Recovery of Principal Metal Values From Waste Hydroprocessing Catalysts

By B. W. Jong, S. C. Rhoads, A. M. Stubbs, and T. R. Stoelting

BUREAU OF MINES

UNITED STATES DEPARTMENT OF THE INTERIOR

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UNITED STATES DEPARTMENT OF THE INTERIOR
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BUREAU OF MINES
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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	lb/yr	pound per year
ft	foot	Mgal	thousand gallon
g	gram	min	minute
g/cm³	gram per cubic centimeter	mL/min	milliliter per minute
g/L	gram per liter	Mlb	thousand pound
h	hour	MMBtu	million British thermal unit
in	inch	pct	percent
kW·h	kilowatt hour	psig	pound per square inch, gauge
L	liter	st	short ton
lb	pound	vol pct	volume percent
lb/d	pound per day	wt pct	weight percent

RECOVERY OF PRINCIPAL METAL VALUES FROM WASTE HYDROPROCESSING CATALYSTS

By B. W. Jong,[1] S. C. Rhoads,[2] A. M. Stubbs,[1] and T. R. Stoelting[3]

With an Appendix on Process Economics by Thomas A. Phillips

ABSTRACT

The U.S. Bureau of Mines investigated anhydrous chlorination and caustic-acid leaching processes to recover Ni, Co, Mo, and W from waste hydroprocessing catalysts. In batch laboratory-scale equipment, the chlorination process extracted 61 to 99 pct of the metals. Final recovery was 65 to 99 pct. The caustic-acid leaching process extracted 81 to 98 pct of the metals. Final recovery was 36 to 99 pct. Chlorination processing included roasting, chlorination, hydrolysis of metal chlorides for recovering Mo or W, water leaching of Ni or Co from the spent charge, purification, and solvent extraction or precipitation of Ni or Co from the purified solutions. Caustic-acid leach processing included NaOH leaching, solvent extraction of Mo or W from the NaOH leach liquor, H_2SO_4 leaching of the NaOH leach residue, purification, and solvent extraction or precipitation of Ni or Co from the purified solution.

The estimated fixed capital cost for a commercial-scale plant processing 39,000 lb/d of waste Ni-Mo-Al catalyst was $8 million for the chlorination process and $9.6 million for the caustic-acid leaching process. The estimated operating cost was about $0.20 and $0.40 per pound of the waste catalyst, respectively, for the two processes.

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INTRODUCTION

An objective of the U.S. Bureau of Mines is to provide the technology that will help to assure an adequate supply of critical metals for the United States. This objective requires meeting U.S. economic and strategic needs and reducing or avoiding total U.S. dependence on foreign supplies. Achieving these goals necessitates evaluation of the potential recovery of metals from secondary sources as well as from domestic mineral resources.

In a 1982 Bureau study (1),[4] waste hydroprocessing catalysts were identified as a potential source of Ni, Co, Mo, W, and V. The study revealed that every year more than 26 million lb of these metals are discharged in waste catalysts and less than half of these metals are recovered or recycled. The hydroprocessing catalysts are used for refining and upgrading crude oils in the petroleum industry. Among the catalysts employed are nickel oxide and molybdenum trioxide (NiO-MoO_3), nickel oxide and tungsten trioxide (NiO-WO_3), and cobalt oxide and molybdenum trioxide (CoO-MoO_3), all on alumina (Al_2O_3) support materials. These catalysts are identified in this report as Ni-Mo-Al, Ni-W-Al, and Co-Mo-Al, respectively. In general, the active life of the catalysts in industry ranges from 6 months to 6 years. The catalysts are deactivated or poisoned by the deposition of sulfur, carbon, and metal impurities. In some cases the metals associated with the waste materials can be recovered from the deactivated catalysts once regeneration is no longer feasible. Current commercial recycling operations emphasize only Mo, V, and W recovery and suggest known technology for Ni and Co recovery. The U.S. Bureau of Mines dealt with deactivated catalysts to recover all of the critical metals, including Ni and Co.

Initial Bureau research screened various approaches for recovery of critical metals from waste Ni-Mo-Al, Ni-W-Al, and Co-Mo-Al hydroprocessing catalysts $(2$-$3)$. These approaches were (1) anhydrous chlorination, (2) leaching with ammonium hydroxide-ammonium sulfate [NH_4OH-$(NH_4)_2SO_4$], sodium hydroxide ($NaOH$), or sulfuric acid (H_2SO_4), and (3) leaching with $NaOH$ followed by leaching the residue with H_2SO_4 (a two-step $NaOH$-H_2SO_4 leaching process). These tests showed that the anhydrous chlorination process and the $NaOH$ leach followed by a H_2SO_4 leach of the residue process were the most effective extraction approaches for recovering critical metals from the three types of waste hydroprocessing catalysts.

This report describes laboratory results of the anhydrous chlorination and the two-step $NaOH$-H_2SO_4 leaching processing schemes on various waste catalysts. Economic evaluations were made for both processes using the Ni-Mo-Al waste catalyst. Also reported are metal extraction results from Co-Mo-Al waste catalysts that contained impurities such as As or Ni and V.

MATERIALS

A Bureau contract with Inco Research & Development Center, Inc., included as tasks identifying waste catalysts types and providing various samples of waste hydroprocessing catalysts (1). Various approaches were evaluated for recovery of critical metals from the representative waste catalysts supplied through the contract. In 1982, the Bureau began research on Ni-Mo-Al, Ni-W-Al, and Co-Mo-Al waste hydroprocessing catalysts. Near the end of the project in 1986, a Co-Mo-Al waste catalyst contaminated with Ni and V was added to the study.

Chemical analyses and X-ray diffraction analyses of these waste catalysts are shown in table 1. Alumina was

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[4]Italic numbers in parentheses refer to items in the list of references preceding the appendix at the end of this report.

Table 1.–Chemical analyses of waste catalysts, weight percent

(X-ray diffraction identified eta alumina crystalline phase for all catalysts)

Waste catalyst	Metal						Nonmetal			
	Ni	Co	Mo	Al	Fe	Si	C	S	P	H_2O
Ni-Mo-Al:										
Sample A	1.7	0.01	8.9	29.6	0.5	0.1	6.7	5.7	1.1	8.5
Sample B	2.0	.02	10.1	31.2	.2	.2	1.6	.4	1.1	8.3
Ni-W-Al: Sample C[1]	3.4	.05	NAp	33.8	.5	.1	1.0	.3	.05	5.0
Co-Mo-Al:										
Sample D[2]	1.1	1.7	5.9	31.1	9.0	.2	7.8	9.1	.5	2.8
Sample E[3]	.1	2.3	6.9	30.4	.7	2.5	1.5	2.6	.03	7.4
Sample F[4]	3.0	1.4	4.6	21.2	.3	.2	20.1	10.1	.02	1.5

NAp   Not applicable.
[1]Contains 13.1 wt pct W.
[2]Contains 2.2 wt pct As, further identified as used in high-temperature oil shale treatment; Fe_9S_{10} crystalline phase identified also.
[3]Contains no As, heat-treated waste.
[4]Contains 9.4 wt pct V.

the only crystalline phase identified by X-ray diffraction for most of these waste hydroprocessing catalysts. However, pyrrhotite (Fe_9S_{10}) was identified in one of the Co-Mo-Al waste hydroprocessing catalysts. Metal contaminants in the final recovery products may include Al, Fe, Si, P, and As. The waste hydroprocessing catalysts contained about 30 wt pct Al and less than 1.1 wt pct Fe, Si, and P. However, one of the Co-Mo-Al catalysts contained 9 wt pct Fe and another contained 2.5 wt pct Si. Half of the spent catalysts received contained over 6 wt pct C, and the other half contained less than 2 wt pct C.

The bulk densities and particle sizes of these waste hydroprocessing catalysts were determined on the as-received samples (table 2). The particle sizes of Ni-Mo-Al and Ni-W-Al ranged from minus 10 mesh to plus 100 mesh, while particle sizes of Co-Mo-Al ranged from minus 4 mesh to plus 28 mesh. Of these waste catalysts, Ni-W-Al had the lowest bulk density.

Table 2.–Bulk density and particle size of waste catalysts

Waste catalyst	Bulk density, g/cm^3	Size Tyler mesh	wt pct
Ni-Mo-Al:			
Sample A	1.06	-10, +100	92.0
		-100	8.0
Sample B	.89	-10, +100	97.2
		-100	2.8
Ni-W-Al: Sample C[1] .	.66	-10, +100	99.0
		-100	1.0
Co-Mo-Al:			
Sample D[2]	.74	-8, +20	99.4
		-20	.6
Sample E[3]	.85	-4, +10	100.0
Sample F[4]	1.10	-10, +28	100.0

[1]Contains 13.1 wt pct W.
[2]Contains 2.2 wt pct As.
[3]Contains no As.
[4]Contains 9.4 wt pct V.

PROCEDURES AND EQUIPMENT

ANHYDROUS CHLORINATION PROCESS

Chemical Reactions

The major chemical reaction equations were formulated for the processing of the waste Ni-Mo-Al, Ni-W-Al, and Co-Mo-Al catalysts by the anhydrous chlorination process. Examples of the equations for processing the Ni-Mo-Al catalyst are shown below:

Chlorination:
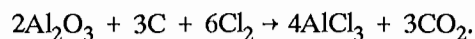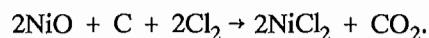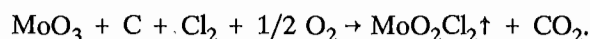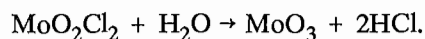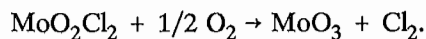
$$MoO_3 + C + Cl_2 + 1/2\ O_2 \rightarrow MoO_2Cl_2\uparrow + CO_2.$$

$$2NiO + C + 2Cl_2 \rightarrow 2NiCl_2 + CO_2.$$

$$2Al_2O_3 + 3C + 6Cl_2 \rightarrow 4AlCl_3 + 3CO_2.$$

Hydrolysis:

$$MoO_2Cl_2 + H_2O \rightarrow MoO_3 + 2HCl.$$

Calcination:

$$MoO_2Cl_2 + 1/2\ O_2 \rightarrow MoO_3 + Cl_2.$$

Water leaching:

$$AlCl_3 \rightarrow Al^{3+} + 3Cl^-.$$

$$NiCl_2 \rightarrow Ni^{2+} + 2Cl^-.$$

Purification:

$$AlCl_3 + 3NH_4OH \rightarrow Al(OH)_3\downarrow + 3NH_4Cl.$$

$$NiCl_2 + 2NH_4OH \rightarrow Ni(OH)_2\downarrow + 2NH_4Cl.$$

$$Ni(OH)_2 + 4NH_4OH + 2NH_4Cl$$

$$\rightarrow Ni(NH_3)_6Cl_2 + 6H_2O.$$

Solvent extraction:

$$Ni(NH_3)_6Cl_2 + 2RH + 4H_2O \rightarrow NiR_2 + 4NH_4OH$$

$$+ 2NH_4Cl\ (extraction).$$

$$NiR_2 + 2HCl \rightarrow NiCl_2 + 2RH\ (stripping).$$

Precipitation:

$$Ni(NH_3)_6Cl_2 + Na_2S \rightarrow NiS\downarrow + 2NaCl + 6NH_3.$$
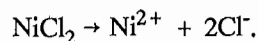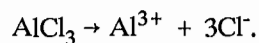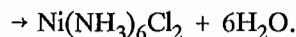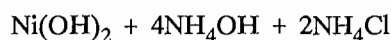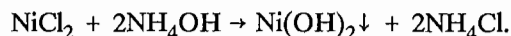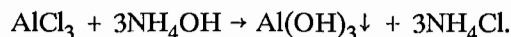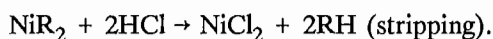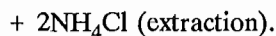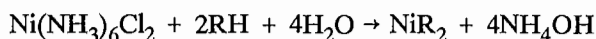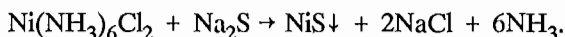
Chlorination

The chlorination studies were carried out in a batch fluidized-bed reactor, a 1.25-in-diam by 48-in-long tube made of Vycor[5] heat-resistant glass, to extract the metals as chlorides. A coarse quartz frit was used as a gas distributor. A Chromel-Alumel alloy thermocouple was submerged into the catalyst bed for measuring temperature.

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

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The bed was expanded from about 3 in high to about 4 in high during chlorination. The chlorinator was connected to a primary condenser and receiver, from there to a secondary condenser and receiver, and then to the exhaust outlet (fig. 1). The exhaust outlet was connected to a bubbler containing H_2SO_4 to prevent backflow of air into the reactor.

Waste Ni-Mo-Al, Ni-W-Al, and Co-Mo-Al catalyst charges were chlorinated. Immediately prior to chlorination, the waste catalysts were roasted at 400° C for 30 min with 300 mL/min N_2 to remove moisture and some sulfur. The most effective chlorination process parameters were determined for these catalysts in the 400° to 600° C temperature range, and from 30 min to 120 min, with Cl_2 plus N_2 or Cl_2 plus other gases (N_2, air, CO, and CO_2). Chlorination of metal oxide requires a reductant such as C or CO. Therefore, waste catalysts containing more than 6.7 wt pct C were chlorinated with only Cl_2 plus N_2 or Cl_2 plus N_2 and air; other waste catalysts were chlorinated with Cl_2 plus N_2 and CO or Cl_2 plus N_2, CO, and CO_2. A 25- or 50-g catalyst charge was used for the chlorination. The flow rates for Cl_2, air, CO, and CO_2 were varied from 30 to 100 mL/min, and the flow rate for N_2 was varied from 200 to 900 mL/min.

Prior to chlorination the transfer lines and both condensers were heated and maintained at 200° C during the N_2 roasting. The waste catalyst in the reactor was heated from the roast temperature to the chlorination temperature, and Cl_2 was passed over the heated charge. Most of the volatile chloride products [molybdenum oxychloride (MoO_2Cl_2) and tungsten oxychloride (WO_2Cl_2)] were condensed in the primary receiver, and the remainder were condensed in the secondary receiver. After the chlorination was completed, the volatile chlorides were washed out of both receivers, both condensers, and the transfer lines with water, and combined into one product (volatile-chloride slurry).

For obtaining the measure of metal extraction during chlorination of the waste catalysts, the chlorinated spent charge was diluted with water to a 15-wt-pct slurry and leached for 1 h at 100° C. The hydrated volatile-chloride slurry and the water-leached spent-charge slurry were vacuum filtered separately. Both filtrates were cooled to room temperature, the volumes were measured, and aliquots were collected for chemical analyses. The solids from leaching the volatile chlorides and the insoluble spent charge were dried at 105° C for 16 h. Both dried solids were ground to minus 60 mesh prior to analyses. The metal extraction was calculated using the equation:

Metal extraction, wt pct

$$= \left(\frac{\text{total metal wt - metal wt in leached spent charge}}{\text{total metal wt}} \right) \times 100,$$

where

total metal wt = metal in volatile product (wt of metal in aqueous + wt of metal in solid) + metal in spent charge (wt of metal in aqueous + wt of metal in solid).

