Report of Investigations 8145

Extraction and Recovery of Molybdenum and Rhenium From Molybdenite Concentrates by Electrooxidation: Process Demonstration

By B. J. Scheiner, R. E. Lindstrom, and D. L. Pool
Reno Metallurgy Research Center, Reno, Nev.

March 3, 1849

UNITED STATES DEPARTMENT OF THE INTERIOR
Thomas S. Kleppe, Secretary
BUREAU OF MINES
Thomas V. Falkie, Director

1a

This publication has been cataloged as follows:

Scheiner, Bernard J

Extraction and recovery of molybdenum and rhenium from molybdenite concentrates by electrooxidation: process demonstration, by B. J. Scheiner, R. E. Lindstrom, and D. L. Pool. [Washington] U.S. Bureau of Mines [1976]

12 p. illus., tables. (U.S. Bureau of Mines. Report of investigations 8145)

Includes bibliography.

1. Molybdenum. 2. Rhenium. I. U.S. Bureau of Mines. II. Lindstrom, Roald, E., jt. auth. III. Pool, Danny L., jt. auth. IV. Title. (Series)

TN23.U7 no. 8145 622.06173

U.S. Dept. of the Int. Library

BIBLIOGRAPHIC DATA SHEET

1. Report No.
BuMines RI 8145

2.

3. Recipient's Accession No.

4. Title and Subtitle
Extraction and Recovery of Mo and Re From Molybdenite Concentrates by Electrooxidation: Process Demonstration

5. Report Date
June 1976

6. Performing Organization Code

7. Author(s)
B. J. Scheiner, R. E. Lindstrom, and D. L. Pool

8. Performing Organization Rept. No.

9. Performing Organization Name and Address
Reno Metallurgy Research Center
Bureau of Mines, USDI
1605 Evans Avenue
Reno, NV 89502

10. Project/Task/Work Unit No.

11. Contract/Grant No.

12. Sponsoring Agency Name and Address
Office of Assistant Director--Metallurgy
Bureau of Mines
U.S. Department of the Interior
Washington, DC 20241

13. Type of Report & Period Covered
Research, FY 1976

14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstracts
The Federal Bureau of Mines has successfully demonstrated an electrooxidation-solvent extraction-carbon adsorption process for recovery of molybdenum and rhenium from off-grade concentrates. The flow sequence consists of dissolution of metal values by electrooxidation, liquid-solid separation by thickening, acidification and chlorate ion removal by SO_2 treatment, solvent extraction to concentrate the molybdenum and rhenium by carbon adsorption, and metal recovery by crystallization. Molybdenum and rhenium were recovered as ammonium paramolybdate and ammonium perrhenate. Electrolysis of brine-concentrate pulps to generate a hypochlorite oxidizing agent in situ resulted in the dissolution of 98.9 and 99.1 pct of the molybdenum and rhenium, respectively, at an energy consumption of 13.7 kwhr/lb of molybdenum extracted.

17. Key Words and Document Analysis. 17a. Descriptors

Metallurgy
Hydrometallurgy
Molybdenum
Rhenium
NaCl
Electrooxidation
Solvent extraction

17b. Identifiers/Open-Ended Terms

17c. COSATI Field/Group 11F

18. Distribution Statement
NTIS release unlimited.

19. Security Class (This Report)
UNCLASSIFIED

20. Security Class (This Page)
UNCLASSIFIED

21. No. of Pages
18

22. Price
3.50

FORM NTIS-35(10-70)

US COMM-DC 40329-P71

INSTRUCTIONS FOR COMPLETING FORM NTIS-35 (10-70) (Bibliographic Data Sheet based on COSATI Guidelines to Format Standards for Scientific and Technical Reports Prepared by or for the Federal Government, PB-180 600).

1. **Report Number.** Each report shall carry a unique alphanumeric designation. Select one of the following types: (a) alphanumeric designation provided by the sponsoring agency, e.g., FAA-RD-68-09; or, if none has been assigned, (b) alphanumeric designation established by the performing organization e.g., FASEB-NS-87; or, if none has been established, (c) alphanumeric designation derived from contract or grant number, e.g., PH-43-64-932-4.

2. Leave blank.

3. **Recipient's Accession Number.** Reserved for use by each report recipient.

4. **Title and Subtitle.** Title should indicate clearly and briefly the subject coverage of the report, and be displayed prominently. Set subtitle, if used, in smaller type or otherwise subordinate it to main title. When a report is prepared in more than one volume, repeat the primary title, add volume number and include subtitle for the specific volume.

5. **Report Date.** Each report shall carry a date indicating at least month and year. Indicate the basis on which it was selected (e.g., date of issue, date of approval, date of preparation.

6. **Performing Organization Code.** Leave blank.

7. **Author(s).** Give name(s) in conventional order (e.g., John R. Doe, or J.Robert Doe). List author's affiliation if it differs from the performing organization.

8. **Performing Organization Report Number.** Insert if performing organization wishes to assign this number.

9. **Performing Organization Name and Address.** Give name, street, city, state, and zip code. List no more than two levels of an organizational hierarchy. Display the name of the organization exactly as it should appear in Government indexes such as USGRDR-I.

10. **Project/Task/Work Unit Number.** Use the project, task and work unit numbers under which the report was prepared.

11. **Contract/Grant Number.** Insert contract or grant number under which report was prepared.

12. **Sponsoring Agency Name and Address.** Include zip code.

13. **Type of Report and Period Covered.** Indicate interim, final, etc., and, if applicable, dates covered.

