RECOVERY OF MOLYBDENUM FROM SUPERALLOY SCRAPS AND WASTE PRODUCTS

by

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STATEMENT BY AUTHOR

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To all those who believe in progress
and are ready to pay the price of
success.

December, 1980

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ABSTRACT

The literature on recovery of metal values from superalloy scraps has been studied, with particular emphasis on the recovery of molybdenum. Experimental work has shown that this metal can be at least 98% recovered as the trioxide and as molybdic acid by precipitation with ammonium chloride and nitric acid. Prior to its ultimate recovery, the moly was solubilized along with nickel, chrome, cobalt and iron, with hot concentrated hydrochloric acid. Experimental techniques are discussed for separating iron, cobalt and moly from the nickel-chrome chloride solution by solvent extraction of selectively oxidized chlorocomplexes in Alamine 336®. The loaded organic was first stripped of its iron and cobalt, then of the moly, to yield a fairly high purity solution of sodium molybdate.

technical feasibility, economic feasibility, and environmental and operational safety. Some of the available options are flotation, pyro- and hydrometallurgical techniques that could be used separately or in combination. In this investigation, hydrometallurgy has been selected because of potential advantages over the others. The process scheme will consist of: (1) chloride leaching of the ground waste products, (2) solvent extraction of cobalt, molybdenum, and iron, and (3) hydrolysis of purified molybdenum stream or crystallization of commercial molybdenum products.

CHAPTER 2

LITERATURE REVIEW

Molybdenum Chemistry

Molybdenum was identified by Carl Wilhem Scheele, a Swedish chemist, in 1788. Its chemistry is among the most complex of the transition elements and it exists in six valence states, viz.: 0, 2, 3, 4, 5, and 6. The hexafluorides, oxides halides, and oxo-anions are volatile (Cotton and Wilkinson, 1972). Molybdenum occurs chiefly as molybdenite (MoS_2) and wulfenite ($PbMoO_4$) (Killeffer and Linz, 1952) though it has been found in thirteen minerals and produced with the associated metals such as copper. Recovery is achieved through oil flotation and roasting the concentrate to obtain MoO_3 (Snell-Ettre, 1966) which is reduced in hydrogen to give the metal.

Significant mechanical property of molybdenum is its retention of strength and hardness at high temperatures with a melting point of 2622 ± 10°C and a boiling point of 4800°C (Kelly, 1935). In the trivalent state, it forms a large number of complexes with hydrochloric, oxalic, thiocyanic, and other solutions; hydrocyanic complexes of the tetravalent states are known while the pentavalent state forms phosphoric, hydrocyanic, thiocyanic, and hydrochloride complexes. Precipitation of molybdenum oxides are inhibited by citric, tartaric, and oxalic complexes of the hexavalent state (Pourbaix, 1974).

Molybdenum bromide, chloride, and sulfides are sparingly soluble in water as are most molybdates except those of the alkali

metals. It is not readily attacked by acids, but it is passivated by oxidizing solutions such as concentrated nitric acid, hydrogen peroxides, and sodium peroxide. A mixture of concentrated nitric acid (HNO_3) and hydrofluoric acid (HF) will dissolve the metal while oxidizing alkaline melts such as fused KNO_3-NaOH or Na_2O_2 attack it rapidly. At ordinary temperatures, Mo is inert to oxygen, but forms the trioxide, MoO_3, at red heat. Hexafluoride of molybdenum is formed at room temperature when molybdenum metal is exposed to fluorine gas, and it gives rapid reaction with hot dilute hydrochloric acid.

Largest consumption of molybdenum is in alloy production because of its high temperature properties. Small amounts cause tremendous increases in hardness and strength. It is an excellent material for glass-metal seals at temperatures between 1,000°C and 1200°C. Trace amounts of molybdenum are considered important to some enzyme-related process in the human body.

Molybdenum Compounds

Important compounds of molybdenum include the oxides, sulfides, halides, molybdates, and organomolybdenum compounds. Compounds having oxidation states of 2+, 3+, 4+, 5+, and 6+ are known although the 2+ and 4+ oxidation states are unstable in aqueous solutions. It has coordination numbers of 4, 6, and 8 with minor variations in controlled conditions capable of bringing about changes in the coordination state. Polymerization and condensation reactions are governed by pH and concentrations.

Oxides

Two regular oxides, MoO_2 and MoO_3, have been fully confirmed (Hägg and Magneli, 1935). Other oxides reported include Mo_3O_8, Mo_4O_{11}, Mo_5O_{12}, and Mo_8O_{23} and some of them seem to be a various mixture of the dioxide (MoO_2) and the trioxide (MoO_3). Molybdenum blue is suggested to be a compound having more than two moles but less than three moles of oxygen to one mole of molybdenum (MoOx where $2 < x < 3$), but controversy over the exact composition of the compounds remains. Also known are two hydroxides, $Mo(OH)_3$ and $MoO(OH)_3$.

Molybdenum trioxide (MoO_3). Molybdenum trioxide is the most important compound of the element and other known compounds can be prepared from it. Formation of MoO_3 can be done by roasting the sulfide in air and by thermal or chemical decomposition of molybdates. For example, reacting hot concentrated nitric acid with normal ammonium molybdates produces molybdenum trioxide:

$$(NH_4)_2\ MoO_4 \xrightarrow{\text{Conc. } HNO_3} MoO_3 + 2\ NH_3 + H_2O$$

Molybdenum dioxide (MoO_2). Partial reduction of either the metal or the trioxide will produce MoO_2. When this oxide is heated in hydrogen at 500°C, it is reduced to the metal while the carbide will form if it is heated in the presence of carbon.

The chemistry of molybdenum blue is not fully known. According to Cotton and Wilkinson (1972), it contains both oxides and hydroxides with the mean oxidation state being between 5 and 6. Mild reduction of Mo(Vl) in acidified solution would produce this blue compound at about

pH of 4 (Snell-Ettre, 1966). Schirmer et al (1942) reported that there has been no satisfactory explanation for the blue oxide formation. However, use is made of this reaction as an analytical reagent for phosphorus.

Hydroxides. There are two hydroxides which are commonly precipitated by alkali, $Mo(OH)_3$ and $MoO(OH)_3$. The first is a powder precipitate that is sparingly soluble in H_2SO_4 and HCl and practically insoluble in water. When it is exposed to air, it takes up oxygen and loses water to become MoO_3. The second compound is a brown precipitate which has about 2 gpl solubility (Snell-Ettre, 1966). Other hydroxides mentioned include $Mo(OH)_2$, $Mo(OH)_4$, and $Mo(OH)_5$, which are not yet confirmed.

Sulfides

There are four known sulfides of molybdenum, viz.: Mo_2S_3, MoS_2, Mo_2S_5, and MoS_3, but the most important is MoS_2, which is the form of the mineral molybdenite. In hot nitric and sulfuric acids, the disulfide is oxidized to MoO_3 but it is dissolved by aqua regia. It is used as a lubricant.

Molybdenum trisulfide, MoS_3, dissolves in alkali sulfides to form thiomolybdenum:

$$MoS_3 + Na_2S \rightleftharpoons Na_2MoS_4$$

When thiomolybdate solution is acidified from basic to acidic range, the trisulfide is precipitated:

$$Mo\ S_4^{=} + 2H^{+} \rightleftharpoons MoS_3 + H_2S.$$

Sulfide precipitate of molybdenum is difficult to filter. Mo_2S_3 is found by heating MoS_2 in the absence of air, and it is soluble in aqua-regia.

Halides

Molybdenum combines with fluorine, bromine, iodine, and chlorine to form a variety of compounds. Most of the investigative work on halide compounds of molybdenum were carried out between 1817 and 1880 with Berzelius (1821) and Blomstrand (1861) working on fluorides and bromides. During the second world war, the hexafluoride and the pentafluorides were used for production of isotopes.

The most important molybdenum chlorides are Mo(V) compounds and the pentachloride can be formed by combining finely divided Mo with chlorine:

$$2\ Mo + 5\ Cl_2 = Mo_2Cl_{10}.$$

The above reactions requires high purity reactants to proceed at room temperature and excess chlorine is necessary for the reaction to go to completion.

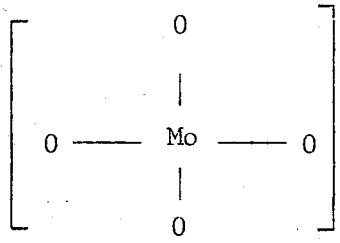
Complexes

Oxo compounds (complexes) are formed when molybdate or MoO_3 is reduced in acidic medium under appropriate conditions of pH and concentration. Reducing solutions of Mo(Vl) or $MoCl_5$ in hydrochloric acid with 8M HCl or more produces $[MoOCl_5]^{2-}$. The predominant complex in 5-6 M HCl is $[Cl_4OMo(OH)_2MoOCl_4]^{4-}$, and in 1-3 M HCl $[Cl_4OMoOMoOCl_4]^{4-}$ is stable. Dissolution of Mo(Vl) oxide in aqueous HCl gives $[MoO_2Cl_4]^{2-}$ at

12 M acid and at 6 M acid [$MoO_2Cl_2(H_2O_2)$] is stable (Griffith and Wilkins, 1967).

Molybdates

Molybdate is an important class of compounds with Mo having a coordination number of 4 in normal molybdates. Structural presentation of molybdate anion is given below:



Under anhydrous conditions, formation of mono-, di-, tri, and tetra-molybdate compounds have been reported (Griffith and Wilkins, 1967). In aqueous solutions, the chemistry is more complex due to ionization, equilibrium condensation, and impurity ions.

Normal molybdates can be prepared in three different reactions:

1. Combination of MoO_3 with metal oxide (hydroxide or carbonates) at high temperature, with or without fusible salt solvent:

   $CaCo_3 + MoO_3 = CaMoO_4 + Co_2$

2. Combination of MoO_3 with metal oxide at low temperature, using water as solvent:

   $Na_2O + MoO_3 + xH_2O = Na_2MoO_3 \cdot x\ H_2O.$

3. Precipitation reaction (double decomposition):

   $(NH_4)_2MoO_4 + Ca(NO_3)_2 = CaMoO_4 + 2\ NH_4NO_2.$

Addition of hydrogen peroxide (H_2O_2) to a molybdate solution yields peroxymolybdate:

1. $H_2MoO_4 + H_2O_2 = H_2MoO_5 + H_2O + \Delta H$ (8,084 cal).

2. $H_2MoO_5 + H_2O_2 = H_2MoO_6 + H_2O + \Delta H$ (4,300 cal)

Evaporation of a peroxymolybdate solution forms amorphous precipitate or thick syrup (Berzelius, 1821).

Molybdenum in the Presence of Other Ions

The chemistry of molybdenum in isolation has shown high degrees of complexity and should be expected to be even more difficult in the presence of other metal ions. To conclude this brief summary of molybdenum chemistry, it seems appropriate to take a look at what might happen when molybdenum is in the presence of other ions.

Since subsequent chapters will be dealing with nickel-based alloy recycling process, it is appropriate to introduce the ions of the major elements in this review. The elements to be considered include nickel, cobalt, chromium, iron, and molybdenum. Under some suitable conditions, the super alloy can be leached to yield the following ions in solution: N_i^{+2}, Mo^{+6}, Mo^{+5}, Mo^{+3}, Co^{+2}, Fe^{+3}, Fe^{+2}, Cr^{+3}, and Cr^{+2}. The final solution from the leaching process will contain species resulting from equilibrium interaction of the above ions.

In Table 1, some thermodynamically possible reactions are listed, and it can be seen that it would be possible to have Mo^{+6}, Mo^{+5}, Fe^{+3}, Fe^{+2}, Ni^{+2}, Co^{+2}, Cr^{+3}, and Cr^{+2} coexisting in the solution. At pH $\simeq$ 3.0, Cr^{+3}, Co^{+3}, and Fe^{+3} would co-precipitate, thus

Table 1. Possible thermodynamic equilibrium conditions in the leach solution

Reactions	E°* (volts)	E** (volts)
$Mo^{+5} + Co^{+3} \rightleftharpoons Mo^{+6} + Co^{+2}$	+1.37	+0.906
$Mo^{+3} + 2Co^{+3} \rightleftharpoons Mo^{+5} + 2Cl^{+2}$	+2.07	+1.143
$Fe^{+2} + Co^{+3} \rightleftharpoons Fe^{+3} + Co^{+2}$	+1.05	+0.033
$Cr^{+2} + Co^{+3} \rightleftharpoons Cr^{+3} + Co^{+2}$	+2.23	+2.385
$Mo^{+5} + Fe^{+3} \rightleftharpoons Mo^{+6} + Fe^{+2}$	+0.32	+0.602
$Mo^{+6} + Cr^{+2} \rightleftharpoons Mo^{+5} + Cr^{+3}$	+0.86	+0.109
$Fe^{+2} + Cr^{+3} \rightleftharpoons Fe^{+3} + Cr^{+2}$	-1.18	+0.082

*Data obtained from Freiser and Fernando (1963) and Weast (1976).

**Values are calculated based on a leach solution concentration (gpl) of: 0.9 Fe (.0179 M), 5.0 Mo (.0521 M), 12.0 Co (.2036M), 18.0 Cr (.346 M), and 43.0 Ni (.732 M).

making hydrolysis inefficient as a method of selective separation. Even when Co, Fe, and Cr co-precipitation would be considered appropriate or desirable, the poor filtration characteristics of hydroxide precipitate would be a serious problem and high entrainment of Mo and Ni would result. In a solution where Mo^{+6} and Cr^{+6} ions are present, it will not be possible to precipitate both elements as hydroxides or oxides, even in very basic solutions (Pourbaix, 1974). Occlusion in other metal hydroxide or oxide precipitate decreases the recovery of Mo^{+6} and Cr^{+6} in hydrolysis of Co^{+3}, Ni^{+3}, and Fe^{+3}. One alternative to hydrolysis is liquid-liquid extraction but the presence of more than one oxidation state for some of the elements could become a problem for efficient extraction.

In spite of the complex nature of the system, many investigators have taken various approaches toward solving or minimizing the problems in order to recover some of the metal values. In the next sections, some of the proposed and practised techniques are reviewed.

Processes and Techniques

Many metallurgical processes have been proposed and developed for separation of metal values from ores, scraps, and other waste products. Those commonly used are pyro-, hydro-, and electrometallurgical techniques as well as flotation. These processes can be used in combination or separately to achieve the desired separation. Application of some of these techniques for recovery of metal values from super alloy scraps and ores are reviewed including possible advantages and limitations.

Pyrometallurgical Techniques

Pyrometallurgy is often used as a pretreatment step to remove volatile waste from ores and scraps. Depending on the medium in which the reaction is carried out, compounds with specific metallurgical properties could be produced. Further processing of such compounds might improve or yield selectivity in the separation scheme.

Reinhardt (1975) reported high temperature treatment of super alloy scraps to remove non-metallic elements and using carbon as reducing agent to form carbides of molybdenum, tungsten, and chromium. In a similar treatment by Aue et al. (1971), the carbides of Mo and W did not dissolve while Fe, Co, and Ni were selectively, anodically leached from the melt.

The sulfide concentrate from molybdenite flotation is treated by pyrometallurgical techniques to produce the metal. Mukherjie and Gupta (1974) discussed the roasting of MoS_2 to obtain MoO_3 and treating it with strongly reactive metals to obtain Mo metal. Further work in this area was carried out using magnesium (Campbell, Block, and Anderson, 1962), aluminum (Schmidt et al., 1971), and calcium (Gilbert and Block, 1955). Aluminothermic reduction of MoO_3 was carried out by Mehra, Bose, and Gupta (1973) while Haver, Uchida, and Wong (1968) investigated the reduction of MoS_3-Al compacts at 800°C. The resulting product was not pure and hydrolysis was used to improve the quality. Vacuum reduction of MoO_3 was investigated by Scholz, Doane, and Timmons (1961). Brooks and Rosenbaum (1963) reduced impure nickel oxide with carbon and obtained results similar to those reported by Reinhardt (1975) and Aue et al. (1971).

The merits of pyrometallurgy include volatilization of non-metallic waste, homogenization of process feed materials, and high temperature carburization for selective dissolution. Many purification processes employ high temperature reduction of the impure compound to obtain the metal. Some of the drawbacks of pyrometallurgy have been the subject of investigation by some researchers. Kenworthy, Nieberlein, and Starliper (1961) surveyed the use of lancing, carburization, and carbonyl processes in pyrometallurgical treatment of Ni-Co based alloys and found that there was significant loss of Ni and Co to the slag due to oxidation. They also reported poor separation of high melting-point carbides as well as metals with similar chemical characteristics such as Ni-Co and Mo-Cr. Successful application of pyrometallurgy is possible in special instances but there has been concern over their use in a mixed alloy system. Baggott, Fletcher, and Kirkwood (1966) considered pyrotechniques as highly complex with low yield of some of the metal values. Hence, application of these techniques to mixed alloy systems was considered very inefficient.

Higley (1963) reported Mo loss in induction melting process and this was recently confirmed by de Barbadillo, Pargeter, and Makar (1980). Also lost in this process were tantalum, columbium, titanium, tungsten, aluminum, and chromium. De Barbadillo et al., however, believed that complete element separation can be achieved. Kawakami, Goto, and Kato's (1975) investigations revealed that high temperature chlorination of Ni-Co alloy resulted in partial separation, a similar result was mentioned by Kenworthy et al. (1961).

Pyrometallurgical techniques offer the choice between efficient recovery and effective separation. Perhaps other techniques can offer both efficient recovery and effective separation.

Flotation and Electrometallurgical Techniques

Flotation Technique

Flotation is one of the most important and commonly practised techniques in mineral dressing, and one which finds wide application with both sulfide and oxide ores. Molybdenum is recovered as sulfide (MoS_2) concentrate in oil flotation of its ore or associated minerals, thus taking advantage of the natural hydrophobicity of molybdenite. In the presence of other sulfide minerals such as copper and iron, molybdenum can be depressed to allow the flotation of these minerals by using starch (Papin, 1955) or dextrine (Last, 1964). Optimum flotation of MoS_2 occurs where the zeta potential is minimum (Chander and Fuerstenau, 1972) and this is between pH 5.5 and 6.5. Flotation of chromium sulfide is one of the process steps in the scheme developed by de Barbadillo et al. (1980).

Oxide flotation has been applied to many oxide ores and selectivity is usually determined by differences in the point of zero charge (PZC) of the minerals (oxides) in the system. The PZC for optimum flotability of some oxides are given in the literature (M. Fuerstenau, 1976; D. Fuerstenau, 1970; Palmer, M. Fuerstenau, and Aplan, 1975; Ney, 1973) and a few of them are listed below.

1. Geothite (FeO(OH)) PZC = 6.8
2. Hematite (Fe_2O_3) 4.8-6.7

3.	Rutile (TiO_2)	5.8-6.7
4.	Eskolaite (Cr_2O_3)	5.0-7.2
5.	Bunsenite (NiO)	2.5-3.0
6.	Cobalt hydroxide ($Co(OH)_2$)	10.0
7.	Molybdenum trioxide (MoO_3)	None

Under appropriate pyrometallurgical pretreatment, oxides of the above metals can be produced and cationic flotation, using collectors and depressants appropriate to the system, can be used to selectively float the oxides. It should be noted the MoO_3 shows negligible flotability (Chander and D. Fuerstenau, 1972; Ney, 1973).

Electrometallurgical Technique

Electrochemical dissolution and deposition of metals have been used by industries and investigators to achieve separation or refining of metals. Reinhardt (1975) employed anodic dissolution for selective leaching of carbide granules and concurrently deposited Co at the cathode. Diaphragm-type electrolytic cells were used by Brooks and Rosenbaum (1963) and Aue et al. (1971) for selective dissolution of super alloy products.

Senderoff and Brenner (1954) successfully electro-deposited Mo from $KCl-K_3MoCl_6$ electrolyte and Mo anode in an inert atmosphere. High purity Mo (99.99%) was obtained by Cumings, Cattoir, and Sullivan (1966) from scrap materials by an inert atmosphere electrolysis. Fused salt electrolysis of molybdenum was reported by Suri, Bose, and Gupta (1974). They found $KCl-K_3MoCl_6$ bath to give more satisfactory results than either $Na_2B_4O_7-NaCl-MoO_3$ or $CaCl_2CaMoO_4$ baths.

The art of electrowinning of Co, Ni, and Cr has been well known in industries. In applications where high purity metals are needed, most of the metals would be produced by electro-deposition to insure required quality.