Hydrolysis or Calcination of Volatile Chlorides

Two methods, hydrolysis and calcination, were evaluated for recovering metal values from the volatile chloride products generated during chlorination of the waste hydroprocessing catalysts.

The Mo-containing chlorides from Ni-Mo-Al and Co-Mo-Al catalysts were hydrolyzed in water at 100° C for 1 h. The W-containing chlorides obtained from the Ni-W-Al catalyst were hydrolyzed at 20° C for 1 h. The hydrolyzed products were vacuum filtered, the filtrate volume was measured, and an aliquot was collected for chemical analyses. The filtered solid was dried at 105° C for 16 h and then weighed and sampled.

Metal recovery by hydrolysis, wt pct

$$= \left(\frac{\text{metal wt in solid}}{\text{metal wt in solid + metal wt in liquid}} \right) \times 100$$

or

$$\left(\frac{\text{metal wt in solid}}{\text{metal wt in feed}} \right) \times 100.$$

The alternative approach was to calcine the volatile chlorides for 2 h at 300° C in an alumina crucible in an electric muffle furnace. The calcined powder was weighed and submitted for analyses. Analytical values were used to calculate metal recovery values and to obtain the purity of products. Metal recovery was calculated using the following equation:

Metal recovery by calcination, wt pct

$$= \left(\frac{\text{metal wt in calcined powder}}{\text{metal wt in feed}} \right) \times 100.$$

Water Leaching of Chlorinated Charge and Subsequent Processing

The spent charge from the chlorination process was leached at 100° C for 1 h with 15 wt pct solids to recover Ni and Co. Accumulated spent charges were used to prepare 400- to 1,500-mL batches of leach solution for purification, solvent extraction, and precipitation tests. The vacuum-filtered leach solution was purified by precipitating Al, Fe, Si, and P by adjusting pH from 3.5 to 5 or 10 with a solution containing 100 g/L NH_4OH and 100 g/L NH_4Cl (ammonium chloride). This purification mixture was held for 1 h at 80° C and then filtered. The Ni and Co remained in the purified solution as ammine complexes.

The Ni and Co were recovered from the purified solution either by solvent extraction of Ni with 10 vol pct LIX 64N, an organic extractant, or by precipitation of Ni or Co as a sulfide. Solvent extraction of the Ni from the purified solution was accomplished with 30-min shakeout tests at room temperature with 10 vol pct LIX 64N in Kermac 470B, an organic solvent. Nickel sulfide (NiS) and cobalt sulfide (CoS) were precipitated with 50 g/L $Na_2S \cdot 9H_2O$ (sodium sulfide) while the solutions were heated at 100° C for 1 h. The appropriate recovery approach can be selected based on market prices of Ni and Co.

Secondary condenser

Primary condenser

Secondary receiver

Exhaust outlet

Deentrainment section

Heating elements

Furnace

Preheating furnace

Primary receiver

Ice bath

Cl$_2$ and other gases

Fluidized-bed chlorinator

Metal chloride collector

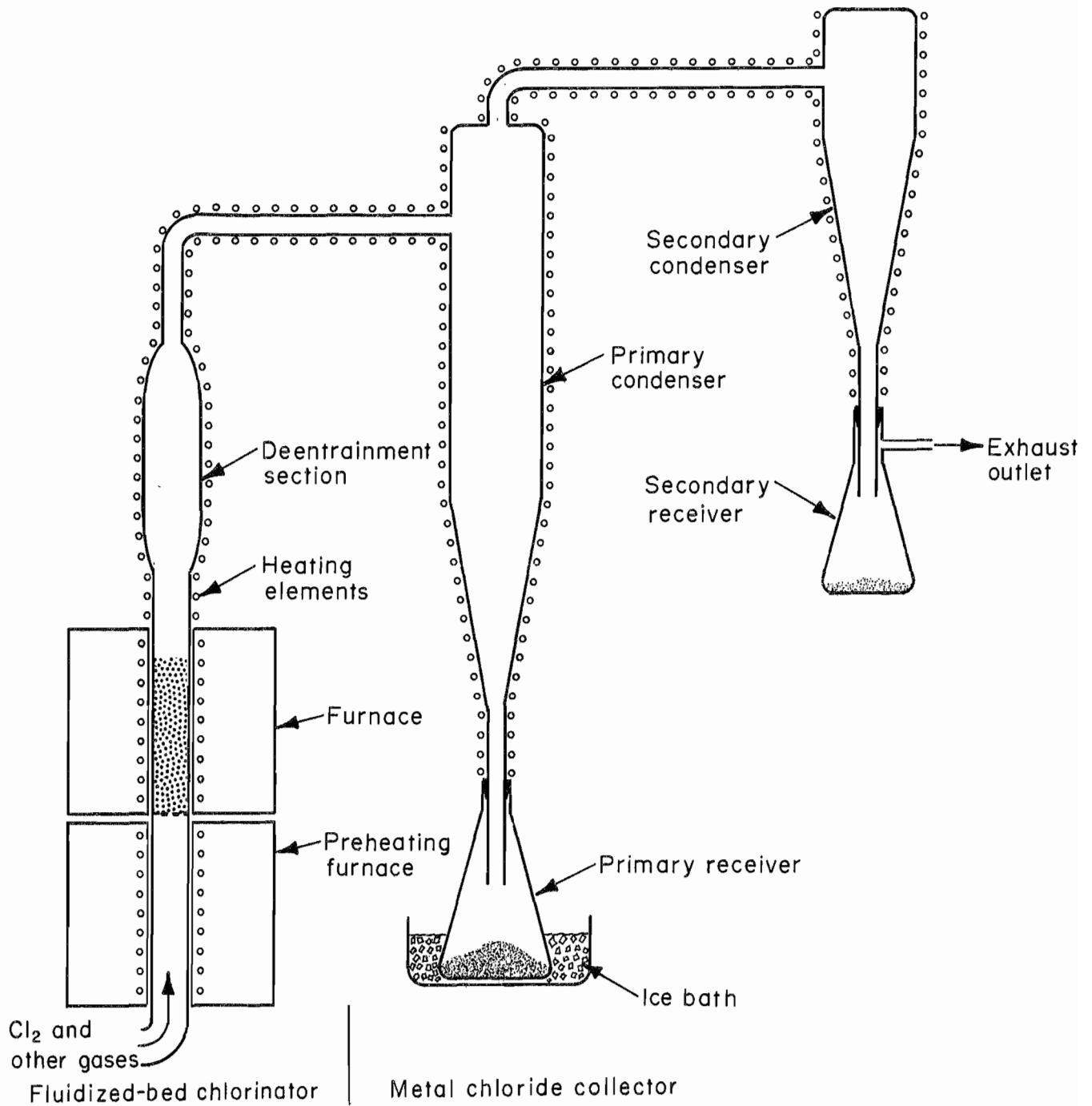Figure 1.–Apparatus for chlorination of waste catalysts.

TWO-STEP NaOH-H$_2$SO$_4$ LEACHING PROCESS

Chemical Reactions

Equations were formulated for processing waste Ni-Mo-Al, Ni-W-Al, and Co-Mo-Al hydroprocessing catalysts by the two-step NaOH-H$_2$SO$_4$ leaching process. The reactions involved in the two-step leaching process of the waste Ni-Mo-Al hydroprocessing catalyst may be represented as

Caustic leaching of Ni-Mo-Al catalyst:

$$MoO_3 + 2NaOH \rightarrow Na_2MoO_4 + H_2O.$$

$$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O.$$
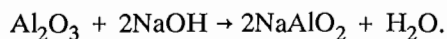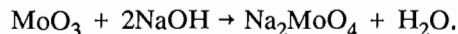
Solvent extraction of Mo from NaOH leach filtrate:

$$Na_2MoO_4 + 2R_3NR'Cl \rightarrow (R_3NR')_2MoO_4 + 2NaCl$$

(extraction).

$$(R_3NR')_2MoO_4 + 2NH_4Cl \rightarrow (NH_4)_2MoO_4$$

$$+ 2R_3NR'Cl \text{ (stripping).}$$
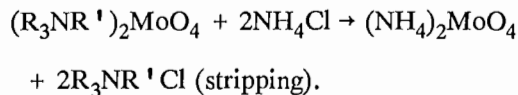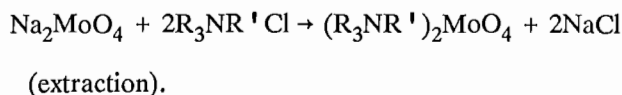
Precipitation of calcium molybdate (CaMoO$_4$) from strip solution:

$$(NH_4)_2MoO_4 + CaCl_2 \rightarrow CaMoO_4\downarrow + 2NH_4Cl.$$
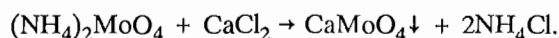
Precipitation of hydrous alumina [Al(OH)$_3$] from raffinate:

$$2NaAlO_2 + 4H_2O \rightarrow 2Al(OH)_3\downarrow + 2NaOH.$$
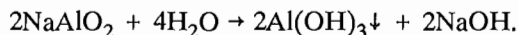
Acid leaching of Al-Ni from caustic leach residue:

$$NiO + H_2SO_4 \rightarrow NiSO_4 + H_2O.$$

$$Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O.$$
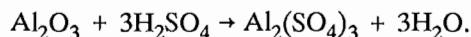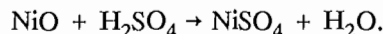
Purification of acid leaching filtrate:

$$Al_2(SO_4)_3 + 6NH_4OH \rightarrow 2Al(OH)_3\downarrow + 3(NH_4)_2SO_4.$$

$$NiSO_4 + 2NH_4OH \rightarrow Ni(OH)_2 + (NH_4)_2SO_4.$$

$$Ni(OH)_2 + 4NH_4OH + (NH_4)_2SO_4 \rightarrow Ni(NH_3)_6SO_4$$

$$+ 6H_2O.$$
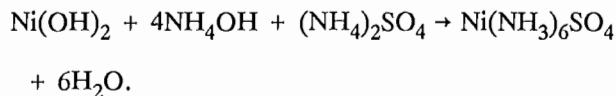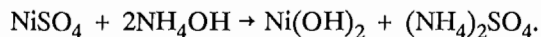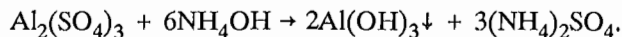
Solvent extraction of Ni from purified filtrate:

$$Ni(NH_3)_6SO_4 + 2RH + 4H_2O \rightarrow NiR_2 + 4NH_4OH$$

$$+ (NH_4)_2SO_4 \text{ (extraction).}$$

$$NiR_2 + H_2SO_4 \rightarrow NiSO_4 + 2RH \text{ (stripping).}$$
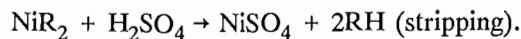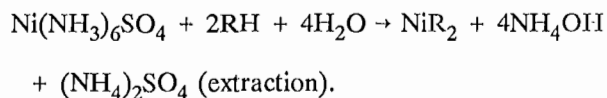
Precipitation of NiS from purified filtrate:

$$Ni(NH_3)_6SO_4 + Na_2S + 6H_2O \rightarrow NiS\downarrow + Na_2SO_4$$

$$+ 6NH_4OH.$$
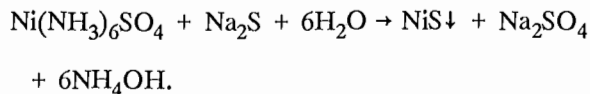
NaOH leaching

NaOH leaching was carried out either (1) at atmospheric pressure in a three-necked Pyrex heat-resistant glass flask equipped with a stirrer, a reflux condenser, and a thermometer or (2) at 150 psig of O$_2$ in a 2-L autoclave. Samples of 50- or 100-g of the fresh waste catalysts were leached with 1 L of 5-, 10-, 20-, 50-, 100-, 120-, or 150-g/L NaOH at 100° C for 2 h. These leach slurries were vacuum filtered, and the filtrate volumes were measured. The leach residues were dried at 105° C for 16 h and weighed. Representative samples of the leach solutions and dry residues were analyzed so metal extraction values and material balances could be calculated. The leach residues were saved for H$_2$SO$_4$ leaching to recover Ni or Co.

Solvent Extraction

Aliquat 336, an organic extractant, was selected for the separation and recovery of Mo (4) or W from caustic leach solutions. The laboratory evaluation of Aliquat 336 involved a series of shakeout tests in the 30° to 60° C temperature range to determine the loading capacity of the solvent for Mo or W. Equilibrium isotherms were constructed for Mo and W extraction from NaOH leach liquors with 10-, 15-, 20-, and 30-vol pct Aliquat 336 extractant plus 2 to 6 vol pct isodecanol in Kermac 470B. It was found that for the Aliquat 336 concentrations used, at least 2 vol pct isodecanol was necessary to inhibit third-phase formation.

The maximum loading capacity of Mo on the solvent was obtained by a "repeating contact" technique (5) with an organic-to-aqueous volume ratio (O:A) of 1:1. Steady-state conditions were achieved during shakeout tests with 2.5 min of contact time.

Molybdenum was extracted from a NaOH leach liquor by solvent extraction using 20 vol pct Aliquat 336 (O:A = 1:2). It was stripped from the loaded organic with a 25-g/L NH$_4$Cl solution (O:A = 2:1). Molybdenum was recovered as a CaMoO$_4$ precipitate by adding stoichiometric amounts of 700 g/L CaCl$_2$ (calcium chloride) to the NH$_4$Cl strip solution. The CaMoO$_4$ was washed with water and dried.

Tungsten-loaded Aliquat 336 organic phase was stripped with 7-wt-pct NH$_4$OH to provide a W-pregnant solution. Tungsten was recovered as ammonium paratungstate [(NH$_4$)$_{10}$W$_{12}$O$_{41}$] by evaporating NH$_4$OH and water at 70° C from the W-strip solution.

H₂SO₄ Leaching and Subsequent Processing

H_2SO_4 leaching of the NaOH leach residue was also done in the three-necked flask equipped with a stirrer, a reflux condenser, and a thermometer. The NaOH leach residues were leached with H_2SO_4 for 1 h at 100° C and at atmospheric pressure. The volumes of the vacuum-filtered leach solutions were measured, and the residue was dried for 16 h at 105° C. Representative samples of the leach solutions and dried residues were analyzed for metal content. The filtered leach solution was purified by precipitation of Al, Fe, Si, and P in a flask equipped with a reflux condenser by adding a solution containing 100 g/L NH_4OH and 300 g/L $(NH_4)_2SO_4$, and then maintaining the temperature at 80° C for 1 h.

The Ni was recovered by solvent extraction with fresh 10-vol-pct LIX 64N at pH 10 and stripped with H_2SO_4, followed by electrowinning the metal from the strip solution. The extraction and stripping tests were conducted in one stage at ambient temperature for 30 min. Alternatively, Ni and Co were recovered by precipitation of NiS and CoS with a 50-g/L $Na_2S \cdot 9H_2O$ solution. This mixture was boiled for 1 h to complete the precipitation at pH 5. Precipitates of CoS or NiS were filtered, washed, dried, and weighed.

