

## Associated Rhenium Extraction in Complex Processing of Productive Solutions of Underground Uranium Leaching\*

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### Abstract

The possibility of associated rhenium extraction during complex processing of productive solutions of underground uranium leaching (UL), by means of precipitation and membrane methods with the use of cationic water-soluble polyelectrolites (PE) is shown. High-molecular nitrogen-containing substances are used as PE (BA series; as well as pilot models, developed in the Mendeleyev Russian Chemical and Technological University). It has been established that rhenium extraction from sulphuric productive solutions of UL with the use of complexation – ultrafiltration method proceeds most effectively on application of polyelectrolite BA-212. Pilot models of polyelectrolites AC-392, AC-412, OP-1-76, AP-392, AP-400 have the best characteristics for rhenium precipitation from industrial nitrate-sulphuric solutions, formed in sorption processing of productive solutions of UL.

### INTRODUCTION

Development of advanced technologies is greatly determined by materials, available for the development of new equipment. Rhenium occupies a special place among strategically important rare metals. It is an irreplaceable component of super alloys, used to make essential parts of machinery that function under extreme conditions. In the recent years world demand for rhenium has overgrown its supply and totaled 44 tons [1]. That is due to rhenium unique properties such as refractoriness, plasticity, high density, corrosive medium resistance and catalytic reactivity. Rhenium share in super alloys for use in alloys for aerodynamic industry has jumped dramatically (up to 80 %).

Rhenium is one of the less-common elements in the Earth's crust (the clark of rhenium being  $7 \cdot 10^{-8}$  % according to A. P. Vinogradov). Because of its particular geochemical properties, rhenium is extracted throughout the world only as a by-product in complex processing of molybdenic and copper ores [2].

Rhenium reserves are almost lacking in Russia. Rhenium content in molybdenic concentrates of the Russian ore mining and processing enterprises (Zhireken, Sor and Tyrnauz) is insignificant (20–100 g/t) [3]. The hope to discover large-scale workable fields (such as copper-porphry deposits and cupriferous sandstones), that constitute the main type of rhenium raw material resources abroad, is limited. After disintegration of the USSR, all the rhenium sources turned out to be outside Russia. Thus development of alternative rhenium sources is urgent.

Industrial development of rhenium containing fields, such as produced by volcanic activity of high-temperature fumarole gases and

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vulcanites (Kudriavy Volcano, Iturup Island, Kuril Islands) is complicated because of lacking infrastructure and severe natural climate in the region.

Uranium raw material with polymetallic properties serves as additional rhenium supply.

Fair quantities of rhenium were produced from uranic ore for the period 1969–1974 (Falls city, Texas, Susquehanna Corp.). Diluted rhenium solutions were transported to Denver where they were worked into ammonium perrhenate [6].

Increased rhenium contents (0.5–3.0 g/t) were determined in numerous uranium deposits of the Colorado Plateau, USA [7].

The possibility of associated rhenium extraction from uranium-noble metal-vanadium ores is shown (Srednyaya Padma deposit, Karelia, Russia) [8], rhenium content being 0.2–0.5 g/t [9].

A progressive way of processing uranium ore deposits is underground leaching (UL).

Multicomponent productive solutions formed during complex processing of polymetallic uranium ores contain 0.1–0.3 mg/dm<sup>3</sup> of rhenium [10, 11]. During hydrometallurgical treatment associated rhenium and uranium are extracted together at strongly-basic anionite at sorption redistribution stage. Separation of these elements and rhenium extraction can be performed during desorption procedure. After uranium selective elution, the strongly-basic anionite turns into rhenium-containing concentrate [10, 11].

Extraction and sorption technologies were developed for associated rhenium extraction from productive solutions of underground uranium leaching [12]. A mixture of TAA and TBF in diluent was used as the extractive agent. The AM-p and AMP strongly-basic anionites and activated carbon were taken to be sorbents. Rhenium extraction from solutions with the use of activated carbon came to 90–95 %, concentrating degree being 400–500 [12]. Rhenium elution from anionites was carried out with the use of sulphuric acid solution under extraction desorption conditions

On the territory of the former USSR (the Navoiy Mining and Smelting Industrial Plant, Uzbekistan) rhenium was extracted during the complex processing of uranic ores and underground leaching solutions with the use of extraction methods and non-standard equipment [13, 14].