Hydrometallurgical Technique

Winning or refining of metals using water or an aqueous solution is becoming increasingly popular in metal recovery processes. Some of the techniques involved are leaching, solvent extractions (SX), hydrolysis, cementation and electro-deposition. In the remaining part of this chapter, attention will be focused on the use of leaching, solvent extraction, and hydrolysis in recovering metal values from ores and scraps.

Leaching. Metals and their compounds are selectively attacked by various chemicals under certain conditions of temperature, pressure, and concentration. Use is made of this phenomena in metal separation. Ashbrook and Ritcey (1971) dissolved cobalt, copper, iron, nickel, silver, and arsenic with a mixture of H_2SO_4 and HNO_3 at a solution potential of 350 mV and a temperature of 90°C. Pressure and oxidation leach of sulfide ores and scraps of Ni was reported by Suetsuna et al. (1980), who found that the amount of iron leached could be controlled by controlling the pressure. Hydrochloric acid had been used to leach Fe, Mo, T, Ni, Cr, and Co and, according to Baggott et al. (1966) about 25 gram per liter of free Hcl was necessary. The oxidant in this process was chlorine gas, and under these conditions, oxides and

carbides of Mo, W, Nb, and Ti were not dissolved. Thornhill, Wigstol, and Van Weert (1971) used highly concentrated HCl to selectively leach nickel from a nickel-copper matte at 65°C in three-stage leach process with a residence time of 11 hours. Chloride leach is not restricted to using HCl as the leachant since chloride salts such as NaCl and $MgCl_2$ can provide the needed chloride concentration. However, chlorine gas is preferred where oxidation of the products is required. Hougen (1975) and de Barbadillo et al. (1980) leached with Cl_2 and reported complete dissolution of nickel and cobalt at a solution potential of + 550 mV. According to de Barbadillo et al. (1980), the presence of cupric chloride accelerated the dissolution rate, thus reducing the residence time to 1 hour. Kenworthy et al. (1961) dissolved S-816 alloy with sulfuric acid (H_2SO_4).

Besides use of chemicals, electrochemical dissolution had been mentioned by Brooks and Rosenbaum (1963) and Aue et al. (1971). The choice of leaching techniques and chemicals depends on the subsequent recovery steps designed for the system. Whatever the method chosen, most leach liquors are refined via hydrolysis or solvent extraction for the recovery of the valuable products.

Solvent Extraction. Ion exchange techniques are applied in hydrometallurgy for sorbing, concentration, or separation of metallic species. Metal ions are exchanged in a solvent selectively, and the metal can be separated from the system. A general equilibrium reaction can be written as below:

$$RX^n + M^n \rightleftharpoons RM^n + X^n$$

where

R is the solvent structure,

X is the functional group,

M is the metal ion, and

n is the charge on the exchange radical and the metal ion (for an equal charge situation).

Regeneration of the solvent can be achieved by shifting the above reaction equilibrium to the left. Extraction and regeneration depend on the characteristics of the solvent and the metal species present. Some solvents extract in strong acid solutions, some extract in weak acids; others extract in basic solutions which could be either strong or weak, and the extraction could be cationic or anionic. Kennedy (1980) outlined a qualitative approach to selection of resins for extraction under a satisfactory concentration and complexation. Further readings on the theory of solvent extraction (SX) can be made from appropriate texts on the subject (Morrison and Freiser, 1967; Samuelson, 1958; Treybal, 1963; Marinsky and Marcus, 1973; Ritcey and Ashbrook, 1979; Marcus, 1971).

The use of solvent extraction for a large-scale separation in metallurgical systems is increasing. Wigstol and Froyland (1972) used triisooctylamine (TIOA) to extract cobalt and copper from chloride solutions. The above investigators used tributylphosphate (TBP) to extract iron from chloride solutions. Brooks, Potter, and Martin (1969) successively used trioctylphosphate (TPF), amberlite LA-1, and TIOA to extract Mo, Fe, and Co, respectively. Ritcey, Ashbrook, and

Lucas (1972) co-extracted Co and Ni from sulphate solutions using D2EHPH at pH between 5 and 6. In the development of a pilot plant for the process, column contactors were used instead of the more usual mixer-settlers and it was possible to achieve selectivity for Co and Ni, as was observed by a Co/Ni ratio of about 280.

Tertiary amine was used by Fischer, Bauer, and Lindstrom (1975) to extract Mo and Re from SO_4^{-2}/Cl^- solution. Molybdenum was separated from Re by passing the strip solution through activated carbon column, and Re was absorbed to the carbon, and was later recovered in a MeOH-H_2O eluate. Brooks and Rosenbaum (1963) extracted Co from chloride solution with TIOA while Reinhardt (1975), Baggott et al. (1966), and Aue et al. (1971) used Alamine 336® (General Mills Chemical, Inc.) to extract Fe and Co from Fe-Ni-Co chloride solutions. In thiocyanate solutions, Hyde and Feick (1959) used methyl isobutyl ketone (MIBK) for separation of Co from Ni. Similar results were reported by Hard and Kummerle (1974). Co-extraction of molybdenum and rhenium with a mixture of dibutyl butyl phosphonate and DEHPA was reported by Peterson (1973). Suetsuna et al. (1975) used versatic acid to co-extract nickel and cobalt from sulphate solutions and the chloride strip solution was contacted with tri-n-octyl amine hydrochloride solution to separate cobalt from nickel. Kim and MacInnis (1980) extracted Fe^{+3} with MIBK from a chloride solution of Co-Ni-Fe, and the raffinate was contacted with Aliquat 336 (General Mills Chemical, Inc.) to separate cobalt from nickel.

By choosing proper chemicals and extraction conditions, it is possible to obtain strip solutions with high concentration of the

desired element. These solutions can be refined and the metal values recovered by electrowinning, hydrolysis, or evaporation.

Hydrolysis. Hydrolysis can be used at any point in hydrometallurgical processes but more often it forms one of the major options in the final product preparation. Since the technique is widely used and understood, it seems appropriate to only cite a few applications relating to recovery of metals such as Fe, Mo, Cr, Co, and Ni.

Addition of H_2S to an acid solution of Mo(Vl) gives sulfide precipitate but strong concentrated HCl would prevent the formation of the precipitate. Co-precipitation of Fe and Mo with $NiCO_3$ as the neutralizer was mentioned by deBarbadillo et al. (1980). Magnesia slurry was used in the precipitation of Fe, Cr, Mo, and Ti as hydroxides at pH of 2.2-2.4 (Ney, 1973; Kunda, Warner, and Mackiw, 1962).

The commonly used agents for hydrolysis include the hydroxides, oxides, and carbonates of the alkali metals. It is possible to use similar compounds of other metals for the precipitation where desired separation is feasible. Selective precipitation can be obtained by varying the solution potential, the pH, and the valence state of the element of interest. The problem of co-precipitation (which might be undesirable in some cases) could be overcome if a process solution contains only one element whose precipitate is needed. This situation is usually attained through hydrometallurgical techniques.

Summary

In designing a recovery scheme, the process metallurgist can draw from the various techniques available in pyro-, electro-, and hydrometallurgy as well as flotation. The difference between a poor and a good scheme lies not only in the technological merits but also in the economy of cost, adaptability, and size.

CHAPTER 3

OBJECTIVES

The general objectives of the research (of which this thesis forms a part) were to explore:

1. A dissolution process for the superalloy (WASPALLOY*) waste products.
2. A method(s) of selective separation of the individual metal values from the leach liquor.
3. Refining schemes for the separated products for the purpose of making commercially marketable products.

Within the broad scope of the research project, the author's thesis is based mainly on the recovery of molybdenum, and as such, details regarding the recovery of other metals will not be covered except where such details are considered necessary by the author in aiding understanding or for emphasis and differentiation.

Experimental

An integrated hydrometallurgical process was designed for the recovery of the metal values from the super alloy grindings and the initial flow sheet is given in Figure 1. The leaching step led into a solvent extraction step for the separation of Co, Fe, and Mo from Cr

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*WASPALLOY is a super alloy whose grindings were supplied by Special Metals Company for this research project.

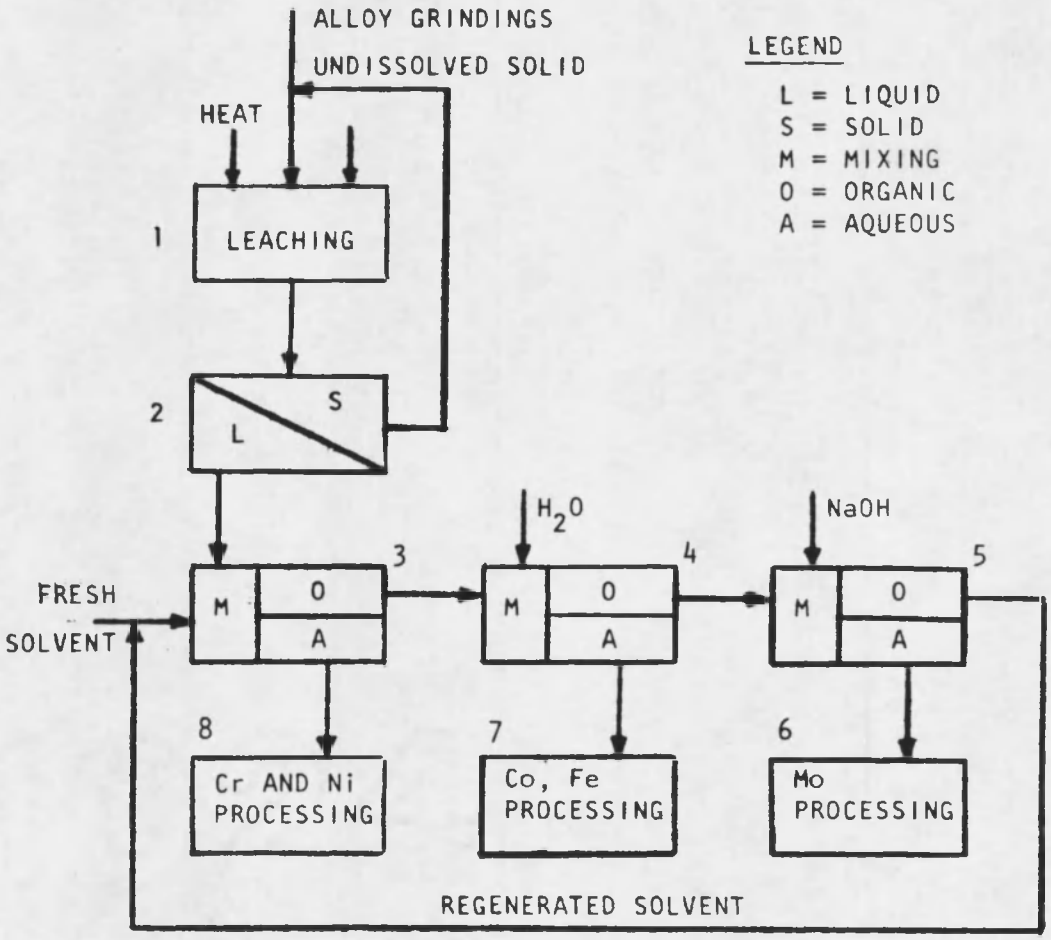


Figure 1. Initial process flow sheet for recovery of Cr, Ni, Co, Fe, and Mo

and Ni. Selective stripping of Co and Fe would be followed by Mo recovery and regeneration of the solvent which would be recycled for reextraction at step 3 of the diagram. The chromium and nickel stream would be processed for Ni and Cr separation and Co will be separated from Fe in Co-Fe stream. The Mo solution would be treated to produce either of the following products: H_2MoO_4, Na_2MoO_4, $CaMoO_4$, or MoO_3.

Apparatus

Leaching

The initial tests were carried out in a 1-liter beaker with 500 mls of solution, heated and stirred with a magnetic hot plate. The beaker was covered with a plastic lid and holes were provided for four glass rods (baffles) and a thermometer, and the experiments were carried out under the fume hood. Production was increased by using a 4-liter beaker with two liters of solution. This unit was equipped and operated in the same manner as the 1-liter beaker except the baffles were plastic bars.

It was necessary to produce about 35-40 gallons of leach solution for the solvent extraction tests; thus, a 12" x 12" pyrex glass vessel, with a capacity of more than 15 liters, was used. A mechanical agitator was used in the vessel and the plastic lid provided holes (ports) for eight glass rods (in 4 pairs), solid and liquid input, pregnant solution withdrawal, a thermometer, and condenser and H_2 exhaust. The equipment was too large to be mounted under the fume hood, hence, it was mounted on a deck in the lab and to prevent exhaust

gas and fumes from the lab environment, proper sealing was required on the vessel. The rim of the reactor was sealed with tape and the agitator shaft post was fitted with a water seal: all other open holes were covered with rubber stoppers. Heat was supplied by a hot plate. Glass wool insulator was wrapped around the reactor to prevent draft due to room temperature. The condenser exhaust was connected to the hood. Input and output solutions were delivered by peristaltic pumps. The diagram of the reactor is given in Figure 2.

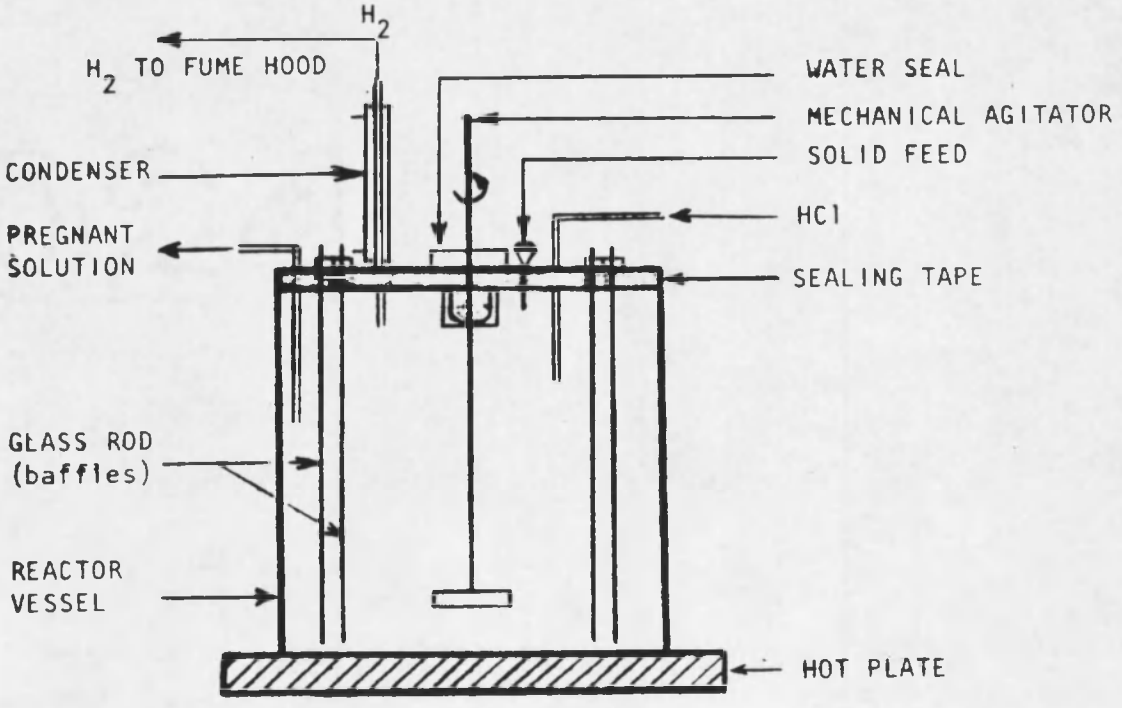


Figure 2. Continuous leach reactor

Solvent Extraction

The shake out tests were carried out in 125-250 ml separatory funnels and mixing was achieved by a mechanical "wrist action" shaker. The continuous tests were performed in a battery of mixer-settler units with mechanical agitators (see picture in Figure 3). Fumes (HCl) from the mixer-settlers were prevented by covering the top of the units with plexiglass. A constant temperature bath was used for temperature control of the feed solutions.

The apparatus for hydrolysis included hot plate and magnetic stirrer, beakers, pH meters, and thermometers. Chemical analyses were carried out on Atomic Absorption unit manufactured by Perkin Elmer, Series 360. Some qualitative checks on solid products were done on a Spectograph.

Solutions

Various concentrations of HCl in distilled water were used as the input solutions in the dissolution tests. Effective extraction of cobalt by tertiary amine such as Alamine 336 requires high chloride concentration ($\simeq$ 300 gpl), hence, at least nine molar (9 M) HCl was needed for the dissolution. In the large-scale continuous runs, three bottles of 37% HCl were mixed with one bottle of distilled water and fed to the reactor. The pregnant solution (containing about 88 gpl Ni, 28 gpl Cr, 19 gpl Co, 8 gpl Mo, and 2 gpl Fe) was withdrawn from the reactor. The above concentrations were reached after four hours in a two-step leach reaction. The large volume production solutions contained half of the stated concentrations due to low solid feed rate at the start of the experiments.

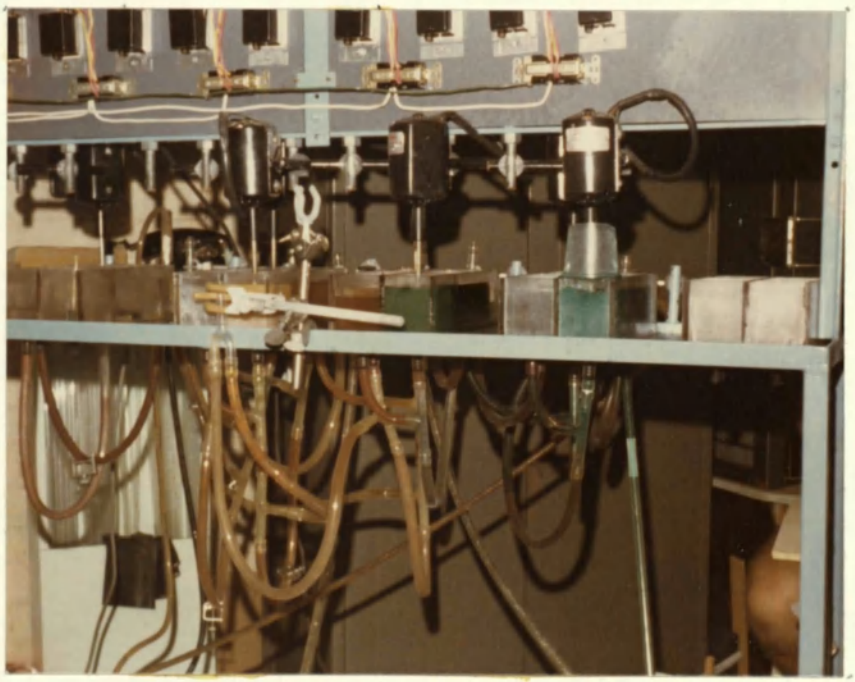


Figure 3. Solvent extraction mixer-settlers batteries

The filtered leach liquor was contacted with a "solvent", i.e., 30% (volume) Alamine 336® [General Mills Chemical Co.], 40% Decyl alcohol and 30% kerosene. After extraction, a Ni-Cr raffinate was obtained and the organic contained Co, Mo, and Fe with some entrained Ni-Cr solution. Cobalt and iron was stripped into a pH 2 solution of HCl, and the organic was finally stripped with one molar alkaline solution of either sodium or calcium compound. The molybdenum solution was refined and hydrolyzed for recovery of molybdenum, and the regenerated organic was recycled to the extraction steps.

