

Article

# Application of Ion Exchange for Preparation of Selected Metal Perrhenates—Precursors for Superalloy Production

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**Abstract:** Methods for the preparation of selected metal perrhenates and their mixtures are presented in this paper. These materials are suitable for reduction, and therefore for production of alloy powders containing rhenium and other superalloy components, i.e., Cr, Ni and Co. Prepared compounds may be also used as substrates for electrowinning of binary and ternary rhenium alloys. All developed methods are based on an ion exchange technique. This technique allows management of waste solutions, limitation of valuable metals losses, and, importantly, production of high-purity components.

**Keywords:** rhenium; nickel; cobalt; chromium; superalloys

## 1. Introduction

Metals are basic materials for all technique branches. Currently, one of its most interesting application areas are superalloys [1–3]. These are alloys of various metals, usually iron-, nickel- and cobalt-based [3–5]. Superalloys possess unique physical and chemical properties, e.g., nickel-based superalloys are resistant to high temperature, dynamic loads and aggressive, corrosive environments. Therefore, they are mainly applied in aviation (engine turbines), rocket and space industries [3,6,7]. It is estimated that ca. 50% of nickel-based superalloys are used for construction of jet engine components. Further improvement of these materials should increase their operating temperature and reduce heat losses as well as improving their durability and reliability. Such improvement may be achieved by optimizing their chemical composition, which would enhance alloy's resistance to creep as well as mechanical and thermal fatigue [3]. The first monocrystalline nickel-based superalloys were prepared in the 1960s. However, their first industrial-scale production was launched in 1975 [1–7]. First-generation superalloys are highly thermal-fatigue- and creep-resistant materials. They are composed of nickel base and other elements, like chromium, cobalt, aluminum, titanium, molybdenum and tungsten. Second-generation superalloys also contain rhenium, which is added to improve material strength under elevated temperature. A small percentage of rhenium already significantly improves almost all technically-important properties of superalloys [6–8]. This is due to so called “rhenium effect”, which is associated with the reduction of grain recrystallisation and inhibition of mean grain size increase. These unfavorable phenomena may increase alloy brittleness, especially during its ageing at high temperatures. Rhenium has a high tendency to form clusters, which inhibit the migration of other atoms and do not disturb alloy uniformity. In the next generations (3rd and 4th) of nickel-based superalloys, the rhenium content is reduced. However, this is due to economic reasons – a high rhenium price. Despite this fact nickel-based superalloys,

containing 1%–6% rhenium, are still produced on industrial scale and widely applied. It is estimated that 70% of the whole world rhenium production is used for superalloys and 20% is applied in catalysis, while the remaining 10% is consumed by the energy and pharmaceutical industries [1,8].

Results of investigation on production technology of selected rhenium compounds are presented in this paper. These compounds (Ni, Co and Cr perrhenates and their mixtures) may be used for preparation of alloy powders and/or electrochemically produced alloys—precursors in manufacturing of nickel-based superalloys. Alloy powders obtained after reduction of perrhenates are intermediates for superalloy production. Electrochemically-obtained binary and ternary alloys, e.g., Re-Ni, Re-Co, Re-Ni-Mo, or Re-Co-Mo are intermediates for preparation of nickel-based alloys, used for construction of aircraft jet engines and energetic turbines. Therefore, strict requirements concerning compounds purity and process conditions need to be taken into account. Currently, rhenium is introduced to superalloys in the form of metallic pellets during the melting process. It requires maintaining a high temperature (which may cause losses of expensive metal released with fumes and dusts) and the application of high-purity rhenium. Introduction of rhenium to superalloys as alloy powder pellets, e.g., Re-Ni, Re-Co, Re-Cr (obtained during reduction of previously prepared compounds), or alloys, e.g., Re-Ni, Re-Co, may limit rhenium losses by reducing the temperature of melt bath [8,9].

## 2. Experimental Section

### 2.1. Materials

Perrhenic acid (IMN, Gliwice, Poland), containing 900.0 g/dm<sup>3</sup> Re, <20 ppm NH<sub>4</sub><sup>+</sup>, 10 ppm Cr, <10 ppm K, 10 ppm Ni, 8 ppm Co, <5 ppm Mo, <5 ppm Pb, 4 ppm Al, <3 ppm Ca, <3 ppm Cu, <3 ppm Fe, <3 ppm Mg, <3 ppm Zn, <2 ppm As, <2 ppm Bi was used as a rhenium source [10–12]. Nickel(II), cobalt(II), chromium(III) nitrates and/or sulphates (Alfa Aesar Chemat, Gdańsk, Poland) were used as sources of other metals. Mineral acids, like sulphuric or nitric acid (Avantor, Gliwice, Poland) were applied for ionite regeneration. Solution of 30% hydrogen peroxide and acetone (Sigma Aldrich, Poznań, Gliwice, Poland) were used for purification. Nickel(II) and cobalt(II) oxides, metallic nickel and cobalt (Merck, Warsaw, Poland) as well as prepared chromium(III) hydroxide (IMN, Gliwice, Poland) were applied for neutralization. Distilled water (<2 µS/cm) was used in the experiments.

### 2.2. General Methodology

Developed hydrometallurgical technologies for preparation of nickel(II), cobalt(II) and chromium(III) perrhenates as well as their mixtures were based on ion exchange. Metal ions (Ni<sup>2+</sup>, Co<sup>2+</sup>, Cr<sup>3+</sup>) were sorbed from aqueous solutions of their salts using strongly acidic cation-exchange resins. In the case of nickel, C160 ionite (Purolite, Gdańsk, Poland) and aqueous solution of nickel(II) nitrate was used, while for cobalt SGC 650 ionite (Purolite, Gdańsk, Poland) an aqueous solution of cobalt(II) sulphate was applied. Nitrate solutions and ionite PFC 100 × 10 (Purolite, Gdańsk, Poland) were employed for chromium sorption. In the next step, sorbed resins were washed with water. Then, metal ions were eluted using aqueous solutions of perrhenic acid. After elution ionites were washed with water and obtained solution, after neutralization, was evaporated to dryness. Neutralization was carried out using metallic nickel and/or cobalt, alternatively using their oxides. Chromium neutralization was performed with application of chromium(III) hydroxide or, for preparation of perrhenates mixture, metallic nickel. Methods of perrhenates purification and waste solution management were also developed. Management of these solutions was a key economic element of this technology. Reduction of metal losses, especially very expensive rhenium and other valuable metals like critical cobalt, should be a priority. Drying and storage methods for prepared salts and their mixtures were also developed.

It should be pointed out that all developed technologies are multistep and consist of the following common elements: solution preparation for sorption, sorption and ionite washing, elution with aqueous HReO<sub>4</sub>, ionite washing after elution, neutralization, evaporation, purification, drying and, importantly, proper storage.

Developed methods allowed to prepare anhydrous forms of chromium(III), nickel(II) and cobalt(II) perrhenates and their mixtures.