14. **Sponsoring Agency Code.** Leave blank.

15. **Supplementary Notes.** Enter information not included elsewhere but useful, such as: Prepared in cooperation with . . . Translation of . . . Presented at conference of . . . To be published in . . . Supersedes . . . Supplements . . .

16. **Abstract.** Include a brief (200 words or less) factual summary of the most significant information contained in the report. If the report contains a significant bibliography or literature survey, mention it here.

17. **Key Words and Document Analysis.** (a). **Descriptors.** Select from the Thesaurus of Engineering and Scientific Terms the proper authorized terms that identify the major concept of the research and are sufficiently specific and precise to be used as index entries for cataloging.
    (b). **Identifiers and Open-Ended Terms.** Use identifiers for project names, code names, equipment designators, etc. Use open-ended terms written in descriptor form for those subjects for which no descriptor exists.
    (c). **COSATI Field/Group.** Field and Group assignments are to be taken from the 1965 COSATI Subject Category List. Since the majority of documents are multidisciplinary in nature, the primary Field/Group assignment(s) will be the specific discipline, area of human endeavor, or type of physical object. The application(s) will be cross-referenced with secondary Field/Group assignments that will follow the primary posting(s).

18. **Distribution Statement.** Denote releasability to the public or limitation for reasons other than security for example "Release unlimited". Cite any availability to the public, with address and price.

19 & 20. **Security Classification.** Do not submit classified reports to the National Technical Information Service.

21. **Number of Pages.** Insert the total number of pages, including this one and unnumbered pages, but excluding distribution list, if any.

22. **Price.** Insert the price set by the National Technical Information Service or the Government Printing Office, if known.

CONTENTS

ILLUSTRATIONS

TABLES

EXTRACTION AND RECOVERY OF MOLYBDENUM AND RHENIUM FROM MOLYBDENITE CONCENTRATES BY ELECTROOXIDATION: PROCESS DEMONSTRATION

by

B. J. Scheiner,[1] R. E. Lindstrom,[2] and D. L. Pool[1]

ABSTRACT

The Federal Bureau of Mines has successfully demonstrated an electrooxidation-solvent extraction-carbon adsorption process for recovering molybdenum and rhenium from offgrade concentrates. The flow sequence consists of dissolution of metal values by electrooxidation, liquid-solid separation by thickening, acidification and chlorate ion removal by sulfur dioxide treatment, solvent extraction to concentrate the molybdenum and rhenium, separation of molybdenum and rhenium by carbon adsorption, and metal recovery by crystallization. Molybdenum and rhenium were recovered as ammonium paramolybdate and ammonium perrhenate.

Electrolysis of brine-concentrate pulps to generate a hypochlorite oxidizing agent in situ resulted in the dissolution of 98.9 and 99.1 pct of the molybdenum and rhenium, respectively, at an energy consumption of 13.7 kwhr/lb of molybdenum extracted.

INTRODUCTION

Conventional flotation and roasting procedures for recovering molybdenum oxide from molybdenum-source materials frequently result in low recovery of molybdenum. This is particularly true in molybdenite flotation from porphyry copper ores where difficulties can be encountered in refloating molybdenite that has been recycled to rougher and cleaner flotation sequences (8).[3] Because copper-molybdenum separation may be less than desired, a portion of the molybdenum may be lost when the copper flotation concentrate is charged to the reverberatory furnace to recover copper.

Rhenium is intimately associated with molybdenite. Consequently, not only do rhenium losses closely parallel molybdenum losses in recovery by flotation, but additional losses are encountered in recovery of rhenium by scrubbing the volatilized rhenium oxide contained in offgases generated

---

[1] Research chemist.

[2] Supervisory chemical engineer.

[3] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

during the roasting of molybdenite to molybdic oxide. Finally, roasting of the molybdenite product to obtain molybdic oxide results in formation of sulfur oxide gases, which are pollutants if discharged into the atmosphere.

Research has been conducted by several investigators to improve molybdenum recovery from ores and concentrates using a sodium hypochlorite-leaching system for dissolving molybdenum as the molybdate ion (1-3). The stoichiometry for the reaction is as follows:

$$MoS_2 + 9OCl^- + 6OH^- \rightarrow MoO_4^= + 9Cl^- + 2SO_4^= + 3H_2O. \quad (1)$$

The process has not been used commercially owing to the high cost of reagents consumed in reaction 1.

The Federal Bureau of Mines has developed an electrooxidation technique for treating carbonaceous gold ores (5), for recovering mercury from cinnabar ores (6), and for recovering mercury and silver from amalgamation tails (7). The process consists of generating hypochlorite in situ in a brine-ore pulp by electrolysis. The chemical reactions involved are as follows:

$$2Cl^- \rightarrow Cl_2 + 2e^- \text{ (anode)}; \quad (2)$$

and

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \text{ (cathode)}. \quad (3)$$

The chlorine and hydroxyl ion produced then combine to form hypochlorite ion

$$2OH^- + Cl_2 \rightarrow OCl^- \pm H_2O + Cl^-. \quad (4)$$

The energy required to produce 1 pound of sodium hypochlorite in the ore pulp is in the 1.5 to 2 kwhr range, indicating that the electrooxidation technique has a potential economic advantage for molybdenum extraction from molybdenum sulfides. A previous paper was published, giving results of laboratory experiments (4). This paper describes the operation of the electrooxidation extraction step and the subsequent molybdenum and rhenium recovery steps.

MATERIALS AND PROCEDURE

The concentrate used in these extraction plant experiments was an off-grade molybdenite concentrate obtained from a commercial operation. The average composition of the dried concentrate is shown in table 1.