Solids

The solid feed to the leach reactor was Waspalloy grindings having the size distribution shown in Table 2 and Figure 4. Sample assay of the solid showed 56% Ni, 18% Cr, 13% Co, 10% Mo, 1% Fe, and some trace levels of Al, Ti, Ta, and W. Tests were conducted to

Table 2. Particle size distribution in Waspalloy grindings

Mesh Size	Weight (%)	Cumm. (%)
+ 20	2.00	2.00
- 20 + 48	20.60	22.60
- 48 + 100	49.30	71.90
- 100 + 200	20.50	92.40
- 200	7.60	99.90

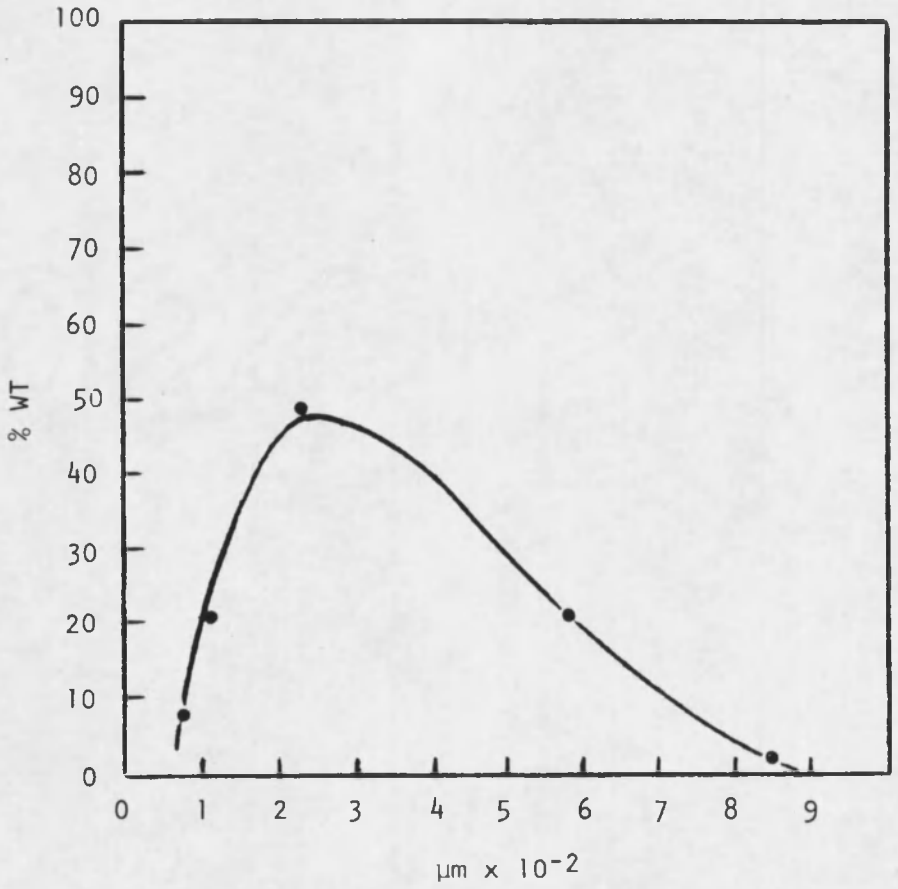


Figure 4. Waspalloy grindings--particle size distribution

investigate the effect of pulp density on the leachability of the solid in acid concentrations containing from 1 to 2.5 stoichiometric requirements. Temperature was varied from ambient to 110°C to observe any effect on the dissolution rate. Sufficient agitation to obtain minimum off bottom suspension was used and the solids were fed in batches. The withdrawn pregnant solution was filtered and the solid particles were returned to the reactor.

The hydrolysis of the molybdenum solution was designed to produce any of the commonly and commercially available molybdates. Evaporation of the molybdenum solution yielded a mixture of NaCl and MoO_3. In dilute acid solutions, NaCl will dissolve but MoO_3 crystals would not, thus providing a method for separating MoO_3 from the mixed crystals. Reduction of the precipitates from the hydrolysis step would yield Mo metal. However, there was no experimental work done beyond the hydrolysis step since the reduction process has been well known by industries.

CHAPTER 4

RESULTS

The work carried out in this study involved leaching, solvent extraction and hydrolysis. It was intended to be a study of the separation and recovery of moly from the various other elements, but work on all three areas was necessary to fully understand the moly chemistry. Thus results of all aspects of the work are included in the following pages.

Leaching

Effect of Temperature on the Kinetics of Dissolution

Tests were conducted to determine the effect of temperature on the leaching rate and the results are summarized in Figure 5. At ambient temperature very little dissolution was observed after about 300 minutes but up to 20% of the material dissolved at 70°C, while 60% dissolution was observed at 90°C after 200 minutes of leaching. About 85% dissolution was observed in the continuous leach runs at 110°C thus showing the pronounced effect of temperature on the rate of dissolution.

An interesting observation was made when a test was carried out on one afternoon, then shut down, letting it cool down overnight and restarted by bringing up the temperature to 95°C the following day.

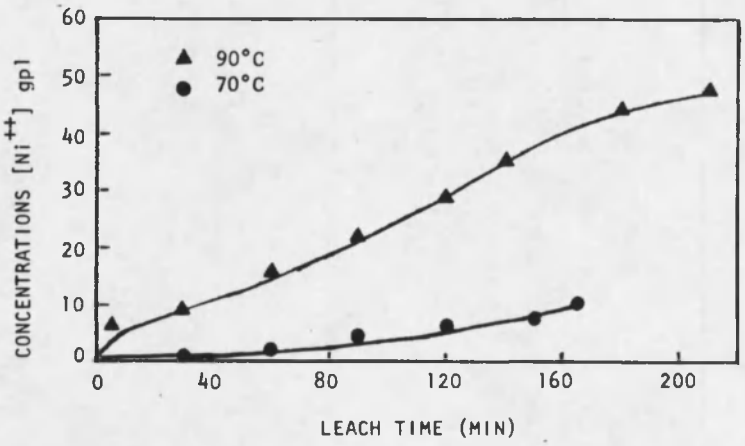


Figure 5. Effect of temperature on leaching rate

Assay of solutions indicated that some precipitation had occurred during the down time, and that the concentration before the shutdown was again obtained on maintaining the previous reaction temperature (95°C) as shown in Figure 6.

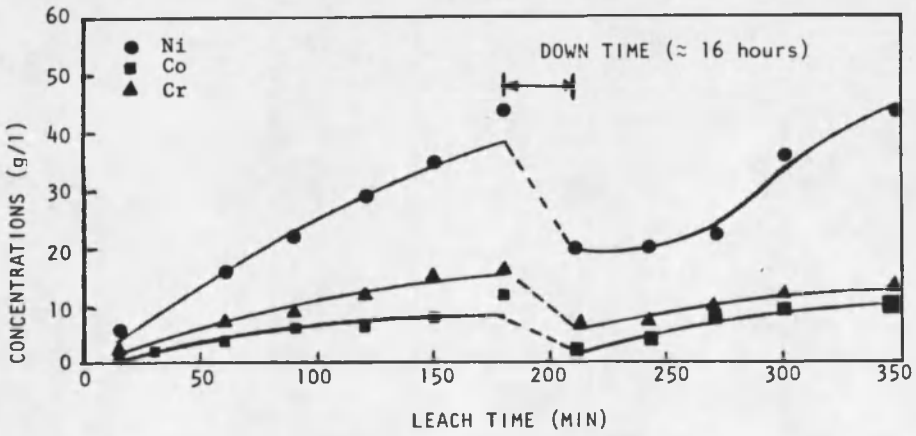


Figure 6. Effect of temperature on concentrations during shutdown and restart of continuous runs

A result similar to Figure 6 was observed during a 15-liter continuous leach run when HCl fumes and heater failure caused the reactor to be shut down for about 3 days. Instead of precipitate, crystals formed on the undissolved solids and analysis show Ni^{+2}, Co^{+2}, Cr^{+3}, Fe^{+3}, and Cl^{-} in the dissolved crystals.

Effect of Particle Size

Particle size did not seem to play any significant role in the dissolution kinetics as can be seen in Figure 7. The extreme size ranges, + 20 and - 200 mesh, were chosen since any intermediate size would reflect one of these classes but from Table 3 and the statistical analysis thereof, there was no difference in the rate of dissolution between the two sizes.

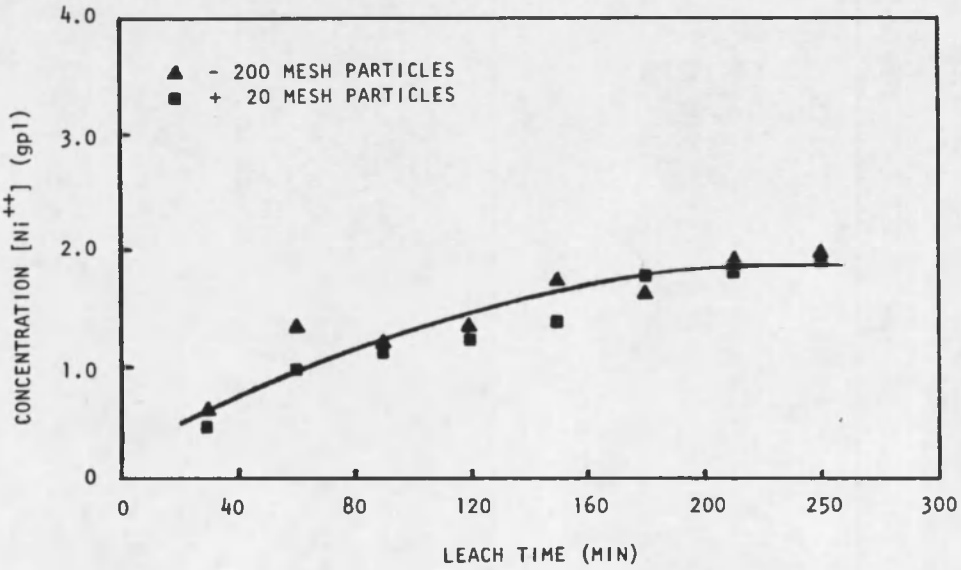


Figure 7. Particle size effect on dissolution

Table 3. Paired difference test for the rate of leaching of cobalt and nickel with ore particle size of + 20 mesh and - 200 mesh

Sample	Co (conc.)(gpl) C_{+20}	Co (conc.)(gpl) C_{-200}	Ni (conc.)(gpl) C_{+20}	Ni (conc.)(gpl) C_{-200}	$\frac{d_{c.Co.}}{C_{-200}-C_{+20}}$	$\frac{d_{c.Ni}}{C_{-200}-C_{+20}}$
1	0.000	0.000	0.450	0.617	0.000	0.167
2	0.007	0.067	0.950	1.317	0.060	0.367
3	0.100	0.087	1.150	1.100	-0.013	-0.050
4	0.093	0.127	1.183	1.283	0.034	0.100
5	0.107	0.207	1.367	1.700	0.100	0.333
6	0.233	0.107	1.683	1.583	-0.126	-0.100
7	0.240	0.273	1.700	1.883	0.033	0.183
8	0.240	0.247	1.733	1.967	0.008	0.234
9	0.267	0.287	2.017	2.217	0.020	0.200
10	0.267	0.327	2.150	2.717	0.060	0.567
11	0.413	0.287	2.183	2.483	-0.126	0.300
12	0.300	0.307	2.350	2.233	0.007	-0.117
				Σd_c	0.056	2.184

$\bar{d}_{c\cdot Co} = 0.0047$ $\quad \bar{d}_{c\cdot Ni} = 0.182$

$S^2_{d\cdot Co} = 0.0047$ $\quad S^2_{d\cdot Ni} = 0.0411$

$H_o : \mu d = 0$ $\quad H_o : \mu d = 0$

$t_{cal} = 0.2887$ $\quad t_{cal} = 0.2592$

At 99% C.I. on two-tailed test with d.f. of 11

$t_{Tab} = 3.106$

$\therefore$ Accept $H_o : \mu_d = 0$

Effect of Pulp Density

Different weights of solids were charged to 500 mls of hot acid and nickel concentration was monitored. The results appear in Figure 8. For 30 gpl and 100 gpl slurry, equilibrium seems to occur at 85.71% dissolution or a nickel to pulp density ratio of 0.48 but only 0.24 ratio was achieved at 200 gpl pulp density, and this represents only 42.86% dissolution. The onset of this equilibrium occurs at about 200 minutes of reaction time.

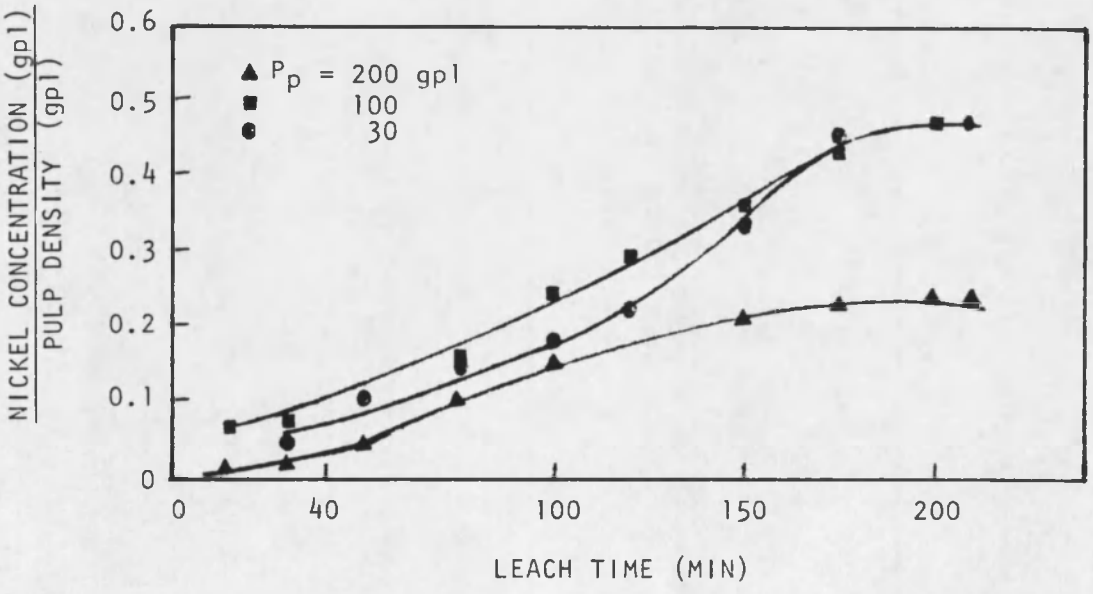


Figure 8. Effect of pulp density on dissolution

Effect of Acid Concentration

With a pulp density of 100 gpl, various stoichiometric concentrations of acid were used to leach the solids. The results are summarized in Figure 9. There is no pronounced difference between using only stoichiometric amounts of HCl and higher concentrations; it thus seems that adequate dissolution can be achieved in the absence of excess acid. Also significant in the plot is the equilibrium concentration earlier observed for reaction time of about 200 minutes.

Optimal Residence Time

Evidence exists in Figures 7, 8, and 9 that the initial dissolution rate is linear within the first 100-150 minutes, and that beyond this time, the rate falls off and finally reaches a dynamic equilibrium

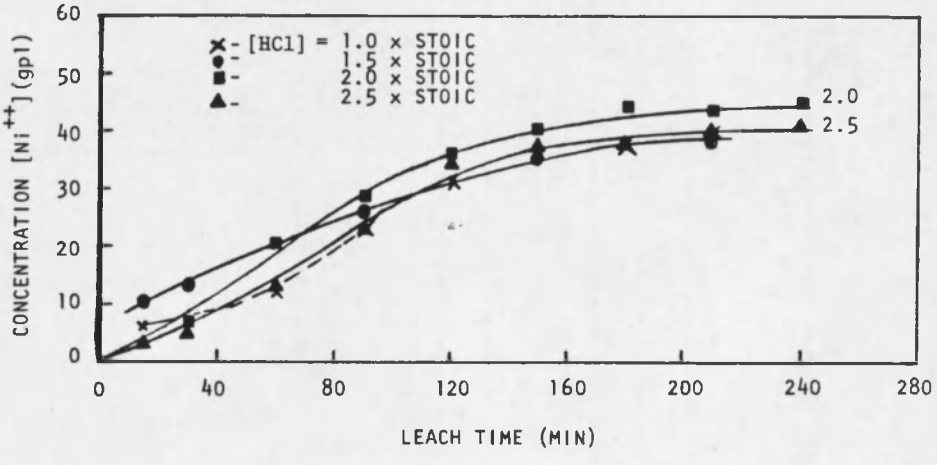


Figure 9. Effect of acid concentration on dissolution

in about 200 minutes of reaction. It would seem unnecessary to sustain the reaction past the linear region. However, it was observed that if fresh solids were added to the solution, a second linear portion was obtained.

The Concept of Two-stage Leach

A two-stage counter current leach would involve contacting fresh solids with partially consumed acid in the first reactor and in the second reactor fresh acid would be fed to partially consumed solid from the first reactor. Work was done on this concept, using 57 gms of sludge from a previous leach and contacting it with 87 gms of fresh HCl. The result appears in Figure 10 as Leach B, and the expected

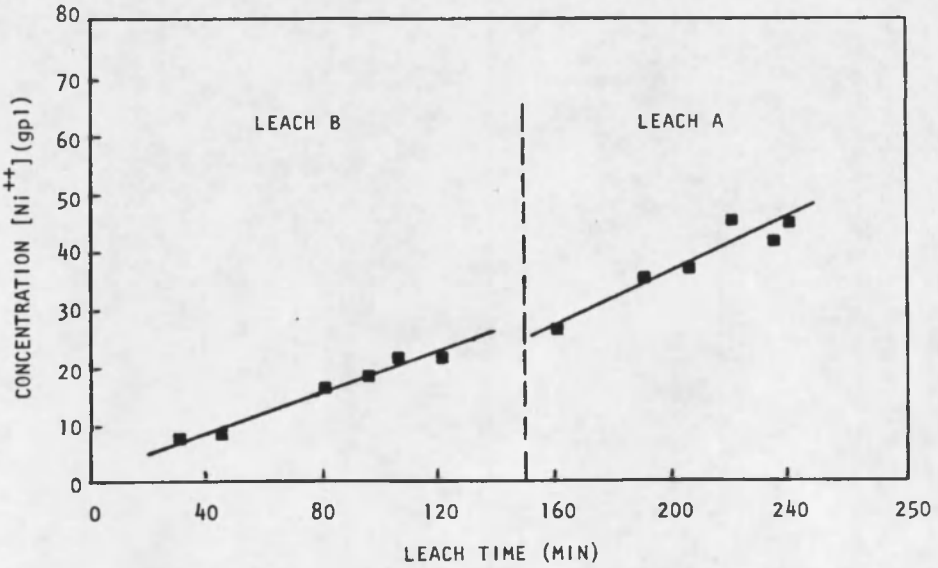


Figure 10. Two-stage leach

linear reaction rate was observed for 120 minutes. A dissolution of 55% of the sludge was achieved. The solution from Leach B was reacted with 84 gms of fresh solid and 16 gms of residue and the linear rate was also observed for 100 minutes, Leach A.

The above data would support a two-stage leach but when consideration is given to materials' handling, especially the leach residue, a single reactor system would be justified. The corrosive and abrasive nature of the residue would cause severe problems in conventional materials' handling techniques such as pumping; and, as such, it would be necessary to keep the solids in a single reactor. Another major consideration in the present system is that the solids contain no gangue and thus must be allowed to attain maximum or complete dissolution in some way.

Modification of the two-stage leach was done in three parts. First, the acid (9M HCl) was charged with desired amounts of solids and allowed to react for two hours after which 55% of the solids dissolved and the second step followed by addition of a new batch of solid to obtain a linear reaction rate. The reaction was allowed to go on for the next two hours and the solution concentration was maintained by regular addition of both solids and fresh 9M HCl. Figure 11 shows that the concentration of the solution can be maintained at 150 gpl for another two hours during this third part of the scheme.