RESULTS AND DISCUSSION

ANHYDROUS CHLORINATION PROCESS

A total processing scheme was devised for recovering metals from waste hydroprocessing catalysts by anhydrous chlorination. An example of processing the waste Ni-Mo-Al hydroprocessing catalyst (sample A) is shown in figure 2. The waste catalyst was roasted to remove moisture and some sulfur and was then chlorinated. During chlorination, the volatile MoO_2Cl_2 was condensed in the condensers while the relatively nonvolatile chlorides of Ni, Al, and the impurity metals remained in the chlorination spent charge. The MoO_3 was recovered by hydrolysis of the MoO_2Cl_2. The hydrochloric acid (HCl) generated by hydrolysis can be neutralized with lime. The remaining nonvolatile residual chlorides were leached with water and filtered. The filtrate was purified by addition of a solution containing NH_4OH and NH_4Cl to precipitate Al and other impurities at either pH 5 or 10. The Ni metal was recovered from the purified pH 10 solution by solvent extraction with LIX 64N solution followed by electrowinning of Ni from the strip solution. In an alternative approach, the Ni in the pH 5 purified solution was recovered by precipitation of NiS with Na_2S. The major constituent in the water-leached residue was Al_2O_3. The hydrous alumina that precipitated during purification with NH_4OH-NH_4Cl was calcined at 600° C for 2 h to recover Al_2O_3.

The same processing scheme was applied to the waste Ni-W-Al and Co-Mo-Al hydroprocessing catalysts. However, since the waste Ni-W-Al and Co-Mo-Al catalysts (samples C and E) contained an insufficient amount of C, when they were chlorinated it was necessary to add CO, or CO plus CO_2, in place of air. These conditions produced WO_2Cl_2 or MoO_2Cl_2, which was hydrolyzed to produce WO_3 or MoO_3. The water-leach solution of the Ni-W-Al chlorination spent charge or the Co-Mo-Al chlorination spent charge was purified by adjusting the pH with NH_4OH-NH_4Cl solution.

Chlorination

Molybdenum or tungsten was recovered from these catalysts by chlorination to yield MoO_2Cl_2 or WO_2Cl_2, which was later converted to MoO_3 or WO_3 via hydrolysis or calcination.

Ni-Mo-Al

Chlorination processing parameters were determined for the waste Ni-Mo-Al catalyst. Chlorination at 450° C for 30 min with a suitable Cl_2-air-N_2 mixture was adequate to convert the Mo to MoO_2Cl_2. This was confirmed from the literature, which reported the formation of MoO_2Cl_2 when MoO_3 was chlorinated with Cl_2 plus a small amount of O_2 (6). Higher temperatures and longer chlorination times produced the unwanted water-soluble molybdenum pentachloride ($MoCl_5$). Chlorination progress was monitored visually by observing the color and flow of the volatile chloride products. MoO_2Cl_2 was yellow-white, WO_2Cl_2 was light yellow, and MCl_x (M = Mo or W, and x = 2, 3, 4, 5, or 6) was brown, red, or black depending on x. Fifty grams of the waste Ni-Mo-Al catalyst was chlorinated using air:Cl_2 ratios (mL/min to mL/min) of 0:120, 40:80, 60:60, and 80:40, plus 700 mL/min N_2 as a carrier gas. Chlorination with Cl_2 (120 mL/min) at 450° C for 30 min extracted 8 wt pct of the Al, while 4 wt pct of the Al was extracted with a 60:60 air:Cl_2 ratio. Results of the air:Cl_2 ratio tests indicated that the Ni, Mo, and Al extraction decreased slightly as the air:Cl_2 ratios were increased.

The Ni-Mo-Al catalyst was also chlorinated at 450° C for 30 min with air:Cl_2 ratios (mL/min to mL/min) ranging from 30:30 to 100:100 (fig. 3). The Mo chlorination increased rapidly as the gas flow rates increased from 30 mL/min to 60 mL/min, but increasing the individual gas flow rates above 60 mL/min produced insignificant increases in Mo chlorination. However, the amount of Ni and Al chlorides increased only very slightly when the Cl_2 and air flow rates were increased from 30 mL/min to 60 mL/min. So, Cl_2 and air flow rates of 60 mL/min were selected for chlorinating 50-g charges of the spent Ni-Mo-Al catalyst at 300 mL/min N_2. MoO_2Cl_2 was identified by X-ray diffraction as the only volatile chloride collected during chlorination tests that used equal flow rates of Cl_2 and air.
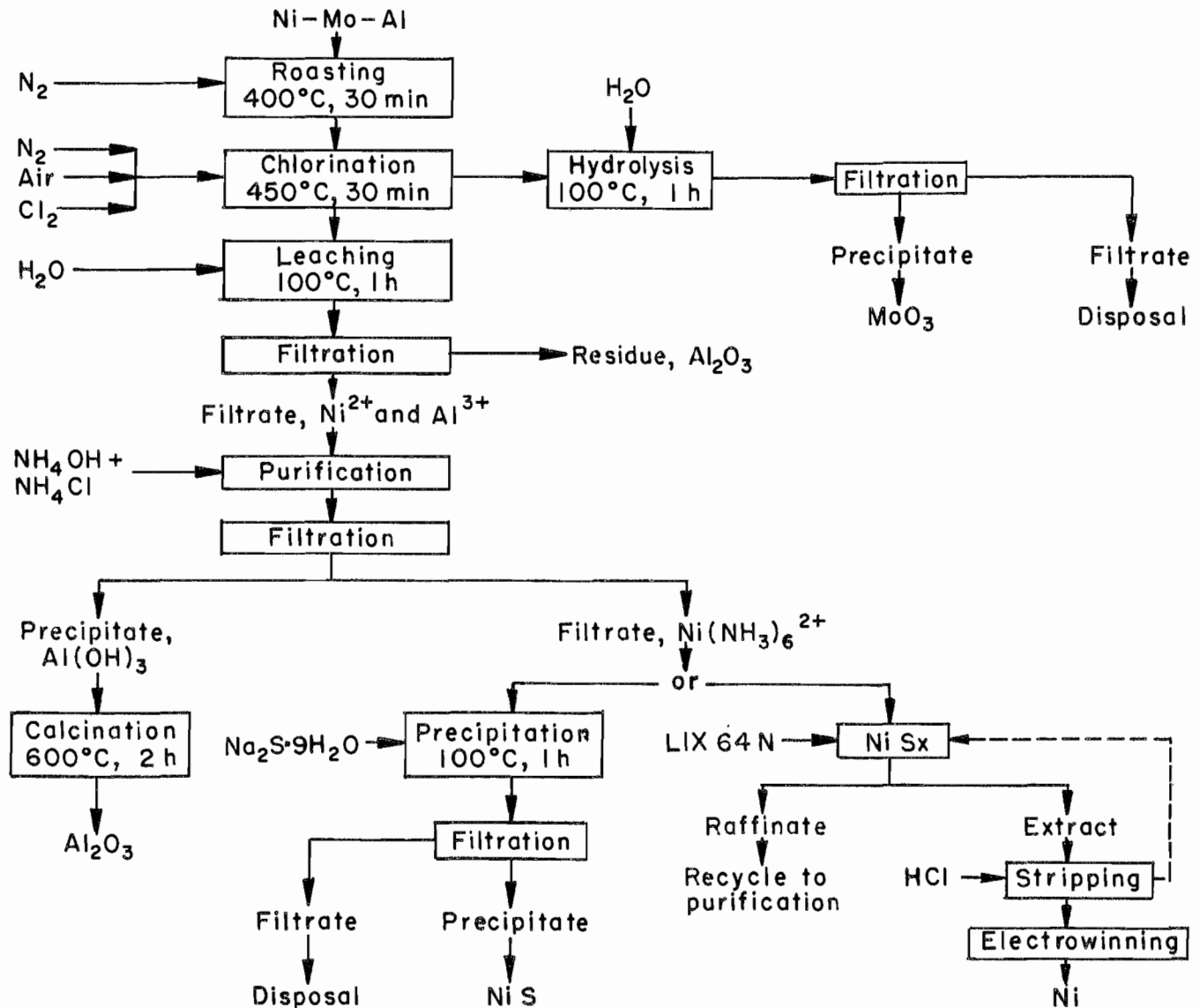
Ni–Mo–Al

Figure 2.–Flowsheet for anhydrous chlorination approach for waste Ni-Mo-Al catalyst.

Ni-W-Al

Chlorination processing parameters were also determined for the waste Ni-W-Al catalyst. Since this catalyst contained only 1.0 wt pct C, CO was added as a reductant. During chlorination, the oxygen content of the gas mixture was controlled by varying the CO_2:CO ratio. The waste Ni-W-Al catalyst was chlorinated at 450° C for 30 min with 50 mL/min Cl_2, 700 mL/min N_2, and CO_2:CO ratios ranging from 0:50 to 40:10 (mL/min to mL/min). The effect of varying CO_2:CO ratios on Ni, W, and Al extraction is shown in figure 4. These results indicate that W extraction decreased as the CO_2:CO ratio was increased and diminished to almost zero at a CO_2:CO ratio of 40:10. The Al extraction was small in all cases and decreased slightly when the CO_2:CO ratios were increased. However, the Ni

extraction dropped from more than 70 wt pct to less than 50 wt pct when the CO_2:CO ratio was increased from 0:50 to 40:10.

The Ni-W-Al chlorination was also studied at Cl_2:CO flow rate ratios ranging from 30:30 to 100:100 (mL/min to mL/min). The temperature, time, and N_2 flow rates were the same as for the previous chlorination test series at various CO_2:CO ratios. Results (fig. 5) indicate that Ni and W extraction increased rapidly as individual Cl_2 and CO flow rates were increased from 30 to 50 mL/min and remained almost constant at higher flow rates. The Al extraction increased from 2 wt pct at 30 mL/min each of Cl_2 and CO to 5 wt pct at 100 mL/min each of Cl_2 and CO. The Cl_2 and CO flow rates of 50 mL/min were selected for chlorinating 25-g charges of the Ni-W-Al catalyst at 300 mL/min N_2. The only volatile chloride

collected during the chlorination of the Ni-W-Al catalyst was identified as WO_2Cl_2.
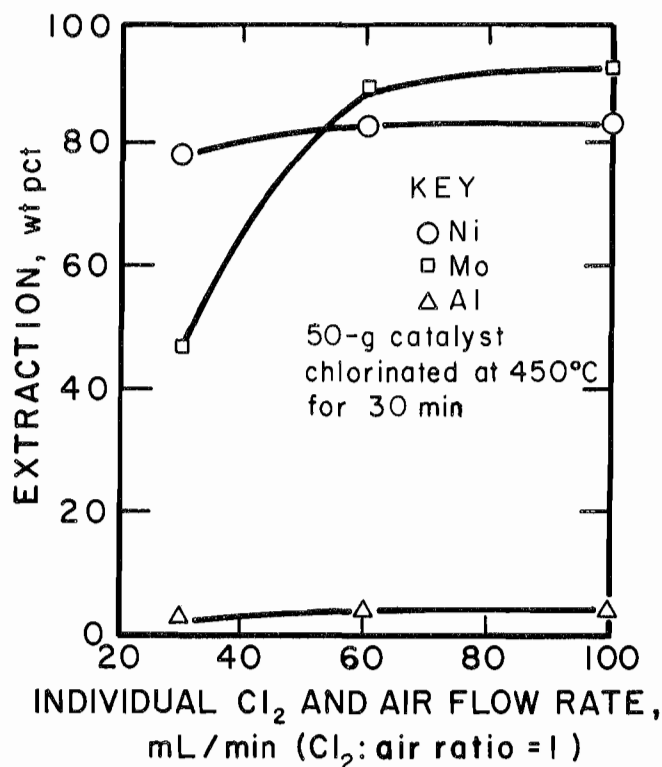
Figure 3.--Extraction of Ni, Mo, and Al from Ni-Mo-Al catalyst with Cl_2, N_2, and air (700 mL/min N_2).
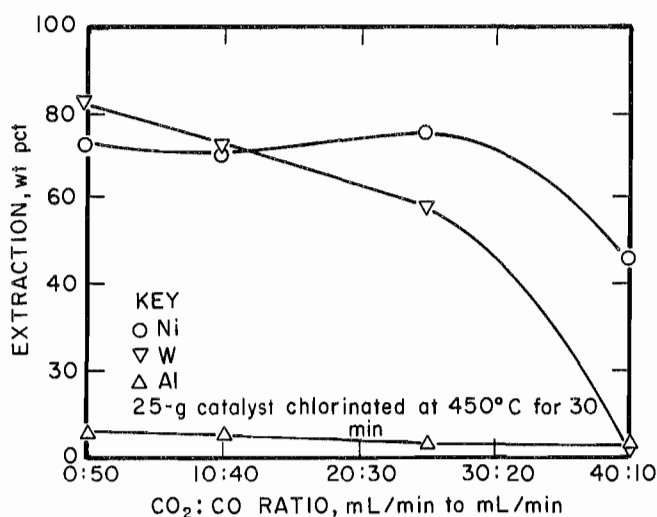
Figure 4.--Extraction of Ni, W, and Al from Ni-W-Al catalyst with Cl_2, N_2, and CO_2:CO (50 mL/min Cl_2 and 700 mL/min N_2).

Ni-Mo-Al and Ni-W-Al

Chlorination of the waste Ni-Mo-Al and Ni-W-Al catalysts in a fluidized bed was compared with chlorination of these catalysts in an expanded bed using lower N_2 flow rates to reduce the consumption of N_2. The expanded bed is defined as a condition in which the particles of catalyst move slightly apart and about in a restricted region. The waste Ni-Mo-Al catalyst was chlorinated at 450° C for 60 min with 60 mL/min Cl_2, 60 mL/min air, and 300 mL/min N_2. The waste Ni-W-Al catalyst was chlorinated at 450° C for 60 min with 50 mL/min Cl_2, 50 mL/min CO, and 300 mL/min N_2. The chlorination reaction ceased after about 30 min for both waste materials. The use of the extra 30 min (total 60 min) for chlorination was an attempt to maximize the metal extraction. Typical results for the fluidized-bed chlorination and the expanded-bed chlorination tests are summarized in table 3. Metal extraction increased when chlorination was performed in the expanded bed. The better extraction in the expanded bed could be attributed to a higher concentration of Cl_2 and/ or a longer chlorination time. After these tests, waste catalysts were chlorinated only in the expanded bed.

