractant and was further tested in a countercurrent solvent extraction circuit.

# **Extraction Chemistry**

During preliminary testing with the five different oxime extractants, both nickel and chloride concentrations in the loaded solvent were determined. Results showed that chloride, as well as nickel, was extracted by each of the oximes, and the extracted chloride-to-nickel mole ratios ranged from 2.01 to 2.09. The closeness of these ratios to 2.0 indicates that  $\text{NiCl}_2$ , a neutral complex, was the extracted nickel species. Thus, nickel was extracted by an ion-pair transfer mechanism. Based on ion-pair transfer and a nickel coordination number of 6, the following equation represents the oxime extraction of nickel.

$$\operatorname{NiCl}_{2} \cdot 4H_{2}O_{(aq)} + 4RCNOH_{(org)}$$
  
= NiCl<sub>2</sub> · 4RCNOH\_{(org)} + 4H\_{2}O\_{(aq)}. (8)

# Extraction with Decanal Oxime

After completing the preliminary testing and selecting decanal oxime (DOX) as the best nickel extractant, research was continued to determine the conditions and design criteria for a countercurrent solvent extraction system. The feed solution used was either actual manganese circuit raffinate or a synthetic solution closely resembling the manganese raffinate. The composition of the manganese raffinate was, in grams per liter, 200 Cl, 0.002 Co, 83.5 Cr, 0.003 Mn, and 12.2 Ni.

#### **Extraction and Stripping Kinetics**

The nickel extraction rate was determined by contacting 1 vol of 1.0-mol/L DOX with 2 vol of synthetic manganese circuit raffinate in a stirred reactor at room temperature. The mixture was sampled at timed intervals ranging from 5 to 300 min, the phases were separated, and the nickel concentration in the solvent phase was determined. The results showed that the initial extraction rate was rapid; however, as equilibrium was approached, the rate markedly decreased. Sixty-five minutes were required to reach an equilibrium loading of 12.4 g/L Ni. The contact times to attain 98 and 99 pct of the equilibrium nickel loading were 20 and 40 min, respectively.

The nickel stripping rate was determined by a similar procedure. One volume of loaded solvent containing 12.0 g/L Ni was contacted with 2 vol of 7.5-g/L-HCl solution in a stirred reactor at room temperature, and the mixture was sampled at timed intervals. The results showed that 120 min were required to attain equilibrium conditions and to produce a stripped solvent containing 0.60 g/L Ni. However, 97 pct of the nickel was stripped in 60 min.

# **Extraction and Stripping Isotherms**

A nickel extraction isotherm was established by eontacting the 1.0-mol/L DOX extractant with synthetic manganese raffinate at various A:O ratios. Contacts were made in a stirred reactor for 60 min at room temperature. The extraction isotherm and a McCabe-Thiele construction are presented in figure 25.

The results show that a countercurrent circuit should contain two extraction stages with an A:O flow ratio of 1.0. The loaded solvent will contain about 11.7 g/L Ni, and the raffinate will be essentially free of nickel.



Figure 25.–McCabe-Thiele diagram for nickel extraction with decanal oxime. Test conditions: solvent, 1.0 mol/L DOX in Cyclo Sol 63 naphtha; aqueous phase, synthetic manganese circuit raf-finate; contact time, 60 min; temperature, 25° C.

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. Contacts were made in a stirred reactor for 60 min at room temperature. The stripping isotherm and a McCabe-Thiele construction are presented in figure 26.

These results show that with an A:O flow ratio of 0.37, stripping will require five countercurrent stages. The strip liquor will contain about 33 g/L Ni, and the stripped solvent will contain only trace amounts 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 two stages 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.

A modified mixer-settler unit was used for nickel extraction because, compared with the amine extraction systems, the extraction rates were slower and the phaseseparation rates were more rapid. Figure 27 shows the dimensions and configuration of the modified mixer-settler, which had a 430-mL mixing volume and a 108-mL settling volume. A loading mixing compartment had a 43-min



Figure 26.—McCabe-Thiele diagram for the stripping of nickel. Test conditions: solvent, 1.0 mol/L DOX in Cyclo Sol 63 naphtha; aqueous phase, 7.5-g/L-HCl solution; contact time, 60 min; temperature, 25° C.

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.