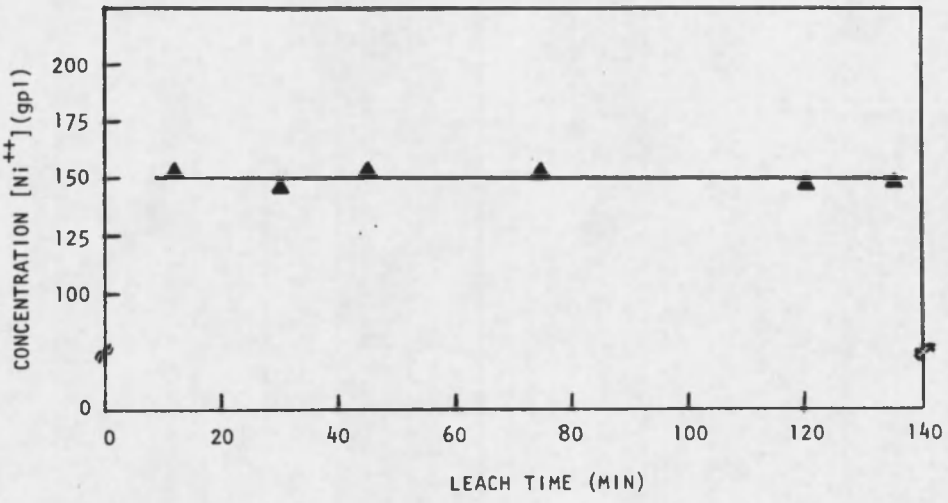


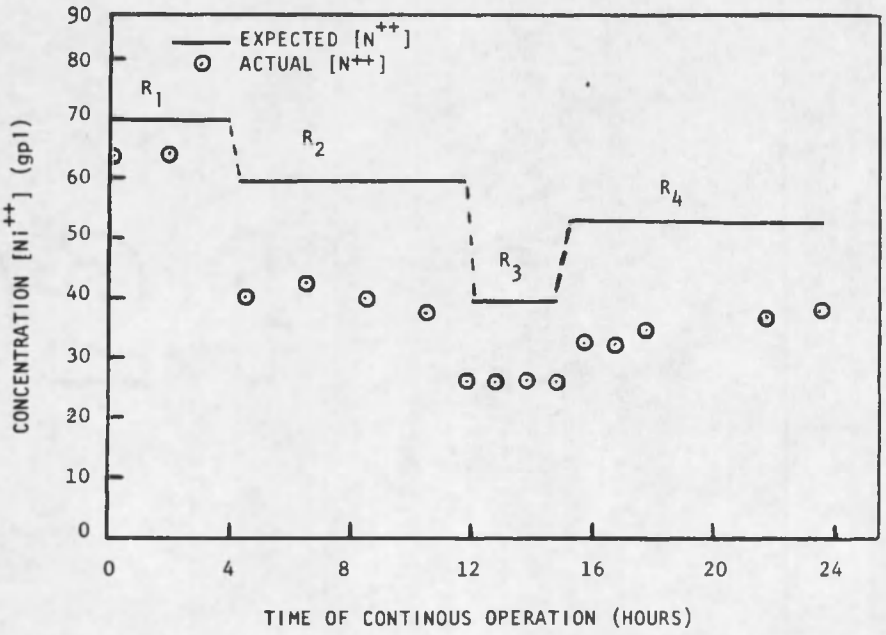
Figure 11. Continuous leach run

Fifteen-liter Pilot Runs

The three-step method described previously was followed in the 15-liter scale-up runs. Acid solution (11.25 liters 37% HCl + 3.75 l H_2O) was brought to the reaction temperature (95°C), 3.00 Kg of Waspalloy grindings were added, and the reaction was allowed to go on for two hours. At the end of the first two hours, 1.65 Kg of solid was added and allowed to react for two hours and then 110 gm of solid was added hourly, with acid solution fed at 1 liter per hour. Pregnant liquor was withdrawn from the reactor at the rate of 960 ml/hr, but was increased to 3,240 mls/hr when the solid feed was raised to 324 gm/hr.

Concentration profiles during the 24-hr continuous runs are shown in Figure 12 along with the expected nickel concentrations. It was observed that lower values were obtained from the leach, but they were consistent, in trend, with the expected values.

The main purpose of the large-scale leach was to provide about 35-40 gallons of pregnant solution, and the target was met with 38 gallons of product. However, the final HCl concentration (> 8 M HCl) was capable of dissolving more solids, hence, a recycling program, to



R_1 = 123 gpl solid + 960 ml HCl/hr
R_2 = 209 gpl solid + 1,960 ml HCl/hr
R_3 = 243 gpl solid + 3,240 ml HCl/hr
R_4 = 324 gpl solid + 3,240 ml HCl/hr

Figure 12. Nickel concentrate profile--15-liter continuous leach

further concentrate the liquor, was considered. After the first 2 hours of successful test run, HCl fumes were discharged to the laboratory atmosphere, thus causing a shut down of the reactor. The concentration of nickel was raised from 56.25 gpl to 100 gpl at the end of the run. Further attempt to resume the test was halted as the sealing problems persisted and the reactor was shut down over night. On the following day the concentration of nickel was determined to have dropped from 100 gpl to 75 gpl, thus confirming a similar result reported earlier in the section on effect of temperature on the kinetics of dissolution. The leaching campaign was finally stopped as the heater failed and the temperature fell below 70°C. The reactor remained for 3 days before the undissolved solids and crystals were separated from the liquor which contained 70 gpl of Ni, a further evidence of the anomolous condition of concentration on shut down.

Characteristics of the Pregnant Solution

The blended batch of 38 gallons in the storage tank was examined to determine some of the physical properties. The following data were obtained at room temperature:

Concentration (gpl): 87.50 Ni, 32.5 Cr, 20.3 Co, 6.65 Mo, 1.60 Fe, 294.59 Cl^-_{total}, 2.0 M HCl

Density (g/cc): 1.280

Color: Dark green

Potential: + 177 mV. (Pt vs. saturated calomel).

The mass balance on the leaching is summarized in Table 4.

Table 4. Material balance on leaching. -- Basis: Ni = 59, Cr = 52, Co = 59, Mo =96, Fe = 56, Cl = 35.5, H = 1.0, O = 16, 1 gal = 3.8 l.

	Ni	Cr	Co	Mo	Fe	Other	Cl	H	O	Total	(CPD) Compound
Input											
Solid	13,647.2	4,874.0	3,168.1	1,218.5	243.7	1,218.5				24,370.0	Grindings
35% HCl HCl							43,009.0	1,211.5		44,220.5	HCl
35% HCl H_2O								9,124.9	72,998.0	82,123.8	H_2O
Water								4,254.0	34,032.2	38,286.2	H_2O
Total Input	13,647	4,874.0	3,168.1	1,218.5	243.7	1,218.5	43,009.0	14,590.4	107,031.1	189,000.5	
Output											
Solution	12,635.0						15,204.8			27,839.8	$NiCl_2$
		4,693.0					9,611.6			14,304.6	$CrCl_3$
			2,931.3				7,055.0	99.4		10,085.7	H_2CoCl_4
				960.3			1,775.5	20.0	160.0	2,915.8	H_2MoOCl_5
					231.0		585.9	8.3		825.2	H_2FeCl_4
							7,725.2	217.6		7,942.8	HCl
								13,358.9	106,871.1	120,230.0	H_2O
Gas								886.2		886.2	H_2
Crystals	485.9	0.02	113.7		6.1		1,051.0			1,656.7	Crystals (mixed)
Undissolved Solid	526.3	94.1	123.1	134.3	6.6	46.5				930.9	Grindings
Fine Black Material		86.88		123.9		1,172.0				1,382.8	FBM
Total output	13,647.2	4,874.0	3,168.1	1,218.5	243.7	1,218.5	43,009.0	14,590.4	107,031.1	189,000.5	

Solvent Extraction--Schedule 1: Co-extraction with Mo and Fe Co-extracted as Impurities

Optimal Conditions

The use of a solvent extraction for recovery of Co from chloride solutions has received commercial applications (Reinhardt, 1975; Wigstol and Froyland, 1972; Fujimori et al., 1980; Ojanen, 1980) and the reports of investigation on the subject abound in the literature. Problems often encountered by use of these techniques include co-extraction of Mo, Cu, and Fe and the subsequent poisoning of the solvent due to the inability to completely strip the extractable species of these elements, even when they are present as minor impurities in the aqueous solution. Secondly, major refining is necessary to reduce the amount of these impurities in the cobalt eluate. In this project attempt was made to capitalize on the above problems by finding selected conditions of solutions, solvents, kinetics, and mass transfer that would result in dependable selectivity in extraction and stripping. The variables investigated were contact time, solvent composition and concentration, agitation, chloride concentration, and solution temperature. Below are some of the results.

Effect of Solvent Concentration. Various solvents were considered and tried in the experiments but the final choice was Alamine 336® (a tertiary amine by General Mills Co.). Methyl isobutyl ketone was not very effective in iron extraction nor was 5% TBP. Both solvents extracted Ni, Cr, Fe, Co, and Mo from the leach solution (pH = -0.30); MIBK was partially soluble in the aqueous, thus solvent

loss was significant. Increasing iron concentrations in the leach solution by addition of $FeCl_3$ solution did not increase the amount of iron extracted from the aqueous solution in competition with the other elements, therefore only a limited amount of iron can be allowed in the leach solution for effective separation. Third phase formation was also a problem with these systems. More investigations were carried out using Alamine 336®.

The solvent consisted of volume ratios of Alamine 336®, isodecanol, and kerosene. Isodecanol, which acted as a third-phase inhibitor, was mixed with the amine to form the "active organic", and the effects of alamine to decanol ratios (A/C) were observed after contacting the solvent with the leach solution for 3 min at room temperature (Table 5). Significant extraction of Ni and Cr occured for values of $A/C \geq 1.0$ thus making it difficult to strip Co even after five contacts with strip electrolyte. Stripping the solvent with a base gave large amounts of emulsion, indicating the existence of Ni, Cr, Co, and Fe that did not strip during H_2O contacts. The optimal active organic was chosen at $A/C = 0.75$.

The diluent (kerosene) plays an important role in the final concentration of the active organic, hence, its effect on extraction was analyzed by maintaining $A/C = 0.75$ and varying the volume of kerosene added. Table 5 shows that cobalt extraction depends directly on the concentration of amine while Mo and Fe show no strong dependence. Concentrated and very dilute solvent seemed to enhance nickel extraction. Figure 13 indicates a linear relationship between the amount of cobalt extracted and the concentration of amine. The slope

Table 5. Extraction and stripping characteristics at various amine to decanol ratios

Process	Amine to Decanol Ratios (A/C) 1.67	1.25	1.0	0.83	0.625
Extraction					
No. of phases	3	3	3	3	2
Vol. free unloaded solvent	10.4 ml	8.5 ml	4.0 ml	2.3 ml	0
Color of loaded solv.	Blue	Blue	Blue	Blue	Blue
Stripping with H_2O					
Color of 1st strip solv.	Green	Green	Green	Light Pink	Deep Pink
No. of phases	3	3	3	3	2
Color of 2nd strip solv.	Green	Green	Light Pink	Deep Pink	Pink
3rd-5th strip solv.	Pink & Blue	Pink & Blue	Pink	Pink	Pink
Stripping with NaOH					
Color of Aqueous	Pink & Blue	Pink & Blue	Pink & Blue	Blue	Blue
Emulsion	Large	Large	Large	Small	None
Regenerated Solvent					
Vol Recovered out of 25 ml	21.0 ml	22.4 ml	22.0 ml	22.0 ml	23.8 ml
% Extraction					
Ni	22.3	26.5	20.7	25.5	9.3
Cr	35.5	41.7	30.0	38.7	13.2
Co	100.0	100.0	100.0	50.0	47.5

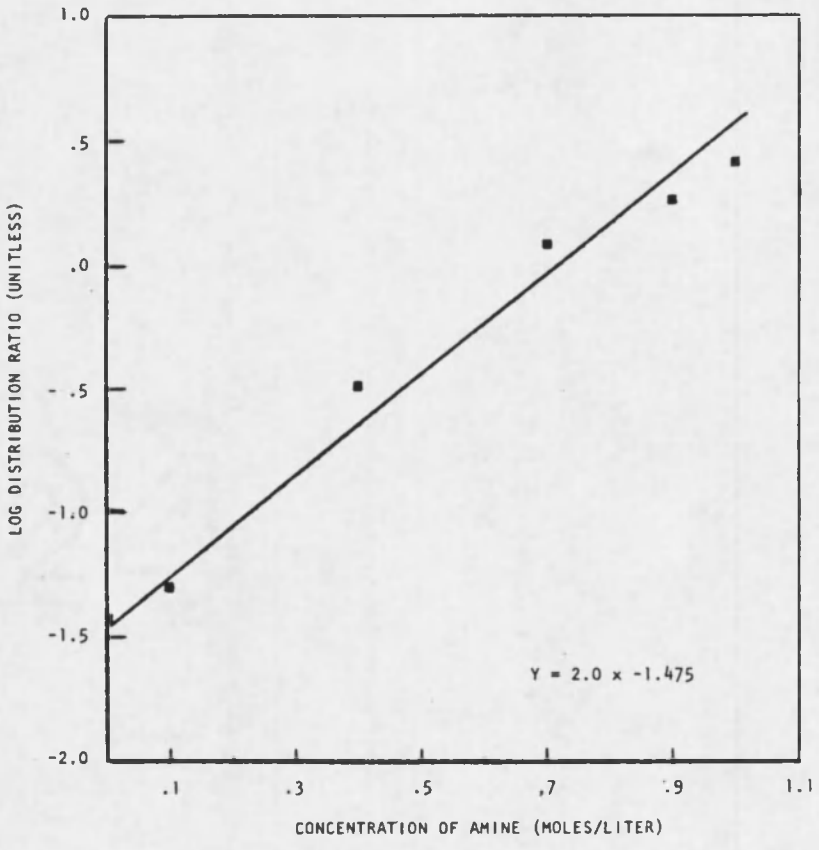


Figure 13. Distribution of Co chloride between leach soln and Alamine 336 as a function of amine concentration

has a value of 2.0 and therefore confirms the presence of $CoCl_4^=$ as the extractable cobalt species.

The result in Table 6 gives the optimal percentage of active organic as 70% and this corresponds to 0.69 M amine.

Effect of Contact Time. The timer on the mechanical shaker (Figure 14) was varied to observe any changes in the amounts and types of elements extracted, and the summary of the results appear in Figure 15. Apparently 3 minutes seems to offer the highest percentage extraction of Co but this was rejected because of the nearly 24% extraction of Cr and Ni; instead, 10 minutes was chosen since only about 2.0% of Cr and Ni was extracted. Between 7 and 10 minutes would be appropriate contact time and beyond 10 minutes all the elements show increasing trend for extraction. The remaining part of the investigation was based on 10 minutes contact time.

Effect of Agitation on Extraction. Like the other parameters considered so far, mixing plays a major part in solvent extraction. Insufficient mixing or excess of it is detrimental to metal extraction since the former does not provide adequate mass transfer and the latter causes the formation of a third phase. Difficulties arise not only in determining what the optimal mixing should be but also in quantifying such conditions for possible scale-up or transfer to different equipment. The author has chosen to express the mixing in terms of angular momentum of the particles:

(1)

Table 6. Effect of diluent on extraction

% Active Organic	Volume of Kerosene	Co			Mo	Fe	Ni	Cr	Conc. Amine (M)
		%E	D	Log D	%E	%E	%E	%E	
100	0 ml	72.5	2.64	0.42	38.2	6.4	18.2	16.2	0.99
90	5	64.5	1.82	0.26	40.7	15.6	15.0	17.9	0.89
70	15	55.4	1.24	0.09	37.6	22.2	12.9	7.3	0.69
40	30	25.0	0.33	-0.48	33.5	21.6	12.6	5.4	0.39
10	45	4.8	0.05	-1.3	39.7	18.2	12.8	11.5	0.099
0	50	3.7	0.04	-1.42	15.2	4.8	4.8	5.9	0.00

Note: $\%E = \%\ \text{Extraction} = \frac{100D}{1+D}$

D = Distribution Ratio

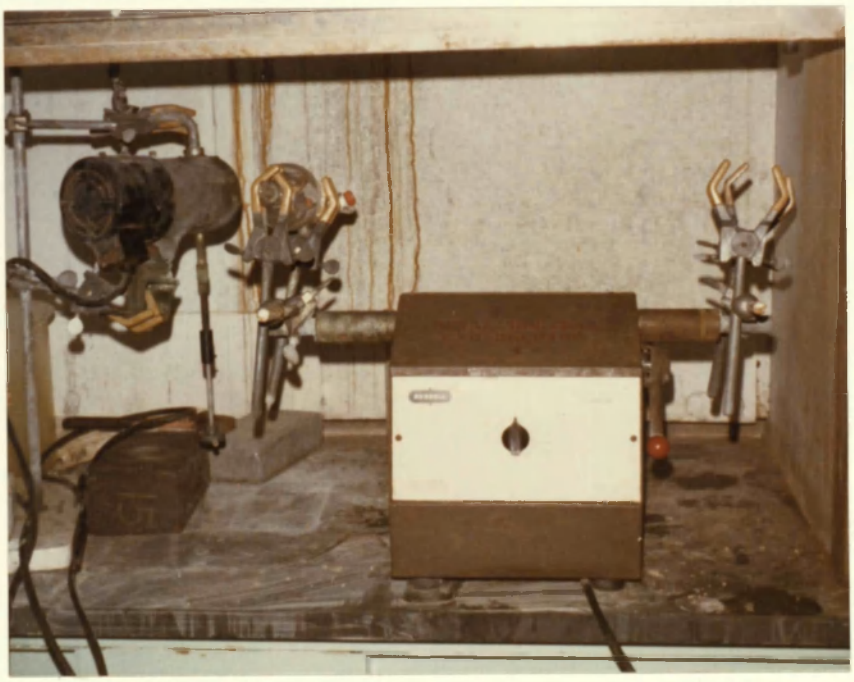


Figure 14. Mechanical agitator

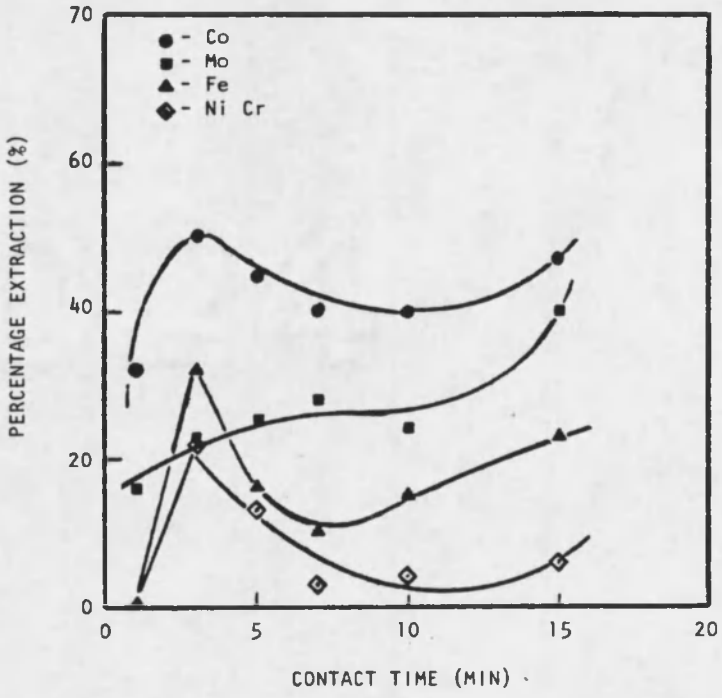


Figure 15. Effect of contact time on extraction

$$l = rp \sin \theta \qquad (1)$$

where

l = magnitude of angular momentum (g cm^2/sec)

r = moment arm (radius)(cm)

θ = angle (rad.)

p = magnitude of the linear momentum (g cm/sec)

By substituting for p in rotational dynamics, the final expression becomes:

$$l = r^2 m \omega \sin \theta$$

where

m = mass of particle (or systems of particles) (rad/sec)

and

ω = angular speed of the particle

From equation (2) above, the product $r^2\omega\sin\theta$ will be referred to as the design variable (DV) and m will be assumed constant for a given mixing system. To vary the momentum, requires changing the values of DV, and by design, only one of three variables (r, ω and θ) can be changed at a time. The optimal condition will be based on the DV value that give the best possible results, thus quantifying the degree of mixing.

The mechanical shaker (Figure 14) can be set to vary θ in DV by varying the throw of the moment-arm, giving $1 \propto DV \propto \text{Sin}\theta$. Various values of $\text{Sin}\theta$ and the percentage extraction of the elements appear in Table 7 and some of the data are plotted in Figure 16. Increased mixing seems to have decreased the extraction of Ni and Cr but optimum extraction of Co, Mo, and Fe occurred when $\sin\theta$ had a value of 0.16. The corresponding numerical value of the DV is given below:

$$DV = r^2\omega \sin\theta = 8.89^2 \times 200 \times 0.16 \text{ cm}^2/\text{min} = 2529.0 \text{ cm}^2/\text{min}$$

Conventional agitators often specify the diameter of the impellar (2 r) and the angle of throw θ; hence by adjusting the rpm of the agitator, the optimal DV value of the system can be reproduced for scale-up or design purposes. The above degree of mixing was equivalent to a setting of 8 on the throw scale of the shaker.

