Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Selective Recovery of Rhenium from Gas-Scrubbing Solutions of Molybdenite Roasting Using Direct Precipitation and Separation on Resins

P. Blazy[a]; E. A. Jdid[a]; A. Floreancig[b]; B. Mottet[b]
[a] Centre De Recherche Sur La Valorisation Des Minerais, Andoeuvre, Cedex, France [b] Centre De Recherche De Voreppe-Pechiney, Voreppe, Cedex, France

To cite this Article Blazy, P. , Jdid, E. A. , Floreancig, A. and Mottet, B.(1993) 'Selective Recovery of Rhenium from Gas-Scrubbing Solutions of Molybdenite Roasting Using Direct Precipitation and Separation on Resins', Separation Science and Technology, 28: 11, 2073 — 2096

To link to this Article: DOI: 10.1080/01496399308016735

URL: http://dx.doi.org/10.1080/01496399308016735

SEPARATION SCIENCE AND TECHNOLOGY, 28(11&12), pp. 2073–2096, 1993

Selective Recovery of Rhenium from Gas-Scrubbing Solutions of Molybdenite Roasting Using Direct Precipitation and Separation on Resins

P. BLAZY and E. A. JDID
CENTRE DE RECHERCHE SUR LA VALORISATION DES MINERAIS, ENSG-INPL, LEM-CNRS URA 235
BP 40 VANDOEUVRE CEDEX 54501, FRANCE

A. FLOREANCIG and B. MOTTET
CENTRE DE RECHERCHE DE VOREPPE-PECHINEY
BP 27 VOREPPE CEDEX 38340, FRANCE

ABSTRACT

Rhenium, a by-product of molybdenum's extractive metallurgy, can be recovered from acidic gas-scrubbing solutions by using the techniques of direct precipitation and separation on resin. Direct precipitation is achieved by using tetraphenylphosphonium bromide (φ_4P). This technique yields an organometallic precipitate containing more than 25% Re and less than 1% Mo and Se. The reaction is fast and selective, with a stoichiometry $\varphi_4P/Re = 1/1$. Separation on resins is achieved with a weak base anionic resin of the tertiary amine type. By using the reflux method, the weakly coadsorbed molybdenum and selenium are removed by a concentrated sulfuric acid solution containing rhenium. Rhenium is then selectively eluted by an ammoniacal solution from which pure ammonium perrhenate is crystallized.

INTRODUCTION

Due to its remarkable physical properties (highest Young's modulus among all refractory metals, high electrical resistivity, very high melting and boiling points), rhenium enters into the composition of many high-tech materials (1–7). It is used in the catalyst industry (bimetallic Re/Pt catalysts for hydrocarbon reforming; hydrogenation or dehydrogenation catalysts in the petroleum industry) and added to tungsten-based alloys used in lamps, high-temperature thermocouples, or photographic flashes. It is also used in the naval industry in electrical connection protectors and in the aeronautical industry in the composition of superalloys for turbines.

A unique and rare rhenium mineralogical species is known as dzhezkazganite. It was first found in the Dzhezkazgan deposit (Community of Independent States, ex-USSR) where it is associated with chalcocite. Its theoretical formula is $CuReS_4$ (8–10). A similar species was found in the copper deposit of Kipushi (Zaire) (11).

Molybdenite ore from porphyric copper deposits represents the main commercial source of rhenium. Rhenium grades in these ores are variable

TABLE 1
Rhenium Content of Selected Molybdenites as 100% MoS_2(6)

Origin	Re (ppm)
United States of America:	
Climax, Colorado	2–5
Questa, New Mexico	12
Bingham, Utah	360
Chino, New Mexico	800
McGill, Nevada	1650
Miami, Arizona	200
Bagdad, Arizona	200
Latin America:	
Cananea, Mexico	700
Chuquicamata, Chile	230
El Salvador, Chile	570
El Teniente, Chile	440
Europe:	
Lainedzhaur, Sweden	2500
Knaben, Norway	10
Mansfeld, Germany	100
Community of Indepenent States (CIS, ex-Soviet Union):	
Koumad, Kazkhstan	510
Akchatausk, Kazakhstan	7
Almalyk, Uzbekstan	230
Kalmatyr, Uzbekstan	290
Kadzharan, Armenia	300
Dastakert, Armenia	80
Daragachaisk, Armenia	280
Aigedzor, Armenia	1000
Dzhindarinsk, Armenia	250
Tyrny Auz, North Caucasus	10
Davenda, Transbaïkal	60
Shakhtominsk, Transbaïkal	20
Umaltinsk, Far East	1
Dzhida, Buriat Mongolia	6

and can reach a few thousand ppm (Table 1). Other quoted sources of rhenium (12) are copper ores (porphyric deposits), uranium ores, colombo-tantalites, oil shales, etc. In order to verify this, we have performed rhenium analyses on several samples from different origins but, unfortunately, the analysis results shown in Table 2 confirm that molybdenites are the only rhenium bearers.

Previous papers dealing with the status of rhenium in molybdenite (13) show a nonhomogeneous substitution of Re for Mo in the MoS_2 lattice. For this reason, rhenium recovery must involve molybdenite roasting, the classic procedure to obtain MoO_3. Thus, rhenium can be considered to be a by-product of molybdenum's extractive metallurgy. When MoS_2 is roasted at 600°C, rhenium is volatilized as rhenium oxides (14). It can then be recovered in gas-scrubbing solutions and extracted later. These scrubbing solutions are concentrated in sulfuric acid (H_2SO_4 of 4 to 6 N).

Several processes have been developed to extracting rhenium from the gas-scrubbing solutions obtained after molybdenite roasting. The published techniques include ion-exchange resins (15–19), adsorption on activated carbon (20), solvent extraction (21–24), cementation on iron or zinc (4–25), and precipitation as rhenium sulfide (26–28). None of these processes is really satisfactory; they are all complex to operate and/or poorly selective.

TABLE 2
Rhenium Content of Some Samples Assumed to be Re Bearers

Samples	Origin	Re (ppm)
Molybdenite concentrates	Chateau Lambert (France)	20
	Beauvin (France)	30
	Bagdad Copper (USA)	300
	Cuajone (Peru)	240
Copper ores and by-products of copper metallurgy	Kipushi (Zaire): Run-of-mine	<1
	Slags	<1
	Flue dusts	1.4
	Anodes slimes (France)	<10
	Salave (Spain)	3.5
Colombo-tantalite concentrates	Echassières (France)	<1
	Maman Lézards, Belle Etoile, Oyapock, Venus (Guyane)	<1
	Penuta, Golpejas (Spain)	<1
Oil shales	Lorraine, Dordogne, Jura, Var, Doubs, Alsace (France)	<1
	Timahdhit (Morocco)	<1

The aim of this paper is to explore the potential of simpler processes for extracting rhenium from the sulfuric acid solutions obtained after molybdenite roasting. Two techniques were studied: 1) direct precipitation by organic compounds and 2) separation on weak base anionic resins (13–29).

EXPERIMENTAL PROCEDURE

The synthetic solutions were prepared using:

Sulfuric acid, H_2SO_4 95% (Prolabo)
Rhenium oxide, Re_2O_7, for direct precipitation experiments (Strem Chemical Inc.)
Ammonium perrhenate, NH_4MoO_4, for separation on resins (Pechiney Electrométallurgie, PEM)
Sodium molybdate, Na_2MoO_4-$2H_2O$ (Prolabo)
Sodium hydroxide, NaOH (Prolabo)
Lime, CaO (Prolabo)
Ammonia aqueous solution, NH_3 32% (Prolabo)
Ammonium chloride, NH_4Cl (Prolabo)

The organic reagents used for direct precipitation experiments were as follows:

Alkyl-phosphoric acids (Hoechst)
Dialkyl-dithiophosphates (Hoechst)
Quaternary ammonium salts (Fluka, Janssen)
Alkyl-phenyl phosphonium organic compounds (Lancaster Synthesis)

The required quantities of these organic reagents were dissolved in distilled water or in ethanol.