The following indicators: sorption efficiency, elution efficiency, degree of ionite saturation were calculated for the performed tests. Sorption efficiency was calculated as a ratio of sorbed metal mass to mass of the metal in the initial solution multiplied by 100%. Elution efficiency was calculated as a ratio of metal mass in the solution before neutralization to metal mass sorbed in an ionite, multiplied by 100%. Degree of ionite saturation was calculated as a sorbed metal mass to ionite mass ratio, multiplied by 100%.

### 2.3. Preparation of Anhydrous Chromium(III) Perrhenate and its Mixtures

Preparation of anhydrous chromium(III) perrhenate was performed using clear aqueous nitric solutions, containing 2–3 g/dm<sup>3</sup> Cr. Appropriate amounts of the solutions required to achieve over 2.5% degree of ionite saturation and 0.05 g/dm<sup>3</sup> chromium in the solution after sorption were used. The solutions were passed through a bed of PFC100X10 ionite in hydrogen form. The bed was placed inside a column and its height to diameter ratio was over 7.5. Tests were carried out using 1 kg portions of PFC100X10 ionite. Six working cycles of the ionite were performed. Sorption was carried out proceeding down the column, at room temperature, while contact time between solution and ionite bed was at the level of 5 dm<sup>3</sup>/h. After the sorption ionite was washed with water, downward from the column, at a flow rate between 2.5–10 dm<sup>3</sup>/h. Solutions generated after sorption and washing were acidic nitric effluent directed for utilization. Washed column with chromium-sorbed bed was subjected to elution. It was carried out using aqueous perrhenic acid solutions containing over 400 g/dm<sup>3</sup> rhenium. For each 1 g of sorbed chromium 30–40 g of rhenium were used, proceeding down the column, at a flow rate of 2.5 dm<sup>3</sup>/h.

Solution generated after elution was collected in two portions. First portion, in the amount of about one bed volume was mixed with second portion of solutions from washing after elution and recycled to eluent preparation step. The second one was directed to neutralization. The ionite bed after the elution was washed with water. The solution generated in this step was also collected in two portions—the first one was mixed with the second portion of solution generated during elution and then neutralized, while the second one was mixed with the first portion of solution from elution step and directed to eluent preparation step. Solutions for neutralization from cycles I–III were joined and subsequently directed to neutralization step with freshly precipitated chromium(III) hydroxide and washed from ammonium ions to the level <0.1%. Whereas, solution generated in cycles IV–VI were combined and subsequently directed to neutralization with nickel(II) oxide. Both neutralizing agents were applied in stoichiometric amounts with respect to rhenium, which was present in excess. Irrespectively of the applied agent, neutralization was carried out below 80 °C, until solution pH reached ca. 6. Solution after neutralization was hot filtered from solid impurities. Concentration of solution after neutralization was also performed at temperature <80 °C, with vigorous mixing until dryness. Obtained solids were purified in two steps—firstly with water of ≤10 °C, using 10 cm<sup>3</sup> of H<sub>2</sub>O per each 1 g of the solid and, secondly, with anhydrous acetone at ≤10 °C using 2 cm<sup>3</sup> of acetone per each 1 g of the solid. The solids remaining after purification were dried at 160 °C, until constant mass and, then, stored in a glass vessel under argon [13]. The scheme of the applied Cr(ReO<sub>4</sub>)<sub>3</sub> preparation method is presented in Figure 1.

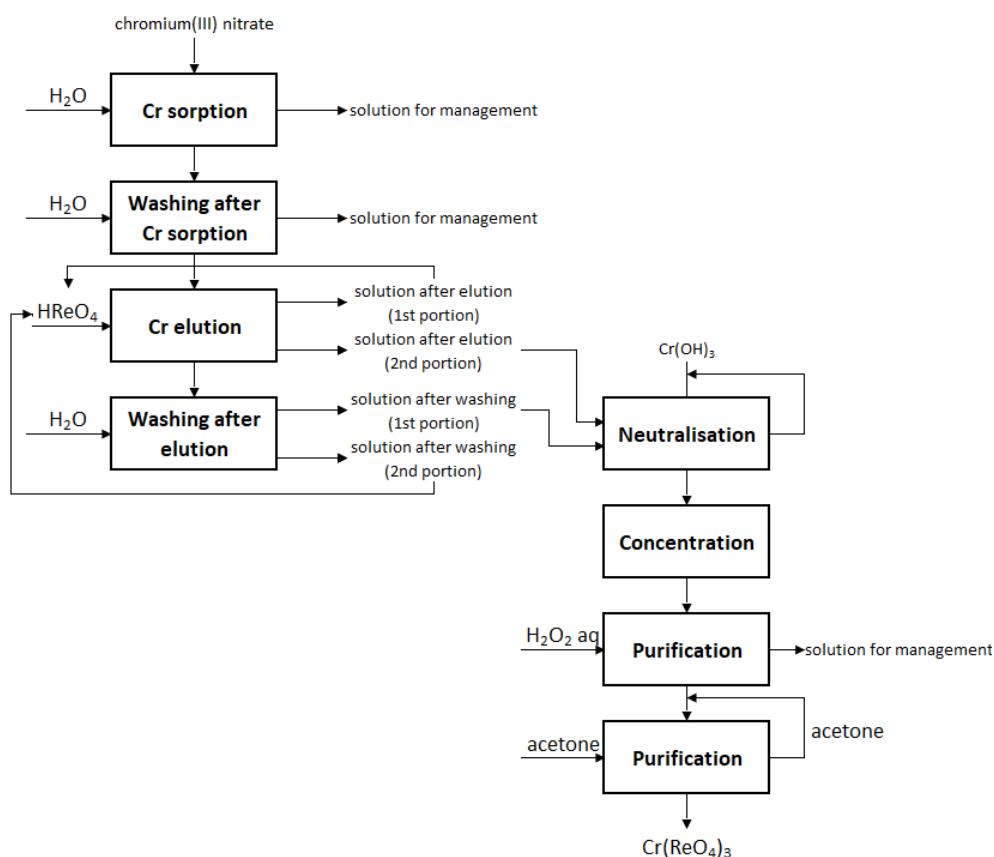
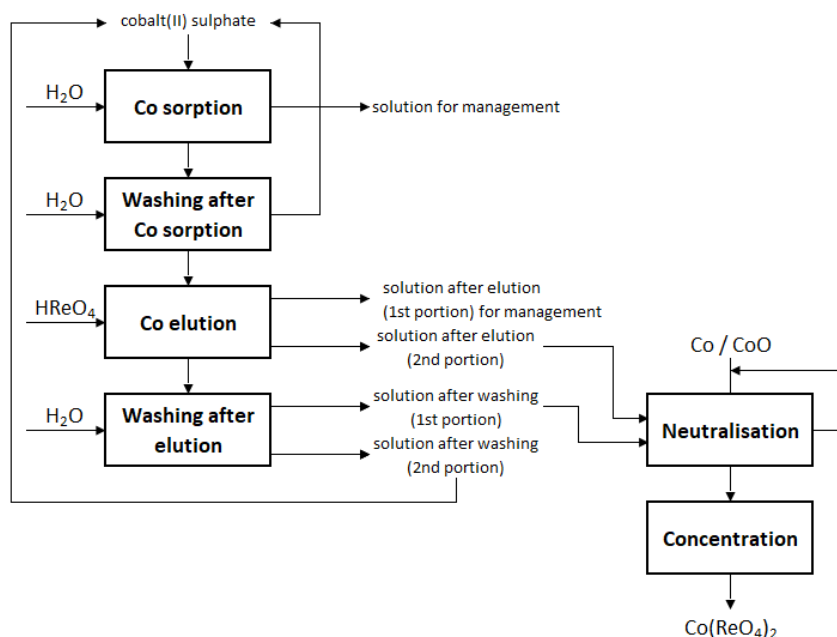


Figure 1. Scheme of  $\text{Cr}(\text{ReO}_4)_3$  preparation.