Table 7. Effect of agitation on extraction

Setting	Total Throw (CM)	Sinθ	Percentage Extraction Co	Mo	Fe	N	Cr	ω (RPM)	γ Cm
1	0.762	0.04285	55.0	20.5	49.4	44.3	42.2	200	8.89
3	1.626	0.09143	64.8	40.0	42.9	31.4	33.1	200	8.89
5	2.337	0.13130	62.8	41.8	42.2	22.3	23.3	200	8.89
7	2.845	0.16000	64.1	46.6	53.1	21.8	23.2	200	8.89
10	3.505	0.19714	59.9	46.6	48.8	12.7	14.3	200	8.89

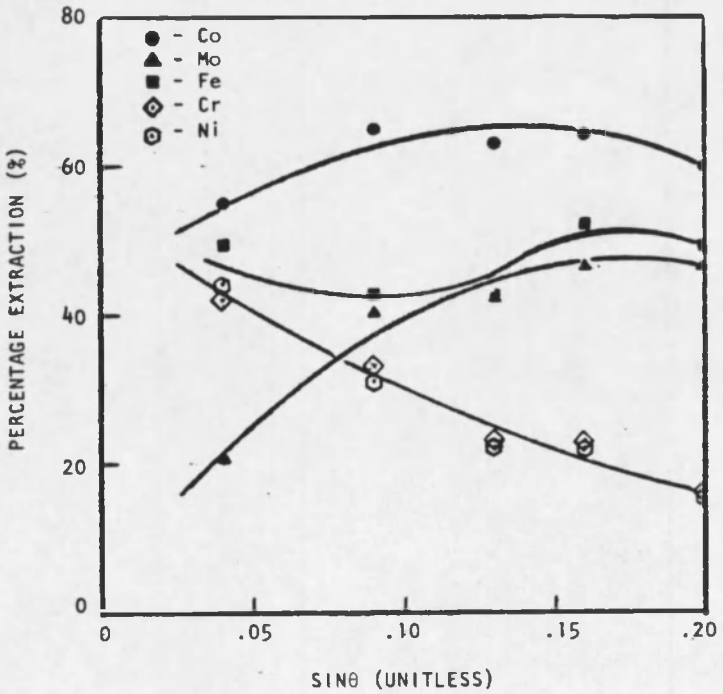


Figure 16. Effect of degree of mixing on extraction. -- Mixing is measured by angular momentum ($l = r^2 m\omega \sin\theta$).

Effect of Chloride Concentration on Extraction. Chemical properties of solutions influence the extraction characteristics of the elements in most solvent extraction systems. In chloride systems, these characteristics are typified by the total chloride concentration in the aqueous phase and to a lesser extent, by the pH of the solution. Investigation by Reinhardt (1975) produced Figure 17, which is a classic result for the indicated systems. Differences in aqueous pH and probable existence of Mo and Fe in more than one valence state necessitated investigation of the influence of Cl^- on the metal extraction.

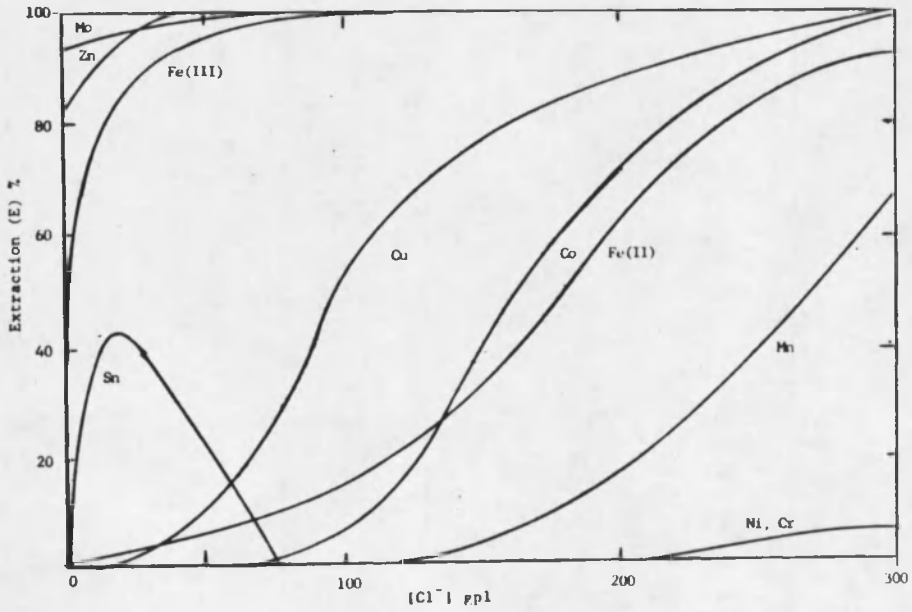


Figure 17. The influence of chloride concentration on the extraction of metals. -- Organic phase = 25% Alamine 336, 15% dodecanol in kerosene. Aqueous phase = $CaCl_2$ solutions. [Metal] = 1 g/l pH = 2).

Solution of the crystals formed during the last phase of the leaching was adjusted for chloride content by adding fresh HCl (37% soln); then contacting the mixture for extraction. Results of the tests appear in Table 8 and Figure 18.

Table 8. Data on chloride concentration effect on metal extraction with Alamine 336

Conc. Cl (g/l)	Metal Extraction (%)				
	Mo*	Co	Fe	Ni	Cr
112.229	NA	25.0	2.65	31.85	3.26
147.394		35.0	0.56	30.03	7.14
166.931		39.17	0.55	34.00	5.36
206.004		42.51	5.14	34.63	0.00
258.100		48.79	8.67	29.86	0.00
291.253		55.23	10.38	35.10	0.00
314.205		49.98	15.44	33.45	2.92
331.036		50.02	24.09	37.35	5.17

*NA--there was no Mo in the dissolved crystals

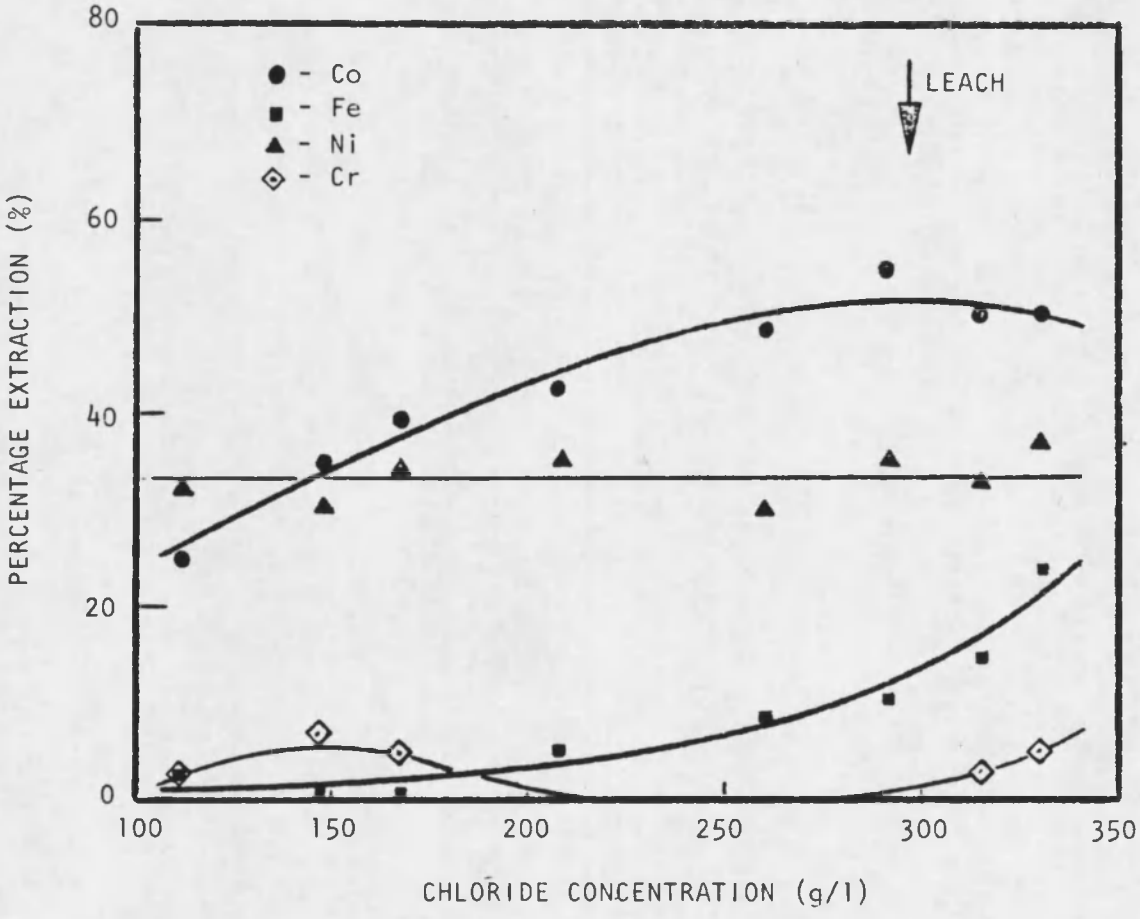


Figure 18. Percentage extraction as a function of aqueous solution chloride concentration

Effect of Temperature on Extraction. Finally, the effect of temperature on the degree of extraction was explored since the previous tests were carried out at room temperature. Table 9 and Figure 19 provide the results. It would possible, as indicated by the above results, to achieve selectivity for extraction of Co, Mo, and Fe from Cr and Ni in addition to increasing the extraction efficiency at 40°C.

Further tests in this schedule were based on the optimum conditions established from the outlined investigations.

Table 9. Data on the effect of temperature on extraction

Temperature (°C)	Metal Extraction (%)				
	Co	Mo	Fe	Ni	Cr
0	81.8	65.1	49.7	27.3	17.4
19	75.4	67.6	41.1	15.4	19.0
28	72.3	57.6	61.1	0.4	4.4
38	69.0	63.4	65.1	0.0	0.0
55	63.6	70.0	100.0	0.0	5.4
68	64.2	73.0	100.0	0.0	6.2

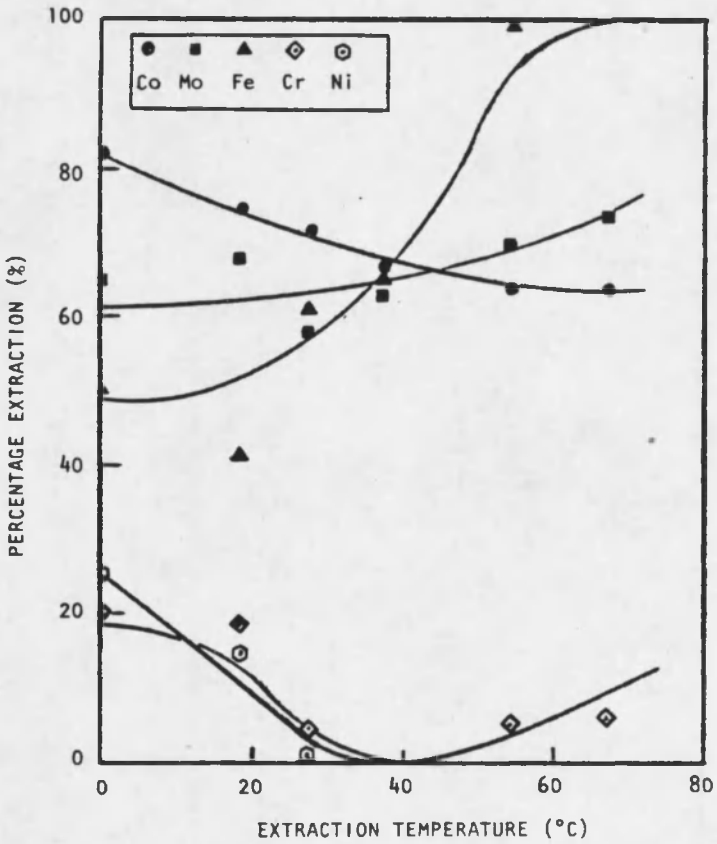


Figure 19. Extraction as a function of temperature

Extraction of Cobalt

Tests were carried out to find out how many stages of extraction would be necessary for effective separation of cobalt from the chloride leach solution. The results (Figure 20 and Table 10) indicate that three practical stages would be needed for complete removal of cobalt.

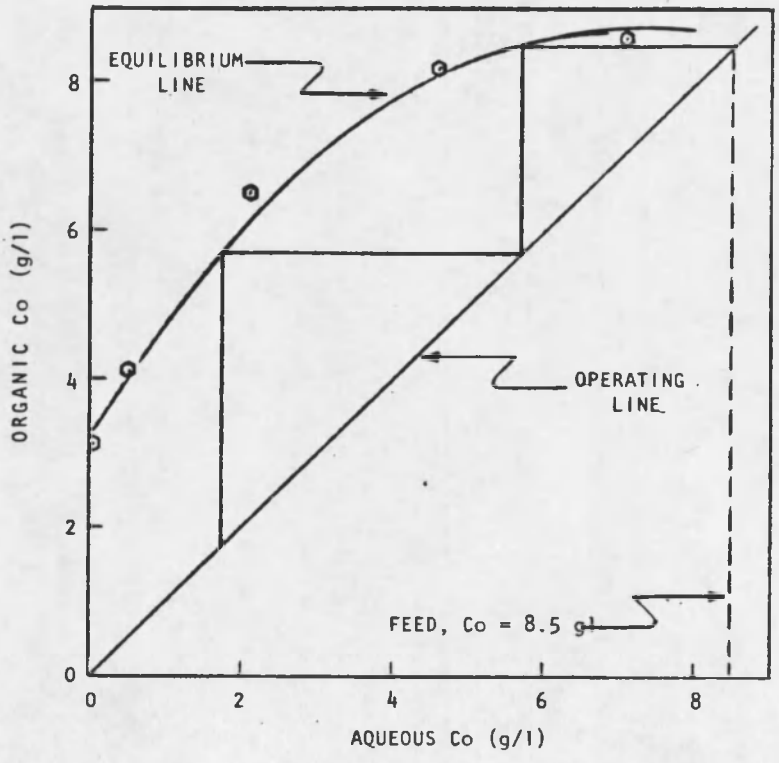


Figure 20. McCabe-Thiele diagram for extraction of cobalt from chloride leach solution

Table 10. Distribution of elements in the solvent and aqueous phases

a. Data for distribution of elements and extraction isotherms

Vo/Va (cc/cc)	Distribution of Elements (g/l)									
	Co		Mo		Fe		Ni		Cr	
	A	O	A	O	A	O	A	O	A	O
1/5	7.06	8.60	2.13	13.48	0.97	3.70	31.56	0.00	15.2	0.00
1/2	4.60	8.24	1.74	6.38	0.63	2.16	28.88	5.36	13.4	3.60
1/1	2.12	6.52	1.64	3.09	0.50	1.19	31.56	0.00	15.2	0.00
2/1	0.50	4.10	1.39	1.69	0.00	0.86	31.56	0.00	15.2	0.00
3/1	0.00	2.91	1.03	1.27	0.00	0.59	24.72	2.10	13.0	0.64
4/1	0.00	2.18	0.95	0.99	0.00	0.43	24.72	1.71	12.0	0.80
5/1	0.00	1.74	0.85	0.78	0.00	0.34	21.64	1.98	11.20	0.80

A = Aqueous (unoxidized leach solution)

O = Organic or solvent

b. Distribution of elements Vo/Va = 1.00

	Co	Mo	Fe	Ni	Cr
D	3.08	1.78	2.38	0.00	0.00
E	75.46	63.98	70.41	0.00	0.00

$$D = \text{Distribution Ratio} = \frac{\text{Conc. Element in Solvent}}{\text{Conc. Element in Aqueous}}$$

$$E = \% \text{ Extraction} = \frac{100D}{1+D}$$

Co-extraction of molybdenum and iron follow the isotherms in Figures 21 and 22. Two stages would result in complete extraction of iron but molybdenum could not be extracted more than about 80% after the third contact. Application of these results to a pilot plant is summarized in Table 11.

Stripping of Co from Loaded Organic

Recovering the extracted species from the solvent requires reversing some of the conditions that favored the formation of organic-metal complexes. The variables that affected extraction were re-examined except the temperature was maintained at 40°C.

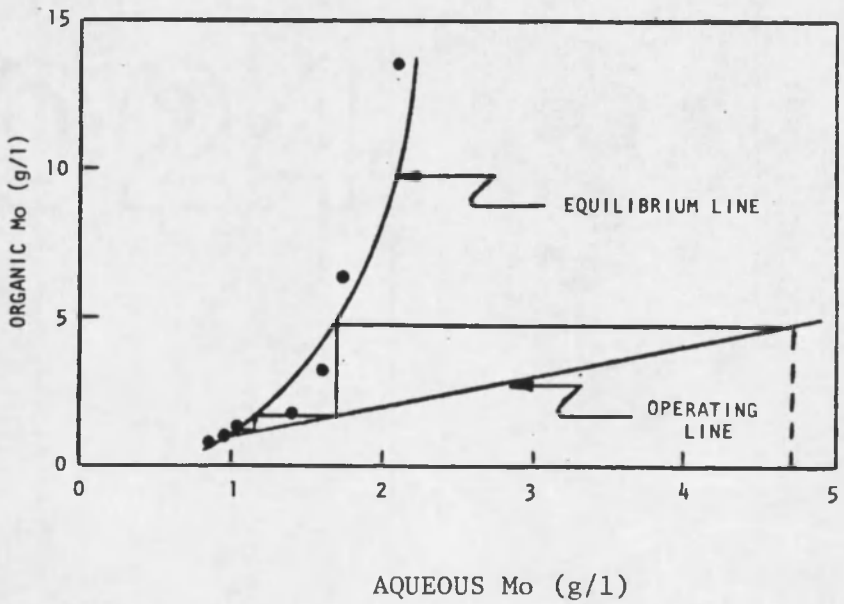


Figure 21. McCabe-Thiele diagram for extraction of molybdenum from chloride leach solution

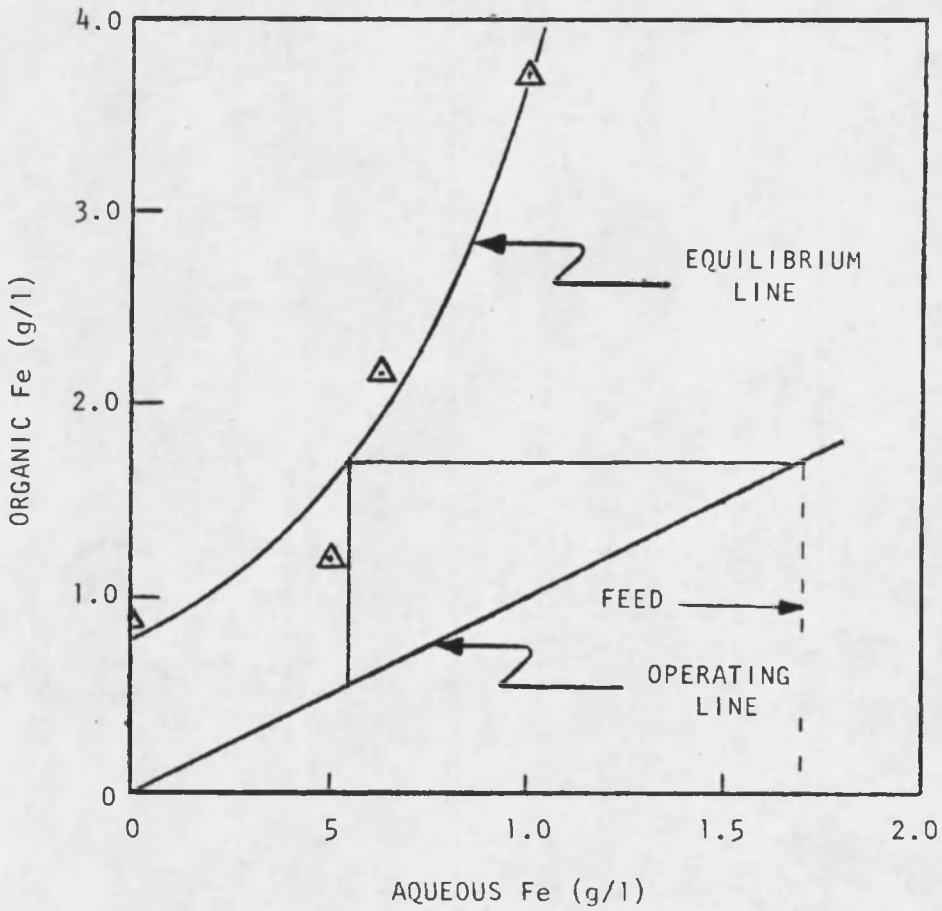


Figure 22. McCabe-Thiele diagram for extraction of iron from chloride leach solution

