



TERTIARY AMINE EXTRACTION OF MOLYBDENUM FROM ACID LEACH LIQUOR CONTAINING NICKEL, CHROMIUM, COBALT AND IRON.

ANIEDI O. ETTE AND DOUGLAS J. ROBINSON*

Mechanical Engineering Department

University of Uyo

P.M.B. 1017, Uyo, Akwa Ibom State

Nigeria.

**DREMCO*

9932 E. Holmes Street

Tucson, Arizona 85715, U.S.A.

ABSTRACT

Molybdenum (Mo) can exist in five oxidation states and its extraction chemistry is further complexed by the presence of metal ions such as nickel (Ni), cobalt (Co), chromium (Cr) and iron (Fe). Efficient extraction of Mo was obtained using Alamine 336[®] with the following conditions:

- *pH = -0.30*
- *300 grams per litre chloride concentration*
- *+360 millivolt solution potential*
- *38°C operating temperature and*
- *10 minutes contact time*

Good selectivity for Ni and Cr was realized as co-extraction of Mo, Co and Fe occurred under the above conditions. Selective stripping of the metal values from the amine solvent was accomplished by varying the pH, chloride concentration, solution potential and the degree of agitation. Molybdenum value was recovered through a two-step precipitation of the strip eluate with NH_4Cl

Keywords: *Molybdenum, superalloy waste, chloride leach, tertiary amine, extraction, Alamine 336[®], solution potential, selectivity, temperature, complex ions, active organic and degree of mixing.*

INTRODUCTION

Molybdenum is a strategic metal and an important alloying element in the production of steel and super alloys. It is used in the chemical, nuclear, missile and aircraft as well as the electronics industries. It is corrosion resistant with good thermal conductivity.

Turnings and other waste from superalloys constitute secondary sources for strategic metals such as Mo, Co, Cr, Ni, Ti and Pt. Effective and efficient separation of the molybdenum value, in the presence of the above metal ions, was the focus of this investigation.

The recovery of Mo from a superalloy waste using a tertiary amine solvent, with specific reference to Alamine 336[®] is presented. The results showed that Mo and other metal values can be recycled using acid digestion and selective solvent extraction techniques.

MATERIALS AND METHOD

Solid Materials: The feed to the leach reactor was waspalloy grindings, obtained from Special Metals Inc; New York. The grindings contained particle size of about 80% finer than 48 mesh and had an assay of 56.7% Ni, 18% Cr, 13% Co, 10% Mo, 1% Fe with some trace levels of Al, Ti, Ta and W by weight

Solutions:

Reagent grade chemicals were used in the preparation of various solutions used in the investigation. Hydrochloric acid was diluted to nine molar (9M) concentration and used for the leaching of the dust. The leach liquor was obtained after leaching and filtering the undissolved valve metals from the solution. This solution was then contacted with a "solvent", i.e. 30% (volume) Alamine 336[®], 40% decyl alcohol and 30% kerosene. The strip solution were various concentrations of HCl and Na₂CO₃.

Methods

The solid grindings were dissolved in a continuous flow reactor designed by the authors (Ette, 1980). Various volumes of the acid solution were heated in the reactor and the grindings introduced into the hot acid at the desired temperature. The reaction temperature was maintained while samples were drawn at regular intervals for analysis. Pregnant liquor was withdrawn continuously when the concentration reached a constant or steady value.

The filtered leach solution was brought in contact with the solvent in a mixer -- settler battery. The metal values were selectively loaded on the solvent forming the loaded organic. The loaded organic was washed with concentrated hydrochloric acid solution before stripping. The stripping solution (electrolyte) contained various concentration of chloride or carbonate, relative to available information published in the literatures. (Ette, 1980; Robinson, 1984; Reinhardt, 1975; Wigital, 1972; Fujimori, et al, 1980; Ojanen, 1980)

RESULTS

The investigation was intended to be a study of the separation and recovery of molybdenum from the other elements contained in the superalloy. Work on leaching and solvent extraction was necessary to fully understand the molybdenum chemistry.