The settling compartments were sized small relative to the mixers, because phase separation was rapid. The capacity of the settlers was 108 mL, which resulted in 11and 15-min retention times in the extraction and stripping settlers, respectively.

#### Initial Circuit Operation

Initially, the circuit was 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 and shut down overnight, and the procedure repeated. The supply of 1.0-mol/L DOX was sufficient to operate the circuit for two 6-h periods before the stripped solvent was returned 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 after three more cycles of solvent through the circuit. The raffinate then 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 ninth cycle. Apparently the DOX extractant was slowly degrading with each cycle of use, eventually producing a condition in which there was insufficient oxime to extract all the available nickel.

## Oxime Degradation and Regeneration

The extent of oxime degradation was determined by comparing the nickel-loading capacity of solvent from the circuit with the nickel-loading capacity of freshly prepared 1.0-mol/L DOX. Results from prior tests showed that nickel-loading capacities of DOX extractants were directly proportional to the extractant concentration. The loading procedure consisted of contacting 1 vol of solvent with 5 vol of simulated manganese circuit raffinate for 1 h at room temperature on a wrist-action shaker. The manganese circuit raffinate was spiked with <sup>63</sup>Ni isotope, and relative nickel loadings were determined by radiochemical techniques. The 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 probably promoted by the acidic conditions in the nickel extraction circuit. Because the oxime was thought to be degrading back to its parent aldehyde, and because aldehydes react with hydroxylamine salts in neutral solutions to form oximes, a sample of the degraded 0.799-mol/L DOX solvent was contacted with a solution containing 17.5 g/L NH<sub>2</sub>OH · HCl and 13.3 g/L Na<sub>2</sub>CO<sub>3</sub> at an A:O ratio of 1.0 for 1 h. The concentration of DOX in the treated solvent was determined to be 0.979 mol/L. Further testing showed that regeneration could not exceed 0.979-mol/L DOX.

# Circuit Operation With In Situ Regeneration

After preliminary tests had indicated that the degraded extractant could be regenerated with a  $NH_2OH$  $\cdot HCl-Na_2CO_3$  solution, the nickel extraction circuit was modified to include a stage for the in situ regeneration of the stripped solvent. The regeneration stage consisted of a single mixer-settler unit in which the stripped solvent was contacted with a  $NH_2OH \cdot HCl-Na_2CO_3$  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 operating procedure was the same as previously described. However, before startup, all of the 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.



Figure 27.-Nickel circuit mixer-settler unit (two separate units). Pyrex heat-resistant glass construction with Teflon fluorocarbon polymer baffle.

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<sub>2</sub>OH · HCl and 2.9 g/L Na<sub>2</sub>CO<sub>3</sub>, which was not sufficient to completely regenerate the DOX. Thereafter, a regeneration solution containing 14.0 g/L NH<sub>2</sub>OH · HCl and 10.7 g/L Na<sub>2</sub>CO<sub>3</sub> was used, and a regeneration range of 1.02- to 1.05-mol/L DOX was achieved. Although this later solution contained an excess of reagents, it was discarded and more efficient use was not studied. Regeneration to molarities greater than 1.0 mol/L was due to exceeding the 1.0 mol/L target when adding DOX to adjust the extractant concentration before starting this 12-day run.

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 average analyses were, in grams per liter of nickel, feed 12.1, raffinate 0.002, loaded solvent 10.3, and stripped solvent 0.018. The average composition of the strip liquor produced was, in grams per liter, <0.001 Co, 0.03 Cr, 0.002 Fe, <0.001 Mn, and 27.2 Ni. Over 99 pct of the grinding

waste nickel was recovered in the NiCl<sub>3</sub> strip liquor. The average extractant concentration before regeneration was 0.92 mol/L, and after regeneration, 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 h of operation. Thus, the degradation rate was great during the first cycle of use, and when the solvent was recycled without regeneration, the degradation rate was materially decreased. Apparently the buildup of aldehyde in the extractant decreases the degradation rate.

#### CHROMIUM RECOVERY

The nickel circuit raffinate was essentially a purified  $CrCl_3$  solution that contained, in grams per liter, 185 Cl, 0.002 Co, 83.5 Cr, 0.003 Fe, 0.003 Mn, and 0.002 Ni. After evaporation to 160 g/L Cr, this solution compared favorably with a commercially marketed  $CrCl_3$  solution. A comparison of the evaporated nickel circuit raffinate and a commercially marketed  $CrCl_3$  solution is given in table 7.