TABLE 1. - Composition of concentrate used in process demonstration plant

Carbon (organic)..........wt-pct..	19.20
Copper..........wt-pct..	.97
Iron..........wt-pct..	5.52
Molybdenum..........wt-pct..	35.60
Oil plus insoluble..........wt-pct..	~9.00
Rhenium..........parts per million..	1,330
Sulfur..........wt-pct..	29.60

Figure 1 shows a conceptual flow diagram developed as a result of laboratory experiments conducted on several different molybdenite concentrates and ores. The flow sequence consists of the following unit operations: (1) Electrooxidation of a brine-concentrate slurry to produce soluble molybdate ion, (2) liquid-solid separation, (3) treatment of the clarified pregnant solution with SO_2 to lower the pH and destroy chlorate ion, (4) recovery of salt and concentration of molybdenum-rhenium by solvent extraction with a tertiary amine, (5) separation of rhenium from molybdenum by selective adsorption of rhenium on activated carbon, (6) stripping of rhenium from the activated carbon and recovery of the Re as NH_4ReO_4, (7) recovery of molybdenum as ammonium paramolybdate $[(NH_4)_6Mo_7O_{24}\cdot 4H_2O)]$ by crystallization, and (8) removal of sulfate ion by crystallization.

The operating procedure consisted of mixing a predetermined amount of concentrate with a 10-pct sodium chloride solution from the barren recycle tank in 55-gal agitated tanks. The resulting slurry (4 pct pulp density) was pumped at a predetermined rate to the first of five rubber-lined, 70-gal stirred vessels with the pump flowing from one tank to the next by gravity.

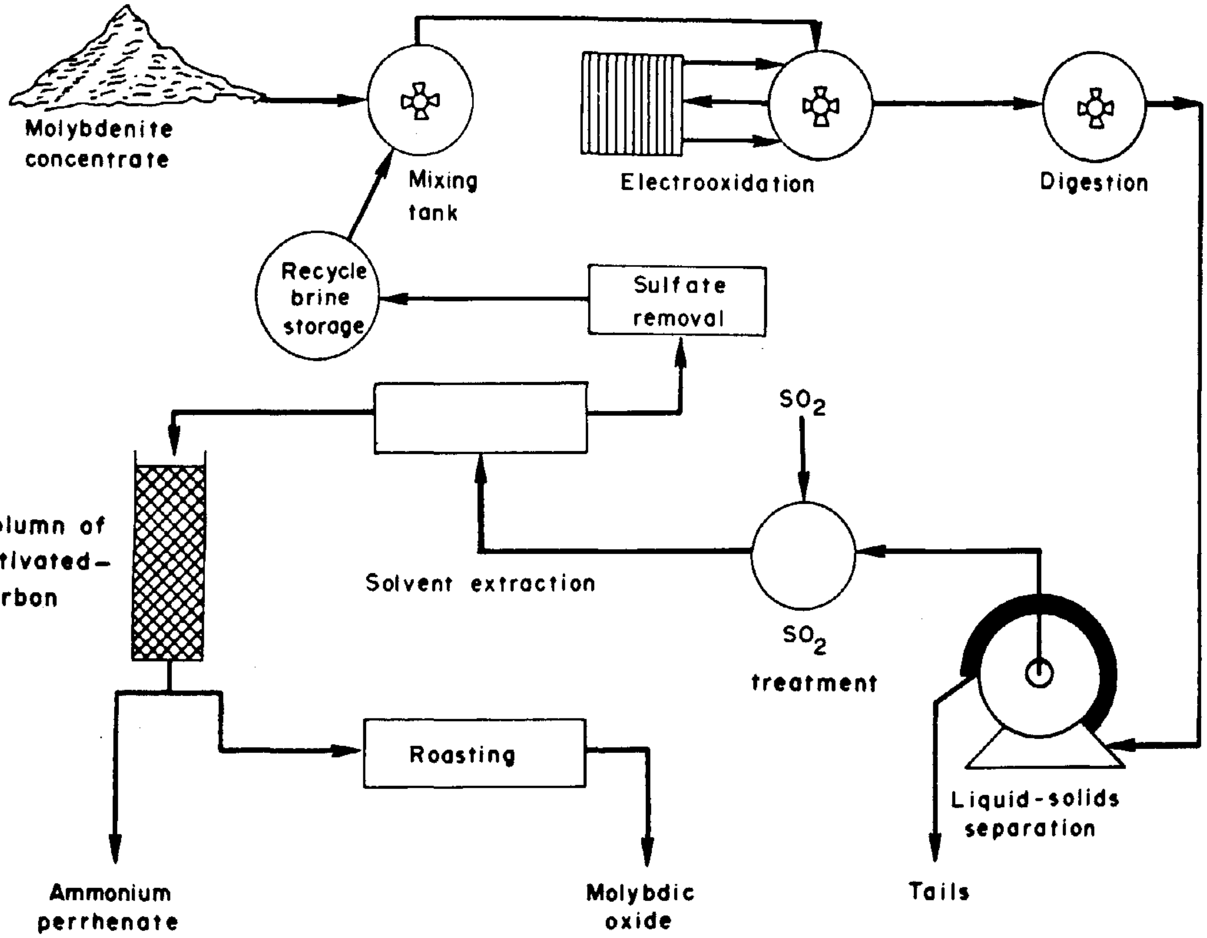

FIGURE 1. - Flowsheet for the recovery of molybdenum and rhenium from ores or concentrates.