The resin used was an Amberlite IRA 93 SP from Rohm & Haas, which is a weak base anion exchanger. Its active group is a tertiary amine. It is macroreticulated and formed of spheres whose diameter varies from 0.37 to 0.47 mm. When used in the separation column (10 mm inner diameter), its height is approximately 600 mm.

A schematic diagram of the separation on resin apparatus is shown in Fig. 1. The solution flow rates were 400 mL/h for fixation steps and 40 mL/h for elution steps.

The industrial solutions were provided by Pechiney Electrometallurgie (PEM, Le Giffre—France). Two samples were used:

Sample 1: Re, 910 mg/L; Mo, 2 g/L; Se, 29 mg/L; acidity 5.8 N
Sample 2: Re, 950 mg/L; Mo, 3 g/L; Se, 38 mg/L; acidity 4.4 N

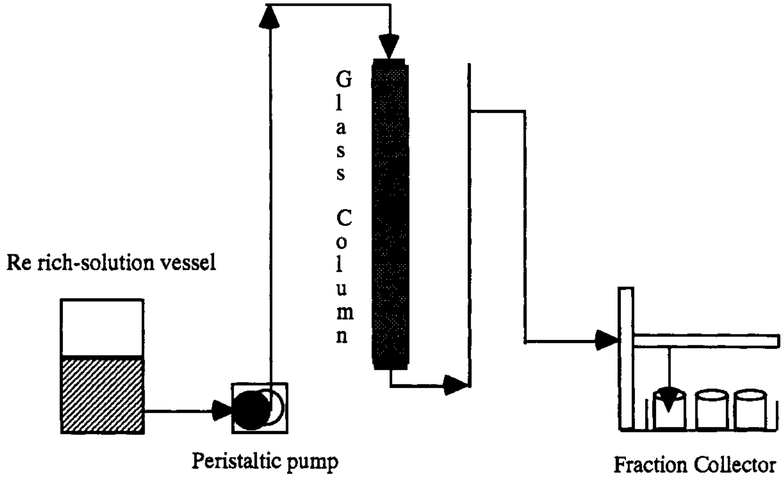


FIG. 1 Schematic diagram of the separation on resin device.

Rhenium, molybdenum, and selenium analyses were done by ICP methods.

FIRST TECHNIQUE: RHENIUM RECOVERY AS AN ORGANOMETALLIC PRECIPITATE

In previous studies dealing with the direct precipitation of rhenium from gas-scrubbing acidic solutions issued from MoS_2 roasting, an impure sulfide, Re_2S_7, was obtained using H_2S or NaHS (27–29). The precipitates were very fine, and thus difficult to separate from the solution. Furthermore, the affinity of these inorganic thiol reagents is almost the same for rhenium, molybdenum, and selenium.

We decided to focus the research toward the use of organic reagents. The precipitates formed by these compounds with metallic cations are generally well flocculated. In some cases they also present hydrophobic properties. For these two reasons, such precipitates should be separable from solution by either filtration or flotation.

Results and Discussion

Rhenium Recovery from Synthetic Media

Several organic compounds were tested. They were chosen according to their stability in acidic media and/or their affinity toward rhenium. The tests were carried out at room temperature using synthetic solutions of 6 N H_2SO_4 containing 1 g/L rhenium or 2 g/L molybdenum. The results obtained show that:

Alkyl-phosphoric acids ($R—PO_3H_2$, where R = octyl or benzyl) react with molybdenum only

Dialkyl-dithiophosphates [$(RO)_2PS_2Na$, where R = ethyl or isobutyl] precipitate both Re and Mo, but their affinity is greater for the latter. Furthermore, the precipitate obtained is greasy and sticky

Quaternary ammoniums, such as octadecyltrimethylammonium bromide and cetylpyridinium chloride, precipitate molybdenum only. These results were unexpected since strong base quaternary ammonium resins are known to adsorb molybdenum as well as rhenium

Alkyl-phenyl phosphonium compounds precipitate rhenium selectively. Thus, these reagents offer the best possibilities for rhenium separation from molybdenum in concentrated sulfuric acid media ($H_2SO_4 \approx 4$ to 6 N)

Phosphonium compounds with hydrocarbon chains presenting different structures and lengths have thus been tested. These tests were performed in a synthetic medium: 6 N H_2SO_4 containing 0.1 g/L rhenium and 0.3 g/L molybdenum (this Mo/Re ratio is similar to that of industrial solutions). The results obtained are given in Table 3. They show that:

The precipitation rates as well as the nature of the precipitates formed depend on both the structure and length of the hydrocarbon chain of the reagent

The best precipitation rates are obtained using the reagent φ_4P whereas the reagent $HD\varphi_3P$ yields a well-flocculated precipitate. However, flotation tests showed that none of the precipitates, even when flocculated, could be separated by this technique

In the case of φ_4P, when the molar ratio Φ ([reagent], M/[rhenium], M) is close to 1, the precipitation efficiency is equal to 75%. This suggests that the reaction has a stoichiometry φ_4P/Re equal to 1/1. In fact, analysis of the precipitate "φ_4P-Re" gives 31.5% Re, which corresponds to the rhenium content of the compound φ_4PReO_4. The reaction should then be written as

$$\varphi_4P^+ + ReO_4^- \rightarrow \varphi_4PReO_4\downarrow \qquad pK_s \approx 7.7$$

This first study on synthetic solutions clearly selected only three interesting phosphonium compounds. These three compounds, φ_4P, $TD\varphi_3P$, and $HD\varphi_3P$, were then used for studying the recovery of rhenium from industrial solutions.

TABLE 3
Rhenium Precipitation by Phosphonium Compounds in Synthetic Media H_2SO_4 6 N, $T = 25°C$

Reagents	Precipitate properties	Φ	Precipitation rates (%)
n-Ethyltriphenylphosphonium-Br ($E\varphi_3P$)	No precipitation		
n-Hexyltriphenylphosphonium-Br ($H\varphi_3P$)	Unstable precipitate even for $\Phi = 40$		
Tetra-*n*-butylphosphonium-Br (B_4P)	No precipitation		
Tetraphenylphosphonium-Br (φ_4P)	Fine, abundant, not flocculated	1.0	75
		2.5	95
		5.0	95
		7.5	95
n-Tetradecyltriphenylphosphonium-Br ($TD\varphi_3P$)	Greasy	2.5	78
		7.5	90
		10.0	91
n-Hexadecyltriphenylphosphonium-Br ($HD\varphi_3P$)	Flocculated	2.5	70
		5.0	83
		10.0	90
n-Hexadecyl tri-*n*-butylphosphonium-Br (HDB_3P)	Very greasy	2.5	87
		5.0	90
		10.0	92

Recovery of Rhenium from Industrial Media

Tests were performed at room temperature and at 60°C using the three selected alkyl-phenyl phosphonium reagents. The results show that compounds with alkyl-phenyl hydrocarbon chains are unusable in industrial media containing high rhenium concentrations. Indeed, for reagent concentrations corresponding to Φ values higher than the stoichiometry of the reaction, the precipitates obtained are very greasy and sticky.

