AMMONIUM PERRHENATE PURIFICATION AND RHENIUM RECOVERY FROM HEAT-RESISTANT RHENIUM-NICKEL SUPERALLOYS

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Abstract
An enterprise for purification of crude ammonium perrhenate purchased at Central Asia region as well as for rhenium recovery from Re-Ni heat resistant superalloys wastes of CMSX–4 & CMSX–10 types, has started its activity at Czech Republic. First type of rhenium raw material - the initial ammonium perrhenate (APR), for example, according to Uzbekistan's Standard TU 48–7-1-90, type AR-0, contains: Re not less than 69 % mass.; impurities, ppm: P 90, S 200, Fe 50, Mn 2; Mg 8, Ni 2, Al 5, Mo 5, Ca 10, Cu 3, K 40–70; Na 40. By means of ion exchange on Purolite resins surface and electrodialysis approach the content of above mentioned impurities in NH₄ReO₄ salt might be significantly reduced (K< 20). Second type of rhenium raw material – metallic wastes of superalloys of CMSX–4 & CMSX–10 type contains, % mass: Re 3–6; Cr 6.5; Co 9; Mo 0.6; W 6; Ta 6.5; Re 3; Al 5.6; Ti 1; Hf 0.1; Ni 61.7. The resulting APR is of high quality too. Powdery metal rhenium might be produced from this APR by means of its high-temperature reduction by gaseous hydrogen. The purity of obtained metallic rhenium is generally determined by purity of APR applied.

Keywords,
Ammonium Perrhenate, Ni-Re Superalloys, Ion-Exchange Resins

1. INTRODUCTION
Alongside with traditional ore sources of rhenium in Uzbekistan: solutions of processing molybdenum and copper concentrates at Almalyk GMK (sorption on weak base anion exchange resin Purolite A170) [1], uranium barren solutions at Navoi GMK (liquid extraction and sorption) [2], new its rising source is a recycling of Re-containing secondary materials. First, dead catalysts of oil refining (additives of 0.3 % Re and 0.3 % Pt at a substrate of Al₂O₃), second, wastes of Re-containing alloys of aerospace industry. Application of Re-based alloys is determined with the mutual solubility of Re and “rhenium effects” [3] - high solubility in Group VI metals leading to W-Re, Mo-Re and W-Mo-Re alloys (characterized with low-temperature ductility) and the ability to increase the high-temperature strength of Ni-Re-base superalloys. Objects of research are wastes of Re-containing alloys of the following types: 1) Fe-Ni-Re; 2) Mo-W-Re; 3) Ni-Re superalloys of CMSX-4, CMSX-10 types (produced by company “Cannon Muskegon” for “Rolls Royce”). The aim of the research is to develop ways of their processing.

2. EXPERIMENTAL
The following equipment and materials were used.
2.1. The element analysis of impurities in samples of metals and ammonium perrhenate (APR) - atomic absorptive spectrometer "Perkin-Elmer" RE 30300 and RE 230300 (USA), ICP masses-spectrometer Elan DRC II (USA-Canada) semiquantitative spectral analysis - diffraction spectroscope PGS-2 (Russia).
2.2. The Measurement of electrode's potential on Ni-Re, Mo-Re, W-Re alloys, counting out comparatively to AgCl electrode, as well as polarization measurements – potentiostate PI-50-1 together with programmer PR-8 (Belarus) with temperature-controlled cell, 200 sm³. Indicator Me-electrode - a disk D =1-20 mm in teflon mount, count electrode - Pt. Kinetics measurements made with method of rotating disc electrode (RDE) on
installation SVA-1 (the engine AVE-042-2/220 V, 50 Hz, 0,28 A St Standard 10799-69), RDE angular rotation velocity 0-2500 1/min.

2.3. Electrodialysis of crude APR solutions for purification were fulfilled in following device: diameter of the cameras and membranes 240 mm, volume of cameras: central 7,2 l, catholytic 2,7 l, anolytic 2,26 l. APR or KReО4 salts were loaded into the central camera. The electrodes made of titanium alloy VT-22 sq area 4,52 dm², membranes: anion exchanging MA 102, cation-exchanging MC 40. Voltage 250 V at the temperature 30°C and 100-150 V at 60-70°C in central camera. Current density 0,3-0,4 A/dm².