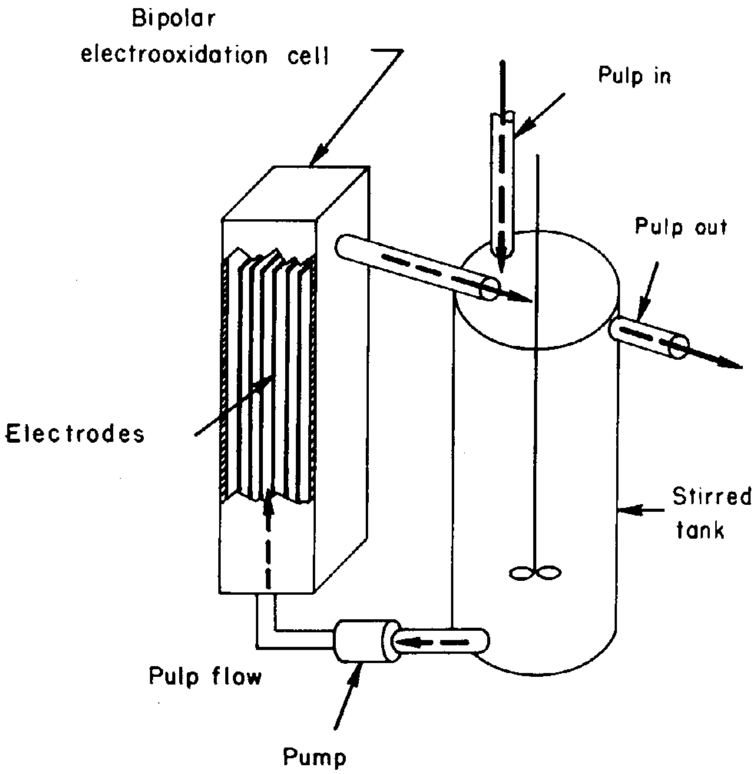

FIGURE 2. - Pulp flow sequence through agitator and bipolar cell.

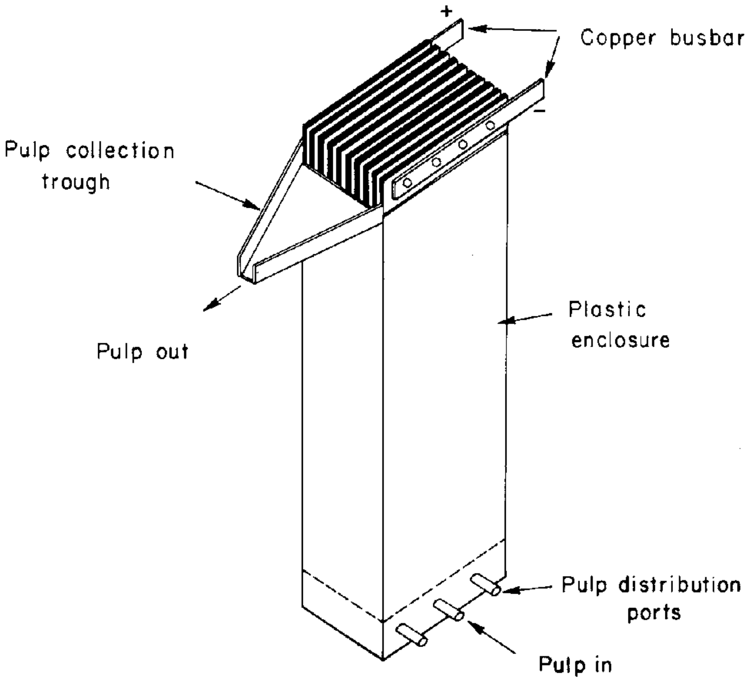

FIGURE 3. - Electrooxidation electrode assemblage.

Pulp from each of the first four vessels was pumped through a bipolar flow-through electrooxidation cell and returned to the same tank by gravity flow. The pulp flow sequence is shown in figure 2. The electrooxidation cell, shown in figure 3, consists of ten 8- by 3/4- by 48-inch graphite electrodes held in a plexiglass container. The effective area for each electrode was 7 inches by 40 inches. Spacing between electrodes was 5/16 inch. The four cells were connected electrically in series and were operated at an electrode current density of 0.5 amp/in^2. The overall voltage drop across the four cells was 125 volts at a current of 140 amp. An operating temperature of 35° to 40° C was maintained by passing the pulp through water-cooled heat exchangers positioned between each stirred vessel and its corresponding cell. Automatic addition of Na_2CO_3 was used to maintain the pH between 6 and 7 in the first three tanks, and between 7 and 8 in the fourth. The pulp from the fourth agitator tank passed to a fifth tank for digestion. The pH of the digestion tank was maintained in the 8.0 to 8.5 range by adding sodium carbonate. The digestion tank functioned as a holding tank to allow the residual hypochlorite ion to react.

The capacity of the electrolytic oxidation section of the plant was approximately 1.5 lb/hr of molybdenum, and the concentrate was fed at a rate that varied between 3.4 and 4.7 lb/hr to determine the effects of process variables on molybdenum extraction.

The pulp density of the plant feed and the overall operating conditions were adjusted to produce pregnant solutions containing 10 to 12 g/l of molybdenum exiting from the liquid-solid separation circuit. These solutions were fed to a solvent extraction circuit where they were concentrated up to approximately 100 g/l of molybdenum. The maximum solubility of ammonium paramolybdate, expressed as molybdenum, is approximately 150 g/l at a pH of 8. The electrooxidation and liquid-solids separation sections of the plant were operated continuously on a 24-hour basis, whereas the remainder of the plant was operated semicontinuously.

