The improvement of rhenium recovery technology from W-Re alloys

O G Kuznetsova, A M Levin, M A Sevostyanov and A O Bolshih

A.A. Baikov Institute of Metallurgy and Materials Science of Russian Academy of Science, 49 Leninsky pr., Moscow, Russian Federation

Abstract. The lack of rhenium raw materials sources on the territory of Russia leads to the necessity of this valuable metal recovery from wastes and secondary raw materials, in particular, from tungsten-rhenium alloys. The using of hydrometallurgical and electrochemical technologies is the most promising way to dissolve and recovery these metals in the form of prospective precursors. It is considered, that the fundamentals of an improved technology of rhenium recovery in the form of perrhenic acid from binary W-Re alloys. It is shown the desirability of avoiding the precipitation of metal in the form of potassium perrhenate. A basic technological scheme of the Re recovery process is proposed. It includes anodic dissolution of W-Re alloys, precipitation of calcium tungstate from the electrolyte and electrodialysis of rhenium in the form of perrhenic acid.

1. Introduction

Rhenium and its alloys find wide application in various fields of modern technology. The basic part of this metal is used to create special alloys for aviation and aerospace industry. So, the demand of Re grows continuously [1, 2]. It results in the task of increasing the volume of rhenium production, which can be solved by expanding the range of raw materials and the application of various types of secondary rhenium-containing raw materials. Also it is very important to create the new efficient technological schemes for recovery this valuable metal [3, 4]. The recovery of rhenium from waste and secondary raw materials is especially important for Russia because of the absence of exploited rhenium deposits [5, 6].

The development of new technological processes for recovery rhenium from technical secondary raw materials and commercial products of Re manufactory is very actual not only for Russian researchers [7-10]. This can be considered as the sources of secondary rhenium not only the metal production wastes, but also its binary alloys with nickel, tungsten, molybdenum, as well as multicomponent high-temperature and heat-resistant rhenium alloys based on nickel, so-called "superalloys" [3-5, 11-14].

One of the most common sources of secondary rhenium is the wastes of tungsten alloys with rhenium (TR alloys). The recovery of rhenium from them can be carried out by various pyro- and hydrometallurgical methods [5]. At the same time, electrochemical methods are the most promising way for fast and effective alloys dissolution with the recovery of individual metals by well-known hydrometallurgical methods [15-18]. In addition, the using of electrochemical technologies, namely, electrodialysis, allows to receive perrhenic acid or ammonium perrhenate (which are the best rhenium precursors from potassium perrhenate).
2. Experimental part

Earlier [17, 18], we investigated the anodic polarization of tungsten, rhenium and the VR 20 alloy in sodium hydroxide solutions, detected the optimal conditions for the alloy dissolution and offered a basic technological scheme for processing a VR 20 alloys waste. The disadvantages of the proposed scheme are:
- the extraction of rhenium in the form of potassium perrhenate, which leads to increased losses of rhenium, the necessity of secondary Re extraction from mother liquor, the irretrievable loss of the precipitant, an increased volume of salt drains;
- considerable energy consumption for electrodialysis due to low solubility of potassium perrhenate;
- the difficulty in utilisation or recycling catholyte - a potassium perrhenate solution.

The weak spot of electrodialysis synthesis of rhenium acid is a high bath voltage, which leads to electrolyte heating and increases the power consumption of the process. Thus, according to [17], the total power consumption of this stage is over 16 W·h/g perrhenic acid.

To analyze the power consumption for carrying out the process of electrodialysis of perrhenic acid from potassium perrhenate, a voltage drop was measured on the elements of a three-chamber electrolytic cell, described in [15, 16]. It was found that the voltage drop in the central chamber (64-73%) contributes most to the voltage balance of the cell, which is due to the low electrical conductivity of the potassium perrhenate solution because of its low solubility in water [5, 9]. In order to reduce the bath voltage it is necessary to:
- increase the temperature of the central chamber solution;
- maintain the concentration of potassium perrhenate at the highest possible level;
- forced mixing of the solution in the central chamber.