The authors of work [15] describe two fundamental schemes of processing multicomponent productive solutions of the UL uranium from ores of the Kyzyl Kum region deposits, Uzbekistan. The first scheme contemplates collective sorption of uranium, molybdenum and rhenium on the anionites AMP, VP-1P, selective molybdenum desorption with ammonia and ammonium sulphate solutions, selective rhenium desorption with ammonium thiocyanate solutions, extraction concentrating, solid-phase re-extraction, recrystallization and obtaining ammonium perrhenate. The first two above-mentioned stages are the same in both the first and the second schemes. Next, according to the second scheme a simultaneous uranium and rhenium desorption with sulphuric ammonium nitrate solutions is conducted, uranium being precipitated with ammonia and polyuranate being obtained. Then, rhenium sorption after-extract out of mother waters of uranium concentrate precipitation on the AM and AMP anionites is carried out, rhenium being desorbed with ammonium thiocyanate solution and ammonium perrhenate being separated from commercial strippant by evaporation.

In the late 1980-ies, field test on rhenium and uranium co-extraction out of productive UL solutions by means of sorption method, with the use of AMP and VP-1P anionite mixture and separate elution, was performed in the Chu-Sarysuy province, Inkay deposit, Kazakhstan [15]. Also a scheme of simultaneous rhenium-scandium sorption from the mother waters of uranium sorption on the AFI-22 ampholyte was tested. Pressure ion-exchange columns with the periodic resin loading and unloading were used as the main equipment.

The estimated technical and economic assessment of processing of the productive uranium UL solutions with the use of sorption method has shown high profitability (over 500 %) of rhenium co-extraction from solutions with rhenium concentration lower than 0.2 mg/dm<sup>3</sup> [10, p. 386].

In the present work the possibility of rhenium extraction during processing of the uranium-containing solutions of such a concentration by means of membrane and precipitation methods with the use of water-soluble polyelectrolytes is studied.

## EXPERIMENTAL

### Rhenium extraction by complexation – ultrafiltration method

Baromembrane methods are very promising for rhenium extraction and thickening from diluted solution. Among these methods, combined complexation – ultrafiltration method (COUF) is of the highest selectivity. It is based on formation of metal compounds with high molecular mass through preliminary injection of water-soluble polymer into the solution and separation of the obtained compounds by passing through ultrafilter [16].

Cationic polyelectrolytes (PE) of the VA-types (VA-2, VA-112 and VA-212), containing quarternary ammonium base groups, were tested as water-soluble polymers to extract rhenium from sulfuric solutions, the latter simulating productive and residual UL solutions [17].

Kinetic method was used to evaluate rhenium concentration in aqueous solutions [18].

Variation in rhenium concentration in solution during ultrafiltration was controlled by radioactive indicator method. Isotope  $^{188}\text{Re}$  ( $T_{1/2} = 16.7$  h), produced in a specially designed generator, was used for radioactive labeling.

The experiments were conducted with the use of ultrafiltration system (Fig. 1). Ultrafiltration tube with separating membranes, made in the form of hollow polysulphone fibres (nominally cutoff molecular mass of solutes being 40 thousand atomic mass units), provides the main part of this system [20]. Filtering was carried out under solution circulation conditions, overpressure of 0.5 atm being kept at the diaphragm module inlet.

The maximum selectivity of the process is observed on application of VA-212 polyelectrolyte, with the following structure of the elementary units:

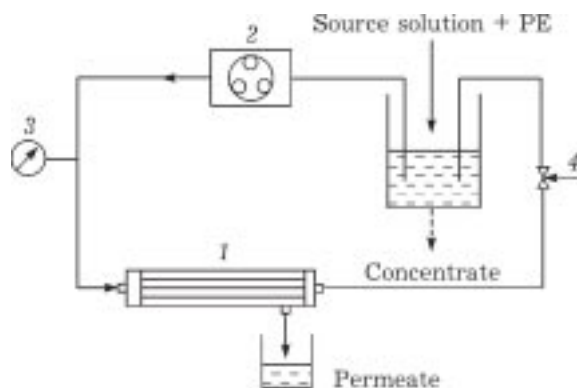
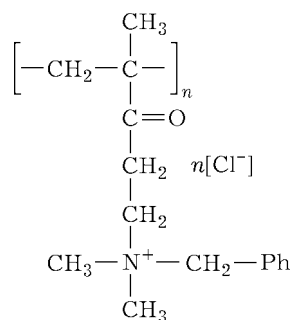


Fig. 1. Basic scheme of ultrafiltration system: 1 – diaphragm module, 2 – pump, 3 – manometer, 4 – valve.