Problems often encountered by use of solvent extraction techniques include co-extraction of Mo, Cr, 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.

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 1. The concentration of Ni was used since it was observed that the concentration of Fe, Cr, Co and Mo in the leach liquor were in the same proportion as their concentrations in the feed (alloy grindings). At ambient temperature, very little dissolution was observed after 300 minutes but up to 20% of the material was dissolved at 70°C. Sixty percent dissolution was obtained at 90°C after 200 minutes of leaching. About 85% dissolution was observed in the continuous leach runs at 110°C. This temperature was achieved in a variation of the Long-Tube Vertical Evaporator (LTV) designed by the authors (Ette, 1980).

Effect of Particle Size, Pulp Density and Acid Concentration

Particle size did not seem to play a significant role in the dissolution kinetics as shown in Figure 2.

At 30 grams per litre (gpl) and 100gpl slurry, equilibrium concentration of nickel seemed to occur at 85.71% dissolution of the nickel value in the grindings. Increasing the pulp density to 200gpl gave only 42.66% dissolution of the nickel content after about 200 minutes reaction in the reactor.

Beyond the stoichiometric amount, acid concentration did not have significant effect on the leaching. Minimum stirring was necessary to expose the particle surfaces to the acid.

Characteristics of the Pregnant Leach Solution

The following data were obtained at room temperature for the pregnant leach solution:

Concentration (gpl): 87.50Ni, 32.50Cr,
20.30Co, 6.65Mo, 1.60 Fe, 294.59Cl⁻ total, 2.0 M HCl.
Density (g/cc): 1.28
Colour: Dark green
Potential (mV): + 177m (pt vs. saturated calomel)

SOLVENT EXTRACTION

Solvent Selection

The following solvents were screened for use in separating the metal values from the leach liquor:

- Methyl isobutyl ketone (MIBK)
- 5% Tributylphosphate (TBP)
- Carbon Tetrachloride (CCl₄) and
- Alamine 336®

MIBK, TBP and CCl₄ did not exhibit selectivity and extracted Ni, Cr, Fe, Co and Mo from the leach solution (pH = -0.30). Partial solubility of MIBK resulted in significant loss of the solvent. Third phase formation was a problem with the above solvents. However, this problem was not as severe with Alamine 336. Further screening of Alamine 336 to exploit this positive characteristic gave rise to the results shown in Table 1.

“Active Organic” A/C), the ratio of Alamine to isodecanol was varied to establish optimal value for fast phase separation and the elimination of emulsion formation. At A/C \geq 1.0, significant extraction of Ni and Cr occurred. The presence of Ni and Cr made it difficult to strip the Co value after five contacts with the electrolyte. Large amounts of emulsion was observed when basic solution were used to strip the organic.

At A/C ratio of 0.75 was selected for the extraction based on the result of Table 1. Using this value, Co was found to exhibit the relationship shown in Figure 3. Also presented in Figure 3 are similar plots for extraction of Mo from the un-oxidized and oxidized leach liquor. The slopes of the lines were 2.1 and - 1.6 for Co and Mo in the un-oxidized solution. The oxidized solution gave 2.1 And 6.0 for Co and Mo, respectively. The potentials were measured prior to extraction and stripping stages. The un-oxidized solution was the solution obtained at the end of the leaching process. Addition of appropriate quantities of the selected oxidant to the “as leached” solution gave the oxidized solution

Three extraction stages were required for cobalt in both the as - leached solution and the oxidized solution decrease in the loading of Mo and Fe was observed with increased contact of the solvent with the un-oxidized solution. It is important to note that a single extraction stage was needed for complete removal of Mo and Fe from the oxidized solution.

Effect of Contact Time

Figure 4 presents the effect of contact time on the extractability of the various elements. Three minutes seemed to give the highest percentage extraction of Co but extraction of about 24% Cr and Ni was objectionable. Extraction of Cr and Ni dropped



to about 20% ten minutes while high values of Co, Mo and Fe were maintained. Beyond ten minutes, selectivity was lost as extraction for all the elements increased. Ten minutes was therefore selected as the contact time.