Table 11. Data on pilot plant operation -- concentration of elements in the raffinate

Run	Raffinate Elements Concentration (gpl)				
	Co	Mo	Fe	Ni	Cr
1	2.375	0.375	0.275	85.069	30.243
2	1.000	0.750	0.586	85.069	29.792
3	0.000	0.500	0.875	71.313	29.792
4	4.800	0.320	0.650	81.550	25.278
5	2.000	1.250	0.875	87.107	32.500
6	0.575	2.000	0.625	87.500	31.823
7	7.750	2.500	0.750	87.500	32.500
8	1.000	1.875	1.250	87.500	32.500
9	0.000	1.250	0.375	79.625	28.438
10	5.000	0.780	0.500	80.500	26.361
Average	2.450	1.160	0.676	83.273	29.923
%E	87.931	82.556	57.744	4.830	7.930

Effect of Contact Time. At short contact times, the degree of selectivity in the stripping of Co, Fe, and Mo was poor. It would be desirable to have two of the elements to co-strip in a single stream as this would afford simple refining steps for complete separation. Though the largest amount of Co stripping occurred at a contact time of 7 minutes, 50% of Mo was co-stripped (Figure 23) on the first contact of the organic with the strip electrolyte. Above 7 minutes Mo showed less

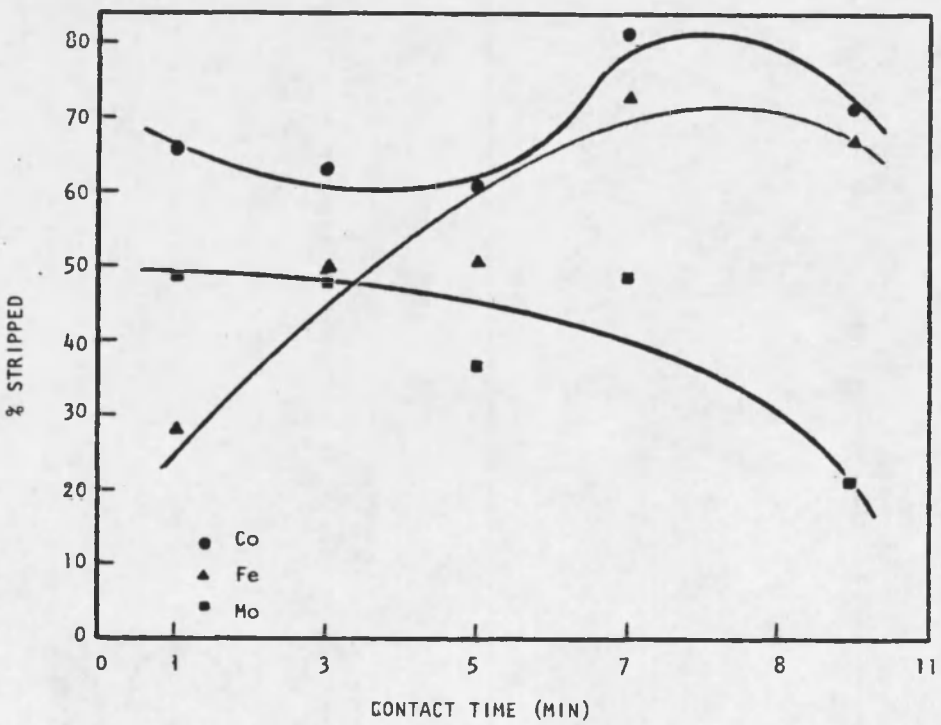


Figure 23. Effect of contact time on stripping Co with H_2O

tendency of stripping with Co and Fe. Similar investigation was done using Mo-strip electrolyte and the results appear in Figure 24. From the above results, 10 minutes was considered as the best contact time in terms of solution characteristics, phase disengagement time, and material recovery.

Effect of Agitation on Stripping. Cobalt stripping seems to be independent of the amount of agitation beyond a certain value (DV = 1739 cm^2/sec), but iron responded positively to increased mixing while molybdenum had a maximum at DV = 2055. The general characteristics of the effect of agitation on stripping of Co, Fe, and Mo appear in Figures 25 and 26. For both maximum stripping (first contact) and selectivity, a DV value of 3,200 was predicted by the results.

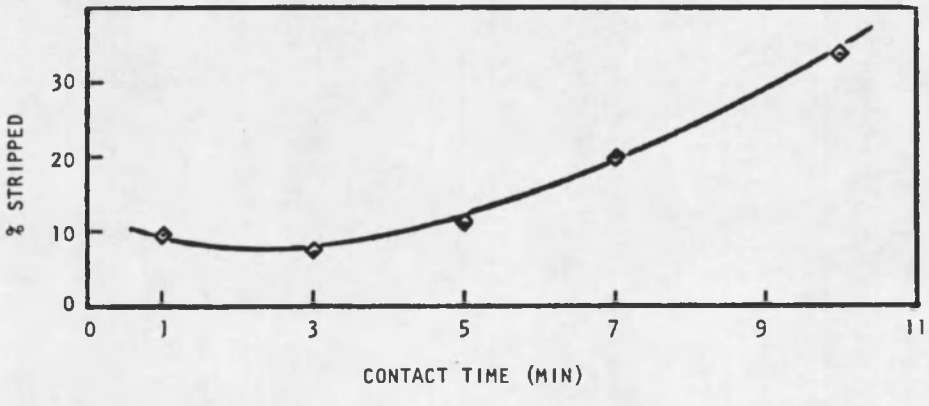


Figure 24. Effect of contact time on Mo stripping

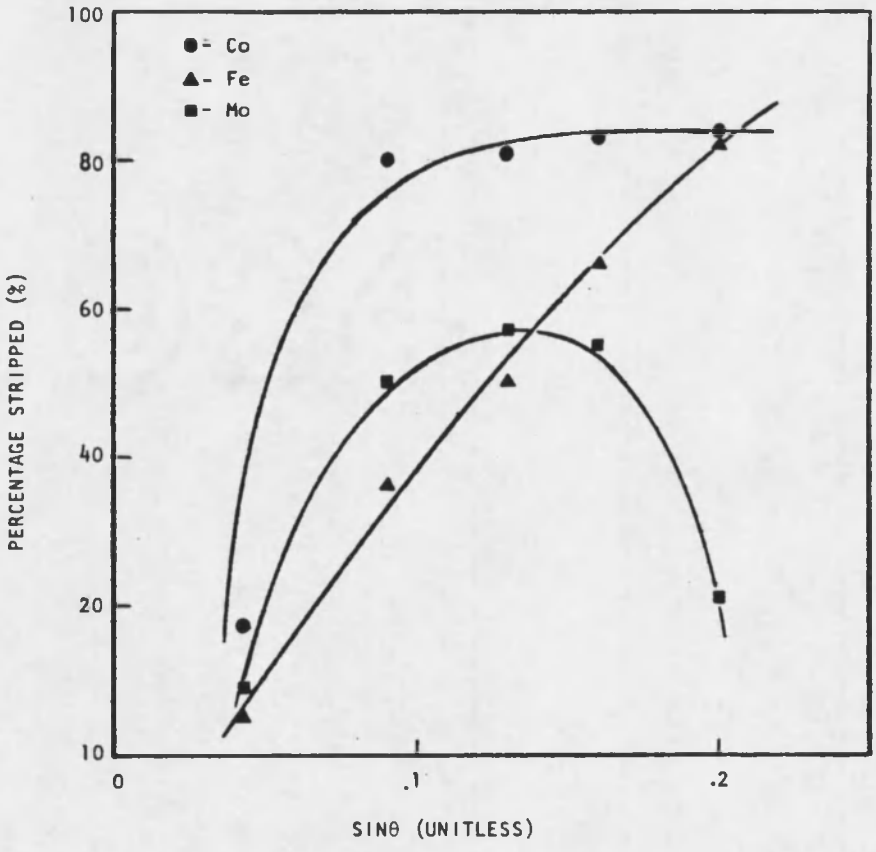


Figure 25. Stripping as a function of mixing (mixing ∝ angular momentum ∝ sinθ)

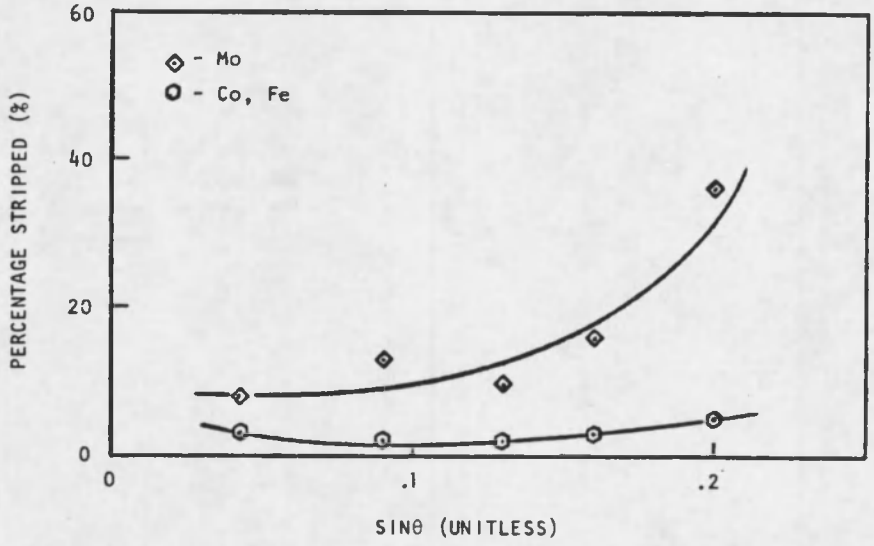


Figure 26. Mo stripping as a function of mixing

Effect of Electrolyte pH on Stripping of Cobalt. pH was not considered a strong variable in the metal extraction step but the situation was different in the stripping steps as shown in Figure 27. The pH of the electrolyte (H_2) was adjusted with HCl and it could be seen that the recovery follows a parabolic trend with a maximum at a pH 2.0. As the electrolyte becomes more acidic, less recovery occurs due to increased chloride concentration in the aqueous which drives the reaction, given below, to the left:

$$(R_3N)_2\ H_2CoCl_4 + H_2O \rightleftharpoons 2R_3N + CoCl_2(aq) + H_2O + 2H^+ + 2Cl^- \qquad (3)$$

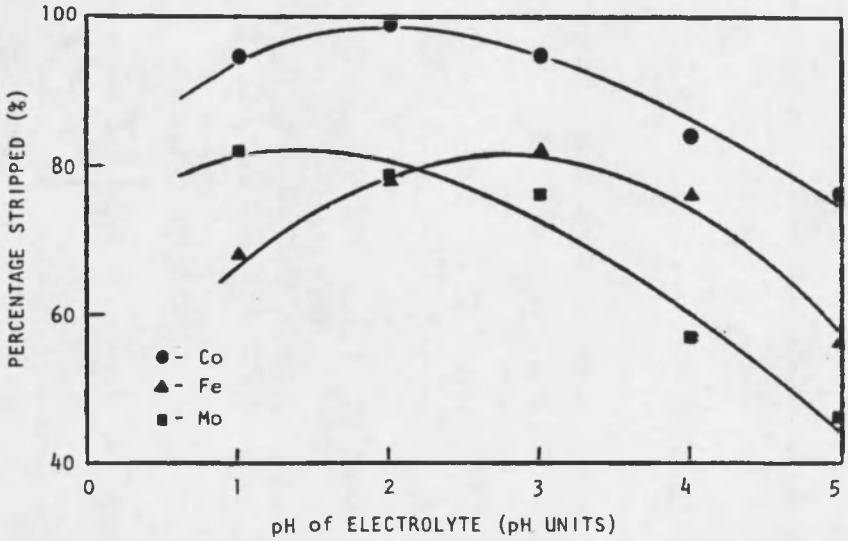


Figure 27. Stripping versus electrolyte pH

Emulsion (third phase) becomes a problem as the pH starts increasing from two towards the basic range.

The solvent that was stripped of Co at the various pH values was contacted with Mo-strip electrolyte to recover the remaining Mo. The results (Figure 28) show the decline in recovery as the pre-extraction pH increases above 2, and such decrease reflect a lower total Mo recovery from both stripping steps. Poisoning of the organic would result in poor recycling and cause increases in costs.

It was obvious (from the results) that the best stripping would be achieved at a pH 2.0, and this was used in subsequent tests.

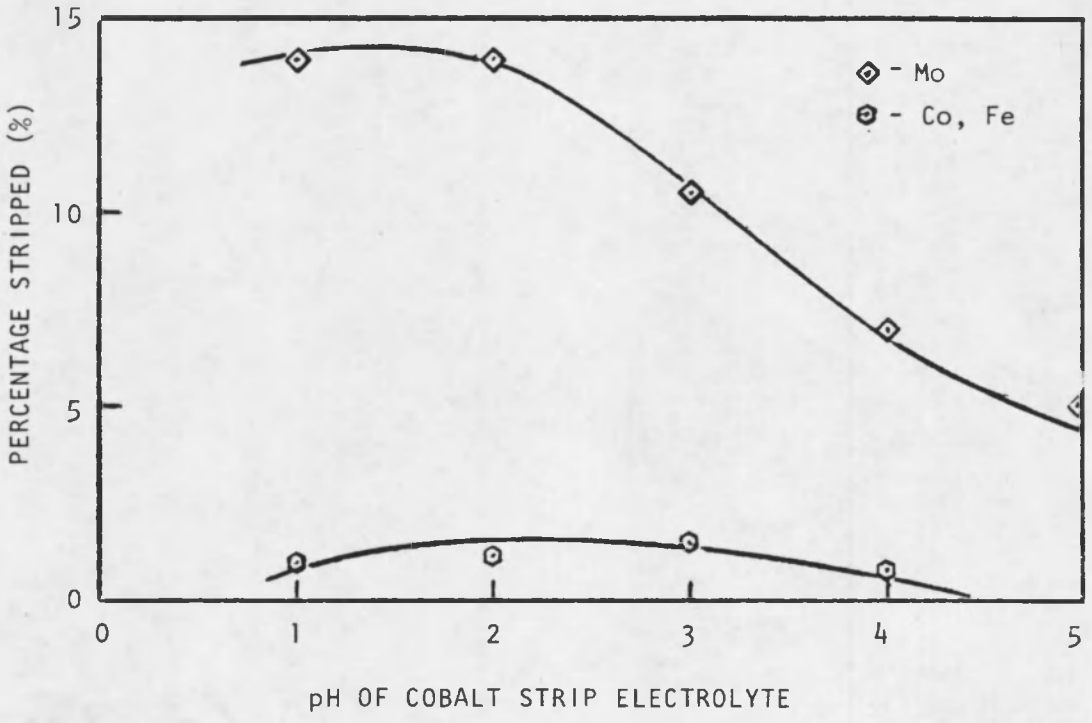


Figure 28. Mo strip as a function of the pH of cobalt strip electrolyte

Stripping Stages

The number of contacts necessary for effective stripping of Co was determined based on the following (optimal) conditions:

1. Solutions temperature = 40°C
2. Electrolyte pH = 2.0
3. Contact time = 10 minutes
4. Design variable (DV) or mixing = 3,200.

Results of the tests show that four practical stages would be required for complete removal of Co from the organic (Figure 29). There was no appreciable selectivity with regards to Mo and Fe and concentrations of the elements in the organic at various phase ratio appear in Figure 30. Iron showed no strong response to increased organic phase ratio but the situation is different for Mo, which shows substantial stripping at a phase ratio of one and less for values above or below one.

The significance of the above results is that even though Co could be removed from the solvent in four stages, Mo and Fe will be substantially stripped thus minimizing selectivity. In Figure 17, Reinhardt (1975) indicated that selectivity would be highly influenced by chloride concentration and the valence states of the elements. The chloride requirements were met in the conduct of the extraction and stripping experiments, hence the possible reason for the lack of selectivity might be the valence states of iron and molybdenum. Complexity in the nature of the species in the leach solution and the need for selective stripping of the extracted elements demanded further investigations to the effect of solution potential on the stripping characteristics of Co, Fe, and Mo. The results of these new sets of experiments are given in the next sections.

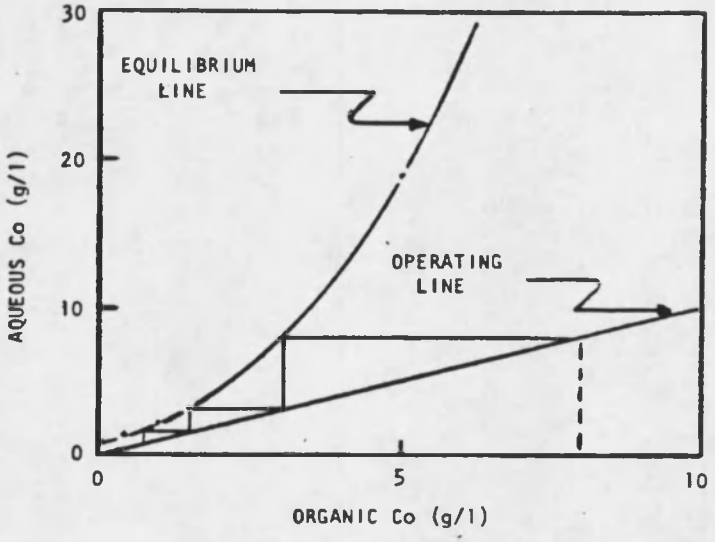


Figure 29. McCabe-Thiele diagram for Co stripping from Alamine 336 (pH = 2.0, T = 40°C)

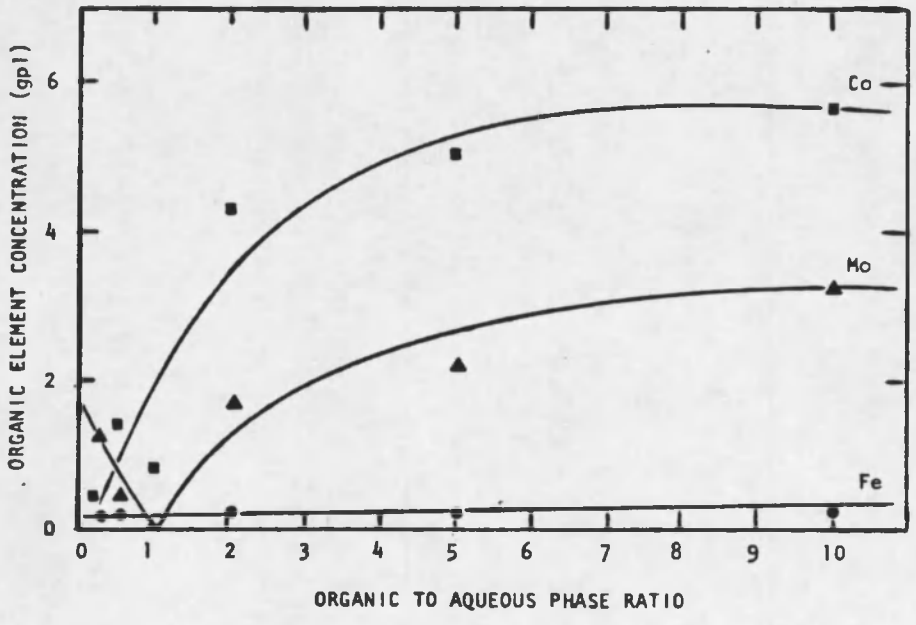


Figure 30. Stripping characteristics of Co-Fe-Mo with H_2O (pH = 2.2, T = 40°C) on single contact

Pilot Tests on Schedule 1

Extension of the bench tests to pilot plant was carried out using mixer-settlers batteries with 3 extraction stages; 3 Co-strip, 3 Mo-strip, and 1 protonation stage. Data collection was hampered by some of the operating problems encountered during the test; such as pump failures and inconsistent feed rate, poor temperature control, and more importantly drifing rpm of the agitators. In spite of the above difficulties, a few short-run data points were collected, which (it is hoped) would reflect the status of continuous operation.

In Table 11, the raffinate at the end of each of the ten runs was analyzed for the various elements as shown. Complete extraction of cobalt from the leach was observed in some of the runs thus confirming the possibility of a three-stage extraction circuit for Co; however, nickel and chromium were also observed to extract as well. On the average, 87.93% of extraction of Co, 56% Mo, 57.74% Fe, and 5.83% Ni, and 7.93% Cr was achieved. These results reflect the fact that the optimal conditions obtained in the bench tests were not adequately attained in the pilot plant due to the problems mentioned earlier in this section.