#### 2.4. Preparation of Anhydrous Cobalt(II) Perrhenate and its Mixtures

Preparation of anhydrous cobalt(II) perrhenate was performed using clear aqueous sulphate solutions, containing  $5 \text{ g/dm}^3$  Co. Appropriate amounts of the solutions required to achieve over 5% degree of ionite saturation and  $0.1 \text{ g/dm}^3$  chromium in the solution after sorption were used. The solutions were passed through a bed of SGC650 ionite in hydrogen form. The bed was placed inside a column which parameters were described in Section 2.3. Tests were carried out according to the methodology similar to chromium(III). The main difference was that sulphate solution generated after sorption was an acidic effluent for utilization, while solution from washing after sorption was recycled to sorption solution preparation step. Aqueous  $\text{HReO}_4$  solution, containing over  $500 \text{ g/dm}^3$  rhenium, was used for elution. For each 1 g of sorbed cobalt 10–20 g of rhenium were used. Solution generated after elution was also collected in two portions. First portion (up to one bed volume) was directed for management using known methods, while the second one was neutralized. The solution generated during washing after elution was collected in two portions—the first one was combined with the second portion of solution from elution and neutralized, while the second one was mixed with washings from washing after sorption and directed to step of sorption solution preparation.

Solutions for neutralization from cycles I–II were joined and subsequently directed to neutralization step with metallic cobalt, solutions generated in cycles III–IV are combined and subsequently directed to neutralization with cobalt(II) oxide, whereas solutions generated during cycles V–VI were also combined and neutralized with nickel(II) oxide. Neutralization was carried out until solution pH was between 7–8. Solution after neutralization was hot filtered from solid impurities. Concentration of solution after neutralization was also performed at temperature  $<80^\circ\text{C}$  with vigorous mixing until dryness. Purification step was not applied. Obtained solid was dried at  $130^\circ\text{C}$  [14]. The scheme of the applied  $\text{Co}(\text{ReO}_4)_2$  preparation method is presented in Figure 2.



**Figure 2.** Scheme of  $\text{Co}(\text{ReO}_4)_2$  preparation.

### 2.5. Preparation of Anhydrous Nickel(II) Perrhenate and its Mixtures

Preparation of anhydrous nickel(II) perrhenate, the basics of which were described in the previous publications [15–17], was performed using clear aqueous nitrate solutions, containing 5 g/dm<sup>3</sup> Ni. Appropriate amounts of the solutions required to achieve over 6% degree of ionite saturation and 0.1 g/dm<sup>3</sup> chromium in the solution after sorption were used. The solutions were passed through a bed of C160 ionite in hydrogen form. The bed was placed inside a column which parameters were described in Section 2.3. Tests were carried out according to the similar methodology as for abovementioned perrhenates. Solution after sorption was recycled to the step of sorption solution preparation. After sorption ionite was washed with water in two steps, proceeding down the column, at a flow rate between 2.5–5.0 dm<sup>3</sup>/h. Combined solutions were recycled to step of sorption solution preparation. Washed column with nickel-sorbed bed was subjected to elution. It was carried out using aqueous solutions of perrhenic acid or solution obtained combining perrhenic acid with the first portion of the washings after elution. Total rhenium concentration in these solutions was over 500 g/dm<sup>3</sup> rhenium. Concentrated nitric acid in an amount of 20 cm<sup>3</sup> per each 1 dm<sup>3</sup> of eluent was added. For each 1 g of sorbed nickel, 20 g of rhenium were used. Solution generated after elution was also collected in two portions. The first one (up to 0.5 bed volume) was directed for management using known methods, while the second proper portion (up to 2 bed volumes) was neutralized. Eluted ionite bed was washed with water, whereas solution from washing after elution was collected in two portions—the first one was recycled to eluent preparation, while the second portion was directed to preparation of sorption solution. Solution for neutralization generated in cycles I–II were combined and subsequently neutralized with metallic nickel, solutions from cycles III–IV were joined and neutralized with nickel(II) oxide, whereas solutions from cycles V–VI were also combined and neutralized with metallic cobalt. All neutralizing agents were used in stoichiometric amounts with respect to rhenium, which was present in excess. Irrespective of the applied agent, neutralization was carried out below 80 °C, until solution pH reached 7–8. Solution after neutralization was hot filtered from solid impurities. Concentration of solution after neutralization was also performed at temperature <80 °C with vigorous mixing until dryness. Then, it was purified with 30% aqueous hydrogen peroxide solution using 2 cm<sup>3</sup> of the solution per each 1 g of the solid. Solids remaining after purification were dried at 160 °C, until constant mass and, then, stored in a

glass vessel under argon [18]. The scheme of the applied  $\text{Ni}(\text{ReO}_4)_3$  preparation method is presented in Figure 3.