Co-Mo-Al

Three types of waste Co-Mo-Al catalysts (see table 1) were chlorinated in an expanded bed under conditions with or without CO. The Co-Mo-Al catalysts were (1) waste
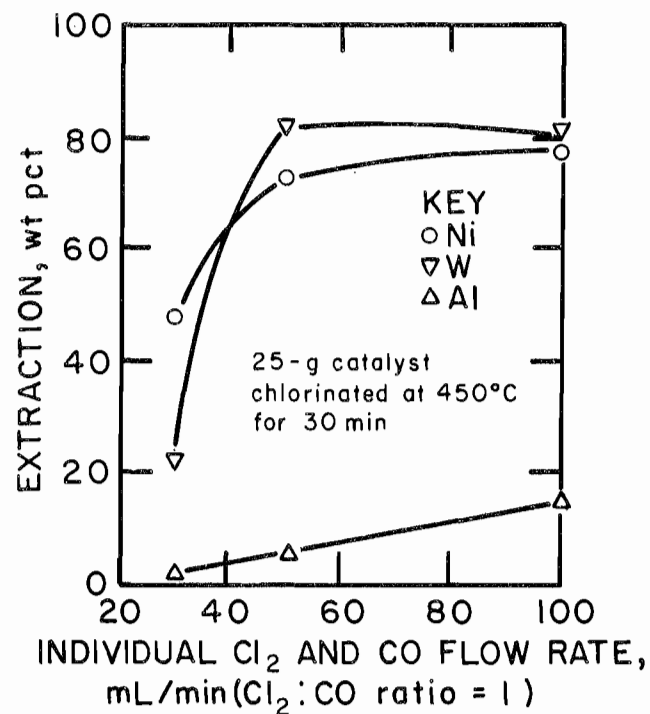
Figure 5.--Extraction of Ni, W, and Al from Ni-W-Al catalyst with Cl_2, N_2, and CO (700 mL/min N_2).

from high-temperature oil shale treatment (sample D), (2) heat-treated waste containing no As (sample E), and (3) waste contaminated with Ni and V (sample F). A 50 g sample of the As-containing waste catalyst (sample D) was chlorinated at 450° C for 1 h with 100 mL/min Cl_2 and 400 mL/min N_2. This resulted in the extraction of less than 50 wt pct of the Co and Mo. Another charge of this catalyst was chlorinated at 450° C for 1 h with 100 mL/min Cl_2, 100 mL/min CO, and 400 mL/min N_2. Extraction levels then increased to about 60 wt pct Co and 70 wt pct Mo. The second type of waste catalyst (sample E) was chlorinated at 450° C with the Cl_2-CO-N_2 gas mixture. This test resulted in extractions of 68 wt pct Co and 87 wt pct Mo. Fifty- and twenty-five-gram samples of the third waste catalyst (sample F) were chlorinated for 2 h at 600° C with 100 mL/min Cl_2 and 200 mL/min N_2. Chlorination of the 25-g sample resulted in the extraction of more than 94 wt pct of the Ni, Co, Mo, and V.

Chlorination data for the Co-Mo-Al catalysts are also summarized in table 3. These results indicate that the Co extraction was less than 70 wt pct for samples D and E, while Co extraction was over 90 wt pct for sample F, which contained Ni and V. The catalysts that had been used for high-temperature hydroprocessing (oil shale) or heat treated were very refractory and difficult to chlorinate. This could be attributed to formation of a stable cobaltous aluminate ($CoAl_2O_4$) compound. The third waste catalyst had not been heat treated. Acetone was used to dissolve oil from the third waste catalyst, which contained Ni and V. After the oil was removed, the catalyst was roasted at 300° C for 2 h with N_2 and chlorinated. Results indicate that anhydrous chlorination is technically feasible for metal extraction from waste Ni-Mo-Al, Ni-W-Al, and Co-Mo-Al catalysts that were not heat treated or were not used for high-temperature processing.

Hydrolysis or Calcination of Volatile Chlorides

Hydrolysis and calcination approaches were evaluated for recovering MoO_3 or WO_3 from volatile MoO_2Cl_2 or WO_2Cl_2 products from the chlorination of waste Ni-Mo-Al, Ni-W-Al, and Co-Mo-Al hydroprocessing catalysts. Five to ten grams of the collected volatile chlorides were used for hydrolysis or calcination studies. X-ray diffraction analysis identified only MoO_3 or WO_3 in the products from the hydrolysis or calcination tests. Recoveries of metal values and product impurities are reported in table 4.

Table 3.–Typical metal extraction from various catalysts by chlorination

Waste catalyst	Bed type	Wt, g	Flow rate, mL/min				Chlorination		Extraction, wt pct					
			Cl_2	Air	CO	N_2	Temp, °C	Time, min	Ni	Co	Mo	W	V	Al
Ni-Mo-Al:														
Sample A ..	Fluidized ...	50	60	60	0	700	450	30	83	NAp	89	NAp	NAp	4
Do.	Expanded ..	50	60	60	0	300	450	60	84	NAp	95	NAp	NAp	11
Ni-W-Al:														
Sample C[1] ..	Fluidized ...	25	50	0	50	700	450	30	73	NAp	NAp	82	NAp	5
Do.[1]	Expanded ..	25	50	0	50	300	450	60	79	NAp	NAp	98	NAp	27
Co-Mo-Al:														
Sample D[2] ..	. do	50	100	0	100	400	450	60	([3])	61	73	NAp	NAp	26
Sample E[4] ..	. do	50	100	0	100	400	450	30	([3])	68	87	NAp	NAp	13
Sample F[5] ..	. do	50	100	0	0	200	600	120	91	94	29	NAp	68	15
Do.[5]	. do	25	100	0	0	200	600	120	99	99	94	NAp	98	36

NAp Not applicable.
[1]Contains 13.1 wt pct W.
[2]Contains 2.2 wt pct As.
[3]Not analyzed.
[4]Contains no As.
[5]Contains 9.4 wt pct V.

Table 4.–Typical products recovered, purity, and impurity content by hydrolysis and calcination, weight percent

Waste catalyst and process	Recovery			Purity		Impurity content						
	Mo	W	Al	MoO_3	WO_3	Cl	Al	Fe	Si	Ni	Co	Pb
Ni-Mo-Al (sample A):												
Hydrolysis	84	NAp	28	96.6	NAp	0.03	0.03	0.5	0.05	0.04	NAp	NAp
Calcination	93	NAp	37	93.0	NAp	.6	2.7	.5	.05	.08	NAp	NAp
Ni-W-Al (sample C[1]):												
Hydrolysis	NAp	90	3	NAp	91.1	.8	1.7	1.0	.2	.04	NAp	NAp
Calcination	NAp	57	8	NAp	76.3	.7	9.4	1.2	1.1	.04	NAp	NAp
Co-Mo-Al (sample E[2]):												
Hydrolysis	65	NAp	4	91.4	NAp	.03	1.4	.6	.06	NAp	0.02	0.3
Calcination	NA	NAp	38	75.3	NAp	1.4	6.0	.9	.3	NAp	.04	.1

NA Not available.
NAp Not applicable.
[1]Contains 13.1 wt pct W.
[2]Contains no As.

Recovery of Mo by hydrolysis of the MoO_2Cl_2 ranged from 65 to 84 wt pct. Ninety weight percent of the W was recovered by hydrolysis of the WO_2Cl_2. Calcination of volatile oxychlorides from the chlorination of the Ni-Mo-Al catalyst yielded a 93-wt-pct recovery of Mo. However, only 57 wt pct of the W was recovered from the volatile oxychloride products from the Ni-W-Al waste catalyst. However, a calcination approach would be recommended, if an effective calcination approach can be developed, because Cl_2 can be more easily recycled.

Hydrolysis of oxychlorides produced by the chlorination of Mo catalysts yielded 91.4 to 96.6 wt pct purity of MoO_3 products, while calcination yielded lower purity 75.3 to 93.0 wt pct MoO_3 products. Hydrolysis of oxychlorides from the catalyst containing W yielded a 91.1-wt-pct WO_3 product, while calcination yielded a 76.3-wt-pct WO_3 product. Higher purity MoO_3 and WO_3 products were produced by hydrolysis than were produced by calcination. Also, oxides produced by hydrolysis had less Al contamination than the oxide products produced via calcination.

Water Leaching of Chlorinated Charge, Purification, and Solvent Extraction or Precipitation

Water Leaching

The spent chlorination charges of waste Ni-Mo-Al, Ni-W-Al, and Co-Mo-Al hydroprocessing catalysts were leached with water to extract the Ni or Co by dissolving unvolatilized nickel chloride ($NiCl_2$) or cobalt chloride ($CoCl_2$). Water leaching also dissolved some of the other impurity metal chlorides. The unadjusted pH of leach solutions was about 3.5. Typical chemical compositions of the water-leached, dried residues are shown in table 5. The residues contained 64 to 80 wt pct Al_2O_3. Before either Ni or Co was recovered from the residue leach solution, the impurities (Al, Fe, Si, and P) needed to be removed. Aluminum was the major impurity. Aluminum was separated from Ni or Co by precipitation with an NH_4OH-NH_4Cl solution. Using just NH_4OH coprecipitated Ni or Co with the Al, while the use of an NH_4OH-NH_4Cl solution produced a good separation of Ni or Co from Al.

A series of tests was made to investigate the effect of pH on the separation of Ni or Co from Al by adding an NH_4OH-NH_4Cl solution to the water-leach solution. Test data for the water-leach solutions of the chlorinated Ni-Mo-Al spent charges are plotted in figure 6. Up to 96 wt pct Al and 4 wt pct Ni were precipitated from the solutions at pH 5.4. Nearly 100 wt pct Al and 4 wt pct Ni were precipitated at pH 9.8. Data for the water-leach solutions of the chlorinated Co-Mo-Al spent charges are shown in figure 7. Results indicate that 80 wt pct Al is precipitated with 20 wt pct Co from the solutions at pH 5.2, and nearly 100 wt pct of the Al and Co are coprecipitated at pH 9.7. These tests show that Ni and Al in solution can be separated at about pH 5 or 10, and Co and Al can be separated only at about pH 5.
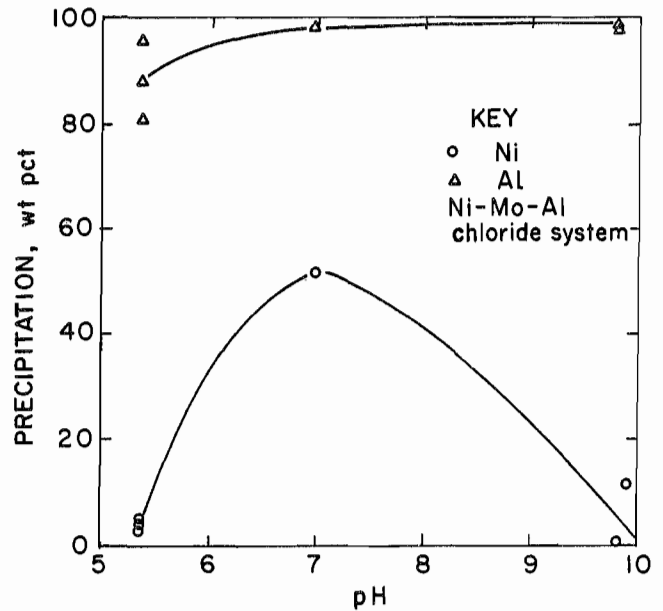
Figure 6.–Effect of pH on separation of Ni and Al from water leachate (chlorinated Ni-Mo-Al catalyst).

Table 5.–Chemical composition range for water-leached residues

(Chlorinated Ni-Mo-Al, Ni-W-Al, and Co-Mo-Al catalysts)

Component	wt pct	Component	wt pct
Al	33.6 -42.6	Fe	0.22-0.32
Al as Al_2O_3	63.5 -80.5	Si	.11-3.01
Ni or Co	.37- 1.35	P	.03-3.7
Mo or W	.16- 1.25		
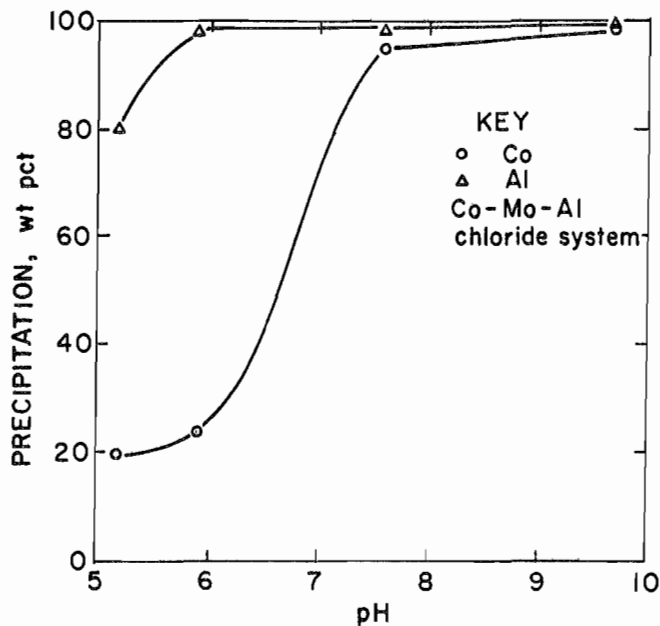
Figure 7.–Effect of pH on separation of Co and Al from water leachate (chlorinated Co-Mo-Al catalyst).

Purification

Purification tests were made to remove metal impurities, other than Al, from water-leach solutions of chlorination residues of the waste Ni-Mo-Al, Ni-W-Al, and Co-Mo-Al catalysts. Purification was accomplished by addition of an NH_4OH-NH_4Cl solution to the leach solution until the pH reached 5 or 10, depending upon the subsequent metal recovery approach. Precipitates of impurities obtained during purification of the leach liquor at pH 5 or 10 were calcined at 600° C for 2 h. This produced an 80-wt-pct Al_2O_3 product (table 6). This material can be either used for a refractory material or discarded.

Solvent Extraction

Solvent extraction was investigated for the recovery of Ni or Co from the purified leach solutions. Using triisooctylamine at pH 3 to extract and separate Ni and Co from these acid-chloride solutions could require eight mixer-settler stages (7-8). However, solvent extraction of Ni with LIX 64N from basic solutions requires only three stages (5). Recovering Ni or Co from acid-chloride solutions by solvent extraction does not appear to be economically feasible. Therefore, recovery of Ni from basic solutions was investigated using LIX 64N.

Water-leach solutions from spent Ni-Mo-Al and Ni-W-Al chlorinated charges were purified by adjusting solutions with NH_4OH-NH_4Cl to pH 10. Test data are shown in table 7. These highly purified solutions contained less than 0.01 g/L each of Mo or W, Al, Fe, Si, and P. A solvent extraction test using 10 vol pct LIX 64N in kerosene was made on the purified leach solution from the Ni-Mo-Al spent charge. The Ni-loaded LIX 64N was stripped with an electrolyte containing 89.6 g/L Ni and 3.7 g/L HCl. Test data are shown in table 8. The results show that over 99 wt pct of the Ni was extracted from the purified solution in one contact. More than 99 wt pct of the Ni was then stripped from the LIX 64N with one contact. The resultant strip solution contained 91.7 g/L Ni, 0.001 g/L Mo, 0.018 g/L Fe, and 0.002 g/L Si and was suitable for electrowinning (9).

Precipitation

As an alternative approach, Ni or Co was precipitated from the pH 5 purified solutions with stoichiometric amounts of Na_2S. The purified leach solutions contained less than 0.08 g/L each of Mo, W, Fe, Si, or P, and less than 1.1 g/L of Al, as shown in table 7. More than 98 wt pct of the Ni or Co was precipitated as a sulfide, leaving less than 0.03 g/L Ni or Co in solution. The dried sulfide precipitates can be processed in existing metal refineries to yield Ni or Co metal.

Table 6.–Typical chemical composition of calcined powder from precipitates obtained by pH 5 and pH 10 purification of water leachate

(Chlorinated Ni-Mo-Al catalyst)

Component	wt pct		Component	wt pct
Al_2O_3	80.1		Fe	1.6
Ni	NA		Si	.4
Mo	.1		P	2.1

NA   Not available.