In order to reduce the number of stages in the technology for processing VR alloys, a direct electrodialysis processing of the electrolyte obtained after anodic dissolution of the alloy has been tested. This would allow the recovery of rhenium in the form of perrhenic acid, excluding the precipitation stage of potassium perrhenate. The process was carried out in a three-chamber cell described earlier [15], the initial concentration of perrhenic acid in the anolyte was 51,6 g/l, the starting solution in the central chamber contained 23,2 g/l Re and 93,0 g/l W. It was established, however, that direct electrodialysis fabrication of electrolyte in HReO₄ can not be carried out because of the sharp and rapid drop in current strength and the increase in bath voltage during the process. This may be related to the appearance of a poorly soluble tungstic acid on the surface and in volume of an anion-exchange membrane, formed by transfer of tungstate ions from the central to the anode chamber, containing a strongly acid electrolyte. The latter can lead to "clogging" of the anion-exchange membrane of non-conductive H₂WO₄.

The observed effect was confirmed by the balance of voltage on the electrodialysis cell. It was found that at the beginning of the process at a voltage of 9,35 V and a strength of current of 750 mA, the voltage drop across the anion-exchange membrane was 4,27 V or 45,67% of the total bath voltage. At the end of half an hour at a voltage of 25,50 V and a strength of current of 250 mA, the voltage drop across the anion-exchange membrane was 21,5 V or 84,31% of the total bath voltage, which prevents the further process and can be explained by the "clogging" anion-exchange membrane by the tungsten acid.

Thus, the presence in the electrolyte tungstate ions does not allow to receive perrhenic acid from accumulated electrolyte with a great efficiency by means of one stage of the electrodialysis.

The removal of tungsten from the electrolyte can be carried out by known methods and, in particular, precipitation of artificial scheelite - CaWO₄.

Tungsten in the form of CaWO₄ was precipitated from the above-obtained electrolyte (C₉, = 23,2 g/l, C₉, = 93,0 g/l) with the aid of Ca(OH)₂, taken in a threefold excess with respect to the stoichiometrically required content with stirring. The degree of tungsten precipitation was 99,2%. Tungsten can be extracted later in the form of tungstic acid from the obtained calcium tungstate. The resulting solution containing sodium perrhenate may be directed to the rhenium recovery by the
method of electrodialysis, excluding the stage of potassium perrhenate precipitation. This will reduce the loss of rhenium with the KReO$_4$ mother liquor and improve the electrodialysis process due to the substantial increasing of rhenium concentration in the central chamber solution (at the temperature of 30°C solubility of sodium perrhenate is 59.6 wt.%, and potassium perrhenate - 1.52 wt.%) [5].

At the same time, the resulting solution of sodium perrhenate contains a significant amount of hydroxide ions, remaining in the electrolyte after anodic dissolution of the VR 20 alloy, which pass from the solution of the central to the anode chamber and are able to interact with the H$^+$ ions contained in the anolyte. It results in power consumption growth of the electrodialysis process, and the dilution of the rhenium acid solution with forming water. In connection with the foregoing, the solution obtained after removing the tungstate ions, containing NaReO$_4$ and NaOH, was sent to the electrochemical neutralization stage carried out by the anodic reaction: $4\text{OH}^- - 4e = 2\text{H}_2\text{O} + \text{O}_2 \uparrow$.

The neutralization process was carried out in an plexiglas electrochemical cell with separation of the anode and cathode chambers with the aid of a cation-exchange membrane. Cathode - stainless steel, anode - platinum plate.

An electrolyte was poured into the anode chamber with a rhenium concentration of 17.98 g/l Re, and into the cathode chamber - the solution of NaOH 100 g/l. Neutralization was carried out for 3 hours. Dependence of the pH of the electrolyte on the passed quantity of electricity (Q, A×h) is shown in figure 1. As a result of the neutralization process, it was possible to decrease the pH of the electrolyte to a value of 6.55. The resulting catholyte, enriched in sodium hydroxide, can be sent to the head of the process to dissolve the alloy VR 20.