Effect of Agitation

In order to obtain optimal mixing condition, Repeatability of results using different mechanical mixing devices, and the need to scale up the process for commercial application necessitated the development of a mixing factor having both the fluid and the mixer parameters factor called Degree of Mixing (D_m) was developed based on the angular velocity of the particles or system of particles, and represented by equation 1.

$$D_m = r^2 mw \sin \theta \text{ -----(1)}$$

- Where r = radius of the mixer blades (cm)
- M = mass of particle or systems of particle (g)
- W = angular speed of the particle (rad/sec)
- θ = angle of throw of the blades (rad)

Consequently, a specific mixing factor (D_s) is defined as the Degree of mixing per unit mass and is given by equation 2.

$$D_s = \frac{D_m}{\text{Mass of Fluid}} = r^2 w \sin \theta \text{ -----(2)}$$

Using a mechanical shaker the effect of mixing on extraction of the elements was measured and displayed in Table 2.

For optimal co-extraction of Co, Mo, Mo, and Fe, setting 7 was chosen and the corresponding values of $\sin \theta$, w, and r were substituted in equation (2). The optimal value of the specific mixing factor D_s was obtained.

$$D_s = r^2 \sin \theta$$

$$= 8.89^2 \times 200 \times 0.16 \text{ cm}^2/\text{min.}$$

$$= 2529 \text{ cm}^2/\text{min.}$$

This value could be obtained by appropriate combination of r, w, and θ specified for a given system of mixer.

The optimum value of D_s was found to be 42.2 $\text{cm}^2/\text{g sec}$. Since r, w and θ are the mixer parameters, appropriate combinations of their values will yield the optimum value of D_s for any given system of mixer. This will ensure repeatability during process scale up or change of the mixing system.

Effect of Chloride Concentration

The influence of chloride concentration on the extraction of metal values from the un-oxidized leach solution is given in Table 3. From Table 3, the extraction of Mo and Fe are much lower than published values (Reinhardt, 1975). The low values could be due to the existence of some of these elements in more than one valence state. Chromium was not extracted at 290 grams per liter of chloride concentration. Hence 300 gpl was selected as the operating chloride concentration, to provide a little excess over the observed value (Table 3). When the operating value was applied to the oxidized solution, complete extraction of Mo and Fe was realized while 53% Co, 0.15% Cr and 0.85% Ni were extracted at a single passes as shown in Table 4.

Effect of Solution Temperature and Potential

Table 5 presents the effect of temperature on the extraction process. Nickel and chromium were not extracted at 38°C. At this temperature about 60% of Co, Mo and Fe, were extracted from the as-leached solution on a single contact. The oxidized solution yielded 100% extraction of Mo and Fe with about 53% Co in a single contact.

A summary of the effect of solution potential is given in Figure 5. As the solution becomes oxidized, selectivity for Cr and Ni is obtained. As the reduction potential increases, mass extraction of the species occur with Co remaining unaffected. The optimum solution potential was + 860mV which corresponds to an oxidation value of 1.0 on the scale (Figure 5).

Stripping of Metal Values

Cobalt was stripped from the loaded organic using an electrolyte (H_2O) at pH = 2 and a chloride concentration between 50 and 100 grams per litre. The iron was stripped using distilled water. Solution of sodium carbonate (Na_2CO_3) at 2-4 M was effective in stripping the Mo without formation of emulsion. Three stages were required for complete stripping of the element.

Recovery of Mo Values from Strip Eluate

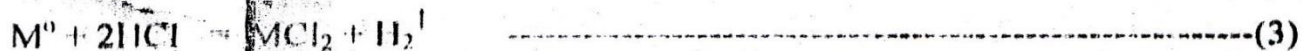
A modified reaction between Na_2MoO_4 and NH_4Cl . In combination with another reaction by Schumb and Hartford (1934) gave fast and repeatable separation of Mo from the strip eluate. Addition of stoichiometric amount of NH_4Cl precipitated 98.1% of the Mo value. The precipitate was highly amenable to filtration with 10.3% being the ratio of recovered Mo to the amount of wash water used.