2.4. Ion exchange in statics was executed in reactor, equipped with mixer and heater, V = 30 l. It was filled with 16 l of water, 2 kgs KReО4 and three times with 2,5 l of resin Rurolite C 100. Duration -2 h, the temperature 70-80°C. Ion exchange in dynamics - at temperature controlled, 45°C 1) column filled with Rurolite C100 resin for rhenium purification or with Purolite A 170 resin for sorption. In case of purification the solution of APR or potassium perrhenate 25,1 g/l (0,087 M) was passing. The capacity of the resin was equal to 4,15 mole /g air-dry ionite. The laboratory ion-exchange installation: made of 3 columns, volume 1,7 l, fuelled with 1 kg of cationite Purolite C100, filtration velocity 4 volumes/h. For increase of APR solubility the source solution, of 87 g/l concentration was heated up to 40°C. To avoid "skip" of K+ ions into the purified rhenium acid solution the test of Nessler reagent was applied indicating the end of conversion process. Regeneration of the Purolite C100 resin was fulfilled with 6,0 % nitric acid.

3. RESULTS AND DISCUSSION

3.1. DISSOLUTION OF METALLIC WASTES AND ELEMENTS SEPARATION

3.1.1. ALLOYS Mo-Re, W-Re, Mo-W-Re

Re in alloys Mo-Re, W-Re leads to increase of an overvoltage of anodic process in the first area of overpassivation: -0,2±0,15 V, braking anodic process. It is more expressed in an alloy at reduction of
concentration Re in it: from 47% up to 4%. The interest was to find out influence of concentration KOH on stationary and equilibrium potentials of electrodes made of Mo, W, Re, alloys Mo-Re-47 (47% Re), W-Re-27 (27% Re).

At fig. 1 dependences of value of stationary potential of above mentioned electrodes with air - oxidized surface are represented. For the specified materials the growth of concentration KOH, from 0,1 up to 5,0 N, led to shift of potential into area of negative values, according to equation of Nernst:

\[ \varphi = \varphi_0 + \frac{RT}{nF} \ln \left( \frac{[ox]}{[red]} \right) \]  

(1)

Where \( z = 6 \) (for Mo, W); \( z = 7 \) for Re. Having opened an expression (1), we receive:

\[ \varphi_{ct, Mo} = \varphi_0 + \left( 0.059/6 \right) \ln \left( \frac{[\text{MoO}_4^{2-}]}{[\text{OH}^8]} \right) \]  

(2)

\[ \varphi_{ct, W} = \varphi_0 + \left( 0.059/6 \right) \ln \left( \frac{[\text{WO}_4^{2-}]}{[\text{OH}^8]} \right) \]  

(3)

\[ \varphi_{ct, Re} = \varphi_0 + \left( 0.059/7 \right) \ln \left( \frac{[\text{Re}_2]}{[\text{OH}^8]} \right) \]  

(4)

Substitution in (2-3) of values of hydroxyl-ions concentration in a solution leads to reduction of values of stationary potentials, as was observed (fig. 2). Curves \( \varphi_{ct, KOH} \) and \( \varphi_{pr, KOH} \) for alloys Mo-W, Mo-Re, W-Re are located between corresponding curves for these pure metals.

Such a picture is typical for dissolution of an alloy at a constancy of concentration of ions of metals: in calculations (1-3) it was accepted \( 10^{-5} \) M. At anodic dissolution of metals there is a falling concentration of alkali in a solution and increase – of ions of metals concentration. According to (1), in a case \( i_a \neq 0 \):

\[ i_{p, Me} = \varphi_{ct, Mo}^0 + \left( 0.059/2 \right) \ln \left( \frac{[\text{MeO}_4^k]}{[\text{OH}]} \right) \]  

(5)

Where \( \varphi_{ct}^0 \) – the potential distinguished from standard on value of polarization of an electrode at \( i_a = 0 \): \( \text{MeO}_4^k \) - molybdate, tungstenate or a perrhenate-ion. It was necessary to expect \( \varphi_{p, Me} \) growth in these conditions. And it is valid, experimental data (tab. 1) have proved these calculations (5).

Table 1

<table>
<thead>
<tr>
<th>№ n/n</th>
<th>Composition, mole/l</th>
<th>( \varphi_{p, V} ) at ( i_a = 0,01 ) A/sm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mo</td>
<td>W</td>
</tr>
<tr>
<td>1</td>
<td>KOH : 1,00</td>
<td>-0,20</td>
</tr>
<tr>
<td>2</td>
<td>KOH : 0,02</td>
<td>Mo 0,25</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>KOH : 0,02</td>
<td>Mo 0,40</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>KOH : 0,02</td>
<td>W 0,40</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Method of RDE was applied to investigate the area of over passivation of alloys (\( j > +0,2 \) B). The value of a limiting current of dissolution of Mo, W (for alloys Mo-Re-47, W-Re-27 value \( i_a \) was fixed at \( j=2,0 \) B). The received linear dependence \( i_a = 0,05 \) for Mo is extrapolated in the beginning of coordinates that testifies for the benefit of over passivational mechanism of kinetics of anodic process in the field of \( 0,6 B < \varphi < 2,0 \) V, with diffusive control of transport of donors of oxygen over the anode. For Mo-Re-47, W-Re-27 \( i_a = 0,5 \) curves are not extrapolated in the beginning of coordinates that specifies the mixed control of process over high anodic potentials.