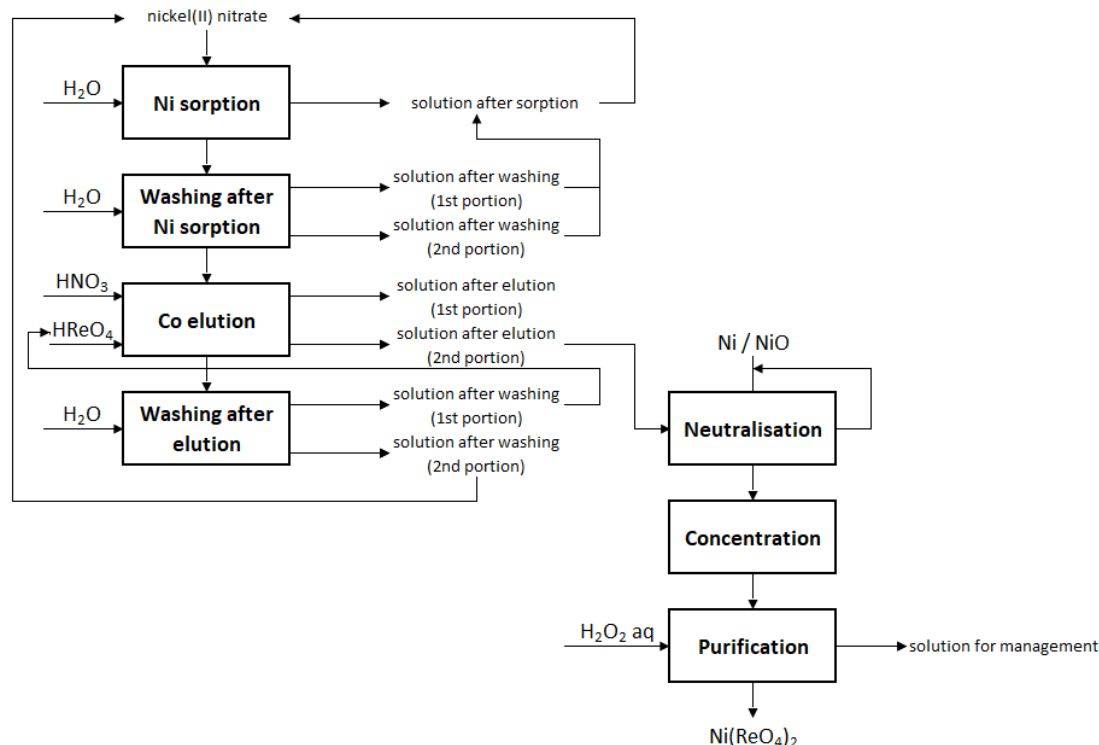


Figure 3. Scheme of  $\text{Ni}(\text{ReO}_4)_2$  preparation.

## 2.6. Analytical Methods

All the necessary analysis was performed by IMN Department of Analytical Chemistry. Content of rhenium, chromium, nickel and cobaltium in products was analyzed using a weight method with tetraphenylarsonium chloride (TPAC) as a precipitating agent, and flame atomic emission spectroscopy (FAES, spectrophotometer AAS novAA400, Analytik, Jena, Germany), respectively. Solutions were analyzed by flame atomic absorption spectroscopy (FAAS, SOLAAR S4, ThermoWaltham, MA, USA) equipped with flame module and deuterium background correction, to establish Re, Co, Ni and Cr content. Analysis of contaminations was performed using various techniques: inductively coupled plasma mass spectrometry (ICP-MS, ICP MS NexION, PerkinElmer, Waltham, MA, USA), inductively coupled plasma—optical emission spectrometer (ICP-OES, ULTIMA 2, Horiba Jobin-Ivon, Kyoto, Japan), graphite furnace atomic absorption spectroscopy (GFAAS, Z-2000, Hitachi, Tokyo, Japan) with graphite cells.

## 3. Results and Discussion

### 3.1. Preparation of Anhydrous Chromium(III) Perrhenate and its Mixtures

Six cycles of chromium(III) perrhenate preparation under dynamic conditions were performed. Balance sheets of conducted trials are shown in Tables 1–6. Changes of sorption and elution efficiency in subsequent cycles of ionite work are presented in Figure 4.

**Table 1.** Chromium(III) sorption and elution balance—1st cycle.

1st CYCLE							
Operation	Materials	Solution Volume, dm <sup>3</sup>	Cr Concentration, g/dm <sup>3</sup>	Re Concentration, g/dm <sup>3</sup>	Cr Mass, g	Re Mass, g	Process Efficiency, %
SORPTION	solution for sorption	15.0	2.000	-	30.000	-	-
	washing water	2.50	-	-	-	-	-
	solution after sorption	15.70	0.002	-	0.031	-	99.87
	washings	1.80	0.005	-	0.009	-	-
ELUTION	ionite	-	-	-	29.960	-	-
	eluent	2.00	-	600.00	-	1200.000	-
	washing water	3.00	-	-	-	-	-
	elution (1st part)	0.70	0.33	1.58	0.230	1.110	-
	elution (2nd part)	2.40	11.10	475.15	26.640	1140.360	99.84
	washings (1st part)	1.10	2.40	50.10	2.640	55.110	-
	washings (2nd part)	0.800	0.50	4.16	0.400	3.330	-

**Table 2.** Chromium(III) sorption and elution balance—2nd cycle.

2nd CYCLE							
Operation	Materials	Solution Volume, dm <sup>3</sup>	Cr Concentration, g/dm <sup>3</sup>	Re Concentration, g/dm <sup>3</sup>	Cr Mass, g	Re Mass, g	Process Efficiency, %
SORPTION	solution for sorption	15.00	2.000	-	30.000	-	-
	washing water	2.50	-	-	-	-	-
	solution after sorption	15.60	0.002	-	0.031	-	99.86
	washings	1.90	0.006	-	0.011	-	-
ELUTION	ionite	-	-	-	30.006 *	-	-
	eluent	3.00	0.21	451.48	0.631	1354.434	-
	washing water	3.00	-	-	-	-	-
	elution (1st part)	0.75	0.35	1.60	0.263	1.200	-
	elution (2nd part)	3.00	9.00	431.00	27.000	1293.000	99.56
	washings (1st part)	1.00	2.30	54.80	2.300	54.800	-
	washings (2nd part)	1.25	0.25	4.16	0.313	5.205	-

\* it is a mass of Cr sorbed in this cycle + mass of Cr which was not eluted during previous cycle.

**Table 3.** Chromium(III) sorption and elution balance—3rd cycle.

3rd CYCLE							
Operation	Materials	Solution Volume, dm <sup>3</sup>	Cr Concentration, g/dm <sup>3</sup>	Re Concentration, g/dm <sup>3</sup>	Cr Mass, g	Re Mass, g	Process Efficiency, %
SORPTION	solution for sorption	15.00	2.000	-	30.000	-	-
	washing water	2.50	-	-	-	-	-
	solution after sorption	15.500	0.005	-	0.078	-	99.69
	washings	2.000	0.008	-	0.016	-	-
ELUTION	ionite	-	-	-	30.038 *	-	-
	eluent	3.20	0.18	362.13	0.575	1158.816	-
	washing water	2.50	-	-	-	-	-
	elution (1st part)	0.80	0.35	1.70	0.280	1.360	-
	elution (2nd part)	3.10	8.71	355.00	27.001	1100.500	99.39
	washings (1st part)	1.10	2.20	48.10	2.420	52.910	-
	washings (2nd part)	0.70	0.22	4.50	0.154	3.150	-

\* it is a mass of Cr sorbed in this cycle + mass of Cr which was not eluted during previous cycle.