DISCUSSIONS

Leaching



Direct use of hydrochloric acid has proven to be effective in the dissolution of the superalloy grindings. No additional chloride injection was required to enable the extraction of cobalt. The dissolution process could be represented by the reaction.



Where M^0 is the divalent metal and MCl_2 is the corresponding chloride formed.

The pulp density affected the leaching reaction as well as the temperature. At 86 gram per litre slurry, 100% dissolution was realized in 200 minutes at 110°C. Only 95% was dissolved at 110gpl under similar conditions.

Acid concentration above one stichiometric amount had no significant effect on the leaching rate. Particle size between 120 mesh and 200 mesh did not have much effect on the leaching process.

The value metals, Ti, Ta, W and Pt where not dissolved but formed "fine black materials" (FBM). No attempt was made to analyze this residue which constituted 0.6% weight of the original dust fed into the reactor.

Hydrogen produced from equation (3) was ignited to prevent explosion in the laboratory. This gas could be utilized for reduction at subsequent process steps where reduction would be required.

Solvent Extraction and Stripping

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 rationing 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 the elements (Co, Mo, Fe, Ni, 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 and Mo. In the continuous extractions, repeated cycling of

organic seemed to decreased the extraction of Fe and Mo relative to Co. The negative slope in Figure 3 confirms this observation in respect of Mo. 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. The oxidation therefore gave rise to the reversal of the plot of the distribution ratio versus amine concentration for Mo, as reflected in Figure 3. the change of slope from - 1.6 (un-oxidized leach solution) to 6.0 (oxidized solution) occurred in the highly acidic solution (pH = -0.30). The cobalt curved remained the same in both solutions showing that the expected Co^{+2} state of oxidization is maintained in both solution. The probable extractable specie for cobalt is CoCl_4 and for Molybdenum, it is MoO_2Cl^- 4 in the oxidized solution. 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 to note that Ni and Cr were extracted to about 30% of their concentration. This result is unexpected since neither Ni^{+2} 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 (1975) 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.

CONCLUSIONS

A study of the recovery of molybdenum values from super alloy scraps was made using waspallyoy grindings. The areas of investigation included alloy dissolution and solvent extraction of Co, Fe, and Mo.

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 ($E_{\text{th}} \leq + 410$ mV) poor extraction of Mo would result And selectivity on stripping would not be realized.
3. The efficiency of extraction and stripping on 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.

REFERENCES



de Barbardillo, J.J., J.K. Pargeter, and H.V. Maker "Recovering Chromium and other metals from superalloy Scrap" U.S. Bur Mines, Rep. Invest. No. 8088,, 1975

ETTE, A. O. ; Recovery of Molybdenum from Superalloy Scraps and Waste Products, M.S. Thesis Submitted to the University of Arizona, Tucson, Arizona, 1980, pp 22-25.

Fujimori, M; N. S. Itasaki, and I. Fukui, "Solvent Extraction in summitomo's cobalt Refining Process", Canadian Institute of Mining and Metallurgy, 10th Annual Hydrometallurgical Meeting, Edmonton, October 26 - 28, 1980.

Ojanen, Asko, "Integrated Treatment of Cobalt - bearing materials at Outokumpu Oy"d. Paper presented at the 10th Annual Hydrometalleugical Meeting, C.I.M, Edmonton, October 26 - 28, 1980.

Reinhardt, Hans, "Solvent Extraction for Recovery of Metal Waste" Chemistry and Industry, March, 1975.

Robinson, D.J. and Aniedi O. Ette. "Separation and Recovery of Metal Alloys from Supper-Alloy Scrap", U.S. Patent No. 4,442, 073, April 10, 1984.

Schumb, W.C., and W.H. Hartford, J. Am, Chem. Soc, 56, 7613 (1934)

Wigstol, E, and K. Froyland, "Solvent Extraction in Nickel Metellingy" U.S. Patent No. 3,887,679, June 3, 1972.