Operation of downstream processing steps involved in recovering molybdenum and rhenium from the electrolyzed pulp is described later in this report.

RESULTS AND DISCUSSION

Electrolytic Oxidation

The effect of electrolysis time, or energy input, on molybdenum-rhenium extraction was investigated by maintaining energy input at 140 amp and varying pulp flow to the system so that current density was constant and the retention time in the electrooxidation system varied. The data in table 2 show that molybdenum extraction ranged from 88.8 to 98.9 pct with power consumption of 10.0 to 13.7 kwhr/lb of molybdenum extracted. Corresponding sodium carbonate consumption for extraction of molybdenum was 3.1 lb/lb of molybdenum extracted. Energy consumption was not linear with respect to molybdenum extraction, and table 3 shows the energy required to extract increasing percentages of molybdenum. The data show that to obtain 88-pct extraction required 10.0 kwhr/lb of molybdenum extracted, whereas to increase extraction from 97.5 to 98.9 pct required 61.4 kwhr for each additional pound of molybdenum extracted.

TABLE 2. - Effect of energy input on molybdenum extraction

Energy consumption, kwhr/lb molybdenum extracted	Molybdenum extraction,[1] pct	Rhenium extraction,[1] pct
13.7	98.9	99.1
13.0	97.5	97.6
10.8	91.9	92.1
10.0	88.0	89.0

[1] Based on 35.6 pct molybdenum and 1,330 ppm rhenium head analysis.

TABLE 3. - Incremental energy consumption

Molybdenum extraction range, pct	Molybdenum extracted, kwhr/lb
0 -88.0	10.0
88.0-91.9	28.8
91.9-97.5	49.2
97.5-98.9	61.4

Rhenium extraction paralleled molybdenum extraction. Therefore, in an operating plant the most economic molybdenum extraction level would depend on the rhenium content of the concentrate. If the concentrate contained favorable amounts or rhenium, it might be economically feasible to expand the energy required to obtain a higher molybdenum extraction even though the cost in terms of kilowatt-hour per pound of molybdenum extracted would be relatively high. For example, the data in table 4 show that an additional 1,400 kwhr/ton of molybdenum extracted is required to increase molybdenum extraction from 97.5 to 98.9 pct. This additional treatment resulted in recovery of an additional 28 lb of molybdenum and 0.04 lb of rhenium. Based on an energy cost of 1 cents/kwhr, the increase in the cost of electricity is $14, whereas the value of the molybdenum and rhenium extracted is $66.40, based on costs of $1.80/lb for molybdenum and $400/lb for rhenium. This calculation only refers to cost of energy; capital cost, recovery cost, etc., are not included.

TABLE 4. - Energy consumption and increased molybdenum and rhenium extraction

Molybdenum extraction range, pct	Molybdenum increase kwhr/ton	Additional molybdenum extracted, lb	Additional rhenium extracted, lb
97.5-98.9	1,400	28	0.04
91.9-97.5	4,400	112	.146
88.8-91.9	1,600	62	.082

During the electrooxidation procedure, the molybdenite was converted to soluble molybdate ion and sulfate ion with an observed 60 pct weight loss based on the original weight of concentrate. The copper, iron, and carbon contents of the concentrate remain insoluble during treatment, and the concentration of these constituents in the tails was approximately 2.5 times greater than in the original untreated concentrate.

Liquid-Solids Separation

Liquid-solids separation of the treated pulp was carried out in a conventional countercurrent-decantation-thickener system. Pulp exiting from the fifth agitator was diluted to a pulp density of 1.6 pct (based on the original pulp weight) and passed to two 3- by 4-foot thickeners. Superfloc 20 flocculant in the amount of 1 lb/ton of concentrate was added to the pulp by means of a Clarkson[4] feeder before it entered the first thickener. The overflow from the first thickener passed through a sand filter, and the resulting clarified solution was pumped to a 400-gal pregnant solution tank for SO_2 treatment to remove chlorate ion and lower the pH. The clarified pregnant solutions contained approximately 10 to 12 g/l of molybdenum.

Sulfur Dioxide Treatment of Pregnant Solutions

Side reactions encountered during electrolysis in brine to produce chlorine or hypochlorite result in production of chlorate ion. Chlorate does not function as an oxidizing agent under neutral or basic conditions, and since the chlorate reports to the organic phase during solvent extraction to concentrate the molybdenum, it is necessary to remove it prior to the solvent-extraction step. Sulfur dioxide was studied for this purpose because in addition to removing chlorate by reduction, it lowers the pH of the pregnant solution that is necessary for subsequent solvent extraction. The reaction of chlorate ion with sulfur dioxide is shown in the following equation:

$$3H_2O + ClO_3^- + 3SO_2 \rightarrow Cl^- + 3H_2SO_4 . \qquad (5)$$

The resulting sulfuric acid lowers the pH of the pregnant solution.

The amount of chlorate ion formed during electrooxidation depended on the pH at which the electrooxidation procedure was conducted. If the pH was allowed to increase from the 6 to 7 range to the 6.5 to 7.5 range in the first three agitators, the chlorate ion concentration increased by 56 pct, from 16.0 g/l to 25 g/l, in the exit flow from the fourth agitator.

If the pH was allowed to decrease below 5.5, excessive amounts of copper were dissolved in the pregnant solution. During electrooxidation, 0.9 to 1.0 lb of $NaClO_3$ was formed for each pound of molybdenum extracted; therefore, the amount of SO_2 required to reduce the chlorate was 1.62 to 1.8 lb/lb of molybdenum extracted.