# SUMMARY AND CONCLUSIONS

Laboratory-scale research has demonstrated that hardface alloy grinding waste can be treated by hydrometallurgical processes to separate and recover chromium, cobalt, manganese, nickel, and tungsten. With the exception of tungsten, which can be recovered as a high-grade scheelite concentrate, various elements can be recovered as relatively pure solutions from which marketable chemicals or high-grade metal products can be produced by available technology. The principal steps in the process and unique considerations follow:

1. Solvent deoiling with perchloroethylene was used to produce a cleaned grinding waste product for subsequent processing. The as-received grindings contained 23.7 pct oil, of which 98.3 pct was removed by the degreasing procedure.

2. The cleaned grindings were dissolved in a two-stage  $HCl-Cl_2$  leaching operation. Optimal leaching required 6 h at 100° to 104° C and 127.2 g of chloride from HCl and 19.9 g of chloride from  $Cl_2$  per 100 g of grinding waste. Nickel, iron, and manganese dissolutions were above 98 pct; cobalt and chromium dissolutions were 98.0 and 79.8 pct, respectively. Tungsten was dissolved and subsequently precipitated as  $H_2WO_4$ , which reported to the leach residue. At optimum conditions, 99.7 pct of the tungsten reported to the leach residue. Leach pulp acidity and oxidation potential were found to be critical for complete precipitation of the tungsten.

3. Tungsten was recovered from the grinding waste leach residue by caustic leaching followed by precipitation

as synthetic scheelite. Caustic leaching, with a small excess of NaOH, extracted 90 pct of the tungsten, and 99.7 pct of the extracted tungsten was recovered in the scheelite product, giving an overall tungsten recovery of 89.5 pct. The synthetic scheelite product exceeded the specifications for commercial tungsten concentrates.

4. The grinding waste leach liquor contained, in grams per liter, 348 Cl, 35.3 Co, 37.8 Cr, 73.4 Fe, 8.5 Mn, and 27.3 Ni. The leach liquor was processed in a continuous countercurrent solvent extraction circuit to remove the iron. The solvent was 0.5-mol/L LA-2 amine dissolved in Cyclo Sol 63 naphtha. Raffinates containing 0.005 g/L Fe were consistently produced; however, to minimize cobalt coextraction, it was necessary to load the solvent to near capacity with iron. The loaded solvent was stripped with water, and an FeCl<sub>3</sub> strip liquor containing over 47 g/L Fe was produced. Over 99 pct of the iron contained in the grinding waste was recovered in the FeCl<sub>3</sub> strip liquor.

5. Cobalt was recovered from iron circuit raffinate by continuous countercurrent solvent extraction. The solvent was 0.6-mol/L TIOA dissolved in Cyclo Sol 63 naphtha and 2.5 vol pct TBP. A satisfactory cobalt-manganese separation was not possible without scrubbing the loaded solvent with a solution containing 18 g/L Co and 265 g/L Cl. Scrubbed solvent contained 0.003 g/L Mn and 17.6 g/L Co and was stripped with water to produce a CoCl<sub>2</sub> strip liquor containing, in grams per liter, 82.3 Co, 0.009 Mn, and 0.026 Mo. Ninety-seven percent of the cobalt contained in the grinding waste was recovered in the CoCl<sub>2</sub> strip liquor.

6. Manganese was recovered from the cobalt circuit raffinate in a continuous countercurrent solvent extraction circuit. The solvent used to extract the manganese was the same as that used to extract the cobalt. Raffinates containing 0.003 g/L Mn were produced. Water was used to strip the loaded solvent, and strip liquors containing 10.9 g/L Mn and 0.2 g/L Cr were produced. The high chromium content of the strip liquor was caused by entrained aqueous solution in the solvent that advanced to the stripping section of the circuit. Passing the loaded solvent through a nylon fabric coalescer aided the removal of the entrained aqueous solution and reduced the level of chromium contamination in the strip liquor to 0.09 g/L. Ninety-nine percent of the manganese contained in the grinding waste was recovered in the MnCl<sub>2</sub> strip liquor.