The situation is very different in the case of tetraphenyl phosphonium reagent. This compound remains effective in industrial media because it yields a flocculated precipitate. The results obtained using φ_4P are reported in Table 4. They show that precipitation rates higher than 90% can be reached even at 60°C, which means that temperature does not affect the formation and stability of the precipitate φ_4PReO_4. It should then be possible to operate directly in gas-scrubbing solutions because their temperature is approximately 60°C.

In industrial media the dry organometallic precipitate "φ_4P-Re" contains 25.6% rhenium, 0.53% molybdenum, and 0.15% selenium. This rhenium content is very close to the theoretical value of 31.6% that should be obtained for a reaction stoichiometry of 1/1. Therefore, the reaction is

TABLE 4
Precipitation of Rhenium by Tetraphenylphosphonium-Br in Le Giffre's Industrial Solution

	Precipitation rates (%) for Φ values of			
Temperature	0.6	1.2	1.8	2.4
Ambient	50	79	94	94
60°C	51	76	91	93

very selective. Furthermore, the precipitation kinetic is fast because the rate of precipitation remains constant (98% for a value of Φ ≈ 2) for times ranging between 15 and 260 minutes.

Solid/Liquid Separation

The precipitate "φ_4P-Re" is not hydrophobic and cannot be separated by ion flotation. Likewise, the precipitate flotation technique, which consists of floating a precipitate by means of another surfactant ion, did not give satisfactory results. Therefore, the separation of tetraphenyl phos-

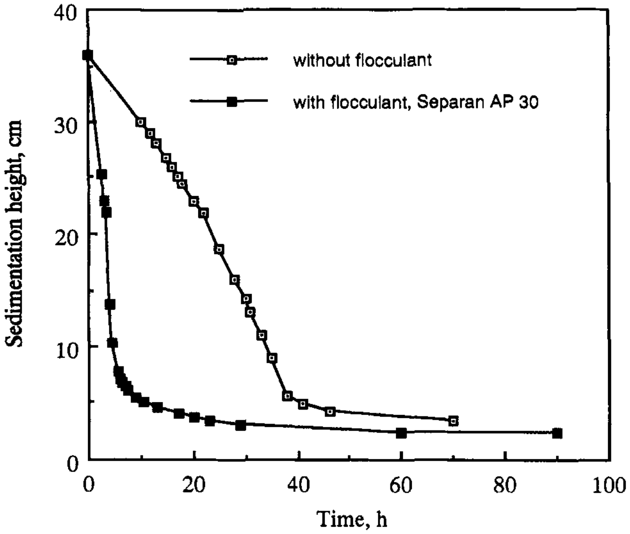


FIG. 2 Sedimentation curves of the precipitate tetraphenyl phosphonium perrhenate, Φ = 1.5; industrial solution.

phonium perrhenate needs either direct filtration or decantation followed by filtration.

Decantation tests showed that the process is relatively slow. It can, however, be accelerated by flocculation, as shown in Fig. 2. In fact, by using a strong anionic flocculant with a hydrolyzed polyacrylamide chain (30) (Separan AP 30), sedimentation velocity can be upgraded from 0.78 to 5.2 cm/min. Then the thickener area, which is inversely proportional to the sedimentation velocity (31), is divided by a factor of $5.2/0.78 = 6.7$.

SECOND METHOD: RHENIUM/MOLYBDENUM SEPARATION USING ION-EXCHANGE RESINS

Kennecott Co. developed two processes using ion-exchange resins to extract rhenium from the gas-scrubbing solutions obtained after molybdenite roasting.

In the first process (15–17), developed in 1957, the 6 N sulfuric acid solution is neutralized to pH 8 by using NaOH and $Ca(OH)_2$ and subsequently oxidized by using hypochlorite. Undesirable ions (such as iron) are precipitated during these steps and then removed by decantation. The clarified solution is exchanged on a strong base resin, Amberlite IRA 400. Molybdenum is eluted first by using sodium hydroxide. Next, rhenium is eluted by using 1 M perchloric acid, and the rhenium-rich solution is acidified with HCl before Re is precipitated with H_2S. The precipitate Re_2S_7 is dissolved in an ammoniacal solution, in the presence of H_2O_2, and after a succession of dissolution–crystallization steps, an ammonium perrhenate, NH_4ReO_4, with a purity higher than 95%, is obtained. However, the overall rate of recovery of rhenium (contained in the initial solution) is only about 85%. Furthermore, this complex process involves numerous stages in both acidic and basic media. Also, the use of perchloric acid is rather hazardous.

The second process (18, 19) utilizes NH_4SCN instead of $HClO_4$ as the eluent agent for rhenium, which allows the direct crystallization of NH_4ReO_4 by evaporation and avoids the steps of precipitation/redissolution of Re_2S_7. As in the first process, the latter presents many drawbacks: ammonium thiocyanate is not a very efficient eluent whose recycling requires a precipitation of copper thiocyanate followed by electrolysis.

Taking into account the inconveniences of the Kennecott processes described above, and in order to adsorb the molybdenum less strongly, it seemed interesting to study the separation of rhenium on an anionic resin less basic than Amberlite IRA 400. Elution operations should be less difficult to achieve on this type of resin. In our study we chose to use

Amberlite IRA 93 SP supplied by Rohm and Haas. It is a weak base tertiary amine.

Operating Conditions

Tests were run in both synthetic and industrial solutions. The characteristics of these solutions follow.

Synthetic Solutions

Solutions at pH = 2: 2 M Na_2SO_4; Mo, 1.96 g/L; Re, 1.05 g/L.
Sulfuric acid solutions, 4 N H_2SO_4; Mo, 2.10 g/L; Re, 1.00 g/L.

Industrial Solutions

Industrial solutions contain different solid particles of molybdenum and selenium compounds as well as organic residues from flotation reagents. These impurities have to be removed by filtration. In order to avoid plugging the filter, the solutions are treated with a solution of lime milk (100 g/L CaO) in a ratio of 1.25 L lime milk to 10 L industrial solution. After gypsum filtration, the filtration cake is washed (2 volumes of water for 10 volumes of solution). The final industrial solutions have the following compositions:

Sample 1, filtered liquor: Mo, 1.6 g/L; Re, 680 mg/L; Se, 23 mg/L; acidity, 3.9 N
Sample 2, filtered liquor: Mo, 2.8 g/L; Re, 850 mg/L; Se, 31 mg/L; acidity, 4.4 N

Results and Discussion

Synthetic Solutions

Adsorption Step. Figures 3, 4, and 5 present the adsorption of molybdenum and rhenium in the column containing the resin Amberlite IRA 93 SP.

At pH 2, rhenium and molybdenum are both strongly adsorbed on the resin. The breakthrough volume, i.e., the volume at which a particular species is detected in the effluent, is equal to 40 BV (BV is the volume of solution equivalent to the volume of resin) for rhenium and to 30 BV for molybdenum (Fig. 4). In Fig. 3 there is a quasi-instantaneous breakthrough volume for molybdenum due to a photochemical reduction of molybdenum in light. To avoid this, the separation column was covered with aluminum foil.