Basing on these data the technology of alloys dissolution was designed.

1-st stage - anodic dissolution of alloys in a solution of caustic potash 1-7 M at temperature 40-85°C, current
density \(i_a > 0.7 \text{ A/sm}^2\), an electrolyte flow along anode surface - up to 1 m/sec. Current efficiency – 95-98%.

In the KOH solution Mo(VI), Re(VII) ions are collected (e.g. Mo-Re alloy). After the anodic dissolution the system is cooled to 2-4 ⁰C and the salt with same cation (K⁺-ion) is added, so as a result on the filter the deposit KReO₄ is separated. From the residuary solution Mo(VI) ions are sorbed on a Purolite A 100 Mo. Resin. Deposit KReO₄ is transferred to distilled water heated up to 50 ⁰C. Then potassium perrhenate is subjected to conversion up to rhenium acid on Purolite C 100 resin being in H⁺ form (tab. 1.), a product obtained is transformed with ammonia into end product APR after its crystallization. From mother waters after their concentrating ammonium paramolybdate (APM) is recovered. The purity of APR and APM accordingly is equal to 99,8; 99,2 %. The result of the ion-exchange of KReO₄ into HReO₄ conversion control is offered (tab. 2).

According to data of tab. 1, the skip of K⁺-ions at the exit is observed after passing of 150 ml of a solution. It complied with value of Purolite C 100 resin’s capacity up to skip equal to 39,3 % from greatest possible. The full capacity has made 52,3 %. This cationite’s property is distributed to all modes of the specific loading expressed by the relation of a solution’s volume past through a column per 1 hour to a volume of resin Purolite C 100 equal to: 5,0; 10,0; 15,0.

![Table 2](image)

Control of HReO₄ at the exit of a column filled with Purolite C 100 in H⁺-form, 45 ⁰C, M

<table>
<thead>
<tr>
<th>Solution passed, ml</th>
<th>specific load, h⁻¹</th>
<th>reproducibility of results at recycles with specific load 5 h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>15</td>
<td>0,087</td>
<td>0,087</td>
</tr>
<tr>
<td>30</td>
<td>0,087</td>
<td>0,087</td>
</tr>
<tr>
<td>150</td>
<td>0,087</td>
<td>0,087</td>
</tr>
<tr>
<td>165</td>
<td>0,003</td>
<td>0,003</td>
</tr>
<tr>
<td>180</td>
<td>0,001</td>
<td>0,001</td>
</tr>
<tr>
<td>195</td>
<td>0,000</td>
<td>0,000</td>
</tr>
</tbody>
</table>

Desorption of Re(VII)-ions from the Purolite C100 resin is fulfilled acting with 6,5 % nitric acid by reverse flow. Leaving column the rhenium acid solution has been neutralized with an ammonia solution and evaporated for crystal APR allocation The content of an potassium impurity in it is supervised after heating NH₄ReO₄ up to 400 ⁰C at the presence of an oxidizer HNO₃ or H₂O₂. The product met the requirements of State Standard for APR of AR-0 mark. Parameters of purification process with potassium impurity control are resulted below (table 3).

![Table 3](image)

Table 3

APR purification process’s parameters

| Amount of purified APR per 1 kg of cationite Purolite C100 resin, g | 700 |
| Concentration of APR in an initial solution, g/l | 87-88 |
| Sorption process’s temperature, ⁰C | 40-50 |
| Speed of a filtration, ml/sm² per hour | 400 |
| The charge of 6,5 % HNO₃ on regeneration of 1 kg of Purolite C100 resin, l | 3,0 |
| Output of the purified APR, % | 95-96 |

The method is suitable for APR purification from potassium impurity as well. The potassium impurity content in APR is supervised with AAS method after preliminary removal of a basis (NH₄ReO₄) transformed by heating to Re₂O₇ in an analyzed sample in a lab’s furnaces at 350-400 ⁰C at the presence of an oxidizer (HNO₃, H₂O₂). The end product meets the requirements of specifications on APR.
3.1.2. Fe-Ni-Re ALLOYS