Table 1: Effect of Diluent on Extraction

% Active Organic	Volume of Kerosene Ml	Co %E	Mo %E	Fe %E	Ni %E	Cr %E	Conc. Amine (M)
100	0	72.5	38.2	6.4	18.2	16.2	0.99
90	5	64.5	40.7	15.6	15.0	17.9	0.89
70	15	55.4	37.6	22.2	12.9	7.3	0.69
40	30	25.0	33.5	21.6	12.6	5.4	0.39
10	45	4.8	39.7	18.2	12.8	11.5	0.10
0	50	3.7	15.2	4.8	4.8	5.9	0.00

Table 2: Effect of Agitation on Extraction

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

Table 3: Effect of Chloride Concentration on Extraction

Conc. Cl ⁻ (gpl)	Metal Extraction (%)				
	Mo	Co	Fe	Ni	Cr
112.229	5.66	25.00	2.65	31.85	3.26
147.394	7.45	35.00	0.56	30.03	7.14
166.931	11.01	39.17	0.55	34.00	5.36
206.004	15.13	42.51	5.14	34.63	0.00
258.100	23.32	48.79	8.67	29.86	0.00
291.253	26.27	55.23	10.38	35.10	0.00
312.205	33.71	49.98	15.44	33.45	2.98
331.036	34.62	50.02	24.09	37.35	5.17

Table 4: Single Stage Extraction in Oxidized Solution

Fluid	Mo (gpl)	Fe (gpl)	Co (gpl)	Cr (gpl)	Ni (gpl)
Leach	6.65	2.75	20.00	24.50	59.63
Raffinate	0.00	0.00	10.80	24.46	59.13
Organic	6.65	2.75	9.20	0.04	0.50
% Extraction	100	100	53	0.15	0.85