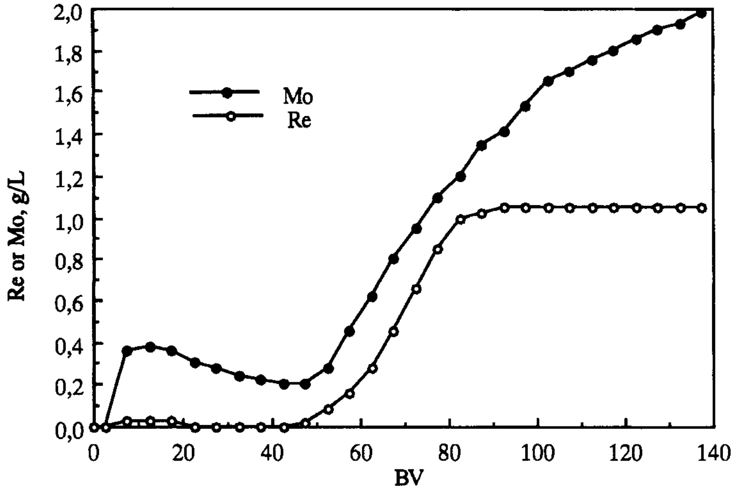


FIG. 3 Adsorption curves of Re and Mo on the resin IRA 93 SP; synthetic solution, pH 2; Re, 1.05 g/L; Mo, 1.96 g/L.

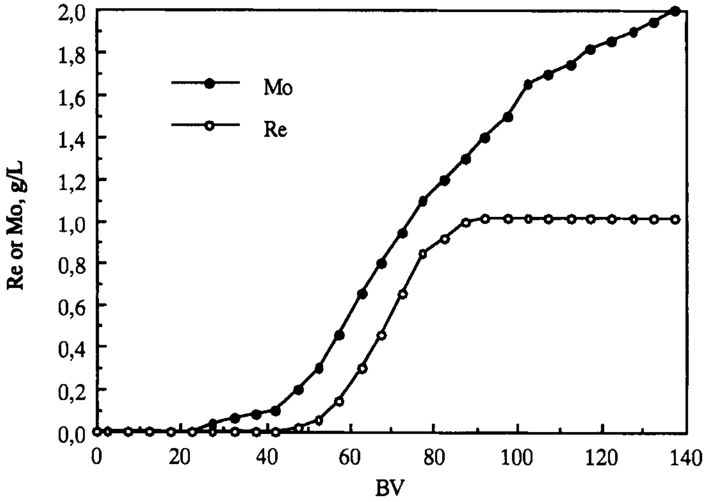


FIG. 4 Adsorption curves of Re and Mo on the resin IRA 93 SP; synthetic solution, pH 2; Re, 1.05 g/L; Mo, 1.96 g/L; column protected from daylight.

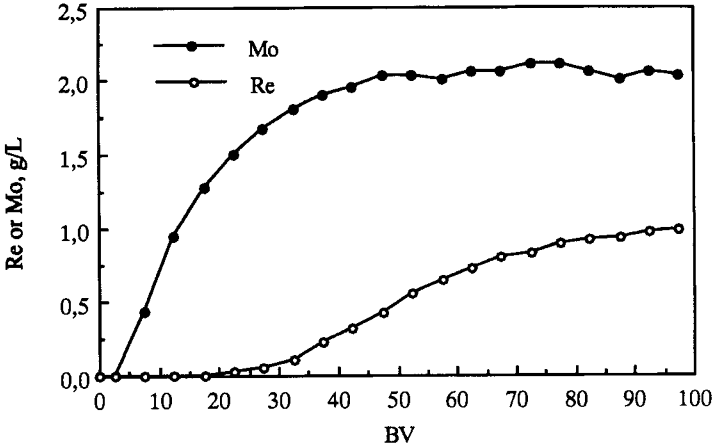


FIG. 5 Adsorption curves of Re and Mo on the resin IRA 93 SP; synthetic solution, 4 N H_2SO_4; Re, 1 g/L; Mo, 2.1 g/L.

In 4 N H_2SO_4 (Fig. 5) the resin still adsorbs rhenium but the loading is less: 50 g/L in 4 N H_2SO_4 instead of 70 g/L at pH 2. On the other hand, molybdenum seems less strongly fixed in very acidic media because, in this case, the breakthrough volume is reached for 1 BV. Concomitantly, the resin is less loaded in molybdenum (35 g/L instead of 190 g/L).

The weak affinity of the resin toward molybdenum in 4 N H_2SO_4 could make it possible to flow back molybdenum using concentrated sulfuric acid solutions containing Re.

Elution Step. Due to the use of a weak base tertiary amine resin, it is possible to elute rhenium using more classical elution agents than those used in the case of the strong base quaternary ammonium resin (Kennecott process).

Figure 6 presents the elution curve of a column previously loaded by the solution at pH 2 (Fig. 4), using an ammoniacal solution (1 M NH_4OH). In the case of this column containing 190 g/L molybdenum and 70 g/L rhenium, both Mo and Re are eluted almost instantaneously by 1 M NH_4OH. In order to recover Re selectively, it is thus necessary to expel molybdenum from the resin before rhenium is eluted. When 2 M NH_4Cl is used for eluting the same column (Fig. 7), molybdenum is not eluted. Unfortunately, this reagent cannot be used for rhenium elution because the elution peak of rhenium does not exceed 2.5 g/L and its elution is incomplete. Increasing the temperature to 60°C does not improve this elution.

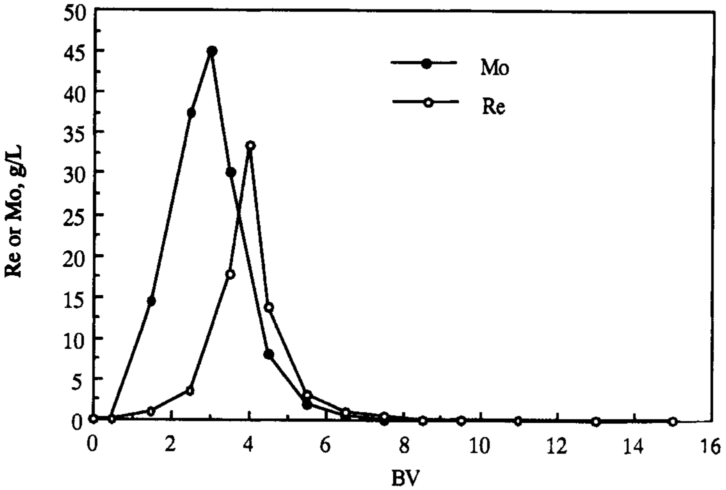


FIG. 6 Elution curves of Re and Mo with 1 M NH_4OH; resin IRA 93 SP loaded with 70 g/L Re and 190 g/L Mo.

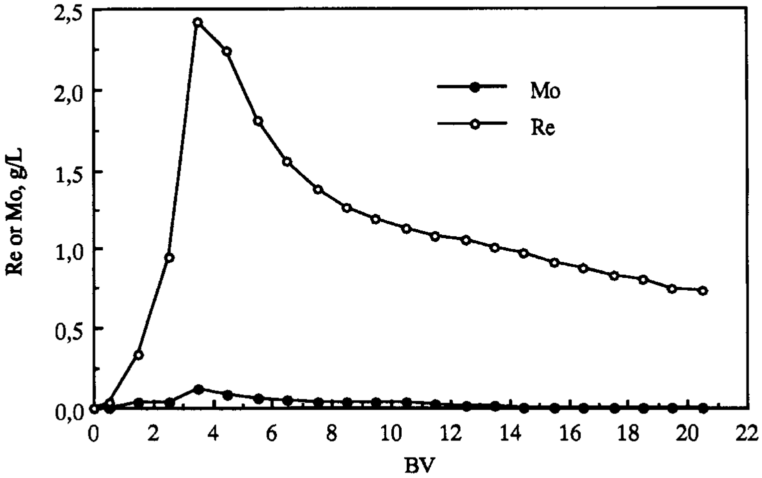


FIG. 7 Elution curves of Re and Mo with NH_4Cl; resin IRA 93 SP loaded with 70 g/L Re and 190 g/L Mo.