Fe-Ni-Re alloy is dissolved in a mixture of sulfuric and nitric acids with conversion of Re(VII) into a sludge, while from joint solution Ni(II) & Fe(III) the ions Ni(II) are selectively semidetached as nickel-ammonium – sulphate compound. It is known, that nickel-ammonium alum - double salt Ni(NH₄)₂(SO₄)₂·6H₂O is received with draining of the hot fat solution of sulfuric salts of nickel and ammonium in an equivalent ratio. Having taken for a basis this reception of one component removal from threefold system, the technology of rhenium solutions clearing from iron and nickel, including dissolution of an alloy in the diluted sulfuric acid with the additive of an oxidizer, sedimentation of nickel as the specified salt, the subsequent division of Re(VII) and Fe(III) in a filtrate based on ion exchange method. Because the completeness of sedimentation of nickel as nickel – ammonium – sulfate was the important technological parameter, the effect of Ni(NH₄)₂(SO₄)₂ concentration in an initial solution on it has been investigated.

Modeling solutions of mixed salts Fe₄(SO₄)₃·9H₂O, NiSO₄·7H₂O, NH₄ReO₄ in I N H₂SO₄ taken in the ratio typical to end product of dissolution of Fe-Ni-Re alloy, namely, %: Ni 42,5; Re 11,1; Fe - the rest. Initial concentration of nickel in all solutions was typical to technological solutions of this alloy processing: 40 g/l. In aliquot parts, 50 ml, of an initial solution various quantities of sulfate ammonium were entered. Thus fine-grained deposit of the double salt of blue-green color was precipitated. Through 30 min a deposit was separated at a filter of Buchner funnel and washed out 2-3 times in the small portions (3-5 ml) of 25 % (NH₄)₂SO₄. solution. A filtrate was analyzed on nickel and rhenium contents (tab. 4).

<table>
<thead>
<tr>
<th>Table 4</th>
<th>The effect of (NH₄)₂SO₄ on sedimentation of Ni in a form of Ni(NH₄)₂(SO₄)₂·6H₂O compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(NH₄)₂SO₄], g/l</td>
<td>[(Ni]ₚαs, g/l (initial 40 g/l)</td>
</tr>
<tr>
<td>80</td>
<td>30,0</td>
</tr>
<tr>
<td>240</td>
<td>2,0</td>
</tr>
<tr>
<td>320</td>
<td>1,3</td>
</tr>
<tr>
<td>400</td>
<td>1,2</td>
</tr>
</tbody>
</table>

The maximal degree of extraction of Ni in a deposit was achieved at concentration of ammonium sulfate ≥ 200 g/l. Residual concentration of Ni = 1.2 g/l, i.e. 97 % of Ni was deposited while the concentration of rhenium in the solution did not vary.

<table>
<thead>
<tr>
<th>Table 5</th>
<th>Solubility of some salts of iron and nickel in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>The formula of a compound</td>
<td>In a solid phase*</td>
</tr>
<tr>
<td>(NH₄)₂Fe(SO₄)₂</td>
<td>6 H₂O</td>
</tr>
<tr>
<td>NH₄Fe(SO₄)₂</td>
<td>12 H₂O</td>
</tr>
<tr>
<td>(NH₄)₂Ni(SO₄)₂</td>
<td>6 H₂O</td>
</tr>
<tr>
<td>FeSO₄</td>
<td>7 H₂O</td>
</tr>
<tr>
<td>Fe₂(SO₄)₃</td>
<td>9 H₂O</td>
</tr>
<tr>
<td>NiSO₄</td>
<td>7 H₂O</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>-</td>
</tr>
</tbody>
</table>

* Number of molecules of water in crystalline hydrate, in balance with the pregnant (saturated) solution

The solubility at 20°C of (NH₄)₂SO₄ and few more simple and double salts of Fe(III), Ni(II) is resulted (tab. 5) [4]. So, for Ni(NH₄)₂(SO₄)₂·6H₂O it is equal to 59 g/l (~9 g/l Ni). Actual decrease of its solubility up to 1.2 g/l for Ni, at the presence of surplus of (NH₄)₂SO₄, is explained with its salting-out effect.
The most suitable way of rhenium recovery from received sulfuric solution and its separation from iron is sorption on ionites of various type (AV-17, AN-21, Purolite A170, A172 etc) [1-2]. We used successfully anionite Lewatit M 500 (analogue of strong base anion resin AV 17).