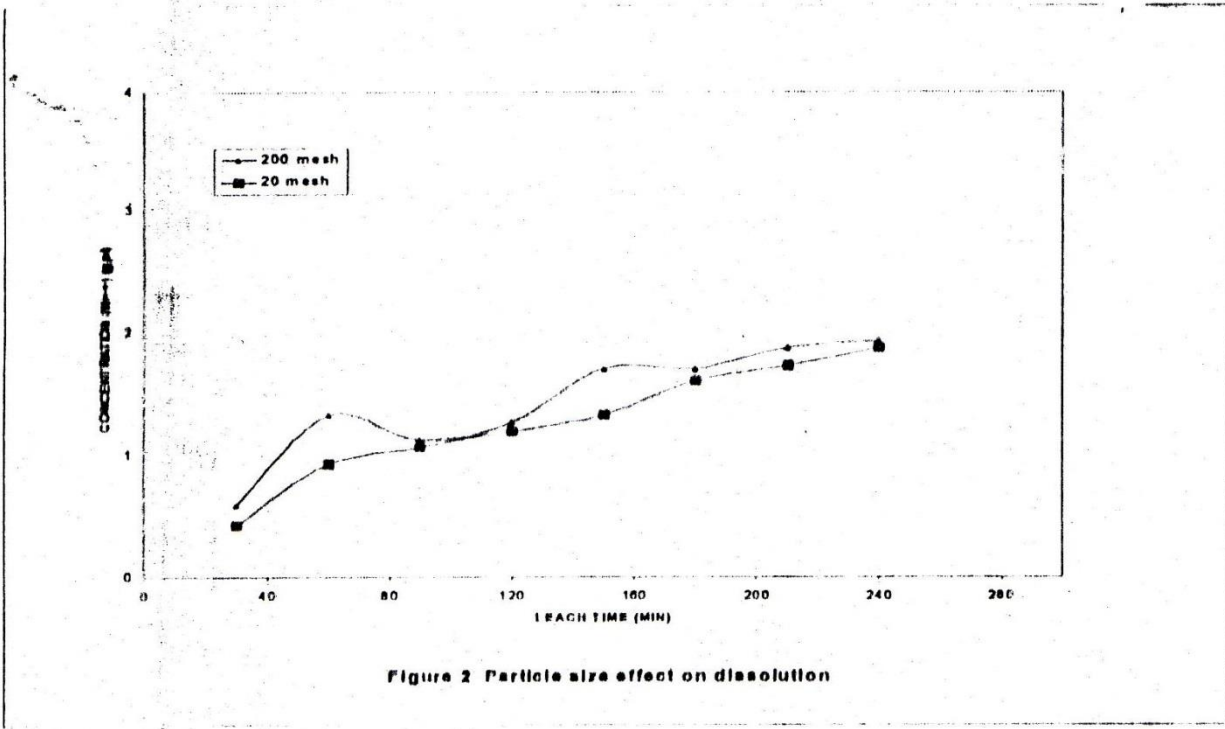


Figure 2 Particle size effect on dissolution

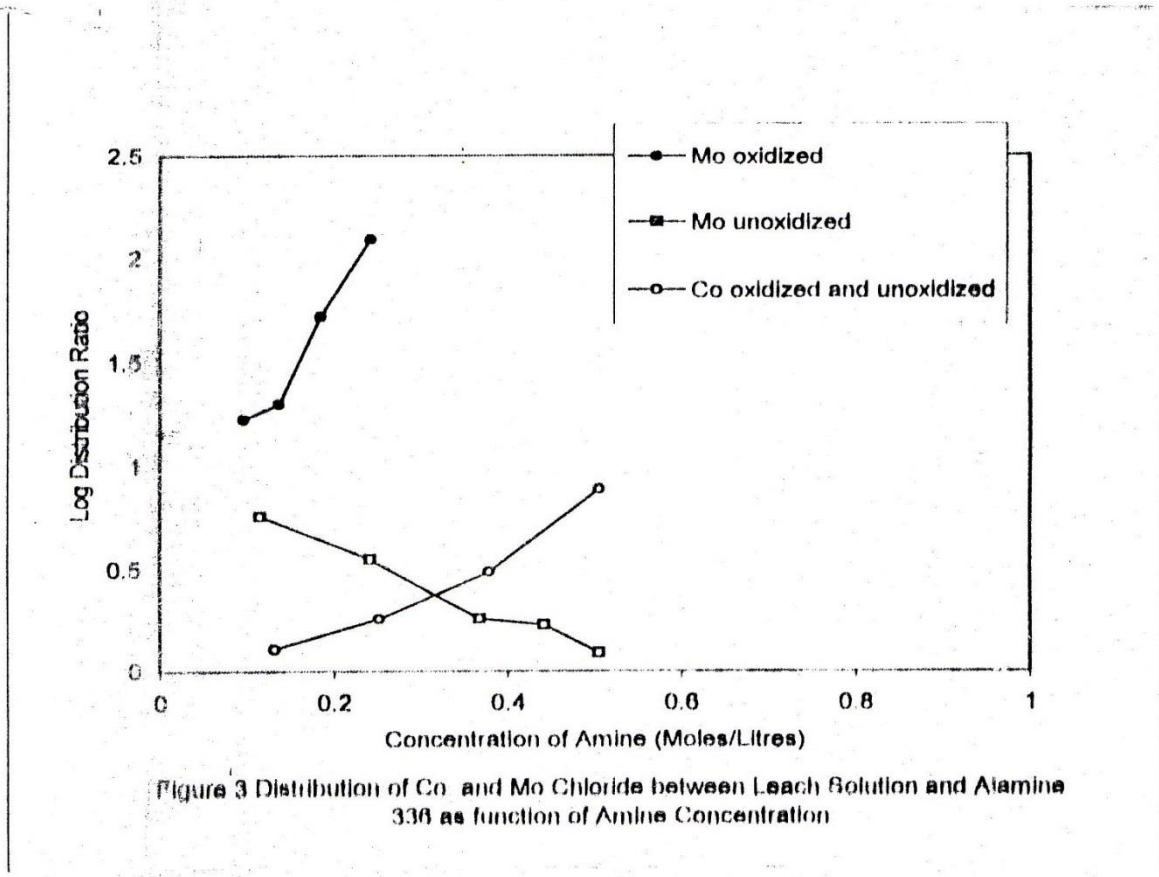


Figure 3 Distribution of Co and Mo Chloride between Leach Solution and Aamine 338 as function of Amine Concentration