**Table 4.** Chromium(III) sorption and elution balance—4th cycle.

4th CYCLE							
Operation	Materials	Solution Volume, dm <sup>3</sup>	Cr Concentration, g/dm <sup>3</sup>	Re Concentration, g/dm <sup>3</sup>	Cr Mass, g	Re Mass, g	Process Efficiency, %
SORPTION	solution for sorption	15.00	3.000	-	45.000	-	-
	washing water	2.50	-	-	-	-	-
	solution after sorption	15.80	0.005	-	0.079	-	99.79
	washings	1.70	0.010	-	0.017	-	-
ELUTION	ionite	-	-	-	45.086 *	-	-
	eluent	3.00	0.14	451.50	0.434	1354.510	-
	washing water	2.50	-	-	-	-	-
	elution (1st part)	0.80	0.320	1.60	0.256	1.280	-
	elution (2nd part)	2.90	14.500	451.00	42.050	1307.900	99.97
	washings (1st part)	1.00	2.500	40.00	2.500	40.000	-
	washings (2nd part)	0.80	0.330	5.20	0.264	4.160	-

\* it is a mass of Cr sorbed in this cycle + mass of Cr which was not eluted during previous cycle.

**Table 5.** Chromium(III) sorption and elution balance—5th cycle.

5th CYCLE							
Operation	Materials	Solution Volume, dm <sup>3</sup>	Cr Concentration, g/dm <sup>3</sup>	Re Concentration, g/dm <sup>3</sup>	Cr Mass, g	Re Mass, g	Process Efficiency, %
SORPTION	solution for sorption	15.00	3.000	-	45.000	-	-
	washing water	2.50	-	-	-	-	-
	solution after sorption	15.90	0.004	-	0.064	-	99.83
	washings	1.60	0.008	-	0.013	-	-
ELUTION	ionite	-	-	-	44.940 *	-	-
	eluent	3.10	0.168	437.24	0.520	1355.440	-
	washing water	2.50	-	-	-	-	-
	elution (1st part)	0.90	0.320	1.70	0.288	1.530	-
	elution (2nd part)	2.80	14.600	465.50	40.880	1303.400	98.31
	washings (1st part)	1.10	2.500	41.00	2.750	45.100	-
	washings (2nd part)	0.80	0.330	5.40	0.264	4.320	-

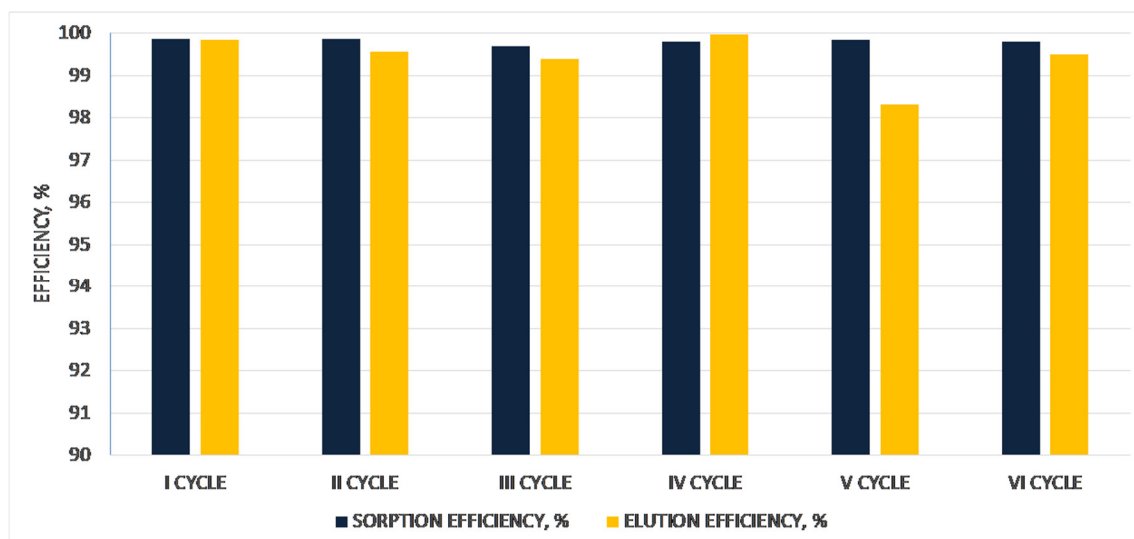
\* it is a mass of Cr sorbed in this cycle + mass of Cr which was not eluted during previous cycle.

**Table 6.** Chromium(III) sorption and elution balance—6th cycle.

6th CYCLE							
Operation	Materials	Solution Volume, dm <sup>3</sup>	Cr Concentration, g/dm <sup>3</sup>	Re Concentration, g/dm <sup>3</sup>	Cr Mass, g	Re Mass, g	Process Efficiency, %
SORPTION	solution for sorption	15.00	3.000	-	45.000	-	-
	washing water	2.50	-	-	-	-	-
	solution after sorption	15.80	0.005	-	0.079	-	99.79
	washings	1.70	0.010	-	0.017	-	-
ELUTION	ionite	-	-	-	45.662 *	-	-
	eluent	3.20	0.173	423.70	0.552	1355.850	-
	washing water	2.50	-	-	-	-	-
	elution (1st part)	0.75	0.330	1.70	0.248	1.275	-
	elution (2nd part)	2.90	14.400	445.00	41.760	1290.500	99.50
	washings (1st part)	1.25	2.500	47.00	3.125	58.750	-
	washings (2nd part)	0.80	0.300	5.40	0.240	4.320	-

\* it is a mass of Cr sorbed in this cycle + mass of Cr which was not eluted during previous cycle.





**Figure 4.** Sorption and elution efficiency of chromium(III) ions in six subsequent cycles of ionite PFC100 × 10 work.

Sorption and elution efficiencies of Cr(III) ions in six subsequent working cycles of PFC100 × 10 ionite were stable and very high. Sorption efficiency was 99.69–99.87%, while elution efficiency was 98.31–99.84%. High stability of sorption and elution efficiencies was also observed when the initial amount of chromium for sorption was increased in cycles IV–VI. Degree of ionite saturation with chromium ions in cycles I–III was ca. 3%, whereas in cycles IV–VI it was over 4%. Concentration of chromium in the solution generated during 2nd part of elution, directed to neutralization, was high enough to isolate a final product, i.e., chromium(III) perrhenate. In the first three cycles it was 8.71–11.10 g/dm<sup>3</sup>, while in the next three—14.40–14.60 g/dm<sup>3</sup>. The proper course of the sorption and elution processes and low metal (Re and Cr) losses (<1%) were the result of adequate recycling of generated solutions. The important part of the proposed technology is minimizing amount of generated waste solutions, containing valuable metals.

Obtained solution were combined, neutralized and appropriate compounds (chromium(III) perrhenate and its mixture with nickel) were separated. Composition of the prepared substances after purification and drying is shown in Table 7.

**Table 7.** Composition of chromium(III) perrhenate and its mixture with nickel.

Material	Re %	Cr %	Ni	NH <sub>4</sub> <sup>+</sup> ppm	NO <sub>3</sub> <sup>-</sup> ppm	Co ppm	Mg ppm	Ca ppm	Na ppm	Zn ppm	Mo ppm	K ppm	Pb ppm
Cr(ReO <sub>4</sub> ) <sub>3</sub>	69.58	6.48	<10ppm	<10	<15	<5	<2	<3	<10	<3	<5	<10	<5
mixture	71.07	3.87	2.28%	<10	<15	<5	<2	<3	<10	<3	<5	<10	<5

The proposed procedure allowed to obtain high purity substances fulfilling the requirements for their application in alloy powder production or as components of baths for alloy electrowinning.