Table 7.–Purification of water leachate by pH adjustment with NH₄OH-NH₄Cl solution

Metal	Solution, g/L		Precipitation,
	Leach	Purified	wt pct
	pH ADJUSTED TO 10[1]		
Ni	3.14 -5.25	2.07 -2.12	0.0-28.6
Mo or W	.02 - .08	.004 - .01	18.8-82.0
Al	1.90 -2.86	.001 - .005	99.6-99.9
Fe	.12 - .19	.0001	99.9
Si	.006- .05	.0001- .0003	92.1-99.6
P	.14	.008	90.7
	pH ADJUSTED TO 5[2]		
Ni or Co	2.73 -5.25	1.93 -4.66	4.8-20.3
Mo or W	.009- .08	.001 - .03	72.5-96.0
Al	1.79 -2.86	.20 -1.05	63.3-87.5
Fe	.10 - .19	.02 - .08	39.7-69.7
Si	.006- .13	.001 - .005	76.8-96.0
P	.14	.020	76.4

[1]Chlorinated Ni-Mo-Al and Ni-W-Al catalysts.
[2]Chlorinated Ni-Mo-Al, Ni-W-Al, and Co-Mo-Al catalysts.

Table 8.–Typical solvent extraction and stripping of Ni from purified pH 10 leachate (chlorinated Ni-Mo-Al catalyst)

Metal	Extraction[1]			Stripping[2]		
	Organic, g/L	Aqueous, g/L	Extraction, wt pct	Organic, g/L	Aqueous, g/L	Stripping, wt pct
Ni .	2.0000	0.008	99.6	0.064	91.7	99.9
Mo .	.0010	.010	9.1	.001	.001	50.0
Al ..	.0010	.004	20.0	.002	NA	92.0
Fe .	.0048	.0001	98.0	.009	.018	66.7
Si ..	.0020	.0008	71.4	.014	.002	12.5

NA   Not available.
[1]Extraction from pH 10 leachate.
[2]Stripped with an electrolyte containing 89.6 g/L Ni and 3.7 g/L HCl.

The most effective ways for recovering Ni and Co from aqueous leach liquors (from the chlorination residue) were by sulfide precipitation from the leach liquor adjusted to pH 5 or by solvent extraction of Ni from the leach liquor adjusted to pH 10, followed by electrowinning Ni from the strip solution. The solvent extraction approach is preferred only if prices of Ni and Co are high enough to make a profit.

TWO-STEP NaOH-H₂SO₄ LEACHING PROCESS

A processing scheme was devised for recovering metals from waste hydroprocessing catalysts by leaching with a NaOH solution followed by leaching the residue with H₂SO₄. An example of this processing scheme is shown in figure 8 for the waste Ni-Mo-Al hydroprocessing catalyst. The procedure consists of first leaching the waste catalyst with a 20-g/L NaOH solution at atmospheric pressure.

The NaOH leach solution extracted Mo and some Al, while the balance of the Al and the Ni remained in the residue with the other metal impurities. The Mo was extracted from the leach solution by solvent extraction with Aliquat 336.

Molybdenum was recovered from that strip solution by precipitation with CaCl₂. When the solvent extraction raffinate stood overnight, Al(OH)₃ precipitated. After filtering off the Al(OH)₃ precipitate, the filtrate can be recycled for further caustic leaching.

In the second step of the procedure, the NaOH leach residue was leached at atmospheric pressure with 100 g/L H₂SO₄ to extract Ni. The resulting solution was then purified by addition of NH₄OH and (NH₄)₂SO₄ to precipitate Al and other metal impurities at either pH 5 or 10. The precipitates obtained from this purification step were leached with water to separate (NH₄)₂SO₄ from Al(OH)₃ and other metal impurity precipitates. During this step, 100 mL H₂O was used for 70 g of precipitates. The (NH₄)₂SO₄ was dissolved from the precipitate and was recovered by evaporation and crystallization as a byproduct. The water insolubles were dried and calcined at 600° C for 2 h to recover Al₂O₃. Nickel was recovered from the purified pH 10 solution by solvent extraction followed by electrowinning Ni from the strip solution. As an alternative, Ni could be precipitated from the purified pH 5 solution with Na₂S.

This processing scheme can also be applied to waste Ni-W-Al and Co-Mo-Al catalysts. However, for the waste Co-Mo-Al catalyst, the acid leach solution can be purified only at pH 5. At pH 10, cobalt hydroxide [Co(OH)₂] precipitates from the solution.

NaOH Leaching

Ni-Mo-Al and Ni-W-Al

Processing parameters such as weight of catalyst charge and concentration of NaOH for the extraction of Mo, W, and Al from waste Ni-Mo-Al and Ni-W-Al hydroprocessing catalysts were evaluated at atmospheric pressure. Fifty-gram samples of the spent Ni-Mo-Al catalyst (sample B) were leached with 1 L of 5-, 10-, 20-, 100-, or 150-g/L NaOH solutions. Extraction values for leaching Ni, Mo, and Al with NaOH are shown in figure 9. Leaching 50 g of Ni-Mo-Al spent catalyst with 20 g/L NaOH resulted in extractions of 96 wt pct Mo, 34 wt pct Al, and 0.08 wt pct Ni. Doubling the amount of waste Ni-Mo-Al catalyst leached to 100 g while leaching with 20 g/L NaOH resulted in extractions of 91 wt pct Mo, 6.9 wt pct Al, and 0.08 wt pct Ni (table 9).
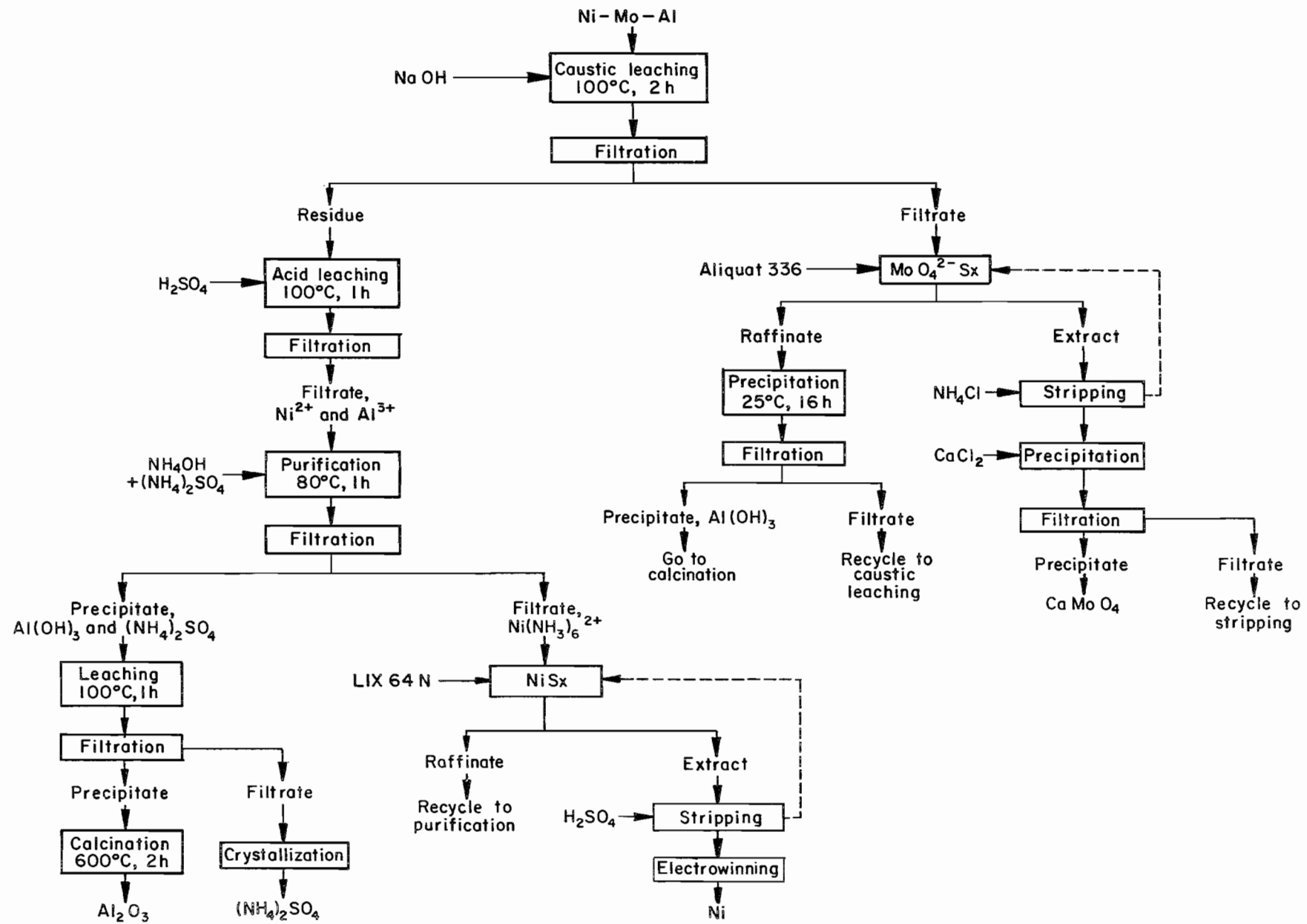
Figure 8.–Flowsheet for two-step NaOH-H$_2$SO$_4$ leach approach for waste Ni-Mo-Al catalyst.

Table 9.–Metal extraction by leaching of various waste hydroprocessing catalysts with NaOH solutions

Waste catalyst	Wt, g	Leaching		Extraction, wt pct					
		NaOH, g/L	Pressure	Ni	Co	Mo	W	V	Al
Ni-Mo-Al: Sample B	100	20	Atmospheric	0.08	NAp	91	NAp	NAp	6.9
Ni-W-Al: Sample C[1]	100	20	. do	.06	NAp	NAp	86	NAp	16
Co-Mo-Al:									
Sample D[2]	50	100	. do	NAp	0.08	46	NAp	NAp	39
Do.[2]	50	20	150 psig O₂	NAp	.08	86	NAp	NAp	26
Sample E[3]	100	100	Atmospheric	NAp	.08	86	NAp	NAp	25
Do.[3]	50	20	150 psig O₂	NAp	.08	91	NAp	NAp	22
Sample F[4]	50	100	Atmospheric	NA	NA	20	NAp	40	NA
Do.[4]	50	100	150 psig O₂	.2	.3	81	NAp	86	95

NA   Not available.
NAp   Not applicable.
[1]Contains 13.1 wt pct W.
[2]Contains 2.2 wt pct As.
[3]Contains no As.
[4]Contains 9.4 wt pct V.

Fifty-gram samples of the waste Ni-W-Al catalyst were leached with 5-, 10-, or 20-g/L NaOH solutions. Extraction values for Ni, W, and Al are plotted in figure 10. The best results were obtained by leaching 50-g samples of the spent Ni-W-Al catalyst with 20 g/L NaOH to produce extractions of 91 wt pct W, 25 wt pct Al, and 0.06 wt pct Ni. Increasing the amount of spent Ni-W-Al catalyst from 50 to 100 g while leaching with 20 g/L NaOH resulted in 86 wt pct W, 16 wt pct Al, and 0.06 wt pct Ni extractions (table 9).

When leaching with 20-g/L NaOH, Al extraction decreased as the amount of waste catalyst used was increased from 50 to 100 g. The Mo or W extractions were more than 86 wt pct.
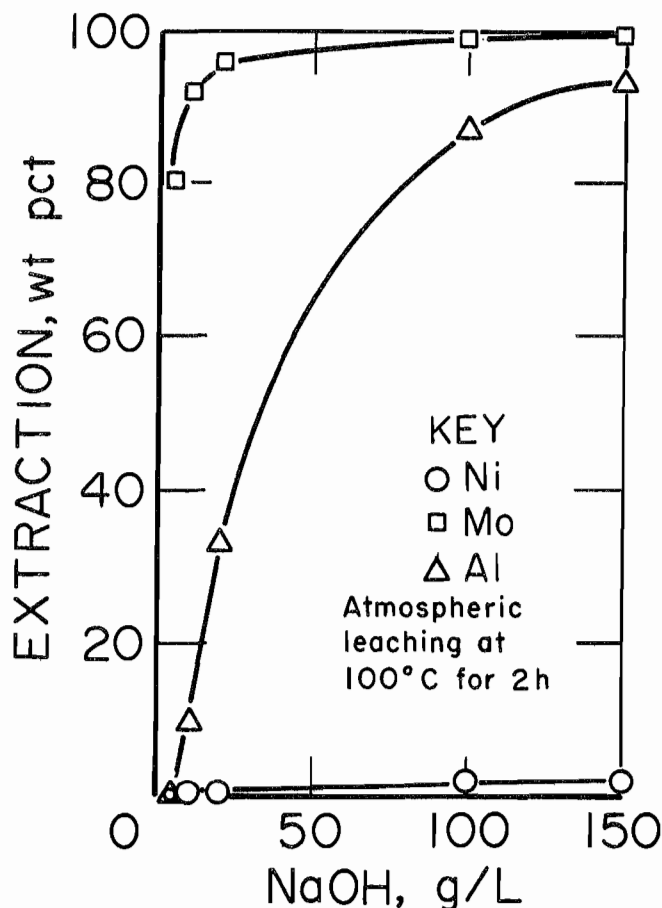
Figure 9.–Extraction of Ni, Mo, and Al from Ni-Mo-Al catalyst with NaOH (50 g Ni-Mo-Al to 1 L of NaOH solution).
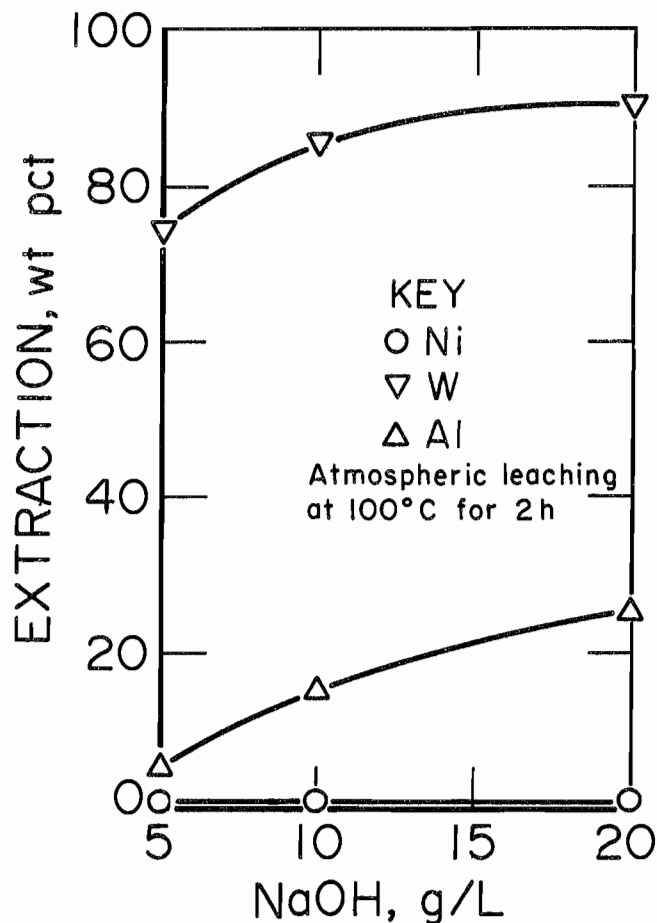
Figure 10.–Extraction of Ni, W, and Al from Ni-W-Al catalyst with NaOH (50 g Ni-W-Al to 1 L of NaOH solution).