The obtained solution containing sodium perrhenate with a rhenium concentration of 17.98 g/l was subjected to electrodialysis according to the procedure [15, 16]. A perrhenium acid solution with an HReO$_4$ concentration of 54,1 g/l was placed in the anode chamber, a sodium perrhenate solution with a rhenium concentration of 17.98 g/l - into the central chamber, a solution of NaOH 100 g/l - into the cathode chamber. The volume of each section solution was ~ 300 ml. The values of the current strength, voltage and temperature were monitored during the electrodialysis. Electrodialysis was performed for 1,25 hours. As a result of the process, the concentration of perrhenic acid in the anolyte increased and reached a concentration of 74,24 g/l. Table shows the material balance of rhenium.

It is established that during electrodialysis the main contribution to the bath balance is made by the voltage drop in the central chamber, which increases with spread of process time. It is related with decrease in sodium perrhenate content in the solution. Recommended process conditions are: current density on membranes ≤ 5 A/dm$^2$, temperature in the anode section < 30 °C, in the central and cathode chambers - up to 50 °C.

It should be noted that the value of consumed electric power of offered process in comparison with the electrolysis of the solution of potassium perrhenate is significantly reduced and comprised 2.79 W×h/g vs. ~ 16 W×h/g [17]. This is due to the increase in the conductivity of central chamber.

![Figure 1](image_url)

**Figure 1.** Dependence of the pH of the electrolyte on the quantity of electricity passed during the electrochemical neutralization of the rhenium-containing electrolyte
Table. Material balance of rhenium in the process of electrodialysis conversion of sodium perrhenate solution to perrhenium acid.

| Product                  | Introduced Re | Received Re |
|--------------------------|---------------|-------------|
|                          | g    | %     | g    | %     |
| Central section solution | 5.39 | 30.9  | 0.67 | 3.8   |
| Anolyte                  | 12.03| 69.1  | 16.51| 94.8  |
| Total                    | 17.42| 100.0 | 17.18| 98.6  |
| Imbalance *              | -    | -     | -0.24| -1.4  |

* The imbalance includes losses of rhenium with washing water and quantitative chemical analysis.

Thus, it has been shown that the production of perrhenium acid by the electrodialysis method is possible directly from the tungsten-free electrolyte (excluding the stage of potassium perrhenate precipitation). So, the scheme for the perrhenic acid production from the VR 20 alloy, described in [17], has become simplified. This will reduce the loss of rhenium with mother liquor and wash water. An improved scheme for VR 20 alloy processing with perrhenic acid production is shown in figure 2.

![Figure 2. Schematic diagram for the recovery of rhenium from a VR 20 alloy in the form of perrhenic acid](image_url)
The most complete purification of sodium perrhenate solution from excess calcium cations (after precipitation of calcium tungstate) should be realized by precipitation of CaCO$_3$ with the aid of a small amount of Na$_2$CO$_3$, as shown in figure 2. This will allow sodium hydroxide solution to be used as a catholyte in the electrodialysis stage of rhenium acid production, which can then be directed to the head of the technological scheme, namely, to the stage of electrolytic dissolution of the VR 20 alloy.

3. Conclusions

A technique for measuring the voltage drop across elements of a three-chamber electrolysis cell in the process of rhenium acid synthesis has been developed. These data have been used to calculate the balance of bath voltage. It has been shown that the main bath voltage drop in the case of the synthesis of rhenium acid from potassium perrhenate takes place in the central chamber of the cell.

It has been established that direct electrodialysis treatment of tungsten-rhenium-containing electrolyte leads to a sharp increase in the voltage drop across the anion-exchange membrane. This is due to its clogging with a poorly soluble tungstic acid, which prevents the effective process of rhenium acid synthesis.

It is shown that preliminary purification of tungsten-rhenium-containing electrolyte from tungsten by its precipitation in the form of an artificial scheelite allows direct extraction of rhenium from the purified solution by electrodialysis in the form of rhenium acid. At the same time, a fivefold reduction in power consumption for electrodialysis process has been achieved.