Since Mo is held less strongly than Re in acidic media, the backflow of molybdenum can be achieved using a sulfuric acid solution containing rhenium. Elution tests carried out with a solution of 6 N H_2SO_4 and 6 g/L Re show that all the molybdenum is expelled by rhenium from the resin loaded with 55 g/L Re and 35 g/L Mo in 11 BV. The results are given in Fig. 8. The sharp peak obtained demonstrates the efficiency of the reflux. The saturation of the resin in rhenium occurs at 20 BV. This suggests that the molybdenum and rhenium anionic complexes are different in sulfuric acid solutions.

Once the resin has been washed (in order to displace the impregnant solution), rhenium is eluted by a molar solution of ammonium hydroxide. Figure 9 shows the elution curves obtained for rhenium and molybdenum. The backflow method appears very efficient for displacing molybdenum from the resin because its concentration is very low in the rhenium elution solutions (Mo = 25 mg/L). Furthermore, rhenium elution is improved because only 9 BV are needed for total recovery of the resin load with an elution peak around 50 g/L.

The collected solutions and the NH_4ReO_4 crystals, obtained by crystallization of the eluting solution, were analyzed. The results show that the ammonium perrhenate is very pure. The Mo/Re ratio decreases from 0.5% in solution to 0.1% in the crystallized product.

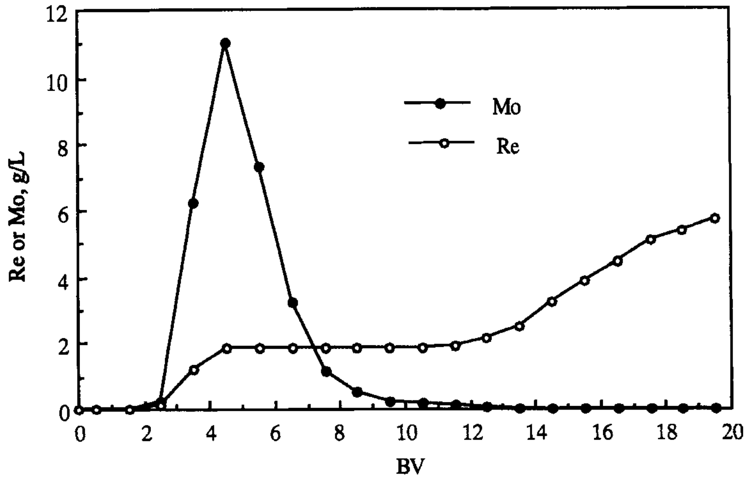


FIG. 8 Selective elution of Mo using the reflux method with concentrated sulfuric acid solution containing Re (H_2SO_4, 6 N; Re, 6 g/L); resin IRA 93 SP loaded with 55 g/L Re and 35 g/L Mo.

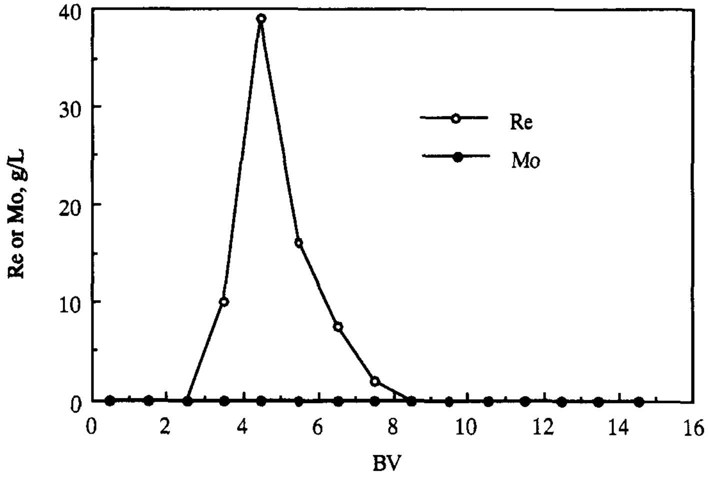


FIG. 9 Selective elution of Re, after Mo elution, with 1 M NH_4OH; resin IRA 93 SP loaded with 55 g/L Re and 35 g/L Mo.

Industrial Solutions

Tests were performed on Sample 1.

Adsorption Step. Fixation curves of molybdenum, rhenium, and selenium on resin Amberlite IRA 93 SP are given in Fig. 10. A comparison between those results and the ones obtained for synthetic solutions (Fig. 5) shows that industrial solutions behave exactly the same as synthetic solutions as far as the fixation of molybdenum and rhenium is concerned. Therefore, the presence of selenium in the industrial solution does not affect their adsorption.

The breakthrough volumes of molybdenum and selenium are almost instantaneous, while that of rhenium ranges between 15 and 20 BV. The resin is saturated with rhenium and molybdenum after feeding 100 and 50 BV, respectively.

Molybdenum Elution. As in the case of synthetic solutions, molybdenum can be eluted by using a 8-N concentrated sulfuric acid solution containing 4.5 g/L Re. The results presented in Fig. 11 confirm those in Fig. 8. The peak of the elution curve is obtained at 3 BV. Molybdenum displacement is almost complete before the resin is totally saturated in rhenium. A part of the selenium is also expelled by rhenium at the same time as molybdenum. Nevertheless, the elution of Se is less satisfactory because the elution curve exhibits a long "tailing-off" period.

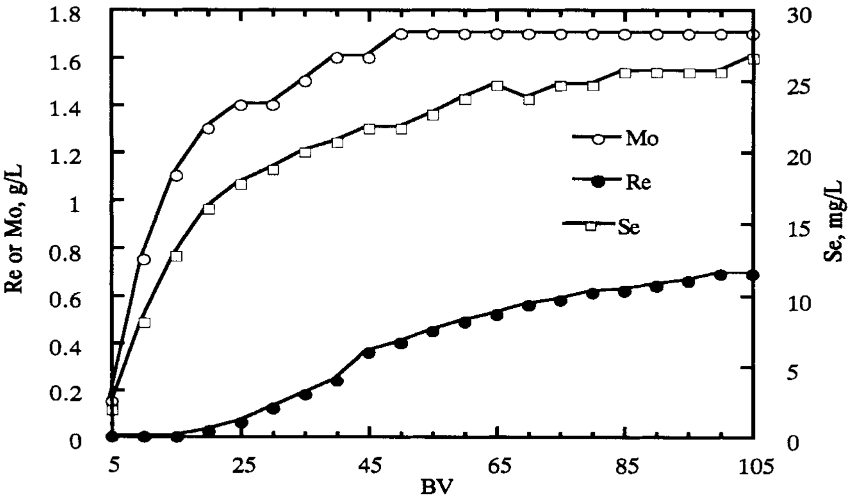


FIG. 10 Adsorption curves of Re, Mo, and Se on the resin IRA 93 SP; industrial solutions with Re (680 mg/L), Mo (1.6 g/L), and Se 23 (mg/L).