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Co-Mo-Al

Processing parameters were evaluated for the extraction of Mo and Al from three types of waste Co-Mo-Al catalysts by NaOH leaching at atmospheric pressure or at 150 psig O_2. The O_2 could help to remove sulfureous or carbonaceous matter. Tests were conducted at 100° C for 2 h. One-hundred-gram samples of a waste Co-Mo-Al catalyst (sample E) were leached with 50-, 100-, 120-, or 150-g/L NaOH at atmospheric pressure (fig. 11). The leach solutions must contain more than 50 g/L of NaOH to extract more than 80 wt pct of the Mo. Samples of the waste Co-Mo-Al catalyst were also leached with 10-, 20-, 50-, or 100-g/L NaOH solutions at 150 psig O_2. Results are shown in figure 12. Leaching 50-g samples of waste Co-Mo-Al catalyst with 20 g/L NaOH at 150 psig O_2 resulted in extractions of 91 wt pct Mo, 22 wt pct Al, and 0.08 wt pct Co (table 9).

The waste Co-Mo-Al catalyst containing As (sample D) and the waste Co-Mo-Al catalyst containing Ni and V (sample F) were leached with 100 g/L NaOH at atmospheric pressure. This resulted in Mo and V extractions of less than 50 wt pct. However, when the Co-Mo-Al catalyst containing As was leached with 20 g/L NaOH at 150 psig O_2, Mo extraction exceeded 80 wt pct. When the waste Co-Mo-Al catalyst containing Ni and V was leached with 100 g/L NaOH at 150 psig O_2, Mo and V extractions of over 80 wt pct were obtained (table 9). It appears that these waste Co-Mo-Al catalysts could be hydrophobic, so they need to be leached under pressure to enhance the metal dissolution during leaching.

Solvent Extraction

Several Mo extraction isotherms were prepared using 20 vol pct and 30 vol pct Aliquat 336 for extraction of Mo from 20-g/L NaOH leach liquors from a Ni-Mo-Al catalyst (fig. 13). The interpretation of these isotherms indicated that 20 vol pct Aliquat 336 plus 2 vol pct isodecanol in Kermac 470B at 40° C were suitable parameters for extracting Mo from the leach liquor. Molybdenum can be extracted from the 6.6-g/L leach liquor in three stages with 20 vol pct Aliquat 336 at 40° C to yield an 88-wt-pct Mo extraction. In two stripping stages, a 25-g/L NH_4Cl solution stripped 95 wt pct of the Mo from the loaded Aliquat. Over 99 wt pct of the Mo was precipitated as $CaMoO_4$ from the NH_4Cl strip solution by adding a stoichiometric amount of $CaCl_2$.

Various types of NaOH leach solutions from waste Co-Mo-Al catalysts (samples D and E) were prepared for evaluating the solvent extraction of Mo with 20 or 30 vol pct Aliquat (table 10). The 100-g/L NaOH leach solution used in tests 1 and 2 was prepared at ambient pressure. The 20-g/L NaOH leach solution used in test 3 was prepared at 150 psig O_2 pressure. The 100-g/L NaOH leach solutions used in tests 4 and 5 were also prepared at 150 psig O_2 pressure. The leach solutions used in test 4 were treated with sodium silicate to remove Al and As.
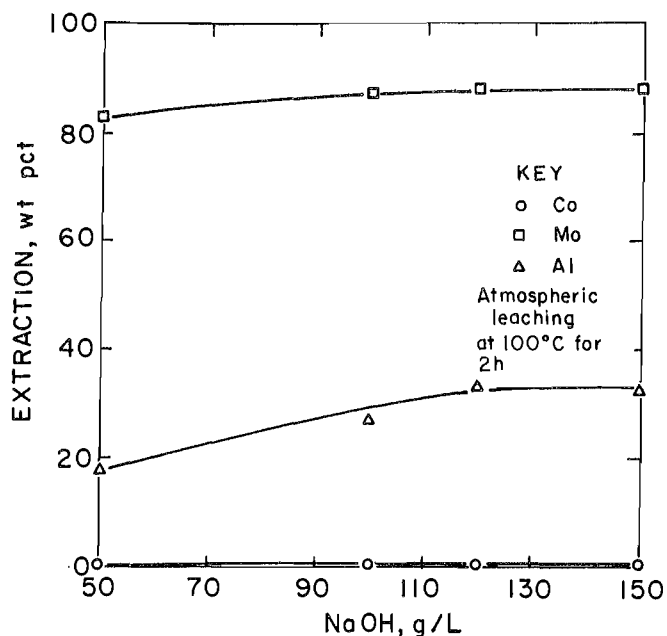
Figure 11.-Extraction of Co, Mo, and Al from Co-Mo-Al catalyst with NaOH by atmospheric leaching (100 g Co-Mo-Al to 1 L of NaOH solution).
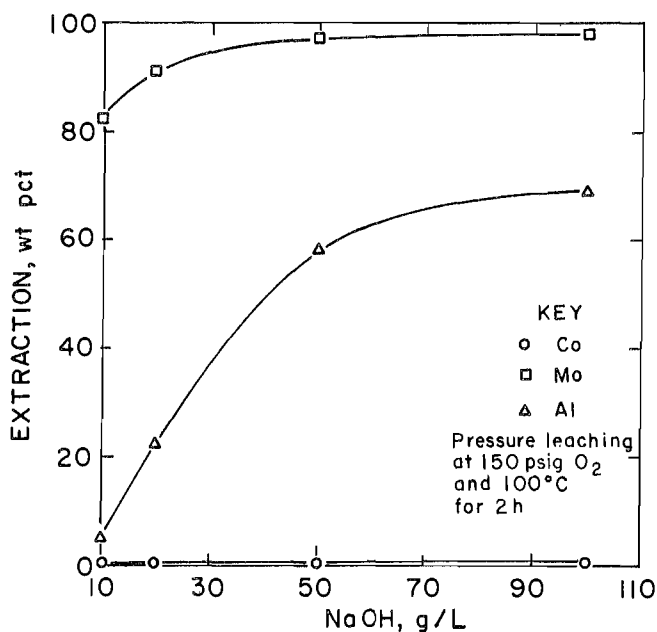
Figure 12.-Extraction of Co, Mo, and Al from Co-Mo-Al catalyst with NaOH by pressure leaching (50 g Co-Mo-Al to 1 L of NaOH solution).

Table 10.–NaOH leachate from waste Co-Mo-Al catalysts used for solvent extraction tests

(All tests conducted at 100° C)

Test	Leaching		Extraction parameters					
	NaOH, g/L	Pressure, psig	Aqueous feed, g/L				Aliquat 336, vol pct	Temp, °C
			Mo	Al	As	Si		
1	100	Atmospheric	2.13	3.15	NAp	NAp	30	30
2	100	. do	2.13	3.15	NAp	NAp	30	60
3	20	150 psig ...	3.01	3.39	NAp	0.001	20	50
4	100	. do	2.55	.16	0.02	.85	20	50
5	100	. do	2.76	13.40	.87	.17	20	50

NAp   Not applicable.

The best Mo solvent extraction results were obtained from the Co-Mo-Al catalyst (sample E) that was pressure leached with a 20-g/L NaOH leach liquor (test 3). More than 80 wt pct of Mo was extracted from the leachate with 20 vol pct Aliquat 336 in two stages using an O:A ratio of 1.1:1 (50° C). The CaMoO$_4$ was produced by stripping Mo from the loaded solvent with an NH$_4$Cl solution and precipitating with CaCl$_2$. However, less than 72 wt pct of Mo was extracted from the 100-g/L NaOH solutions (tests 1, 2, 4, and 5). This could be attributed to a lower concentration of Mo (tests 1 and 2), a higher concentration of Si (test 4), and a higher concentration of Al and As (test 5), which affected the Mo extraction.

Tungsten was extracted from the 20-g/L NaOH leach liquor of the Ni-W-Al catalyst by extraction with 20 vol pct Aliquat 336 (fig. 14) in three extraction stages. Three strip stages using a 7-wt-pct NH$_4$OH strip solution stripped the W from the loaded extractant. The solvent was loaded at

40° C, using an O:A ratio of 1.1:1, with 85 wt pct of the W being extracted from the leach liquor. Three stages of stripping with 7 wt pct NH$_4$OH and an O:A ratio of 2:1 removed 94 wt pct of the W from the loaded solvent. The raffinate, containing 16 wt pct of the W, can be adjusted to 20 g/L NaOH, and returned to the leaching circuit. Tungsten-barren solvent is recycled to the solvent extraction circuit. Recycling the raffinate to the leaching circuit and recycling the stripped solvent to the solvent extraction circuit minimizes the loss of W. Evaporation of the NH$_4$OH strip solution at 70° C yielded the commercial product $(NH_4)_{10}W_{12}O_{41}$.
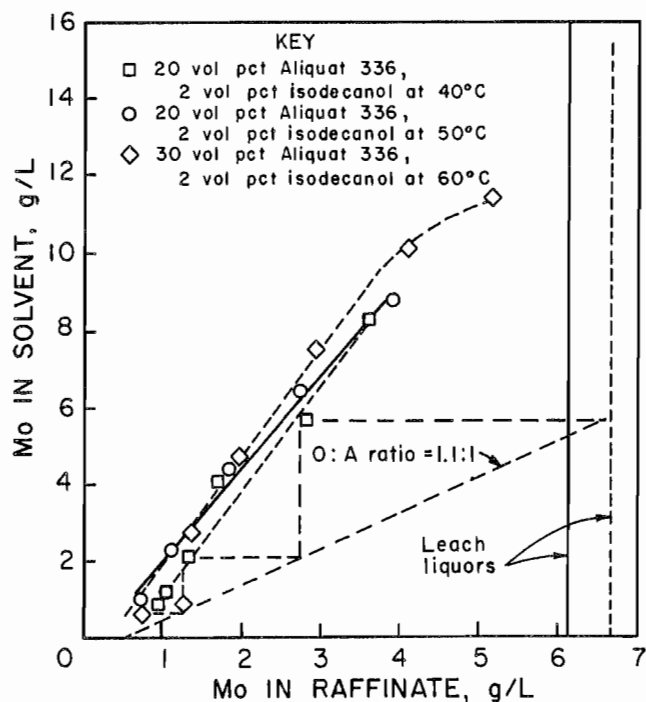
Figure 13.–Molybdenum extraction isotherms–Aliquat 336 versus Ni-Mo-Al NaOH raffinate.

Figure 14.–Tungsten extraction isotherm–Aliquat 336 versus Ni-W-Al NaOH raffinate.

H₂SO₄ Leaching, Purification, and Solvent Extraction or Precipitation

H₂SO₄ Leaching

NaOH leach residues from the waste Ni-Mo-Al, Ni-W-Al, and Co-Mo-Al hydroprocessing catalysts were leached with H_2SO_4 to recover Ni or Co. The pH of the leach solutions was about 1.1. Fifty- or one-hundred-gram samples of the NaOH leach residues were leached with 1 L of either 100-g/L or 50-g/L H_2SO_4 at atmospheric pressure. Results are summarized in table 11. More than 86 wt pct of the Ni or Co and more than 58 wt pct of Al were extracted from the 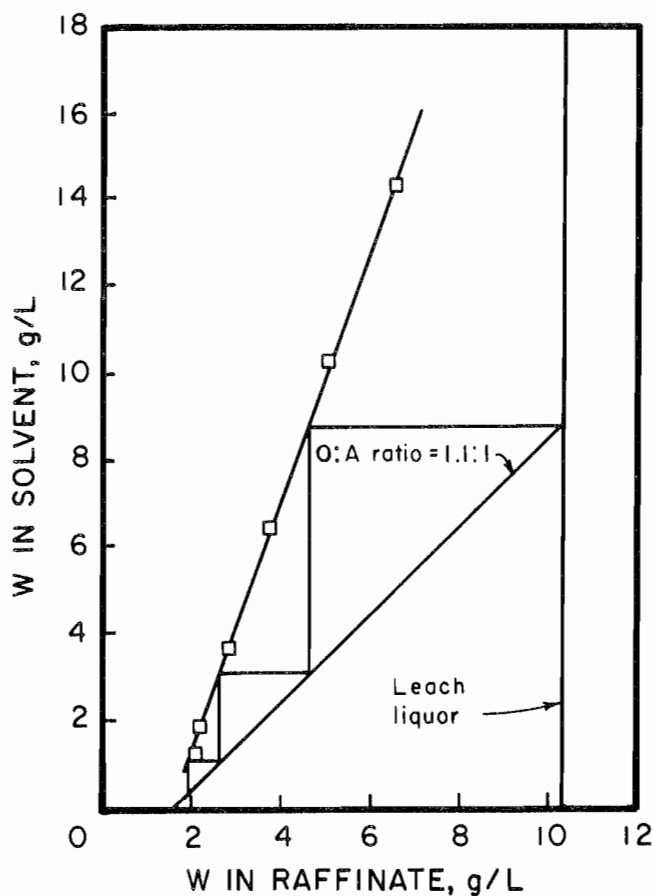NaOH leach residues. These H_2SO_4 leach residues, which contained 55 to 70 wt pct Al_2O_3, can be discarded after acid neutralization.

Aluminum, the major impurity, and other metal impurities needed to be removed from the H_2SO_4 leach solutions prior to recovery of Ni or Co. The effect of pH on the separation of Ni or Co from Al in the leach solutions was investigated by adjusting pH with a NH_4OH-$(NH_4)_2SO_4$ solution. Test data for the H_2SO_4 leach solutions from the NaOH leach residues (Ni-Mo-Al catalyst, sample B) are plotted in figure 15. More than 96 wt pct of the Al and 12 wt pct of the Ni were precipitated from these solutions at pH 5.2. Almost 100 wt pct of the Al and 6 wt pct of the Ni were precipitated at pH 10. Test data for the H_2SO_4 leach solutions from the NaOH leach residues (Co-Mo-Al catalyst, sample E) are plotted in figure 16. These results indicate that 92 wt pct of the Al and 3 wt pct of the Co were precipitated from the solutions at pH 5, and almost 100 wt pct of the Al and 40 wt pct of the Co were precipitated at pH 9.5. The tests showed that Ni could be separated from Al in solutions at pH's of 5 and 10; however Co and Al could be separated only at a pH of about 5.
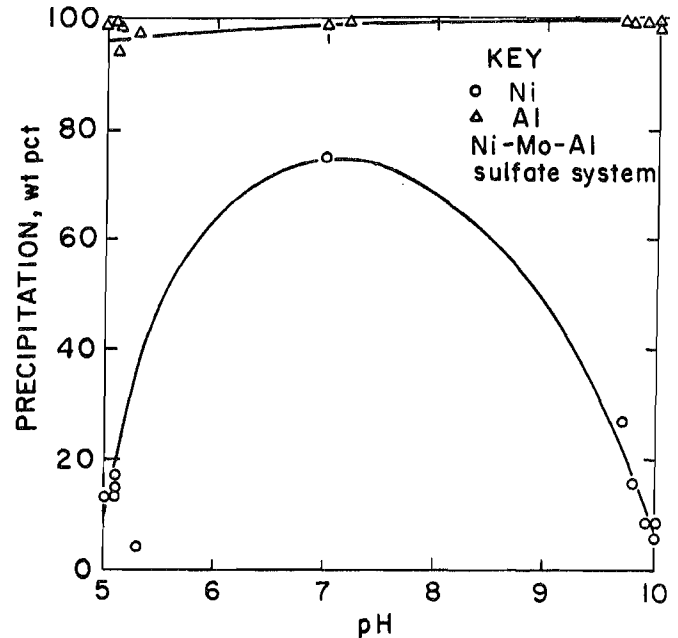
Figure 15.-Effect of pH on separation of Ni and Al from H_2SO_4 leachate (NaOH-leached Ni-Mo-Al residues).