7. Nickel was recovered from the manganese circuit raffinate in a continuous countercurrent solvent extraction circuit. The solvent was 1.0-mol/L DOX diluted in Cyclo

Sol 63 naphtha. DOX is a noncommercial extractant that was developed during this study. The DOX extracted nickel as NiCl<sub>2</sub>, a neutral complex, by an ion-pair mechanism. Raffinates and strip liquors containing 0.002 and 32 g/L Ni, respectively, were produced. Over 99 pct of the nickel contained in the grinding waste was recovered in the NiCl<sub>2</sub> strip liquor. The DOX extractant partially degraded when contacted with acidic manganese circuit raffinate; however, effective in situ regeneration of the DOX was achieved with a NH<sub>2</sub>OH · HCl solution that was neutralized with Na<sub>2</sub>CO<sub>3</sub>.

8. The nickel circuit raffinate was essentially a purified  $CrCl_3$  solution that contained 83.5 g/L Cr, giving an overall chromium recovery of 79 pct. The purified  $CrCl_3$  solution was concentrated to 160 g/L Cr by evaporation. The composition of the concentrated solution compared favorably with the composition of commercially available  $CrCl_3$  solutions.

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# APPENDIX.-PROCESS STREAM COMPOSITIONS

Tables A-1 through A-5 give the composition of the various process streams depicted in figure 2. Stream compositions and relative stream volumes or weights are based on optimum conditions for the unit operations described in the body of this report. Stream volumes and weights were calculated based on processing 1,000 kg of deoiled hardface alloy grinding waste. Solution concentrations of  $\leq 0.005$  g/L were generally not included in the tables.

Stream <sup>1</sup>	Volume,	Weight,	Acid				W	/eight, kg				
	L	kg	insol	CI	Co	Cr	Fe	Mn	Мо	Ni	WO <sub>3</sub>	H₂O
1	ND	1,000.0	131	ND	151.0	198.0	310.0	36.0	2.0	115.0	<sup>2</sup> 64.3	0.0
2	<sup>3</sup> 2,958	3,505.2	0	1,269.9	0	0	0	0	0	0	0	2,200
3	ND	199.1	0	199.1	0	0	0	0	0	0	0	0
4	ND	4134.8	0	10.8	0	0	0	0	0	0	0	124
5	1,758	1,814	0	81.2	8.1	9.3	16.1	1.8	.09	6.2	.01	1,692
6	1,692	1,692	0	0	0	0	0	0	0	0	0	1,692
7	4,188	5,905.4	0	1,456.4	148.0	158.1	307.4	35.6	1.5	114.2	.2	3,684
8	ND	341.8	131	1.8	3.0	39.9	2.6	.4	.5	.8	64.1	84
9	ND	<sup>3</sup> 25.6	0	0	0	0	0	0	0	0	0	0
10	561	572	0	ND	ND	ND	ND	ND	.1	ND	17.7	550.5
11	606	606	0	0	0	0	0	0	0	0	0	606
12	ND	276.9	131	ND	3.0	39.9	2.6	.4	.15	.8	6.4	87.9
13	577	630.5	0	1.8	.001	.001	.001	.0005	.35	.001	57.7	570.4
14	ND	°28.9	0	18.5	0	0	0	0	0	0	0	0
15	298	298.5	0	.5	ND	ND	ND	ND	.001	ND	ND	298
16	298	298	0	0	0	0	0	0	0	0	0	298
17	859	882.4	0	20.3	ND	ND	ND	ND	.24	ND	.2	850.4
18	ND	89.4	0	ND	ND	ND	ND	ND	.11	ND	57.5	18

TABLE A-1. - Grinding waste dissolution and tungsten reccovery

ND Not determined. Streams are identified in figure 2. 250.9 kg W. 37.25-pct-HCl solution.

<sup>4</sup>Condenser offgas.

<sup>5</sup>NaOH.