Nitrate solutions were used for regeneration of the rhenium containing PE. Polyelectrolyte, coagulating in the process, was transformed into dissolved state by introducing the reducing agent into the solution [21].

### Rhenium extraction by precipitation method

Precipitation method with the use of water-soluble PE was tested for rhenium extraction from productive nitrate-sulphate solutions, formed during sorption processing of productive solutions (PS). The authors of [22] present the data on coagulation threshold of cation PE, containing quarternary ammonium base groups, in mineralized solutions. It has been shown that the least coagulation threshold is observed in the presence of nitrate ions.

High-molecular compounds based on copolymers of amine-alkyl esters of methacrylic acid, vinyl methyl pyrazole and ethyl thioethyl methacrylate (AC-392, AC-412, AP-392, AP-400, AP-411-1, AP-411-2, AP-411-3, AP-411-4, AP-312, AP-312-2, CP-112, OP-1-76, OP-3-78)\* were used as PE for rhenium precipitation from industrial nitrate-sulphate solutions.

Rhenium extraction by PE precipitation was carried out by the following procedure. Polyelectrolyte (2 % solution in distilled water) was introduced into the solution on mixing. The

\* Synthesized by A. S. Tevlina, N. I. Skripchenko at the Department of Applied Chemistry of Plastics, Mendeleev University of Chemical Technology.

TABLE 1

Rhenium precipitation by polyelectrolytes from nitrate-sulphate solutions, formed during sorption processing of productive solutions of underground uranium leaching

No.	PE type	Rhenium precipitation rate, %, for a given PE : Re mass ratio				
		4.3	21.7	43.0	130	430
1	AC-392	2.4	16.8	6.8	34.1	67.1
2	AC-412	10.2	18.6	26.9	49.7	71.3
3	OP-1-76	–	–	18.6	–	63.5
4	OP-3-78	0	5.4	10.2	37.1	64.1
5	AP-312	7.2	4.2	7.2	19.8	41.3
6	AP-312-2	8.0	13.8	10.2	23.4	40.1
7	AP-392	0	4.2	5.4	37.1	58.1
8	AP-400	4.2	15.0	19.8	35.3	68.3
9	AP-411-1	4.2	4.2	5.4	10.2	16.8
10	AP-411-2	6.0	1.2	2.4	10.2	22.3
11	AP-411-3	4.2	0	0	7.2	10.2
12	AP-411-4	7.2	8.4	8.4	12.6	–
13	CP-112	16.8	8.4	13.8	21.0	40.1

resulting pulp with the precipitated PE was mixed for 20 min, then filtered. Variation in rhenium concentration in the solution was controlled by radioactive indicator method.

Rhenium precipitation from industrial nitrate-sulphate solution with pH 7.2 was studied under changes of polyelectrolyte to rhenium mass ratio from 4.3 : 1 to 430 : 1 (Table 1). As can be seen from the Table 1, rhenium concentration in the filtrate decreases with increasing PE to rhenium ratio. The maximum level of rhenium extraction during one contact (58–71 %) is observed with the use of the following PE types: AC-392, AC-412, OP-1-76, AP-392, AP-400 (see Table 1, positions 1, 2, 3, 7, 8).

## RESULTS AND DISCUSSION

Methods of associated rhenium extraction during complex processing of productive solutions of uranium underground leaching, based on the use of the synthetic water-soluble cation polyelectrolytes have been studied.

Because of low power inputs and continuous complexation – ultrafiltration process, this method is very promising for rhenium extraction from productive and residual sulphuric solutions of uranium underground leaching. Of all the polyelectrolytes under study, the maximum selectivity of the process is observed

on application of VA-212 polyelectrolyte. Considering a relatively high PE cost, economically sound application of this method is possible providing regeneration and reuse of the polyelectrolyte.

Rhenium extraction by precipitation method from industrial nitrate-sulphate solutions, formed during sorption processing of productive UL solutions, in the presence of polyelectrolyte, yields a high concentration rate of rhenium. This method does not require any complicated equipment or high power inputs. The maximum level of rhenium extraction (up to 71 % during one contact) is observed with the use of the following PE types: AC-392, AC-412, OP-1-76, AP-392, AP-400.

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