### 3.2. Preparation of Anhydrous Cobalt(II) Perrhenate and its Mixtures

Six cycles of cobalt(II) perrhenate preparation, under dynamic conditions using sulphate solutions were performed. Balance sheets of conducted trials are shown in Tables 8–13. Changes of sorption and elution efficiency in subsequent cycles of ionite work are presented in Figure 5.

**Table 8.** Balance for cobalt(II) sorption and elution—1st cycle.

1st CYCLE							
Operation	Materials	Solution Volume, dm <sup>3</sup>	Co Concentration, g/dm <sup>3</sup>	Re Concentration, g/dm <sup>3</sup>	Co Mass, g	Re Mass, g	Process Efficiency, %
SORPTION	solution for sorption	12.00	5.000	-	60.000	-	-
	washing water	3.00	-	-	-	-	-
	solution after sorption	12.50	0.001	-	0.013	-	99.95
	washings	2.50	0.007	-	0.018	-	-
ELUTION	ionite	-	-	-	59.970	-	-
	eluent	2.00	-	500.00	-	1000.000	-
	washing water	3.50	-	-	-	-	-
	elution (1st part)	0.50	0.200	0.03	0.100	0.015	-
	elution (2nd part)	2.00	26.400	475.15	52.800	950.300	99.88
	washings (1st part)	1.00	6.000	42.10	6.000	42.100	-
	washings (2nd part)	2.00	0.500	0.20	1.000	0.400	-

**Table 9.** Balance for cobalt(II) sorption and elution—2nd cycle.

2nd CYCLE							
Operation	Materials	Solution Volume, dm <sup>3</sup>	Co Concentration, g/dm <sup>3</sup>	Re Concentration, g/dm <sup>3</sup>	Co Mass, g	Re Mass, g	Process Efficiency, %
SORPTION	solution for sorption	12.00	5.000	0.033	60.000	0.400	-
	washing water	3.00	-	-	-	-	-
	solution after sorption	12.40	0.003	0.032	0.037	0.400	99.72
	washings	2.60	0.050	<0.001	0.130	-	-
ELUTION	ionite	-	-	-	59.903 *	-	-
	eluent	2.00	-	500.00	-	1000.000	-
	washing water	3.20	-	-	-	-	-
	elution (1st part)	0.50	0.190	0.03	0.095	0.015	-
	elution (2nd part)	2.10	25.200	456.0	52.920	957.600	98.79
	washings (1st part)	0.90	6.000	42.50	5.400	38.250	-
	washings (2nd part)	1.70	0.450	0.18	0.765	0.306	-

\* it is a mass of Co sorbed in this cycle + mass of Co which was not eluted during the previous cycle.

**Table 10.** Balance for cobalt(II) sorption and elution—3rd cycle.

3rd CYCLE							
Operation	Materials	Solution Volume, dm <sup>3</sup>	Co Concentration, g/dm <sup>3</sup>	Re Concentration, g/dm <sup>3</sup>	Co Mass, g	Re Mass, g	Process Efficiency, %
SORPTION	solution for sorption	12.00	5.000	0.026	60.000	0.306	-
	washing water	3.00	-	-	-	-	-
	solution after sorption	12.40	0.002	0.025	0.025	0.306	99.93
	washings	2.60	0.006	<0.001	0.016	-	-
ELUTION	ionite	-	-	-	60.682 *	-	-
	eluent	2.00	-	500.00	-	1000.000	-
	washing water	3.10	-	-	-	-	-
	elution (1st part)	0.40	0.180	0.03	0.072	0.012	-
	elution (2nd part)	2.20	24.200	431.50	53.240	949.300	98.77
	washings (1st part)	1.00	5.800	45.00	5.800	45.000	-
	washings (2nd part)	1.50	0.550	0.18	0.825	0.270	-

\* it is a mass of Co sorbed in this cycle + mass of Co which was not eluted during the previous cycle.

**Table 11.** Balance for cobalt(II) sorption and elution—4th cycle.

4th CYCLE							
Operation	Materials	Solution Volume, dm <sup>3</sup>	Co Concentration, g/dm <sup>3</sup>	Re Concentration, g/dm <sup>3</sup>	Co Mass, g	Re Mass, g	Process Efficiency, %
SORPTION	solution for sorption	12.00	5.000	0.015	60.000	0.180	-
	washing water	3.00	-	-	-	-	-
	solution after sorption	12.10	0.004	-	0.048	-	99.68
	washings	2.90	0.050	<0.001	0.145	-	-
ELUTION	ionite	-	-	-	60.552 *	-	-
	eluent	2.00	-	500.00	-	1000.000	-
	washing water	3.10	-	-	-	-	-
	elution (1st part)	0.60	0.18	0.005	0.108	0.003	-
	elution (2nd part)	2.10	25.40	456.00	53.340	957.600	97.98
	washings (1st part)	0.90	5.60	45.00	5.040	40.500	-
	washings (2nd part)	1.50	0.56	0.200	0.840	0.300	-

\* it is a mass of Co sorbed in this cycle + mass of Co which was not eluted during the previous cycle.

**Table 12.** Balance for cobalt(II) sorption and elution—5th cycle.

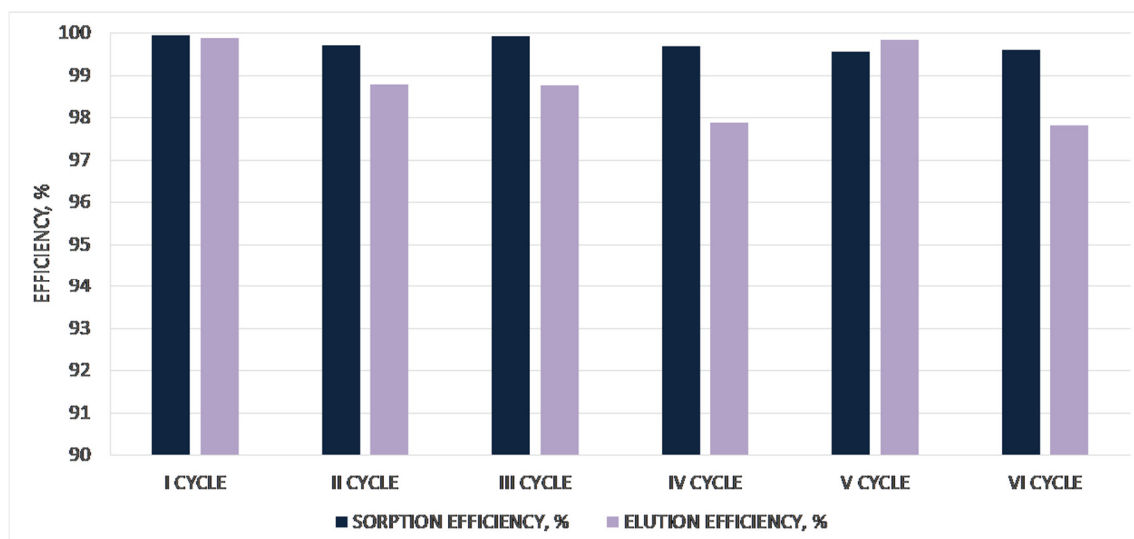
5th CYCLE							
Operation	Materials	Solution Volume, dm <sup>3</sup>	Co Concentration, g/dm <sup>3</sup>	Re Concentration, g/dm <sup>3</sup>	Co Mass, g	Re Mass, g	Process Efficiency, %
SORPTION	solution for sorption	12.00	5.000	0.025	60.000	0.300	-
	washing water	3.00	-	-	0.000	-	-
	solution after sorption	12.20	0.005	-	0.061	-	99.57
	washings	2.80	0.070	<0.001	0.196	-	-
ELUTION	ionite	-	-	-	60.967 *	-	-
	eluent	2.00	-	500.00	-	1000.000	-
	washing water	3.10	-	-	-	-	-
	elution (1st part)	0.50	0.20	0.52	0.100	0.260	-
	elution (2nd part)	2.20	25.40	436.00	55.880	959.200	99.85
	washings (1st part)	0.80	5.00	44.00	4.000	35.200	-
	washings (2nd part)	1.60	0.56	0.23	0.896	0.368	-