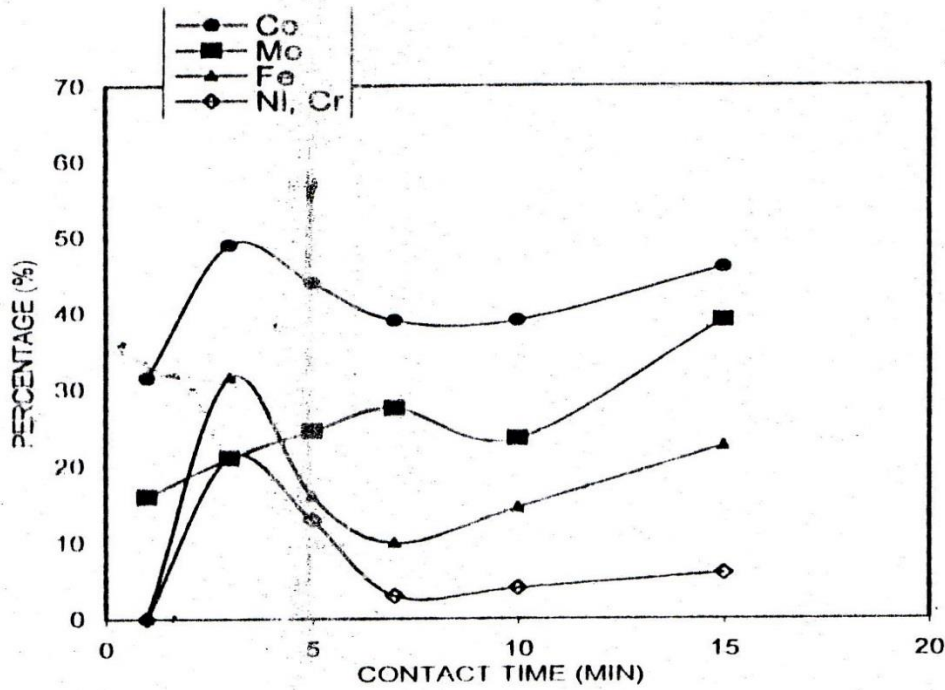


Figure 4 Effect of contact time on extraction

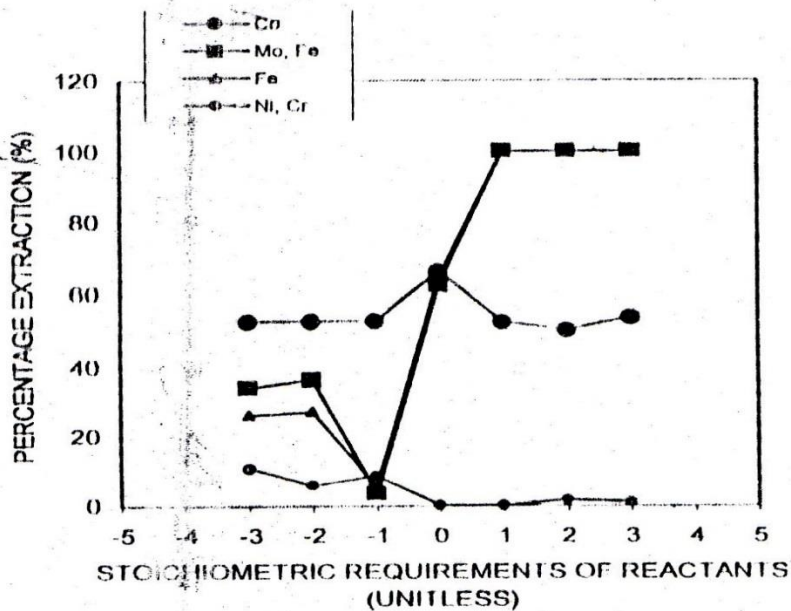


Figure 5 Extraction as a function of reduction and oxidation of the leach solution