Thus the technology was as follows. Mother water solution after the separation of double salt of nickel has been neutralized with ammonia up to pH 1 and passed through a column (size 0,9x11,5 sm) filled with specified anionite in $SO_4^{2-}$ - form with speed of passing equal to 2 volumes per hour. Rhenium was desorbed with 6 volumes of 5 N $HNO_3$ solution with the same speed (98 % of Re eluated). The above mentioned results have allowed to offer the following technological circuit of Fe-Ni-Re alloy processing.

Alloy is dissolved at heating in a sulfuric acid (440 g/l) so that Ni(II) and Re(VII) ions’ concentrations made accordingly 40 and 10 g/l. For activization of alloy decomposition process small portions of nitric acid (d=1,4) in the quantity equal to 20 % of total solution’s amount* are added to a boiling solution. The formatted solution is neutralized with ammonia up to acidity 50 g/l (in respect of $H_2SO_4$). The deposited double salt of nickel is separated with filtering and from mother water preliminary neutralized up to pH ~1, rhenium is sorbed on anionite resin Lewatit M 500 charged in $SO_4^{2-}$ - form with the subsequent desorption with solution of nitric acid (315 g/l). From nitrate column effluent by means of evaporation and neutralization with ammonia the pure APR salt is allocated.

The general recovery of rhenium into commodity salt makes 90 % weight. Some incompleteness of its extraction is explained with presence at solution of $NO_3^-$ ions negatively effected on its sorption. The Ni(II)-salt nickel ammonium sulfate obtained at an initial stage of technological process is a commodity product too.

So, the way of Fe-Ni-Re alloy reagent processing is developed by means of its dissolution in a mixture of sulfuric and nitric acids, with following removal of rhenium into a sludge and the subsequent selective recovery of nickel from the common with Fe(II) solution into a deposit as a complex double salt $Ni(NH_4)_2(SO_4)_2\cdot 6H_2O$.

* at $HNO_3$ introduction the losses of Re because of coprecipitation with Ni salt are not observed.

### 3.1.3. Ni-Re SUPERALLOYS (CSMX-4)

CSMX-4 superalloy composition is the following, %: Cr 6.5; Co 9.0; Mo 0.6; W 6.0; Ta 6.5; Re 3.0; Al 5.6; Ti 1.0; Hf 0.1; Ni 61.7. Complexity of its processing consists in its extremely high corrosion stability, therefore at its processing the following methods are applied: nitrohydrochloric acid decomposition, liquid phase chlorination. We used an anodic dissolution with removal Re in a liquid phase and following sorption on resin Purolite A 170. Industrial line with productivity of processing an alloy of 500-700 kg per month with Re recovery 75-80 % is introduced. As a result of processing the following products turn out:

1. APR of AR-0 type
2. Sludge of powder tantalum with impurity of tungsten, molybdenum etc.
3. Cake consisting of sulfate and hydroxides of nickels, cobalt and impurities.

In total 3 tones of wastes are processed.

### 3.2. APR PRODUCT PURIFICATION

APR - crude initial ammonium perrhenate obtained by re-crystallization often has to be purified. The best way for its purification is electrodialysis of its solution (tab. 6).

#### Table 6

Results of electrodialysis of crude APR (AR-0 mark) solution, ppm

<table>
<thead>
<tr>
<th>state</th>
<th>Re, %</th>
<th>K</th>
<th>Na</th>
<th>S</th>
<th>P</th>
<th>Si</th>
<th>Mg</th>
<th>Mn</th>
<th>Al</th>
<th>Fe</th>
<th>Ca</th>
<th>Mo</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>69,2</td>
<td>32</td>
<td>11</td>
<td>2</td>
<td>11</td>
<td>0,5</td>
<td>0,5</td>
<td>0,2</td>
<td>2</td>
<td>0,6</td>
<td>21</td>
<td>1</td>
<td>1</td>
<td>0,5</td>
</tr>
<tr>
<td>purified</td>
<td>69,2</td>
<td>1,5</td>
<td>0,5</td>
<td>2</td>
<td>10</td>
<td>0,4</td>
<td>0,1</td>
<td>0,05</td>
<td>1</td>
<td>0,06</td>
<td>2,5</td>
<td>1</td>
<td>1</td>
<td>0,5</td>
</tr>
</tbody>
</table>
Washed by ethanol the purified APR was reduced at high-temperature with gaseous hydrogen with output of Re in the metal not less than 99.996 %.

4. CONCLUSION

The recycling wastes of Rhenium containing alloys might be successfully dissolved electrochemically with following separation of Re(VII) ions from other alloy’s components in common solution. The recovery of rhenium from the solution might be fulfilled without liquid extraction method using ion-exchange approach only. The best APR purification method is the electrodialysis of its solution

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LITERATURE