Purification

Purification tests were made to remove metal impurities, other than Al, from the H_2SO_4 leach solutions. These impurities were precipitated by the addition of an NH_4OH-$(NH_4)_2SO_4$ solution until the pH reached 5 or 10, depending upon the subsequent metal recovery approach. Precipitates from the pH 5 or pH 10 purification steps were calcined at 600° C for 2 h to yield products containing over 84 wt pct Al_2O_3 (table 12). These products can be either used for a refractory material or discarded.

Table 11.-Metal extraction by leaching of NaOH-leached residues with H₂SO₄ solutions

(1 L H₂SO₄ solution and atmospheric pressure used in each test at 100° C for 1 h)

Waste catalyst leach residue	Wt, g	H₂SO₄, g/L	Extraction, wt pct					
			Ni	Co	Mo	W	V	Al
Ni-Mo-Al: Sample B	50	100	98	NAp	65	NAp	NAp	90
Ni-W-Al: Sample C[1]	50	100	92	NAp	NAp	50	NAp	76
Co-Mo-Al:								
Sample D[2]	50	100	([3])	92	43	NAp	NAp	76
Sample E[4]	50	100	([3])	86	48	NAp	NAp	58
Sample F[5]	100	50	96	93	16	NAp	96	76

NAp Not applicable.
[1]Contains 13.1 wt pct W.
[2]Contains 2.2 wt pct As.
[3]Not analyzed.
[4]Contains no As.
[5]Contains 9.4 wt pct V.

Table 12.–Typical chemical compositions of calcined powder from precipitates obtained by pH 5 or pH 10 purification of H_2SO_4 leachate

(NaOH-leached Ni-Mo-Al residues)

Component	wt pct		Component	wt pct
Al_2O_3	84.5		Fe	NA
Ni	.4		Si	0.4
Mo	.2		P	3.0

NA   Not available.

Solvent Extraction

Studies were also conducted to recover Ni or Co from the purified H_2SO_4 leach solutions by solvent extraction. Separation and recovery of Co and Ni from the acid sulfate leach solution with di(2-ethylhexyl) phosphoric acid requires a 40-ft sieve-plate pulse column (10). This approach appears not to be economic for recovering metal from these leach liquors. Cyanex 272, an organic extractant, has been successfully used at pH 5 for solvent extraction of Co from Ni in leach liquors that contained less than 30 g/L SO_4 (11). However, less than 2 wt pct Co was extracted from the purified 100-g/L sulfate-leach solution at pH 5. The high resultant sodium sulfate (Na_2SO_4) concentration of the leach solution may have blocked Co extraction with Cyanex 272.

As an alternative approach, Ni was recovered from basic solutions by a technique similar to the one used for leach solutions from anhydrous chlorination spent charge. H_2SO_4 leach solutions from the NaOH leach residues of Ni-Mo-Al and Ni-W-Al were purified by addition of NH_4OH-$(NH_4)_2SO_4$ solution to pH 10. Data for these tests are shown in table 13. The purified solutions contained less than 0.16 g/L of Mo or W and less than 0.04 g/L each of Al, Fe, Si, and P. Nickel was removed from the purified leach solutions (Ni-Mo-Al catalyst) with 10 vol pct LIX 64N in kerosene. The Ni-loaded organic was then stripped with an electrolyte containing 91.2 g/L Ni and 9.7 g/L H_2SO_4 (table 14). These results showed that 99 wt pct of Ni in the purified solution was extracted in one contact, and nearly 100 wt pct of Ni was stripped from the organic in one contact. The pregnant electrolyte, which contained 91.7 g/L Ni, 0.01 g/L Mo, 0.006 g/L Al, 0.006 g/L Fe, and 0.004 g/L Si, was suitable for electrowinning (9).
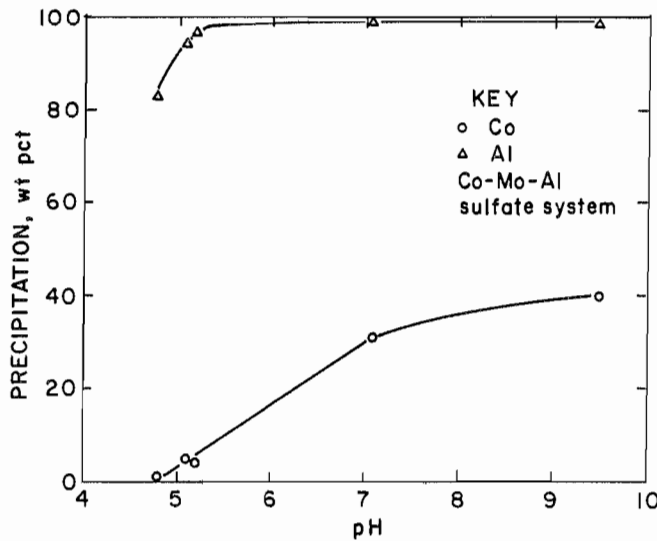
Figure 16.–Effect of pH on separation of Co and Al from H_2SO_4 leachate (NaOH-leached Co-Mo-Al residues).

Table 13.–Purification of H_2SO_4 leachate by pH adjustment with NH_4OH-$(NH_4)_2SO_4$ solution

Metal	Solution, g/L		Precipitation, wt pct
	Leach	Purified	
pH ADJUSTED TO 10[1]			
Ni	1.06- 2.01	0.50 -0.74	9.2-13.2
Mo or W	.36- .61	.14 - .16	13.1-25.1
Al	9.6 -14.2	.005 - .011	99.8-99.9
Fe	.06- .27	.0003- .002	95.0-99.4
Si	.07- 1.28	.004	87.5-95.4
P	1.14	.04	93.8
pH ADJUSTED TO 5[2]			
Ni or Co	1.06- 2.01	0.70 -1.00	5.2-14.8
Mo or W	.36- .61	.09 - .24	17.8-63.1
Al	9.6 -14.2	.21 - .71	93.9-97.6
Fe	.06- .27	.007 - .06	68.5-93.1
Si	.07- 1.28	.003 - .005	74.7-99.2
P	1.14	.02	97.6

[1]Leachate produced from NaOH-leached residues of Ni-Mo-Al and Ni-W-Al catalysts.

[2]Leachate produced from NaOH-leached residues of Ni-Mo-Al, Ni-W-Al, and Co-Mo-Al catalysts.

Table 14.–Typical solvent extraction and stripping of Ni from purified pH 10 leachate (NaOH-leached Ni-Mo-Al residues)

Metal	Extraction			Stripping[1]		
	Organic, g/L	Aqueous, g/L	Extraction, wt pct	Organic, g/L	Aqueous, g/L	Stripping, wt pct
Ni .	0.49	0.005	99.0	0.001	91.7	100
Mo .	.015	.12	11.1	.016	.012	42.9
Al ..	.011	.004	13.3	.001	.006	85.9
Fe .	.005	.0003	94.3	.0062	.0006	8.8
Si ..	.012	.080	13.0	.004	.004	50.0

[1]Stripped with an electrolyte containing 91.2 g/L Ni and 9.7 g/L H_2SO_4.

Precipitation

As an alternative approach, Ni or Co remaining in the pH 5 purified solutions was recovered by precipitation with Na_2S. The purified leach solutions contained less than 0.71 g/L Al, less than 0.24 g/L of Mo or W, and less than 0.06 g/L each of Fe, Si, and P, as shown in table 13. Stoichiometric amounts of Na_2S were added to precipitate either Ni or Co as NiS or CoS. The Ni and Co recoveries were 36 wt pct and 61 wt pct, respectively. In comparison, more than 98 wt pct of the Ni or Co was recovered by precipitation from the purified water-leach solutions of chlorination spent charge. The low recovery of metals from the acid sulfate system could be attributed to formation of thiosalt from oxidation of Na_2S by the H_2SO_4 solution. The recovery of Ni and Co by sulfide precipitation from acid sulfate solution was unacceptably low. More research is needed to improve the economics of recovering Ni and Co from acid sulfate solutions. Based upon the tests conducted, it appears that the solvent extraction of Ni from basic solutions is the most effective method for separating and recovering Ni in the two-step $NaOH-H_2SO_4$ leaching process.

PROCESS ECONOMICS

A preliminary economic evaluation for comparison of the two processes to recover Mo and Ni from a waste Ni-Mo-Al catalyst was prepared by the Bureau's Process Evaluation Group. The chlorination process with solvent extraction to recover Ni (fig. 2) and the caustic-acid leach process (fig. 8) were evaluated. Capital and operating costs were estimated based on plants that were sized to handle 39,000 lb of waste Ni-Mo-Al catalyst per day, or 12.9 million lb/yr on 330 days of operation per year. The estimated fixed capital costs for the two processes are $8 million and $9.6 million, respectively, for the chlorination process and caustic-acid leach process. The estimated operating costs for the two processes are about $0.20 and $0.40 per pound of waste catalyst, respectively. The chlorination process produces $15,600 per day of products, while the caustic-acid leach process produces $15,000 per day of products. The chlorination process appears to have an economic advantage over the caustic-acid leach process. Lower raw material costs, $0.03 versus $0.203 per pound of waste catalyst, are the primary advantages of the chlorination process.

A summary of the economic evaluation is presented in the appendix. A brief description of the two processes is given, followed by a discussion of the capital cost, operating cost, product value, and process comparison. Tables detailing these costs are provided. This cost study is intended as a source of information to guide future research to improve the processes, and significant process changes are still likely.

SUMMARY AND CONCLUSIONS

Using batch laboratory-scale data, this investigation has developed two processing approaches for recovering metal values from waste hydroprocessing catalysts. An anhydrous chlorination process and a caustic-acid leaching process both appear to be technically feasible.

For the anhydrous chlorination process, a waste catalyst was roasted at 400° C for 30 min to remove sulfur and moisture. The roasted catalyst was then chlorinated at 450° C for 30 min to separate volatile MoO_2Cl_2 or WO_2Cl_2 from less volatile $NiCl_2$, or $CoCl_2$, and $AlCl_3$. The MoO_2Cl_2 or WO_2Cl_2 was hydrolyzed to recover MoO_3 or WO_3 as a final product. Hydrolysis recovered 65 to 84 wt pct of Mo and 90 wt pct of W. The chlorinated spent charge was leached with water. The leach liquor was purified with an NH_4OH-NH_4Cl solution to precipitate Al and other metal impurities. At about pH 10, Ni was recovered by solvent extraction. The Ni or Co was precipitated from the purified solution at about pH 5 with

Na_2S. The chlorination step extracted from 73 to 99 wt pct of the Ni, from 61 to 99 wt pct of the Co, from 73 to 95 wt pct of Mo, and from 82 to 98 wt pct of the W. In the final recovery step, solvent extraction recovered over 99 wt pct of the Ni from the purified solution. Over 98 wt pct of the Ni or Co was recovered by sulfide precipitation. The maximum overall recoveries for Ni, Co, Mo, and W in weight percent were 98 (by solvent extraction) or 97 (by precipitation), 97, 80, and 88, respectively. These numbers were obtained by multiplication of percent of extraction during the chlorination step and percent of recovery during the final recovery step.

For the caustic-acid leaching process, the waste catalyst was first leached with NaOH to solubilize Mo or W and some of the Al. Then the NaOH leach residue was leached with H_2SO_4 to solubilize Ni or Co. Molybdenum was recovered from the caustic leach liquor by solvent extraction followed by precipitation of Mo with a $CaCl_2$

solution to yield $CaMoO_4$. Tungsten was recovered by evaporation of the ammoniacal strip solution to yield $(NH_4)_{10}W_{12}O_{41}$. The acid leach liquor was purified with an NH_4OH-$(NH_4)_2SO_4$ solution to precipitate Al and other metal impurities. At about pH 10, Ni was recovered by solvent extraction. From the pH 5 purified leach solution, the Ni or Co was recovered by precipitation with Na_2S. The NaOH leaching step extracted from 81 to 91 wt pct of the Mo, or about 86 wt pct of the W. The H_2SO_4 leaching step extracted from 92 to 98 wt pct of the Ni, or from 86 to 93 wt pct of Co. In the final recovery step, over 84 wt pct of the Mo or W was extracted by solvent extraction. The Mo was precipitated from the solvent extraction strip solution and the W was recovered by evaporation of the strip solution. Over 99 wt pct of the Ni was recovered by solvent extraction. From 36 to 61 wt pct of the Ni or Co was recovered by sulfide precipitation. The maximum overall recoveries for Ni, Co, Mo, and W in weight percent were 97 (by solvent extraction) or 60 (by precipitation), 57, 76, and 72, respectively.

A preliminary economic evaluation estimates the fixed capital cost for a plant processing 39,000 lb of waste Ni-Mo-Al catalyst per day at $8 million for the chlorination process and $9.6 million for the caustic-acid leaching process. The estimated operating cost is about $0.20/lb and $0.40/lb waste catalyst, respectively, for the chlorination process and the caustic-acid leaching process. The anhydrous chlorination process appears to have both technical and economic advantages over the caustic-acid leaching process. The chlorination process produces more valuable products (MoO_3 and WO_3) and recovers Ni and Co by a simple approach (water leaching followed by solvent extraction or precipitation). The chlorination process has lower capital and operating costs than the caustic-acid leaching process. However, the chlorination process generated a large quantity of waste from the hydrolysis of MoO_2Cl_2 and WO_2Cl_2. The waste products were generated from neutralization of solutions with lime. The major component of the waste was $CaCl_2$.

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APPENDIX.–PROCESS ECONOMICS

By Thomas A. Phillips[1]

PLANT DESCRIPTIONS

Two plant designs to recover both Mo and Ni from a spent hydroprocessing catalyst are presented. Each is based on a flowsheet and material balance supplied by research personnel. Each plant is sized to handle 12.9 Mlb of spent Ni-Mo catalyst per year, containing about 250 Mlb Ni and 1.2 Mlb Mo. This capacity is approximately equivalent to the entire annual generation of spent catalyst for the United States as reported by Inco $(1)^2$ in 1982. Operation of each plant is assumed to be 1 shift per day, 7 days per week, 330 days per year.

Chlorination Process

This process is based on the anhydrous chlorination of the spent catalyst. The process description is arbitrarily divided into four sections: chlorination, leaching, Ni recovery, and Mo recovery.

Chlorination Section

Spent catalyst is received by truck and stored in open bins. A front-end loader picks up the catalyst and dumps it into a hopper from which it is conveyed to a hammer mill where it is crushed to pass a 10-mesh screen. Crushed catalyst is roasted in a fluidized-bed to remove moisture and deleterious elements, such as sulfur. The catalyst is fluidized with a stream of combustion products and air at 400° C. Offgases are scrubbed with lime to collect the SO_2, and the sludge is discarded.

The hot roasted catalyst is then fed by gravity to a fluidized chlorination vessel where it is heated to 450° C by contact with a Cl_2-N_2 gas mixture. The gas mixture is a combination of recycled N_2 carrier gas, unreacted Cl_2, and makeup Cl_2. A natural-gas-fired heater is used to preheat the chlorination gas mixture. Most of the metals, with the exception of Al_2O_3, react with the Cl_2 to form chlorides. MoO_2Cl_2 volatilizes at the operating temperature and is collected from the offgases.