Treatment of 300 gal of pregnant solution with SO_2 to reduce the chlorate ion to chloride ion usually took 6 to 8 hours. Sulfur dioxide was bubbled into the uncovered tank as rapidly as possible without emission of SO_2. The amount of SO_2 required was approximately 1.8 lb/lb of contained $NaClO_3$, which corresponded to the theoretical amount required by equation 5. The resulting pH of the treated pregnant solution was usually 1.

Solvent Extraction

The solvent extraction step served two purposes in the process sequence: (1) The concentration of molybdenum and rhenium in the pregnant solutions was increased by a factor of 10, and (2) molybdate and perrhenate compounds were separated from the salt solutions to produce a barren brine solution that could be recycled back to the electrooxidation step.

---

[4] Reference to specific brand names is for identification only and does not imply endorsement by the Bureau of Mines.

The organic extractant employed for the tests consisted of a mixture of 7 vol-pct tertiary amine (Alamine 336) and 7 vol-pct decyl alcohol dissolved in Socal 355L solvent. Molybdenum and rhenium were stripped from the organic phase with 1.0- to 3.0-N NH_4OH solution.

The solvent extraction circuit consisted of four mixer-settler units, 6 inches wide by 36 inches long by 14 inches high. The mixing chamber was 6 by 6 by 12 inches high. The mixing chamber had a volume of 8 liters, and the settler had a volume of 24 liters. The stripping section consisted of three plexiglass mixer-settlers, 4 inches wide by 28 inches long by 14 inches high. The mixing chamber was 4 by 4 by 12 inches high. The volume of the mixing chamber and the settler were 3 liters and 10 liters, respectively.

The extraction section was operated with an aqueous phase flow rate of 3.3 l/min at pH 1. The corresponding flow rate for the organic phase was 1.65 l/min. The stripping section was operated with an organic phase flow rate of 1.65 l/min and the aqueous strip solution was fed to the system at 330 ml/min. The resulting organic-to-aqueous phase ratios were 0.5 for extraction and 5 for stripping. The stripped organic phase was washed with 1-N HCl prior to being recycled back to the extraction section. The pregnant strip solution was passed to a carbon adsorption system for separation of molybdenum from rhenium. A flow diagram for this process sequence is shown in figure 4. The raffinate was passed to further processing for removal of sulfate prior to being recycled back to the electrooxidation section. This is described in a subsequent section of this report.

The solvent extraction section was operated approximately 5 hours per day, and a total of 5,884 gal of pregnant solution was processed during the demonstration campaign. The average concentrations of molybdenum and rhenium in the feed solution were 11.56 g/l and 32 ppm, respectively, with an average extraction of 98.4 pct molybdenum and 99.7 pct rhenium. The percentage of molybdenum extracted per stage was 48, 48, 3, and 1 for stages 1 through 4, with a maximum organic phase concentration of 30 g of molybdenum/l. Operation of the extraction section proceeded smoothly, and no problems were encountered in either the extraction or phase disengagement steps.

Molybdenum and rhenium were stripped from the extractant with ammonium hydroxide. The effect of ammonium hydroxide concentration on stripping efficiency was investigated over the range 1.0- to 3.0-N NH_4OH and found to be independent of the initial ammonium hydroxide concentration. However, it was found that to prevent precipitation of molybdenum in the aqueous phase while in contact with the organic phase, a minimum pH of 8.5 must be maintained. An initial ammonium hydroxide concentration of 1.7 N was required to obtain the required equilibrium pH. The molybdenum stripped in mixer-settlers 1 through 3 was 98.9, 1.0, and 0.1 pct. Strip solutions contained 15 to 20 g/l sulfate, 2 to 4 g/l chloride ion, 90 to 110 g/l molybdenum, and 270 to 450 ppm rhenium. Average reagent consumption for the solvent extraction amounted to 0.270 lb NH_3 and 0.04 lb HCl per pound of molybdenum extracted.

The organic phase was reused 26 times during the demonstration plant experiments with no detectable decrease in efficiency.