All the cobalt that was extracted was recovered in both the Co-stream and the Mo-stream, with about 95% recovery in the H_2O strip. Also contained in the cobalt stream were 30% Mo, 59% Fe, 73% Ni, and 41.4% Cr. The total recovery of Mo, Fe, Ni, and Cr from both streams was less than the respective amounts of these elements that were extracted (Tables 12 and 13).

Table 12. Data on pilot plant operation--Cobalt tank analysis at end of each run

Run	Elements Concentration in Co Strip (gpl)				
	Co	Mo	Fe	Ni	Cr
1	16.950	2.328	0.693	1.825	0.750
2	16.500	0.798	0.427	1.400	0.875
3	13.535	1.968	0.341	8.875	1.000
4	15.000	0.665	0.000	6.250	2.300
5	17.500	1.330	0.427	0.025	0.000
6	17.500	0.998	0.800	0.000	2.050
7	13.750	3.192	0.427	0.000	0.000
8	25.000	0.931	0.688	0.000	0.000
9	17.000	4.250	0.880	7.000	1.800
10	16.500	0.000	0.760	5.500	1.900
Average	16.924	1.646	0.544	3.085	1.068
%R	94.81	29.98	58.88	73.00	41.44

Table 13. Data on pilot plant operation--Mo tank analysis at end of each run

Run	Elements Concentration in Mo Strip (gpl)				
	Co	Mo	Fe	Ni	Cr
1	0.900	3.059	0.060	0.345	0.339
2	1.110	4.003	0.096	0.465	0.420
3	2.500	0.293	0.130	1.630	0.441
4	1.600	5.720	0.065	0.925	0.474
5	1.300	3.275	0.175	0.355	0.000
6	1.180	0.130	0.095	0.000	0.845
7	0.235	0.984	0.025	0.000	0.000
7	0.000	0.692	0.025	0.000	0.000
9	1.000	1.500	0.085	0.800	0.677
10	1.420	2.155	0.095	0.640	1.720
Average	1.124	2.181	0.085	0.516	0.492
%R	6.32	39.73	9.20	12.21	19.09

In Table 14, results of regular analysis of the cobalt stream during test run #1 is shown and it can be seen that beyond two hours, the steady trend observed at the early part of the run was lost. It was found that between the second and third hours the agitator-pump had gone out of set-speed thus causing the raffinate to overflow into the loaded organic stream, and resulted in increased concentration of Ni and Cr in the strip solution. Even though these problems were encountered, it seems that a successful extraction and stripping can be achieved for Co based on schedule 1 process specifications. The cobalt solution from the pilot process was electrolyzed for Co, after some refining.

Table 14. Test run #1--variation of elements concentration with time

Time (hr)	Elements Concentration in Co Stream (gpl)				
	Co	Mo	Fe	Ni	Cr
0.5	15.625	0.000	0.250	1.375	0.250
1.0	17.625	0.000	0.375	1.375	0.375
1.5	16.875	0.125	0.125	1.625	0.375
2.0	16.750	0.125	0.250	1.625	0.375
3.0	14.250	0.125	0.125	3.625	0.750
3.5	14.375	0.250	0.000	3.000	1.000
4.0	16.000	0.125	0.000	3.500	1.125
Average	15.929	0.107	0.161	2.304	0.607
Day's Average	16.950	2.328	0.693	1.825	0.750

Solvent Extraction Attempts on the Co-Fe Stream

Various solvents were contacted with the Co-Fe-Cl solution obtained from the first extraction process, and the results appear in Table 15. Except for MIBK, the solvents showed only a little extraction of Fe and Co from the solution. This negative result (especially with Almine 336) suggested that the iron must probably be in the ferrous form, hence confirming the assumption made in Table 21 regarding the Fe species stripped. The CCl_4 extracted almost equal amounts of both Co and Fe but it was not possible to strip either element with H_2O and Na_2CO_3. Five percent TBP was used in the test and the amount of Fe extracted was very small (14.52%) the same value was observed for Alamine 336 and CCl_4. The uniform extraction shown by these three solvents could indicate the possibility of having only 14.52% Fe as Fe^{+3} in the feed solution.

The positive aspect of the results is equally important as it offers an alternative route toward refining the cobalt solution by extraction with MIBK. In this process, efficient extraction and stripping of Fe would be possible, and the loss of Co will be less than what would be encountered by hydrolysis.

Table 15. Refining of Co solution by solvent extraction

Solutions	SOLVENTS							
	Alamine		MIBK		CCL_4		TBP	
	Co(gpl)	Fe(gpl)	Co	Fe	Co	Fe	Co	Fe
Co-Fe Feed	20.00	3.10	20.00	3.10	20.00	3.10	20.00	3.10
Raffinate	18.29	2.65	18.29	0.00	17.14	2.65	17.14	2.65
H_2O Strip	1.60	0.19	0.19	3.02	0.00	0.00	0.46	0.00
No_2CO_3 Strip	0.04	0.00	0.00	0.078	0.00	0.00	0.00	0.00
% Acc.**	99.65	91.61	92.40	99.94	85.70	85.48	88.00	85.48

**% Acc. = % Accountability based on single extraction and stripping with solvents and solutions shown.

Schedule 2--Solvent Extraction of Mo with Co and Fe as Impurities

Reduction and Oxidation of Leach Solution

The unsatisfactory selectivity shown by results of schedule 1 indicated that there might be some valency effect which adversely affected proper separation. It was assumed that molybdenum was probably not in the hexavalent state which had been shown to extract and strip with adequate selectivity. Since it was not possible to determine, analytically, the amount of Mo^{+6}, Mo^{+5}, or any lower valence molybdenum present in the leach solution, it was further assumed that all the molybdenum existed in valence 5. Stoichiometric amounts of $SnCl_2$ and H_2O_2 were determined for reduction and oxidation of one mole of Mo^{+5} to Mo^{+4} and Mo^{+5} to Mo^{+6}, respectively. The result of the reduction and oxidation tests appear in Figure 31. Reduction favored co-extraction of all the metals to some degree but only Mo, Fe, and Co were extracted from the oxidized solutions. One stoichiometric amount of H_2O_2 was needed to give 100% extraction of both Mo and Fe, and about 53% of Co.

The above results were very encouraging and more tests were carried out to determine the extraction and stripping isotherms for Mo.

Extraction of Mo

Oxidized leach solution was used to determine the number of extraction stages that would be required for complete removal of Mo from the aqueous, and the results are shown in Table 16 and Figure 32.

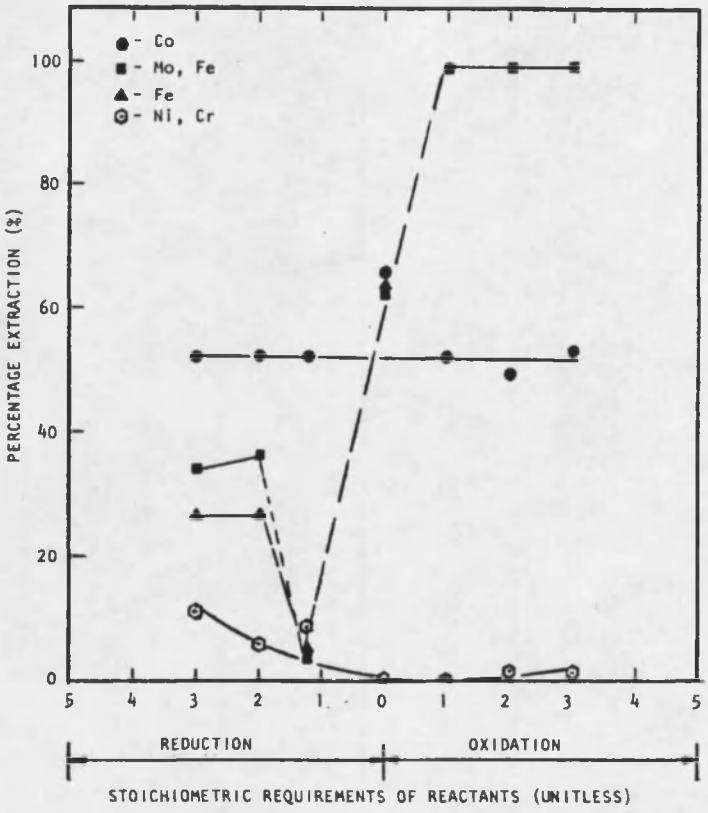


Figure 31. Extraction as a function of reduction and oxidation of the leach solution

Table 16. Data for Mo extraction isotherm

A/O	Mo Concentration	
	Aqueous (g/l)	Organic (g/l)
1/10	0	0.665
1/5	0	1.33
1/3	0	2.22
1/2	0	3.33
1/1	0	6.65
2/1	0.1	13.20
3/1	0.35	19.60
4/1	1.25	25.35
5/1	1.75	31.50
6/1	2.08	37.83
7/1	2.50	44.05
8/1	3.23	49.98
9/1	3.55	56.30
10/1	4.25	62.25

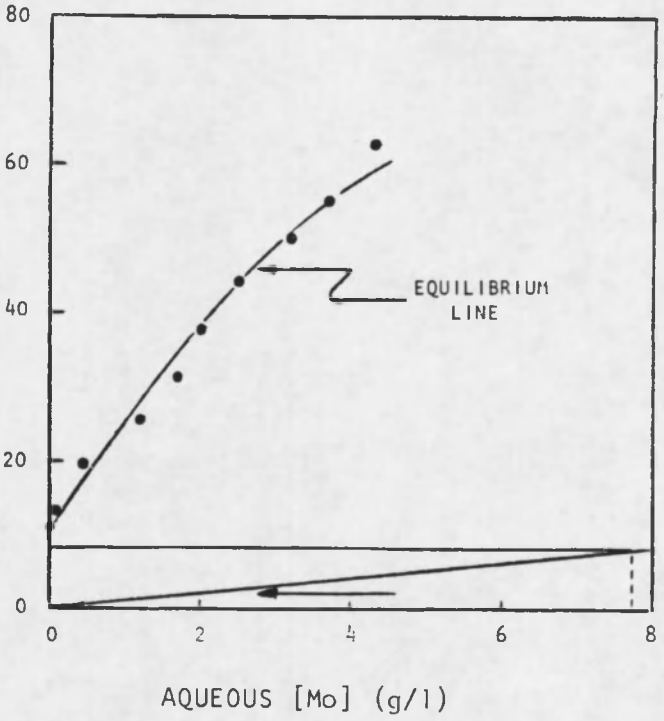


Figure 32. McCabe-Thiele diagram for Mo extraction from oxidized leach solution

It will require only a single extraction stage to completely remove Mo and at the same time extract about 46% Co and 100% Fe (Tables 17 and 18). In Table 19, the separation factors, β, show that Cr and Ni should not extract along with Mo and Fe therefore the amounts of Ni and Cr shown in Tables 17 and 18 would probably come from entrainment since the organic was not scrubbed at the end of the extraction.

It should be noted that the solvent was not saturated in Mo even at a phase ratio (A/O) of 10:1 as indicated by Table 16.

Table 17. Data for determinations of extraction factors, D and β

Fluid	Mo		Fe		Co		Cr		Ni	
	wt(g)	gpl	wt(g)	gpl	wt(g)	gpl	wt(g)	gpl	Wt(g)	gpl
Leach	1.995	6.65	0.825	2.75	6.00	20.00	7.35	24.50	17.89	59.63
Raffinate	0.000	0.00	0.000	0.00	3.24	10.80	7.34	24.46	17.74	59.13
Organic	1.995	6.65	0.825	2.75	2.76	9.20	0.01	0.04	0.15	0.50

Table 18. Distribution Ratio, D: oxidized leach solution, O/A = 1.0

Element	D_{Mo}	D_{Fe}	D_{Co}	D_{Cr}	D_{Ni}	%E
Mo	∞					100.00
Fe		∞				100.00
Co			0.852			46.00
Cr				0.00147		0.147
Ni					.00861	0.854

Table 19. Separation factor β (where $\beta = \frac{Di}{Dj}$)

i → / j ↓	Mo	Fe	Co	Cr	Ni
Mo	1	1	0	0	0
Fe	1	1	0	0	0
Co	∞	∞	1	0.0017	0.010
Cr	∞	∞	579.60	1	5.857
Ni	∞	∞	98.95	0.1707	1

Moreover, all the experiments in this schedule were carried out on the basis of the mass transfer and optimal conditions established in schedule 1.

Molybdenum Stripping

Stripping of molybdenum by H_2O (pH = 2) was observed in schedule 1 when Co and Fe were stripped, but it would be expected, if hexavalent molybdenum species were extracted, that Mo should strip in a basic medium with very low or no chloride. Cobalt stripping followed the four-stage procedure established in the first schedule and virtually all the iron was removed, leaving mostly molybdenum in the solvent. To strip Mo, various chemicals and solutions were used and the degree of success varied.

Among the chemicals used were: NH_4OH, NaOH, CaO, $CaCo_3$, CaOH, and Na_2CO_3. Formation of emulsion and low recovery were commonly encountered with most of the chemicals except Na_2CO_3. Vapor pressure was a problem with the ammonium hydroxide while low solubility of the calcium compounds prevented further considerations of the calcium chemicals. Various concentrations of sodium carbonate (Na_2CO_3) were used but it was found that sufficient stripping could be obtained with 2-4 molar solutions and that higher concentrations did not seem to improve the recovery.

The solvent that had been stripped of Co and Fe was contacted in various phase ratios with Na_2CO_3 solutions, and the results are graphed in Figure 33. Three stripping stages will result in a

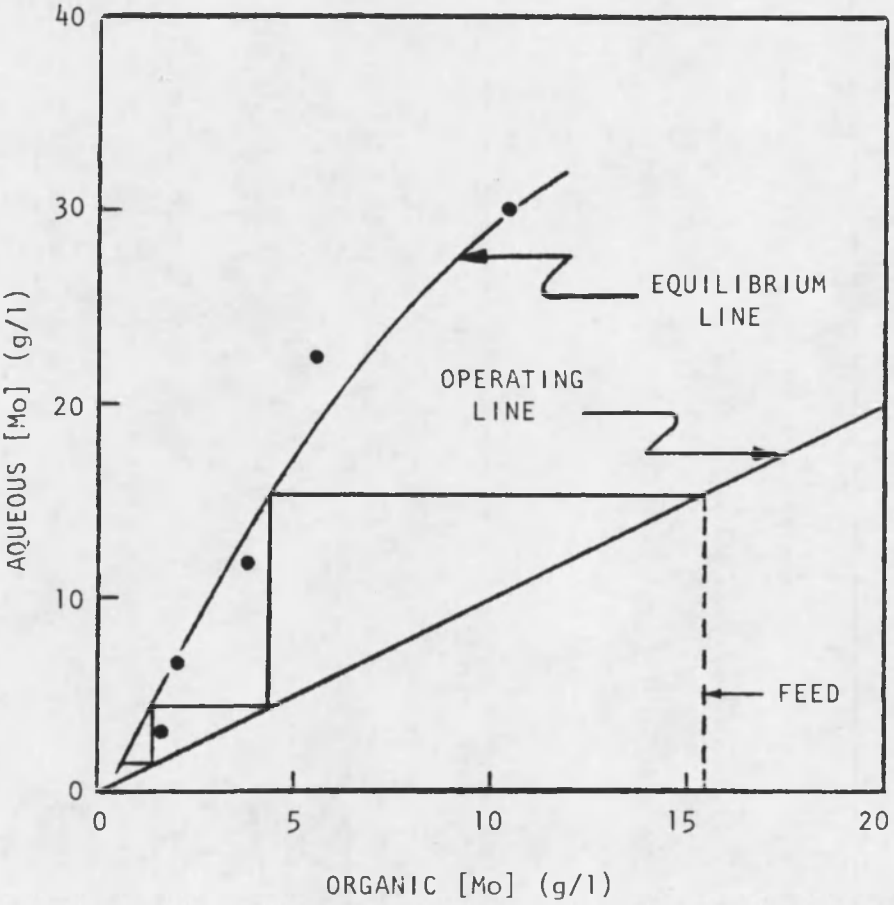


Figure 33. McCabe-Thiele diagram for stripping of Mo from Alamine 336®

concentration of 0.5 gram per liter in the solvent and it should be possible to effectively recover Mo with four practical counter-current stages.

Material Balance on Schedule 2

Material balance for the oxidized leach solution was done on the basis of one liter of processed solution and the results of the bench test on solvent extraction. Table 20 shows the extraction based on single-stage contact. Table 21 shows Co-Fe stripping using three stages of counter current flow and Table 22 Mo stripping using 3 stages of counter current flow is shown. The Co-Fe stream had a cobalt concentration of 20 gpl and 3 gpl Fe while 30 gpl of molybdenum was obtained in the Mo stream. Because of the alkaline nature of the Mo strip solution, the regenerated organic was basic and would require protonation before recycling for further extraction. The Mo solution contained NaCl-H_2MoO_4 or NaCl-Na_2MoO_4 depending on the concentration of the Na_2CO_3 strip solution used. Molybdic acid is obtained with less than 1.5 M Na_2CO_3 strip electrolyte and Na_2MoO_4 is present in higher concentrations of the electrolyte. Refining and making of a commercial molybdenum product can be carried out with either of the solutions.

Hydrolysis of Mo Solution

After successful stripping of molybdenum from the solvent, recovery becomes much simpler since only a single element or two need be dealt with. In this experiment, the task was to separate molybdenum from NaCl in the solution.

Table 20. Material balance on solvent extraction. -- Extraction basis: 1 liter of leach solv processed; Ni = 59, Cr = 52, Co = 59, Mo = 96, Fe = 56, Cl = 35.5, Na = 23.0, C = 12.0, H = 1.0, O = 16.0; H_2O_2 used as oxidant.

	Ni	Cr	Co	Mo	Fe	Na	Cl	H	O	C	Alamine	Decanol	Kerosene	Total	(CPD) Compound
Input															
Leach (aqueous)	87.5						105.30							192.80	$NiCl_2$
		32.5					66.56							99.06	$CrCl_3$
			20.30				48.86	0.69						69.85	H_2CoCl_4
				6.65			12.30	0.14	1.11					20.20	H_2MoOCl_5
					1.60		4.06	0.06						5.72	H_2FeCl_4
							53.44	1.51						54.95	HCl
								92.42	739.32					831.74	H_2O
H_2O_2 (Oxidant)								0.14	2.22					2.36	H_2O_2
Organic (protonated)							24.62	0.69			244.80			270.11	Alamine, HCl
												331.60		331.60	Decanol
													150.00	150.00	Kerosene
Total Input	87.5	32.5	20.3	6.65	1.60	—	315.14	95.65	742.65	—	244.80	331.60	150.00	2,028.39	
Output															
Raffinate	87.5						105.30							192.80	$NiCl_2$
		32.5					66.56							99.06	$CrCl_3$
			10.15				24.43	0.35						34.93	H_2CoCl_4
							53.44	1.51						54.95	HCl
								92.56	740.43					832.99	H_2O
Evolved Gas (Cl_2)							2.46								Cl_2
Loaded Organic			10.15				24.43	0.34			121.70			156.62	$H_2Co(Alamine)Cl_4$
				6.65			9.84	0.14	2.22		49.00			67.85	$H_2MoO_2(Alamine)Cl_4$
					1.60		4.06	0.06			20.21			25.93	$H_2Fe(Alamine)Cl_4$
							5.42	0.15			53.89			59.46	(Excess)Alamine HCl
												331.60		331.60	Decanol
													150.00	150.00	Kerosene
							19.20	0.54						19.74	HCl
Total Output	87.5	32.5	20.30	6.65	1.60		315.14	95.65	742.65		244.80	331.60	150.00	2,028.39	

Table 21. Mass balance on Co-Fe stripping

	Co	Mo	Fe	Cl	H	O	Alamine	Decanol	Kerosene	Total	(CPD) Compound
Input											
Organic	10.15			24.43	0.34		121.70			156.62	H_2Co (Alamine) Cl_4
		6.65		9.84	0.14	2.22	49.00			67.85	H_2MoO_2 (Alamine) Cl_4
			1.60	4.06	0.06		20.21			25.93	H_2Fe (Alamine) Cl_4
				5.42	0.15		53.89			59.46	Excess Alamine HCl
								331.60		331.60	Decanol
									150.0	150.00	Kerosene
				19.20	0.54					19.74	HCl
H_2O					56.21	451.29				507.50	H_2O
H Cl				0.17	0.01					0.18	HCl (pH 2.0)
Total Input	10.15	6.65	1.60	63.12	57.45	453.51	244.8	331.60	150.0	1,318.88	
Output											
Organic		6.65		9.84	0.14	2.22	49.00			67.85	H_2MoO_2 (Alamine) Cl_4
				19.69	0.55		195.80			216.04	Excess Alamine HCl
								331.60		331.60	Decanol
									150.00	150.00	Kerosene
				4.93	0.14					5.07	HCl
Aqueous (20 gpl Co)	10.15			12.21						22.36	$CoCl_2$
			1.60	2.03						3.63	$FeCl_2$
					56.21	451.29				507.50	H_2O
				14.42	0.41					14.83	HCl
Total Output	10.15	6.65	1.60	63.12	57.45	453.51	244.80	331.60	150.00	1,318.88	

Table 22. Material balance on Mo stripping

	Mo	Na	Cl	H	O	C	Alamine	Decanol	Kerosene	Total	(CPD) Compound
Input											
Organic	6.65		9.84	0.14	2.22		49.00			67.85	H_2MoO_2 (Alamine) Cl_4
			19.69	0.55			195.80			216.04	Excess Alamine HCl
								331.6		331.60	Decanol
									150.00	150.00	Kerosene
			4.93	0.14						5.07	HCl
$N_a C O_3$		22.33			23.30	5.83				51.46	Na_2CO_3
$H_2 O$				19.96	159.72					179.68	H_2O
Total Input	6.65	22.33	34.46	20.79	185.24	5.83	244.80	331.6	150.00	1,001.7	
Output											
Aqueous (30 gpl Mo)	6.65			0.14	4.43					11.22	H_2MoO_4
		22.33	34.46							56.79	NaCl
				20.65	165.2					185.85	H_2O
Barren Organic					15.55	5.83				21.38	CO_2
							244.8			244.8	Alamine
								331.6		331.60	Decanol
									150.00	150.00	Kerosene
Total Output	6.65	22.33	34.46	20.79	185.18	5.83	244.8	331.6	150.0	1,001.64	

Even though the solution contained very insignificant amounts of Co (.04%), it was necessary to remove this impurity by raising the pH to 10.5 and filtering off any precipitate. Evaporation of the purified solution produced NaCl and Na_2MoO_4 crystals and since both are soluble in water, physical separation was not possible. Though NaCl is insoluble in very strong hydrochloric acid, a large quantity of acid would be required to neutralize the solution and to build up the concentration necessary for separation of the salt. Use of H_2S or any alkali metal sulfide to precipitate MoS_3 was avoided on safety grounds, and because it would require further heating of the MoS_3 at about 500°C to produce MoO_3, a commercially marketable product. Finally, a method of double decomposition to produce oxide compounds was considered.