Leaching Section

Solids from the chlorinator are leached with water to dissolve the $NiCl_2$. Filtration of the resulting slurry

separates the unreacted oxides, which are mostly Al_2O_3, from the filtrate. The filtrate is mixed with NH_4OH to precipitate the small amount of dissolved Al_2O_3 as $Al(OH)_3$. After a second filtration, the solution is pumped to the Ni recovery section. The $Al(OH)_3$ precipitate is dried and calcined at 600° C to produce Al_2O_3. This product is cooled and conveyed to a storage bin prior to shipment.

Nickel Recovery Section

The Ni-bearing solution from the leaching section is fed to a mixer-settler and contacted with an organic extractant (12-wt-pct LIX 64N in kerosene). An organic to aqueous ratio of 1 to 1 is used. The loaded organic is stripped in a second mixer-settler using a recycled HCl electrolyte as the strip liquor. The stripped organic is recycled to the extraction stage.

Nickel is electrowon on Ni starting sheets from the chloride strip liquor in a single electrowinning cell. A separate cell uses stainless steel cathodes and anodes to make the Ni starter sheets used as cathodes in the primary cell. Electrolyte overflowing the cells is recycled to strip additional Ni from the organic extractant.

Molybdenum Recovery Section

Chlorine and chloride gases from the chlorination section are cooled in a heat exchanger to 150° C, causing the metal chlorides to sublime, which are separated from the gas stream in a cyclone. Gases from the cyclone, mostly unreacted Cl_2 and N_2, are compressed and stored in a pressure vessel until they are recycled to the chlorinator. The solids are leached with water to dissolve most of the chlorides. Heating this solution to 100° C for 30 min hydrolyzes the Mo, creating an impure MoO_3 precipitate, which is collected on a pressure-leaf filter and fed to a tray dryer-calciner to produce a molybdate product. The chloride filtrate is neutralized with lime to produce a mixed hydroxide-$CaCl_2$ waste.

Caustic-Acid Leach Process

In this process, Ni-Mo catalyst is first leached with caustic to dissolve the Mo, which is recovered by solvent extraction. The solids are releached with H_2SO_4 to solubilize the Ni, which is recovered in a solvent extraction circuit, and the Ni is electrowon.

The plant design is arbitrarily divided into four sections: leaching, Ni recovery, Al_2O_3 recovery, and solvent extraction–Mo recovery.

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[2]Italic numbers in parentheses refer to items in the list of references preceding the appendix.

Leaching Section

Spent catalyst is assumed to be trucked to the plant site and dumped into open storage bins. A front-end loader moves the catalyst from the storage bins to a hopper, from which it is conveyed to the caustic leach tank. The catalyst is leached with a 2-pct caustic solution at 100° C for 2 h. Most of the Mo is dissolved as sodium molybdate (Na_2MoO_4), along with a small quantity of Al_2O_3. The resulting slurry is gravity fed to a vacuum filter where the Mo-rich filtrate is separated from the residue and then pumped to the Mo recovery section.

The filter cake is fed to a second leach tank and leached with H_2SO_4 for 1 h at 100° C, dissolving most of the Ni and Al_2O_3. The resulting slurry is gravity fed to a second vacuum filter where undissolved solids are recovered and conveyed to a disposal site.

Filtrate from the acid leach filter is fed to a tank and mixed with NH_4OH to neutralize the acid. Holding the neutralized solution for 1 h at 80° C provides time for the Al to precipitate as $Al(OH)_3$. Some of the $(NH_4)_2SO_4$ formed by the neutralization reaction also precipitates. The combined precipitate is recovered by filtration and conveyed to the Al_2O_3 recovery section. The resulting filtrate contains about 0.5 g/L Ni and is pumped to the Ni recovery section.

Nickel Recovery Section

Ammoniacal solution from the leaching section is fed to a mixer-settler where it is contacted with an organic solvent (10-vol-pct LIX 64N in kerosene). The Ni is selectively sorbed by the organic, and the raffinate is recycled to the precipitation step in the leaching section.

Nickel is stripped from the organic in a second mixer-settler by a recycled H_2SO_4 electrolyte. The stripped organic is then pumped back to the extraction mixer-settler. The strip liquor is fed to an electrowinning cell. The electrolysis reaction deposits Ni on Ni starter sheet cathodes and regenerates H_2SO_4 for recycle to stripping. A second electrowinning cell using stainless steel cathodes and anodes produces Ni starter sheets for use in the primary cell.

Alumina Recovery Section

The $Al(OH)_3$ precipitate from the leaching section is fed to an agitated tank and water leached to dissolve the $(NH_4)_2SO_4$. Filtration of the resulting slurry recovers the undissolved $Al(OH)_3$, which is calcined in a rotary kiln at 600° C. The hydrate is decomposed to Al_2O_3, which is cooled and conveyed to a storage bin prior to shipment.

The $(NH_4)_2SO_4$ filtrate is fed to an evaporative crystallizer. Mother liquor is separated from the $(NH_4)_2SO_4$ crystals by filtration and recycled to the evaporator. The crystals are dried and conveyed to a storage bin, then loaded into trucks for shipment as fertilizer.

Solvent Extraction–Molybdenum Recovery Section

Molybdenum-loaded solution from the caustic leach in the leaching section is fed to a mixer-settler and mixed with an organic extractant (Aliquat 336 dissolved in Kermac with a small quantity of isodecanol). The raffinate is pumped back to the caustic leach step in the leaching section.

Molybdenum is stripped from the organic in a second mixer-settler with an NH_4Cl solution. The stripped organic is pumped back to the extraction step, while the Mo-rich strip liquor is pumped to an agitated tank and mixed with $CaCl_2$ to precipitate the Mo as $CaMoO_4$. Filtration of the resulting slurry recovers the $CaMoO_4$ product, which is dried and packed in bags for shipment. The resulting filtrate is pumped back to the stripping mixer-settler to strip additional Mo.

ECONOMICS

Capital and operating cost estimates for plants based on the preceding descriptions are presented. This cost study is provided as an estimate of major cost items. It is hoped that future research can be guided by this information to select and improve the processes.

Capital Costs

The capital cost estimates are of the general type called a study estimate by Weaver and Bauman (12).

Estimated fixed capital cost for the chlorination process is about $8 million. The estimated fixed capital cost for the caustic-acid leach process is about $9.6 million. These costs are based on a third quarter 1988 basis [Marshall and Swift (M and S)] index of 856.5 and are presented in tables A-1 and A-2.

Equipment costs used in this estimate are based on informal cost quotations from equipment manufacturers and on capacity cost data. In developing the plant capital costs, corrosion-resistant materials of construction are used where appropriate. Capitalized startup costs are estimated as 1 pct of the fixed capital cost. Land investment is not included in these estimates.

Working capital is defined as the funds in addition to fixed capital, land investment, and startup costs that must be provided to operate the plant. Working capital, shown in tables A-1 and A-2, is estimated from the following items: (1) raw material and supplies inventory (cost of raw material and operating supplies for 30 days), (2) product and in-process inventory (total operating cost for 30 days), (3) accounts receivable (total operating cost for 30 days), and (4) available cash (direct expense for 30 days).

Table A-1.–Estimated capital cost,[1] chlorination process

Fixed capital:	
Chlorination section	$1,943,900
Leaching section	1,446,900
Ni recovery section	776,900
Mo recovery section	2,049,000
Steamplant	65,700
Subtotal	6,282,400
Plant facilities, 10 pct of above subtotal	628,200
Plant utilities, 12 pct of above subtotal	753,900
Total plant cost	7,664,500
Land cost	0
Subtotal	7,664,500
Interest during construction period	319,400
Fixed capital cost	7,983,900
Working capital:	
Raw material and supplies	38,700
Product and in-process inventory	250,800
Accounts receivable	250,800
Available cash	145,400
Working capital cost	685,700
Capitalized startup costs	79,800
Subtotal	765,500
Total capital cost	8,749,400

[1]Basis: M and S equipment cost index of 856.5.

Table A-2.–Estimated capital cost,[1] caustic-acid leach process

Fixed capital:	
Leaching section	$2,280,300
Ni recovery section	812,000
Al_2O_3 recovery section	2,724,100
Solvent extraction–Mo recovery section	1,485,300
Steamplant	224,400
Subtotal	7,526,100
Plant facilities, 10 pct of above subtotal	752,600
Plant utilities, 12 pct of above subtotal	903,100
Total plant cost	9.181,800
Land cost	0
Subtotal	9,181,800
Interest during construction period	382,700
Fixed capital cost	9,564,500
Working capital:	
Raw material and supplies	240,900
Product and in-process inventory	495,700
Accounts receivable	495,700
Available cash	371,000
Working capital cost	1,603,300
Capitalized startup costs	95,600
Subtotal	1,698,900
Total capital cost	11,263,400

[1]Basis: M and S equipment cost index of 856.5.

Operating Costs

The estimated operating costs are based on an average of 330 days of operation per year over the life of the plant. The remaining 35 days are for scheduled and unscheduled downtime. The operating costs are divided into direct, indirect, and fixed costs.

Direct costs include raw materials, utilities, direct labor, plant maintenance, payroll overhead, and operating supplies. Raw materials and utility requirements per pound of catalysts are shown in tables A-3 and A-4. Raw water has been used for cooling water. The direct labor cost is estimated on the basis of assigning 1.4 employees for each position that operates 8 h per day, 7 days per week. Payroll overhead includes vacation, sick leave, social security, and fringe benefits.

Indirect costs include the expenses of control laboratories, accounting, plant protection and safety, plant administration, marketing, and company overhead. Research and overall company administrative costs outside the plant are not included.

Fixed costs include the cost of taxes (excluding income taxes), insurance, and depreciation. Depreciation is based on a straight-line, 10-year period.

The estimated operating cost for the chlorination process is about \$0.20/lb of spent catalyst, as shown in table A-3. However, the estimated operating cost for the caustic-acid leach process is about twice as high, \$0.40/lb of spent catalyst, as shown in table A-4. No cost is included for the spent catalyst.

Product Value

The quantity of each product and its value are shown for each process in table A-5. It is assumed that all products are marketable. The Ni is cathode-grade metal selling at \$6.50/lb. The value of $CaMoO_4$ is based on its contained Mo value as a concentrate of \$2.80/lb of contained Mo. The Al_2O_3 products contain impurities, such as phosphates, and can not be marketed as cell-grade Al_2O_3. Therefore, they have been assigned a value of \$100/st to be sold for metallurgical use. The MoO_3 and $(NH_4)_2SO_4$ products are given published values of \$2.65/lb and \$0.03/lb, respectively.

Table A-3.--Estimated annual operating cost, chlorination process

	Annual cost	Cost per pound Ni-Mo catalyst
Direct cost:		
Raw materials:		
Cl_2 at \$0.10/lb	\$231,200	\$0.017
NH_4OH at \$260/st	122,100	.009
Lime at \$0.03/lb	47,200	.003
Chemicals for steamplant water treatment	200	.001
Total	400,700	.030
Utilities:		
Electric power at \$0.05/kW·h	107,100	.008
Process water at \$0.20/Mgal	1,700	.001
Raw water at \$0.50/Mgal	2,200	.001
Natural gas at \$3.00/MMBtu	124,900	.009
Total	235,900	.019
Direct labor:		
Labor at \$10.50/h	415,000	.030
Supervision, 15 pct of labor	62,300	.005
Total	477,300	.035
Plant maintenance:		
Labor	159,500	.012
Supervision, 20 pct of maintenance labor	31,900	.002
Materials	159,500	.012
Total	350,900	.026
Payroll overhead, 35 pct of above payroll[1]	234,000	.017
Operating supplies, 20 pct of plant maintenance	70,200	.005
Total direct cost	1,769,000	.132
Indirect cost, 40 pct of direct labor and maintenance	331,300	.024
Fixed cost:		
Taxes, 1 pct of total plant cost	76,600	.006
Insurance, 1 pct of total plant cost	76,600	.006
Depreciation, 10-year life	798,400	.059
Total operating cost	3,051,900	.227

[1]Direct labor and supervision, maintenance labor and supervision.

Table A-4.–Estimated annual operating cost, caustic-acid leach process

	Annual cost	Cost per pound Ni-Mo catalyst
Direct cost:		
Raw materials:		
NaOH at $230/st	$261,400	$0.019
H_2SO_4 at $75/st	674,900	.050
NH_4OH at $260.00/st	1,764,900	.130
$CaCl_2$ at $217/st	139,100	.010
Chemicals for steamplant water treatment	1,900	.001
Total	2,842,200	.210
Utilities:		
Electric power at $0.05/kW·h	40,700	.003
Process water at $0.20/Mgal	11,200	.001
Raw water at $0.50/Mgal	1,500	.001
Natural gas at $3.00/MMBtu	326,400	.024
Total	379,800	.029
Direct labor:		
Labor at $10.50/h	436,800	.032
Supervision, 15 pct of labor	65,500	.005
Total	502,300	.037
Plant maintenance:		
Labor	200,600	.015
Supervision, 20 pct of maintenance labor	40,100	.003
Materials	200,600	.015
Total	441,300	.033
Payroll overhead, 35 pct of above payroll[1]	260,100	.019
Operating supplies, 20 pct of plant maintenance	88,300	.006
Total direct cost	4,514,000	.334
Indirect cost, 40 pct of direct labor and maintenance	377,400	.028
Fixed cost:		
Taxes, 1 pct of total plant cost	91,800	.007
Insurance, 1 pct of total plant cost	91,800	.007
Depreciation, 10-year life	956,500	.070
Total operating cost	6,031,500	.446

[1]Direct labor and supervision, maintenance labor and supervision.

Table A-5.–Products and product value

	Production, lb/d	Value, $/day
Chlorination process:		
Ni metal	551.5	3,585
MoO_3	4,408.0	11,681
Al_2O_3	20,367.4	1,018
Waste slurry	65,015.0	-650
Total		15,634
Caustic-acid leach process with solvent extraction–Mo recovery:		
Ni metal	659.6	4,287
$CaMoO_4$	6,027.8	8,096
Al_2O_3	20,106.8	1,659
$(NH_4)_2SO_4$	70,492.0	1,005
Waste solids	7,952.1	-80
Total		14,967

PROCESS COMPARISON

Although additional data are required to fully evaluate both processes, it is possible to compare the two to see if one has a significant advantage over the other. In this case, it is apparent that the chlorination process is the lower cost process, as conceived. As shown in tables A-3 and A-4, raw material costs are the primary reason the chlorination process has a lower operating cost than the caustic-acid leach processes ($0.03/lb compared with $0.20/lb). Electric power for the chlorination process is higher, although not enough to offset the higher costs for natural gas used to produce steam in the caustic-acid leach processes.

Another advantage of the chlorination process is that it recovers Mo as MoO_3, which has a higher value than $CaMoO_4$. This offsets the lower recoveries of Ni, Mo, and Al_2O_3. A negative point is that the chlorination process produces much more waste than the caustic-acid leach processes—65,000 lb/d versus 8,000 to 11,000 lb/d. This is not a problem unless the waste were declared hazardous, which would increase disposal costs at least tenfold.