\* it is a mass of Co sorbed in this cycle + mass of Co which was not eluted during the previous cycle

**Table 13.** Balance for cobalt(II) sorption and elution—6th cycle.

6th CYCLE							
Operation	Materials	Solution Volume, dm <sup>3</sup>	Co Concentration, g/dm <sup>3</sup>	Re Concentration, g/dm <sup>3</sup>	Co Mass, g	Re Mass, g	Process Efficiency, %
SORPTION	solution for sorption	12.00	5.000	0.031	60.000	0.368	-
	washing water	3.00	-	-	-	-	-
	solution after sorption	12.00	0.005	-	0.060	-	99.60
	washings	3.00	0.060	<0.001	0.180	-	-
ELUTION	ionite	-	-	-	59.851 *	-	-
	eluent	2.00	-	500.00	-	1000.000	-
	washing water	3.10	-	-	-	-	-
	elution (1st part)	0.40	0.11	0.60	0.044	0.240	-
	elution (2nd part)	2.10	25.40	456.00	53.340	957.600	97.82
	washings (1st part)	0.90	4.60	44.00	4.140	39.600	-
	washings (2nd part)	1.70	0.60	0.22	1.020	0.374	-

\* it is a mass of Co sorbed in this cycle + mass of Co which was not eluted during the previous cycle



**Figure 5.** Sorption and elution efficiency of cobalt(II) ions in six subsequent cycles of ionite SGC650 work.

Sorption and elution efficiencies of cobalt(II) ions in six subsequent working cycles of SGC650 ionite were stable and very high. Sorption efficiency was 99.57–99.95%, while elution efficiency was 97.79–99.89%. Degree of ionite saturation with chromium ions was ca. 6%. Concentration of chromium in the solution generated during 2<sup>nd</sup> part of elution, directed to neutralization, was high and between 24.2–26.4 g/dm<sup>3</sup>. The proper course of the sorption and elution processes and low metal (Re and Co) losses (<1%) were the result of adequate recycling of generated solutions. The important part of the proposed technology is a minimized amount of generated waste solutions, containing valuable rhenium and cobalt.

Obtained solutions were combined, neutralized and appropriate compounds (cobalt(II) perrhenate and its mixture with nickel) were separated. Compositions of the prepared substances after drying are shown in Table 14.

**Table 14.** Composition of cobalt(II) perrhenate and its mixture with nickel.

Material/ Neutralizing Agent	Re %	Co %	Ni	NH <sub>4</sub> <sup>+</sup> ppm	Cr ppm	Mg ppm	Ca ppm	Na ppm	Zn ppm	Mo ppm	K ppm	Pb ppm
Co(ReO <sub>4</sub> ) <sub>2</sub> /CoO	66.55	10.55	20ppm	<10	<5	5	4	11	<3	<5	11	<5
Co(ReO <sub>4</sub> ) <sub>2</sub> /Co <sub>met</sub>	66.55	10.55	<10ppm	<10	<5	<2	<3	<10	<3	<5	<10	<5
mixture/NiO	66.57	3.92	6.60%	<10	<5	<2	<3	<10	<3	<5	<10	<5

As previously shown in this case, the proposed procedure also allowed us to obtain high purity substances that fulfilled the requirements. It should be pointed out that metallic cobalt is a more active neutralizing agent than cobalt(II) oxide. Moreover, the product of neutralization with metallic nickel is a purer substance than the product obtained using cobalt(II) oxide.

### 3.3. Preparation of Anhydrous Nickel(II) Perrhenate and its Mixtures

Six cycles of nickel(II) perrhenate preparation, under dynamic conditions using nitrate solutions were performed. Balance sheets of conducted trials are shown in Tables 15–20. Change of sorption and elution efficiencies in subsequent cycles of ionite work are presented in Figure 6.

**Table 15.** Balance for nickel(II) sorption and elution—1st cycle.

1st CYCLE							
Operation	Materials	Solution Volume, dm <sup>3</sup>	Ni Concentration, g/dm <sup>3</sup>	Re Concentration, g/dm <sup>3</sup>	Ni Mass, g	Re Mass, g	Process Efficiency, %
SORPTION	solution for sorption	14.00	5.000	-	70.000	-	-
	washing water	3.00	-	-	-	-	-
	solution after sorption	14.10	0.002	-	0.028	-	99.93
	washings	2.90	0.008	-	0.023	-	-
ELUTION	ionite	-	-	-	69.949	-	-
	eluent	2.00	-	500.00	-	1000.000	-
	washing water	2.00	-	-	-	-	-
	elution (1st part)	0.50	1.200	6.00	0.600	3.000	96.29
	elution (2nd part)	2.00	32.000	482.00	64.000	964.000	
	washings (1st part)	0.50	4.000	47.00	2.000	23.500	
	washings (2nd part)	1.50	0.500	0.20	0.750	0.300	

**Table 16.** Balance for nickel(II) sorption and elution—2nd cycle.

2nd CYCLE							
Operation	Materials	Solution Volume, dm <sup>3</sup>	Ni Concentration, g/dm <sup>3</sup>	Re Concentration, g/dm <sup>3</sup>	Ni Mass, g	Re Mass, g	Process Efficiency, %
SORPTION	solution for sorption	14.00	5.000	0.021	70.000	0.300	-
	washing water	3.00	-	-	0.000	-	-
	solution after sorption	14.20	0.002	-	0.028	-	99.89
	washings	2.80	0.009	-	0.007	-	-
ELUTION	ionite	-	-	-	72.563 *	-	-
	eluent	2.00	1.300	463.25	2.600	926.500	-
	washing water	3.20	-	-	-	-	-
	elution (1st part)	0.30	0.26	1.20	0.078	0.360	99.73
	elution (2nd part)	2.10	30.10	450.00	63.210	945.000	
	washings (1st part)	0.90	6.20	162.00	5.580	145.800	
	washings (2nd part)	2.25	0.55	5.00	1.238	11.250	

\* it is a mass of Ni sorbed in this cycle + mass of Ni which was not eluted during the previous cycle.