An advanced technological scheme for processing the waste products of tungsten-rhenium alloys with the recovery of rhenium in the form of perrhenic acid of high concentration was developed and proposed. The main stages of the proposed process have been tested in a large laboratory scale.

The work was carried out according to the state task № 007-00129-18-00

4. References

[1] Paretksy V M, Besser A D and Gedgagov E I 2008 Ways to increase rhenium production from ore and technogenic raw materials Non-ferrous metals 10 17-21
[2] Kasikov A G and Petrova A M 2010 Recycling of rhenium from waste heat-resistant and special alloys Technology of metals 10 2-12
[3] Agapova L Y, Abisheva Z S and Kilibaeva S K 2017 Electrochemical processing of technogenic wastes of rhenium-containing high-temperature nickel alloys in sulfuric solutions Non-ferrous metals 10 69-73
[4] Petrova A M, Kasikov A G and Gromov P B 2011 Extraction of rhenium from waste of complex alloy high-temperature nickel-base alloys Non-ferrous metals 11 39-43
[5] Palant A A, Troskhina I D, Chekmarev A M and Kostylev A I 2015 Rhenium technology (Moscow: OOO "Halley-print") p 47
[6] Bykhovsky L Z and Tignon L P 2015 Strategic mineral raw materials: ways to solve the problem of deficiency Mineral resources of Russia. Economics and management 5 43-49
[7] Elesemov T B, Chernyshova O V and Shakirova D T 2015 Electrochemical dissolution of nickel-rhenium-containing alloys Fine Chemical Technologies vol X 2 53-60
[8] Palant A A, Bryukvin V A and Levin A M 2013 Electrochemical processing of metal waste of non-ferrous and rare metals Inst. of Metallurgy and Material Science A. A. Baikova is 70 years old (Moscow: Intercontact Science) pp 176-182
[9] Guro V P and Belov A A Purification of ammonium perrhenate and rhenium extraction from the rhenium containing alloy Conf. "Resource-reproducing, low-waste and environmental technologies for subsoil development" 2012 September 17-21 Moscow - Ust-Kamenogorsk pp 165-166
[10] Petrushin N V, Ospennikova O G and Elyutin E S 2014 Rhenium in single-crystal high-temperature nickel alloys for gas turbine engine blades Aviation Materials and Technologies. 5 5-16
[11] Tingyu C, Ning X and Kaiyuan P 2009 Technology of production and application of rhenium and its alloys Rare Metal Mater. and Eng. 38 2 373-376
[12] Singh Gaur R P, Wolfe T A and Braymiller S A 2015 Recycling of rhenium-containing wire scrap International Journal of Refractory Metals and Hard Materials 50 79-85
[13] Fleischmanna E, Millerb M K and Affeldtc E 2015 Quantitative experimental determination of the solid solution hardening potential of rhenium, tungsten and molybdenum in single-crystal nickel-based superalloys Acta Materialia 87 350-356
[14] Lessard J D, Gribbin D G, Shekhter L N 2014 Recovery of rhenium from molybdenum and copper concentrates during the Looping Sulfide Oxidation process Int. Journal of Refractory Metals and Hard Materials 44 1-6
[15] Palant A A, Levin A M and Bruckvin V A 2010 Preparation of concentrated solutions of rhenium acid by electrodialysis Non-ferrous metals 11 62-64
[16] Palant A A, Bryukvin V A and Levin A M 2011 Combined process for obtaining concentrated solutions of rhenium acid Electrometallurgy 7 23-25
[17] Levin A M and Levchuk O M 2017 Electrochemical recovery of rhenium from W-Re alloys in the form of perrhenic acid: 1. Fundamentals of the process Russian metallurgy (Metally) 1, 47-53
[18] Levin A M, Kuznetsova O G and Levchuk O M Comparison of the anodic behavior of the alloy WR-20 and its components in NaOH solutions Conf. "Innovation, technology, science". 2017 January 25 Perm (Ufa: AERTERNA) part 3 pp 67-70