6CaCl<sub>2</sub>

#### TABLE A-2. - Iron solvent extraction

Stream <sup>1</sup>	Volume,	Weight, kg							
	L	CI	Co	Cr	Fe	Mn	Мо	Ni	
7	4,188	1,456.4	148.0	158.1	307.4	35.6	1.5	114.2	
19	3,798	853.6	146.6	158.0	.02	35.6	.4	114.1	
20	10,878	193	0	0	.8	0	0	0	
21	10,878	795.8	1.4	<sup>2</sup> .1	308.2	0	1.1	<sup>2</sup> .1	
22	<sup>3</sup> 6,328	0	0	0	0	0	0	0	
23	6,559	602.8	1.4	<sup>2</sup> .1	307.38	ND	1.1	<sup>2</sup> .1	

<sup>1</sup>Streams are identified in figure 2.

<sup>2</sup>Primarily from aqueous entrainment in the loaded solvent.

<sup>3</sup>H<sub>2</sub>O strip solution.

Stream <sup>1</sup>	Volume,			Weight	t, kg	13	
	L	CI	Co	Cr	Mn	Mo	Ni
19	3,798	853.6	146.6	158.0	35.6	0.4	114.1
24	9,397	2,321.6	233.2	785	38.3	.4	114.1
25	9,397	2,039.1	.06	784.7	35.58	.01	114.1
26	5,599	1,468	86.54	627	2.35	ND	ND
27	14,020	582.5	233.14	NC	2.38	.39	NC
28	5,599	1,485.5	102.6	627.2	.011	ND	ND
29	14,020	300	.028	0	.014	.31	0
30	14,020	600	249.2	<sup>3</sup> .5	.041	.39	NC
31	<sup>2</sup> 2,959	0	0	0	0	0	0
32	1,247	123.6	102.6	<sup>3</sup> .2	.011	.08	NC
33	1,781	176.4	146.5	<sup>3</sup> .3	.016	.05	NC
40	4,352	1,361.9	0	627	0	0	0

TABLE A-3. - Cobalt solvent extraction

NC Not considered.

ND Not determined.

<sup>1</sup>Streams are identified in figure 2.

<sup>2</sup>H<sub>2</sub>O strip solution. <sup>3</sup>Primarily from aqueous entrainment in the scrubbed solvent.

TABLE A-4. - Manganese solvent extraction

Stream <sup>1</sup>	Volume,		v	/eight, kg	(		Stream <sup>1</sup>	Volume,	Weight, kg				
	L	CI	Co	Cr	Mn	Ni		L	CI	Co	Cr	Mn	Ni
25	9,397	2,039.1	0.06	784.7	35.58	114,1	36	12,496	460.2	0.05	<sup>2</sup> 0.3	35.57	<sup>2</sup> 0.1
34	9,397	1,878.9	.02	784.4	.03	114	37	<sup>3</sup> 3,222	0	0	Q	0	Q
35	12,496	300	.01	0	.02	0	38	3,361	160.2	.04	<sup>2</sup> .3	35.55	<sup>2</sup> .1

 $^1$  Streams are identified in figure 2.  $^2$  Primarily from aqueous entrainment in the loaded solvent.  $^3\mathrm{H_2O}$  strip solution.

TABLE A-5 Nickel solver	it extraction and	chromium	recovery
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Stream <sup>1</sup>	Volume,		Weight, kg		Stream <sup>1</sup>	Volume,	Weight, kg			
	L	CI	Cr	Ni		L	CI	Cr	Ni	
34	9,397	1.878.9	784.4	114.0	44	9,397	138,2	<sup>4</sup> 0.1	114.17	
39	9,397	1,760.9	784.3	.02	45	3,547	163.4	4.1	113.98	
40	4,352	1,361.9	627	.016	46	9,397	.2	0	.19	
41	<sup>2</sup> 4,057	43.1	ND	ND	47	<sup>5</sup> 9,397	67.2	0	0	
42	988	335.9	157.3	.004	48	9,397	.2	0	.19	
43	<sup>3</sup> 3,477	25.4	0	0	49	<sup>6</sup> 9,397	67.2	ND	ND	

ND Not determined. Streams are identified in figure 2. Evaporated water and HCI. <sup>3</sup>7.5-g/L HCI strip solution. <sup>4</sup>Primarily from aqueous entrainment in the loaded solvent. <sup>5</sup>Regeneration solution containing 131.6 kg NH<sub>2</sub>OH·HCI and 100.5 kg Na<sub>2</sub>CO<sub>3</sub>.

<sup>6</sup>Spent regeneration solution.