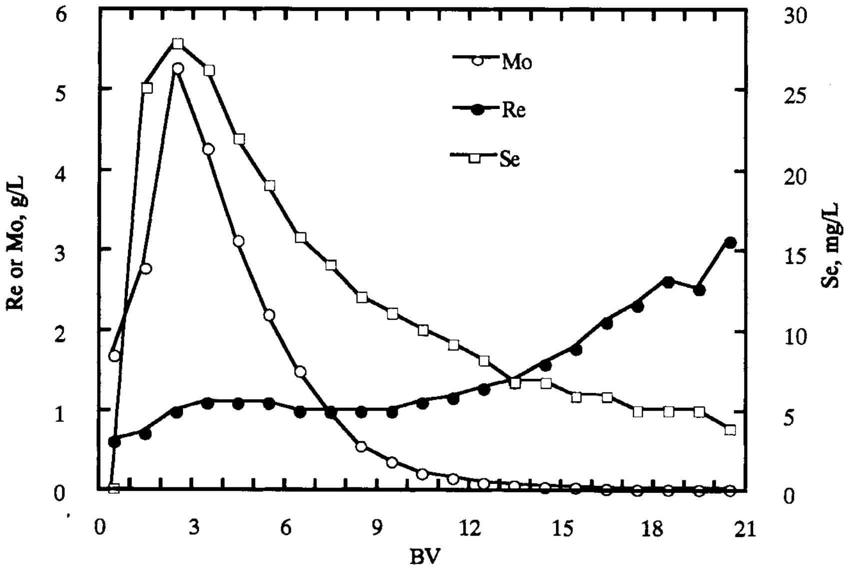


FIG. 11 Selective elution of Mo (and Se) with concentrated sulfuric acid containing Re (6 N H_2SO_4, 4.5 g/L Re); resin IRA 93 SP loaded from industrial solution.

Rhenium Elution. Elution of rhenium is realized by means of a molar solution of ammonium hydroxide. Figure 12 presents the elution curves of rhenium. Residual molybdenum and selenium are also present. Their concentration follows that of rhenium very closely. Thus, to obtain a pure solution of ammonium perrhenate, the backflow of Mo and Se in the previous step has to be complete. Nevertheless, by crystallization of such a solution, it is possible to obtain very pure crystals of ammonium perrhenate.

Recycling of the Resin

The effect of recycling the same volume of resin on its efficiency in Mo/Re separation was tested four times for each step of the process, i.e., adsorption, Mo (and Se) elution, and Re elution. After rhenium elution, the resin was simply washed with water before reuse. The tests were performed on industrial solutions (Sample 2). The results regarding adsorption are given in Figs. 13, 14, 15, and 16; those regarding Mo (and Se) elution in Figs. 17, 18, 19, and 20; and those regarding Re elution in Figs. 21, 22, 23, and 24.

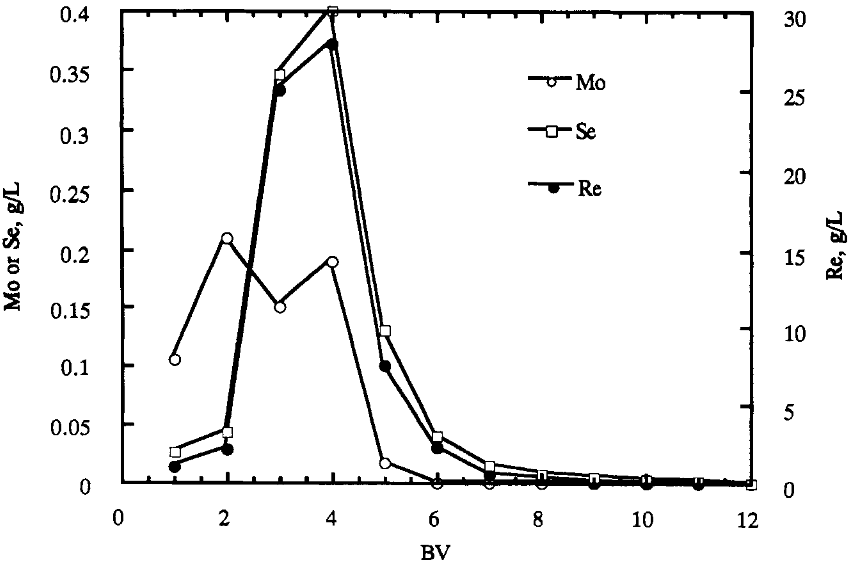
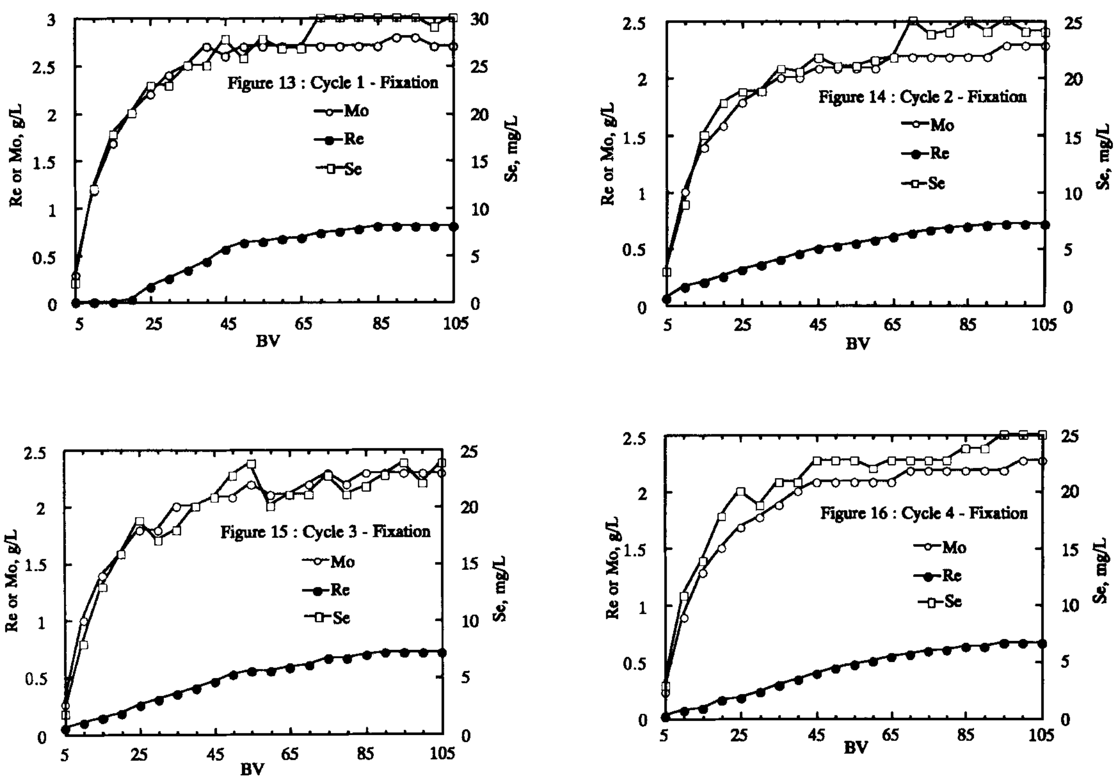
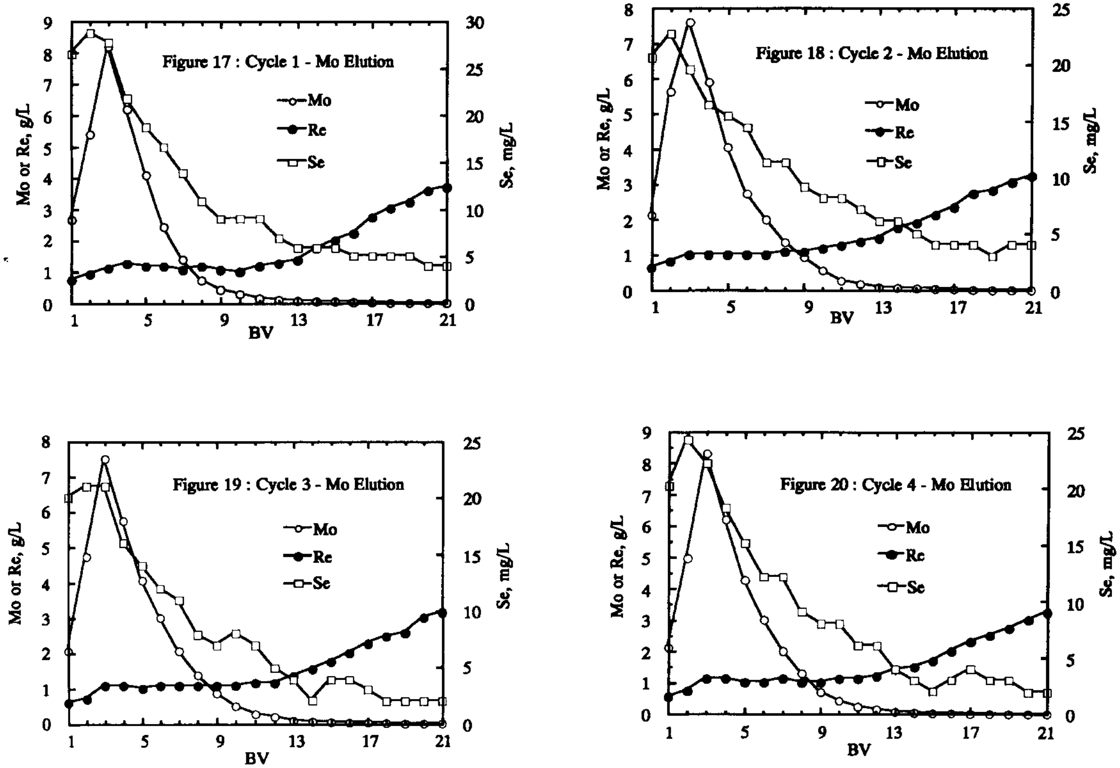