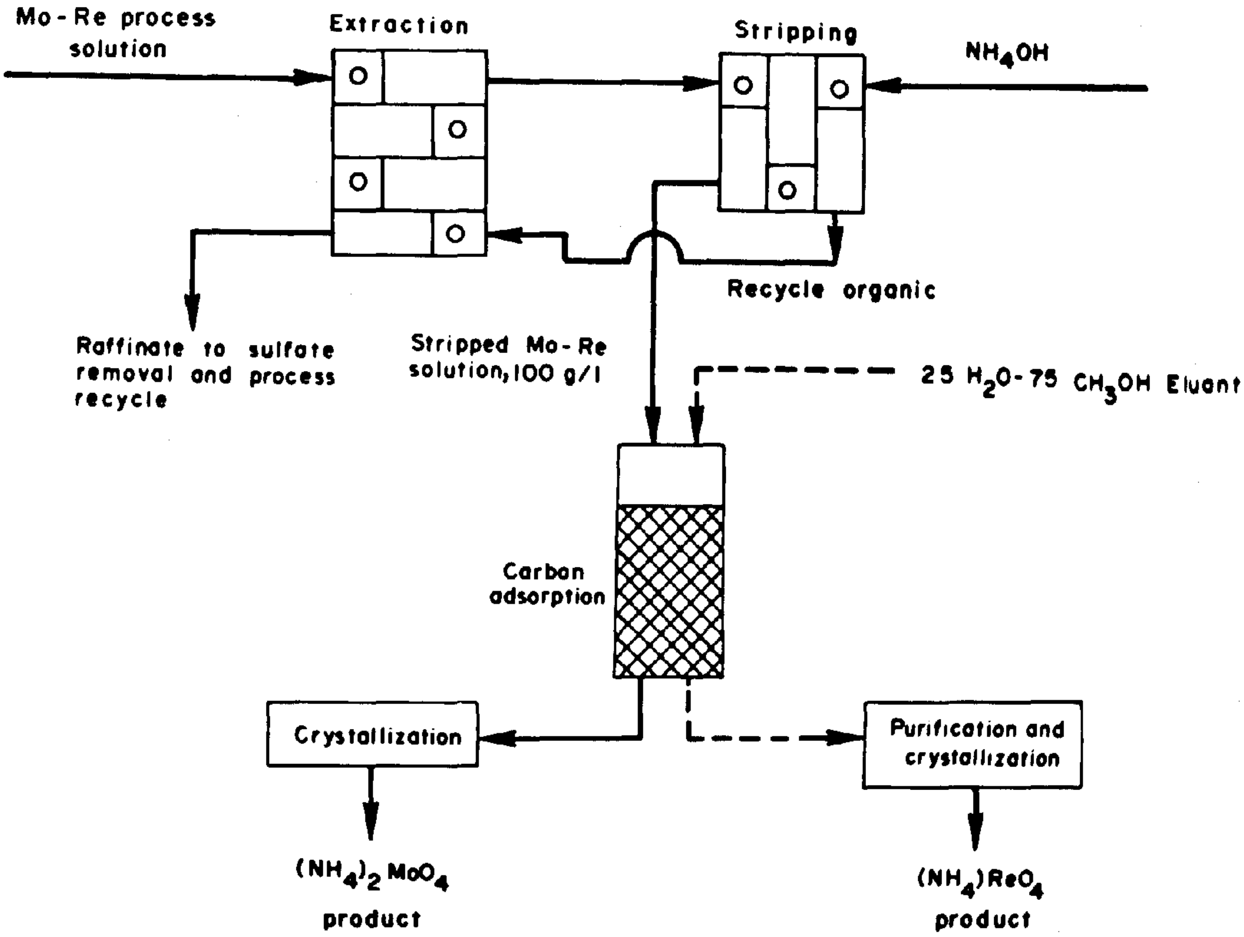

FIGURE 4. - Flow diagram for separation and recovery of molybdenum and rhenium.

Rhenium Adsorption on Activated Carbon

The carbon adsorption system consisted of two glass columns 4 inches in diamater containing 17 lb of dry 8 by 30-mesh coconut carbon per column. The two columns were arranged in series so that the solution flowed downward through the carbon. Strip solution from the solvent extraction system was fed to the carbon column at a rate of 330 ml/min. Under these conditions rhenium loading on the carbon reached 1 wt-pct of the carbon before breakthrough was observed. Average rhenium concentration in the effluent solution during loading was less than 0.1 ppm rhenium.

Rhenium was stripped from the carbon by first washing the physically entrained molybdenum from the carbon with 3 bed-volumes of 25-pct salt solution, and then stripping the adsorbed rhenium with 3 bed-volumes of a 75-25 pct methanol-water mixture. The carbon was regenerated with 4 bed-volumes of water.

An elution curve showing rhenium concentration versus effluent volume is given in figure 5. The data show that rhenium first appeared in the effluent after 0.5 bed-volume had been collected, after which the rhenium concentration increased rapidly to a maximum of 12.4 g/l, followed by a rapid decrease to

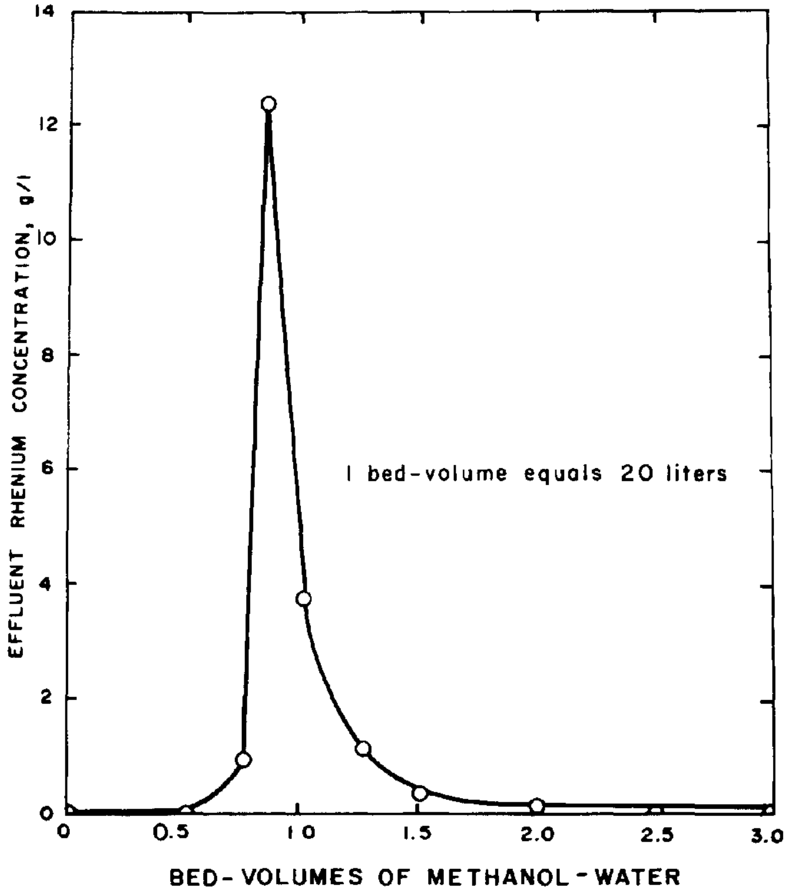

FIGURE 5. - Elution curve of rhenium from loaded activated carbon.