Reduction with $NaBH_4$ between pH of 8 and 11 did not give quantitative recovery of molybdenum even when five time stoichiometric requirements of the reductant was used. A similar attempt to produce $CaMoO_3$ by reacting $CaCl_2$ with the solution of pH = 9.5 was not effective for quantitative separation. Modification of a reaction by Jean (1874) and in combination with another reaction by Schumb and Hartford (1934) was found to be fast and dependable in separating Mo from the strip solution. The reaction steps are represented in the equations below:

$$5\ Na_2MoO_4 + 10\ NH_4Cl = 6\ NH_3 + 10\ NaCl + 2\ (NH_4)_2\ MoO_4 \cdot 3\ MoO_3 \cdot H_2O + 2\ H_2O$$

$$2\ (NH_4)_2\ MoO_4 \cdot 3\ MoO_3 \cdot H_2O + H_2O = 2\ (NH_4)_2\ MoO_4(aq) + 3\ MoO_3(S) + 2\ H_2O$$

$$(NH_4)_2\ MoO_4(aq) + HNO_3\ (conc) = MoO_3 \cdot H_2O_{(s)} + 2NH_4NO_3$$

The first reaction occurs between pH of 6 and 8 and the solution must be brought to boiling, then the ammonium salt formed is washed with slightly acidic solution to obtain partial dissolution of the salt. The filtrate from the second step was reacted with concentrated nitric acid and brought to just below boiling to produce molybdic acid (anhydrous) and ammonium nitrate. The reactions were quantitative but strongly dependent on specified temperature and solution pH.

Material balance on the hydrolysis reactions are given in Tables 23, 24, and 25. The addition of stoichiometric amount of NH_4Cl precipitated 98.07% of the molybdenum and the final recovery as molybdic acid was 97.93%. The characteristic of the precipitate was favorable for filteration and about 50% moisture was retained in the filtered cake. The ratio of recovered molybdenum to amount of wash water used was 10.3%; a significant improvement over hydroxide precipitates which would not only require a larger amount of water but would be very difficult to filter.

Table 23. Material balance on hydrolysis; precipitate of ammonium salt

	Mo	Na	Cl	H	O	N	Total	(CPD) Compounds
Input								
Strip Solution	30.0	14.38			20.0		64.38	Na_2MoO_4
		74.12	114.41				188.53	NaCl
				103.25	826.0		929.25	H_2O
NH_4 Cl (XTLS)			22.19	2.50		8.75	33.44	NH_4Cl
Washing				16.40	131.20		147.6	H_2O
Total Input	30.0	88.50	136.60	122.15	977.20	8.75	1,363.20	
Output								
Soln		88.22	136.60				224.82	NaCl
				114.5	916.00		1,030.50	
	0.58	0.28			0.39		1.25	Na_2MoO_4
Gas				1.14		5.32	6.46	NH_3
Solid	29.42			1.10	17.65	3.43	51.60	$2(NH_4)_2MoO_4 \cdot 3Mo \cdot H_2O$
				5.41	43.16		48.57	H_2O
Total Output	30.0	88.50	136.60	122.15	977.20	8.75	1,363.20	

Table 24. Material balance on partial precipitate of MoO_3 from ammonium salt.

	Mo	Na	Cl	H	O	N	Total	Compound
Input								
Solid	29.42			1.10	17.65	3.43	51.60	$2(NH_4)MoO_4 \cdot 3MoO_3 \cdot H_2O$
				5.41	43.16		48.57	H_2O
Soln H_2O				43.59	348.74		392.33	H_2O
Soln HCl			0.36	0.01			0.37	HCl
Wash Water				8.84	70.61		79.45	H_2O
Total Input	29.42		0.36	58.95	480.16	3.43	572.32	
Output	11.77			0.98	7.85	3.43	24.03	$(NH_4)_2MoO_4$
Soln				55.02	440.0		495.02	H_2O
			0.36	0.1			0.37	HCl
Solid	17.65				8.81		26.46	MoO_3
				2.94	23.50		26.44	H_2O
Total Output	29.42		0.36	58.95	480.16	3.43	572.32	

Table 25. Material balance on precipitate of MoO_3 with HNO_3

	Mo	Na	Cl	H	O	N	Total	Compound
Input								
Soln	11.77			0.98	7.85	3.43	24.03	$(NH_4)_2MoO_4$
				55.02	440.00		495.02	H_2O
			0.36	0.01			0.37	HCl
Acid				0.12	5.89	1.72	7.73	HNO_3
Washing				6.6	52.77		59.37	H_2O
Total Input	11.77		0.36	62.73	506.51	5.15	586.52	
Output								
Soln				0.73	8.81	5.14	14.68	NH_4NO_3
				59.0	472.04		531.04	H_2O
	0.04			0.003	0.03	0.01	0.083	$(NH_4)_2MoO_4$
			0.36	0.01			0.37	HCl
				0.77			0.77	H_2
	11.73			0.24	7.82		19.79	$MoO_3 \cdot H_2O$
				1.98	17.81		19.79	H_2O
Total Output	11.77	0.00	0.36	62.73	506.51	5.15	586.52	

The products, MoO_3 and $MoO_3 \cdot H_2O$ were of high quality and did not contain any detectable amount of other metallic elements. The final flow sheet for Mo recovery is given in Figure 34.

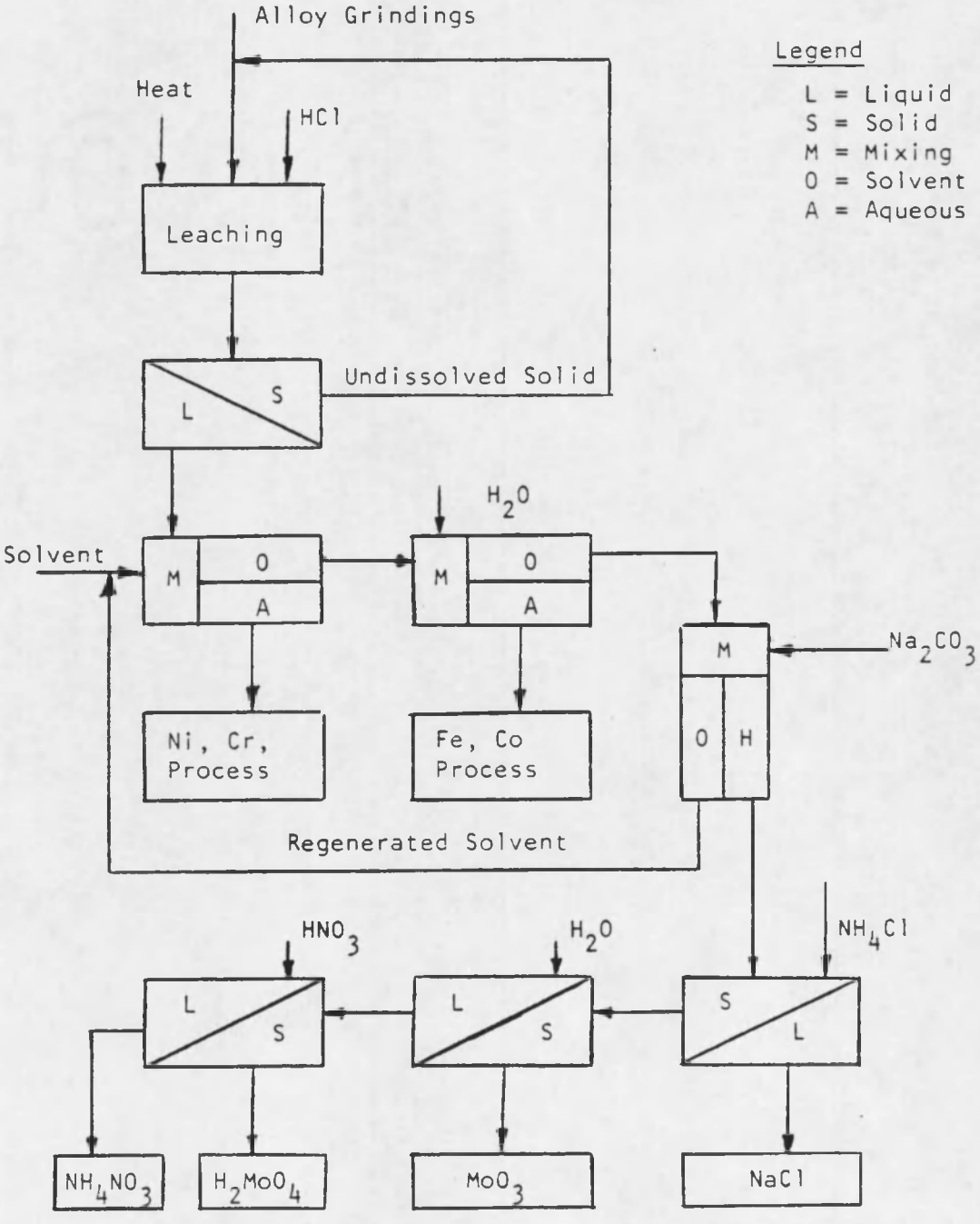


Fig. 34. Final Flowsheet for Molybdenum Recovery

CHAPTER 5

DISCUSSION

Overview

Many researchers have carried out investigations on the recovery of metal values from super alloy scraps. In most cases, Mo was eliminated through some pretreatment technique which unfortunately resulted in partial loss of Mo values. When moly could not be completely removed, difficulties were encountered in separating the element from other metals due to its complex chemistry. In attempting to solve the problem, toxic chemicals and complex methods have been used (Brooks et al., 1969; Fischer et al., 1975). The present research was undertaken to find an alternative method using commonly available chemicals to achieve high moly yield.

Leaching

Direct use of hydrochloric acid has proven to be effective in the dissolution of the super alloy grindings. It has eliminated some of the need for injection of chlorine gas or the introduction of other elements in order to satisfy the chloride requirement for cobalt extraction (Cf 300 gpl total Cl^-). The dissolution process could be represented by the reaction

$$M^\circ + 2HCl \rightarrow MCl_2 + H_2$$

where M° is a divalent metal, and MCl_2 is the corresponding chloride formed.

Variables which affected the dissolution were temperature and pulp density. As the leaching temperature increased, the dissolution rate increased; for example, almost complete dissolution was observed above 110°C, in about 240 minutes. Saturation of the leach solution after cooling to room temperature was about 87 gpl of dissolved nickel, but this concentration was exceeded at the higher leach temperatures. The solution, on cooling to ambient temperature, formed chloride crystals of Co, Ni, Cr, and Fe. These crystals did not contain moly possibly because its concentration did not reach saturation. Formation of these crystals in the process would not present a problem if the leach was maintained below the saturation point (≈ 87 gpl Ni), or if the super saturated solution was diluted as it overflowed from the leach reactor. Though more dissolution would be realized at temperatures above 95°C, solution evaporation and loss of HCl gas would occur. (A condenser and scrubber would undoubtedly be required to prevent this loss.) Use of a pressure reactor would create a reducing environment due to hydrogen gas build-up, the dissolution kinetics would be slowed, longer time and higher temperature would be needed to achieve results similar to those obtained with the open reactor.

Pulp density, defined here as the grams of solid charged per volume of acid, in some way affected the saturation concentration phenomenon. According to the results in Figure 8, a "saturation" point is reached when a constant amount of material is in solution regardless of the amount of charged solid. Material dissolved in a

200 gpl pulp density reaction was observed to be half of what was realized in 100 gpl density; the "equilibrium" concentration of dissolved nickel was 48 gpl in both cases. The limiting value suggested by the results of Figure 8 was 86 gpl pulp density and this would give 100% dissolution at the solution "saturation" point. However, the continuous leach was carried out at 95°C (average temperature) and 95% dissolution was obtained with 110 gpl pulp density.

Acid concentration above one stoichoimetric amount had no significant effect on the dissolution, nor did particle size nor residence time beyond four hours. The minor elements formed a precipitate which was referred to as "fine black material (FBM)." The weight of which was larger than the anticipated weight of the undissolved residue. This could be an oxide or chloride precipitate which formed due to the leaching conditions; there was no attempt made to determine the actual composition of the precipitate, nor its influence on the dissolution kinetics. The controlling mechanism was determined to be a first order chemical reaction with an activation energy of 7.74 kcal.

Hydrogen produced in the process might be used for reduction of various oxide products in other stages of the process.

Solvent Extraction

The solvent extraction step was the essence of the project, and therefore extensive studies of the parameters were carried out. The effects of temperature, agitation, chloride concentration and solvent composition were in general agreement with the results published in the literature for the Alamine system. Special mention of the solvent

composition is warranted, since it was found that proper ratioing of alamine-decanol and kerosene allowed very rapid phase separation during extraction. Such a result has not been previously recorded. Neutralization from the very strong acid solution (4MHCl) would not have been economic, so pH was not used as a variable, but this strong acid was the main reason for the phase ratio studies. Ratios reported in the literature gave serious emulsion problems.

In other studies Mo and Fe were largely removed prior to Co extraction, but even minor remaining concentrations were reported to poison the organic. Hence the mutual interaction of all of the elements (Co, Mo, Fe, N, and Cr) were followed in detail in this work. The ultimate remedy to interaction problems was determined to be control of the state of oxidation in the solution going into extraction. Notably, Fe as Fe^{+3} and Mo as Mo^{+6} were vital to the overall control of the system. The as-leached solution, with a potential of +177 mV (pt vs. calomel) gave complete extraction of Co in 3 stages, but only partial extraction of Fe + Mo. In the continuous extractions, repeated cycling of organic seemed to decrease the extraction of Fe and Mo relative to Co. Conversely, when the leach solution was oxidized to +860 mV (pt vs. calomel), Co was still extracted in 3 stages but Fe and Mo were completely extracted in one stage. When the leach solution was reduced with $SnCl_2$, Co again was extracted in 3 stages, but Mo and Fe were even less extracted than in the as-leached solution. In this reduced solution sequence, it might be important that Ni and Cr were extracted to about 30% of their concentration. This result is unexpected since neither Ni^{++} nor Cr^{+3} is known to exist as an anion and

alamine is supposedly selective to anion extraction. Oxidation did not affect Co extraction, and this result is supported by de Barbadillo et al. (1980) who reported 3-stage extraction at +550 mV. Qualitatively, it was observed that the reduced and as-leached solution yielded a blue organic, characteristic of cobalt loading, while the oxidized solution yielded a green organic apparently due to the mutual presence of Fe, Co, and Mo.

Stripping

After oxidation iron and cobalt could be stripped together using distilled water or Co could be selectively stripped ahead of Fe and Mo with a content of 50-100 gpl chloride. This use of a controlled chloride content during stripping has a beneficial effect in that as the solution is recycled to build up the Co concentration, Fe is rejected from the Co strip.

The organic, freed of its Fe and Co, could be stripped of 91% of its Mo with pH 11.5 solution of Na_2CO_3, at an oxidation potential of 225 mV. When this caustic solution had a potential of +410 mV, four stages were required to strip Mo, even though the organic would be expected to be completely deprotonated. Thus control of the aqueous solution potential, and secondarily the chloride content, were found to be of ultimate importance in controlling the behavior of the solvent extraction system.

Sodium chloride and sodium molybdate crystals have similar solubility characteristics and hence separation could not be achieved by evaporation. The high potential of the purified solution (+ 550 mV) would consume a larger amount of reductant if low valence oxides or

hydroxides of Mo were to be precipitated. Neutralization and precipitation of molybdic acid from the strip solution would consume a large quantity of acid. Production of $CaMoO_4$ is very slow at room temperature and even in boiling solutions, it does not seem to give quantitative precipitation.

The solution to the above problems was a stepwise precipitation procedure where an ammonium salt of moly is quantitatively precipitated at pH between 6 and 8 by NH_4Cl. The precipitate is partially dissolved in acidic solution to recover MoO_3 as precipitate and $(NH_4)_2MoO_4$ in solution. Treating the solution with concentrated nitric acid, at boiling point, gave a precipitate of molybdic acid and ammonium nitrate solution. The procedure was quantitative with by-products of NaCl, NH_3, and NH_4NO_3.

No work was carried out beyond this point since methods are readily available to further process, the MoO_3 and any of the by-products.

Recommendations

Solvent extraction of the oxidized leach solution has opened some areas where further investigations should be carried out. The following studies are necessary to better understand the possible applications of this overall process to mixed scraps.

1. Further work on the effect of solution potential on the extraction and stripping of iron should be carried out.
2. Influence of iron concentration on extraction of Co and Mo should be investigated.

3. Pilot tests on the oxidized leach solution should be conducted and complete extraction of cobalt should be considered as a modification.
4. Work on Cr and Ni separation should be completed as well as the economic analysis of the entire recovery process.

CHAPTER 6

CONCLUSIONS

A study of the recovery of metal values from super alloy scraps scraps was made using waspalloy grindings. The areas of investigation included alloy dissolution, solvent extraction of Co, Fe, and Mo, and hydrolysis of product solution.

The following conclusions may be drawn from the research project.

1. Hydrochloric acid can be used to effectively dissolve Ni, Cr, Co, Fe, and Mo from the alloy leaving a precipitate of what might be Al_2O_3, Ti_2O_3, W_2O_5, and Ta_2O_5; and that leaching can be done at a potential of about + 180 mV.
2. Under appropriate mass transfer and kinetic conditions, Co, Fe and Mo could be removed from the leach solution by solvent extraction with a tertiary amine. At low solution potential ($E_h \leqslant + 410$ mV) poor extraction of Mo would result and selectivity on stripping would not be realized.
3. The efficiency of extraction and stripping of Mo is greatly enhanced at high solution potential and 100% extraction would be obtained in a single stage extraction at + 860 mV. Effective stripping of Mo requires solution potential of about + 225 mV.
4. Precipitation of MoO_3 from NaCl and Na_2MoO_4 solution stepwise reaction of the solution with NH_4Cl and HNO_3.

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