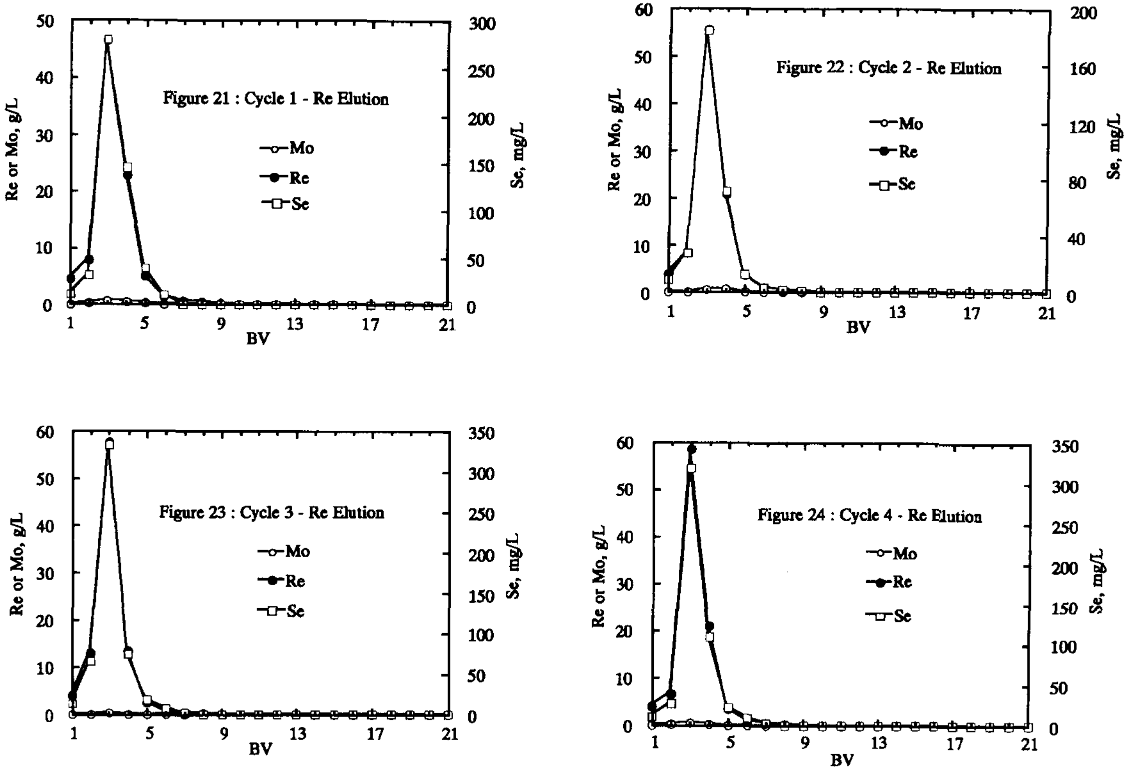
FIG. 12 Elution curves of Re, and residual Mo and Se, using 1 M NH_4OH. Resin IRA 93 SP loaded from industrial solution.



FIGS. 13–16 Effect of recycling on resin IRA 93 SP performance; adsorption cycles; industrial solution with Re (850 mg/L), Mo (2.8 g/L), and Se (31 mg/L).



FIGS. 17–20 Effect of recycling on resin IRA 93 SP performance; Mo elution cycles; industrial solution with Re (850 mg/L), Mo (2.8 g/L), and Se (31 mg/L).



FIGS. 21–24 Effect of recycling on resin IRA 93 SP performance; Re elution cycles; industrial solution with Re (850 mg/L), Mo (2.8 g/L), and Se (31 mg/L).