near zero after 2 bed-volumes of eluting solution was required to desorb 99 pct of the rhenium. Methanol was recovered from effluent solutions by distillation and recycled in the system. The distillation raffinate contained up to 40 g/l rhenium, up to 240 ppm molybdenum, and 3 to 5 g/l chloride ion. Rhenium was recovered from this solution by conventional ion exchange methods, and ammonium perrhenate of 99+ pct purity was obtained as a product.

Molybdenum Recovery

Molybdenum was recovered from the carbon column effluent solutions as ammonium paramolybdate $[(NH_4)_6Mo_7O_{24}\cdot nH_2O]$ by evaporating the solution to 1/26 of its original volume. The crystallization was conducted in 55-gal vessels and continued until the vessel was approximately 1/3 full of crystals. This crystal slurry was then filtered and the filtrate was recycled back to the evaporation vessel. At the end of the experiment, only 20 gal of solution remained of the original 520 gal produced. This solution contained 55 g/l molybdenum, 85 g/l chloride ion, and 243 g/l sulfate ion. A total of 780 lb of ammonium paramolybdate was recovered representing an overall recovery of 98 pct. The analysis of the ammonium paramolybdate recovered was as follows, in percent: Mo 53.40 to 55.13, $SO_4^{=}$ 0.11 to 1.06, Cl 0.1 to 0.4, and NH_4^+ 9.56 to 10.87. A single recrystallization of this crude material resulted in an ammonium paramolybdate product having a major impurity of 0.06 pct sulfate ion. All other impurities, such as chloride, are found only in trace amounts. A second recrystallization yielded a product of 99.9+ pct purity.

Sulfate Removal

Electrolytic oxidation of molybdenite results in production of approximately 2 lb of sulfate ion per pound of molybdenum extracted, and it is necessary to remove the sulfate prior to recycling the solution to prevent buildup of sodium in the system.

Rejection of sulfate from the barren solvent extraction raffinate prior to recycle was accomplished by raising the pH of the raffinate between 8 and 9 by adding 1.9 lb of sodium carbonate per pound of molybdenum extracted during electrooxidation and cooling the solution to between 10° and 12° C for 5 hours to precipitate sodium sulfate. Feed solutions to the precipitation sequence contained 70 to 80 g/l of sulfate ion, while exit solutions contained 40 to 50 g/l.

CONCLUSIONS

Molybdenum and rhenium can be recovered effectively from offgrade concentrates by this procedure. Molybdenum and rhenium extractions of 98.9 and 99.1 pct, respectively, were obtained by electrooxidation with an energy consumption of 13.7 kwhr/lb of molybdenum extracted. Reagent consumption per pound of molybdenum extracted included 5.0 lb of sodium carbonate (includes extraction and neutralization of raffinate), and 1.62 to 1.8 lb of sulfur dioxide. Corresponding reagent consumption for the solvent extraction amounted to 0.270 lb NH_3 and 0.04 lb HCl/lb molybdenum extracted. Recovery of molybdenum and rhenium as $(NH_4)_6Mo_7O_{24} \cdot nH_2O$ and NH_4ReO_4 from process solutions was in the 96- to 98-pct range.

REFERENCES

1. Bhappu, R. B., D. H. Reynolds, R. J. Roman, and D. A. Schwab. Hydrometallurgical Recovery of Molybdenum From the Questa Mine. N. Mex. BuMines and Miner. Res. Circ. 81, 1965, pp. 1-24.

2. Bhappu, R. B., D. H. Reynolds, and W. S. Stahmann. Studies on Hypochlorite Leaching of Molybdenite. Ch. in Unit Processes in Hydrometallurgy. Gordon and Breach Science Pub., New York, v. 24, 1963, pp. 95-113.

3. Cox, H., and A. K. Schellinger. An Ion Exchange Approach to Molybdic Oxide. Eng. and Min. J., v. 159, No. 10, 1958, p. 101.

4. Lindstrom, R. E., and B. J. Scheiner. Extraction of Molybdenum and Rhenium From Concentrates by Electrooxidation. BuMines RI 7802, 1973, 12 pp.

5. Scheiner, B. J., R. E. Lindstrom, W. J. Guay, and D. G. Peterson. Extraction of Gold From Carbonaceous Ores: Pilot Plant Studies. BuMines RI 7597, 1972, 20 pp.

6. Scheiner, B. J., R. E. Lindstrom, and D. E. Shanks. Recovery of Mercury From Cinnabar Ores by Electrooxidation. BuMines RI 7750, 1973, 14 pp.

7. Scheiner, B. J., D. L. Pool, and R. E. Lindstrom. Recovery of Silver and Mercury From Mill Tailings by Electrooxidation. BuMines RI 7660, 1972, 9 pp.

8. Sutulov, A. Molybdenum and Rhenium Recovery From Porphyry Coppers. University of Consepcion, Chile, 1970, pp. 1-242.

INT.-BU.OF MINES,PGH.,PA. 21242

☆U.S. GOVERNMENT PRINTING OFFICE: 1976-603-755/121