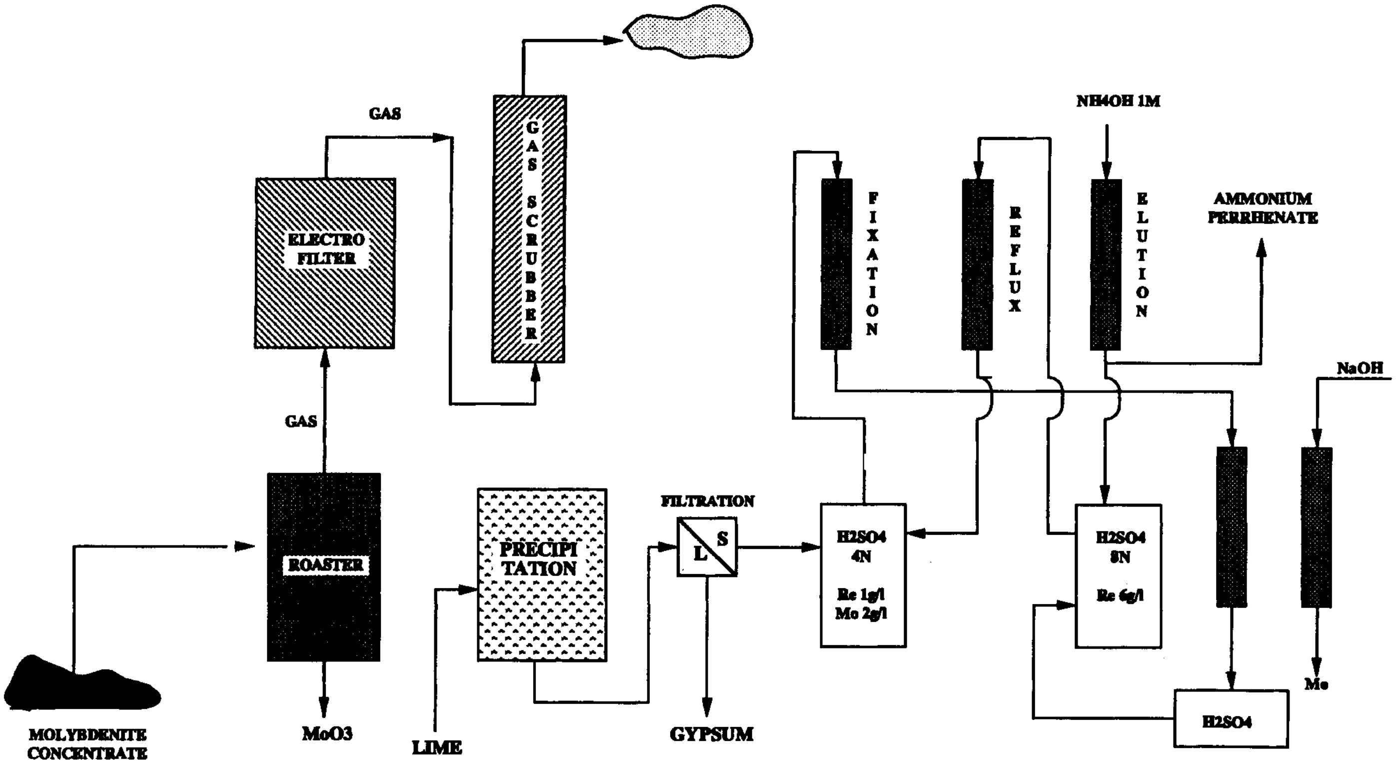


FIG. 25 Process for selective separation of rhenium from molybdenum contained in gas scrubbing solutions of molybdenite roasting, using the weak base anionic resins.

During the adsorption step, the breakthrough volume of rhenium appears early for Cycles 2, 3, and 4 (Figs. 14, 15, and 16). This proves that complete washing of the resin and optimization of the column length are crucial. Pilot tests will be required to solve these two problems.

On the other hand, the elution of molybdenum, selenium, and rhenium is less affected by resin recycling. The curves of elution corresponding to the fourth cycle (Figs. 20 and 24) are nearly the same as those obtained with a fresh resin (first cycle, Figs. 17 and 21).

Design of a Separation Process Using a Weak Base Resin

Based on the results obtained using resin Amberlite IRA 93 SP, we propose a new process for recovering rhenium from molybdenite. The scheme of this process is given in Fig. 25. Its principal steps are:

Molybdenite roasting
Washing of roasting gases
Clarification of the sulfuric acid solution, containing rhenium, by filtration after precipitation of sulfates by lime
Rhenium and molybdenum fixation
Molybdenum, and if necessary selenium, elution by the backflow method using a sulfuric acid solution containing rhenium
Rhenium elution by a solution of NH_4OH, and crystallization of a pure ammonium perrhenate from the eluate
Adsorption of molybdenum contained in the backflow solution on a strong base quaternary amine resin and subsequent elution as sodium molybdate by NaOH

CONCLUSION

The results indicate that the two techniques investigated in this paper (direct precipitation by organic reagents and separation on weak base resins) represent simple and efficient means for selectively recovering rhenium from acidic solutions ($H_2SO_4 \approx 4$ to 6 N) issued from the gas scrubbing of molybdenite roasting.

Direct precipitation using tetraphenyl phosphonium bromide yields a very pure organometallic precipitate, composed of approximately 25% rhenium and less than 1% molybdenum and selenium. Recovery rates higher than 90% can be obtained with reagent consumption of about twice the stoichiometry of the reaction. The precipitate can be separated by decantation followed by filtration.

The direct precipitation technique offers the possibility of obtaining a rhenium-rich product at the molybdenite roasting site. This rhenium concentrate can then be transported to a specialized plant at a much lower cost than can the solutions.

Weak base tertiary amine resins adsorb rhenium and molybdenum less strongly than strong base quaternary ammonium resins. This allows molybdenum to be expelled from the resins by Re contained in acidic solution. The rhenium can then be eluted using an ammoniacal solution. Crystallization of this solution yields a very pure ammonium perrhenate. A process based on these resins uses classical and inexpensive reagents (H_2SO_4, NaOH, CaO, NH_4OH). It requires fewer operating stages than the Kennecott processes.

The two proposed techniques may be complementary. Indeed, the organometallic precipitate can be decomposed thermally. The volatilized rhenium can then be absorbed in acidic solution and recovered by separation on resins.

REFERENCES

1. *Gmelins Handbuch*, "Masrium-Rhenium," 69/70, 1941.
2. W. Gonser, *Rhenium*, Elsevier, 1964.
3. R. Colton, *The Chemistry of Rhenium and Technetium*, Wiley, 1965.
4. K. B. Lebedev, *The Chemistry of Rhenium*, Butterworths, 1962.
5. J. G. F. Druce, *Rhenium*, Cambridge University Press, 1948.
6. A. Sutulov, *Molybdenum Extractive Metallurgy*, University of Concepcion, Chile, 1965.
7. S. Tribalat, *Rhénium et Technétium*, Gauthier-Villars, 1957.
8. P. Pascal, "Technétium-Rhénium," *Nouveau traité de chimie Minérale, Complément 10*, Masson, 1978.
9. E. M. Povlavko, *Inst. Mineralog. Geokhim. i Kristallokhim. Redkikh. Elementov*, *2*, Vlasov, Moscow, 1964, pp. 739–740.
10. I. D. Marchukova and S. Sh. Zak, *Dokl. Akad. Nauk SSSR*, *146*, 433–436 (1962).
11. M. Capitant, J. Francotte, P. Picot, and G. Troly, *C. R. Acad. Sci.*, *257*, 3443–3444 (1963).
12. *Handbook of Geochemistry*, II-5, Wedepohl, 1978.
13. P. Blazy, A. Floreancig, and E. A. Jdid, Internal Report, Research and Technology Ministry (France); Contract 88 R 0733, 1991.
14. L. Coudurier, I. Wilkomirsky, and G. Morizot, *Trans. Inst. Min. Metall.*, *79*(760), C34–40 (1971).
15. S. A. Fisher and V. W. Meloche, *Anal. Chem.*, *24* (1952).
16. V. W. Meloche and A. F. Preuss, *Ibid.*, *26* (1954).
17. S. R. Zimmerley and E. E. Malouf, U.S. Patent 2,809,092 (Kennecott Copper Corp.), 1957.
18. J. D. Prater and R. N. Platzke, U.S. Patent 3,558,268 (Kennecott Copper Corp.), 1971.
19. J. D. Prater and R. N. Platzke, Annual Meeting, AIME, New York, February–March 1971.
20. D. J. Bauer, D. D. Fisher, and R. E. Lindstrom, U.S. Patent 3,862,292, 1975.
21. L. R. Quatrini and M. B. MacInnis, U.S. Patent 4,185,078, 1980.
22. L. Karagiosov and C. Vasiliev, *Hydrometallurgy*, *4* (1979).

23. H. B. Pietsch, Ion and Solvent Extraction, Oslo Symposium, 1982.
24. H. D. Peterson, U.S. Patent 3,751,555, 1973.
25. K. J. Richard and C. N. Wright, U.S. Patent 3,894,866, 1975.
26. D. Douglas and K. T. Reilly, U.S. Patent 4,584,185, 1986.
27. H. G. Nadler and P. Borchers, *Erzmetall*, *40*(6), 293–298 (1987).
28. I. K. Taimi and G. B. S. Salaria, *Anal. Chim. Acta*, *12* (1955).
29. A. Floreancig and E. A. Jdid, French Patent 91 02876 (06/03/1991).
30. P. Blazy, *Ind. Miner.*, *Spéc. Mineralurgie*, pp. 1–13 (1973).
31. P. Blazy, *La Valorisation des Minerais*, Presse Universitaires de France, Paris, 1970.

Received by editor April 20, 1992
Revised November 4, 1992