**Table 17.** Balance for nickel(II) sorption and elution—3rd cycle.

3rd CYCLE							
Operation	Materials	Solution Volume, dm <sup>3</sup>	Ni Concentration, g/dm <sup>3</sup>	Re Concentration, g/dm <sup>3</sup>	Ni Mass, g	Re Mass, g	Process Efficiency, %
SORPTION	solution for sorption	14.00	5.000	0.023	70.000	0.324	-
	washing water	3.00	-	-	-	0.000	-
	solution after sorption	12.40	0.004	0.026	0.050	0.324	99.88
	washings	4.60	0.008	<0.001	0.037	-	-
ELUTION	ionite	-	-	-	70.111 *	-	-
	eluent	2.45	1.76	452.25	4.312	1108.013	-
	washing water	3.10	-	-	-	-	-
	elution (1st part)	0.30	0.26	0.10	0.078	0.030	99.99
	elution (2nd part)	2.10	30.10	501.00	63.210	1052.100	
	washings (1st part)	0.90	6.20	54.00	5.580	48.600	
	washings (2nd part)	2.25	0.55	0.80	1.238	1.800	

\* it is a mass of Ni sorbed in this cycle + mass of Ni which was not eluted during the previous cycle.

**Table 18.** Balance for nickel(II) sorption and elution—4th cycle.

4th CYCLE							
Operation	Materials	Solution Volume, dm <sup>3</sup>	Ni Concentration, g/dm <sup>3</sup>	Re Concentration, g/dm <sup>3</sup>	Ni Mass, g	Re Mass, g	Process Efficiency, %
SORPTION	solution for sorption	14.00	5.000	0.057	70.000	0.800	-
	washing water	3.00	-	-	-	-	-
	solution after sorption	14.50	0.004	-	0.062	-	99.88
	washings	2.50	0.009	<0.001	0.023	-	-
ELUTION	ionite	-	-	-	69.920 *	-	-
	eluent	2.00	2.572	431.20	5.144	862.391	-
	washing water	2.50	-	-	-	-	-
	elution (1st part)	0.50	0.20	0.60	0.100	0.300	-
	elution (2nd part)	2.00	32.0	452.00	64.000	904.000	99.00
	washings (1st part)	1.00	4.600	40.00	4.600	40.000	-
	washings (2nd part)	1.00	0.52	0.20	0.520	0.200	-

\* it is a mass of Ni sorbed in this cycle + mass of Ni which was not eluted during the previous cycle.

**Table 19.** Balance for nickel(II) sorption and elution—5th cycle.

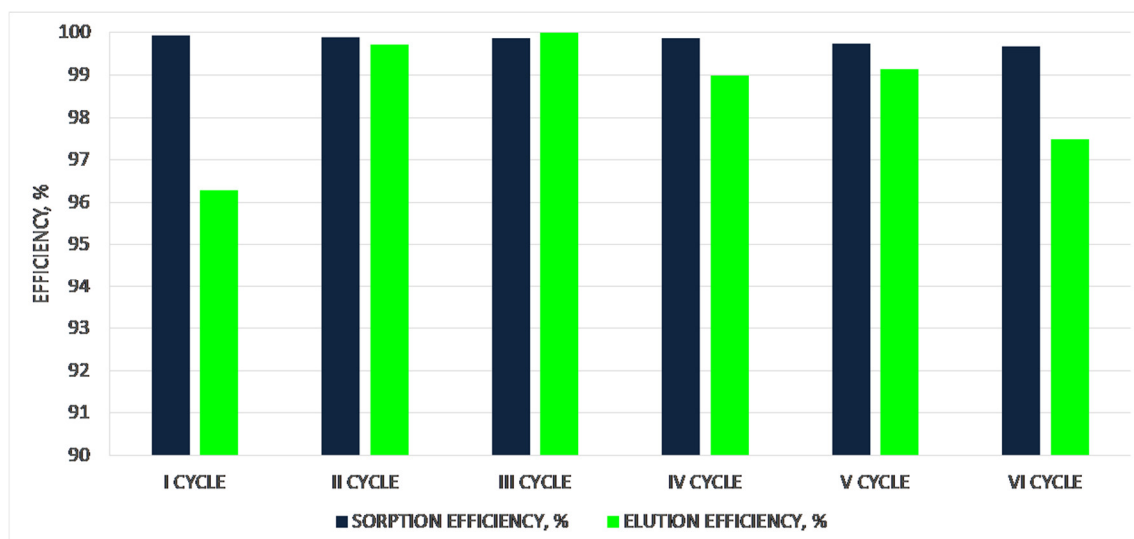
5th CYCLE							
Operation	Materials	Solution Volume, dm <sup>3</sup>	Ni Concentration, g/dm <sup>3</sup>	Re Concentration, g/dm <sup>3</sup>	Ni Mass, g	Re Mass, g	Process Efficiency, %
SORPTION	solution for sorption	14.00	5.000	0.014	70.000	0.200	-
	washing water	3.00	-	-	-	-	-
	solution after sorption	13.90	0.010	-	0.139	-	99.74
	washings	3.10	0.015	<0.001	0.047	-	-
ELUTION	ionite	-	-	-	70.515 *	-	-
	eluent	3.00	1.567	463.43	4.700	1390.300	-
	washing water	2.00	-	-	-	-	-
	elution (1st part)	0.50	0.23	1.2	0.115	0.600	-
	elution (2nd part)	2.75	24.00	463.000	66.000	1273.250	99.15
	washings (1st part)	0.80	4.0	136.00	3.200	108.800	-
	washings (2nd part)	0.95	0.630	1.10	0.599	1.045	-

\* it is a mass of Ni sorbed in this cycle + mass of Ni which was not eluted during the previous cycle.

**Table 20.** Balance for nickel(II) sorption and elution—6th cycle.

6th CYCLE							
Operation	Materials	Solution Volume, dm <sup>3</sup>	Ni Concentration, g/dm <sup>3</sup>	Re Concentration, g/dm <sup>3</sup>	Ni Mass, g	Re Mass, g	Process Efficiency, %
SORPTION	solution for sorption	14.00	5.000	0.075	70.000	1.045	-
	washing water	3.00	-	-	-	-	-
	solution after sorption	15.00	0.006	-	0.090	-	99.67
	washings	2.00	0.070	<0.001	0.140	-	-
ELUTION	ionite	-	-	-	70.371 *	-	-
	eluent	2.30	1.441	438.87	3.315	1009.400	-
	washing water	3.10	-	-	-	-	-
	elution (1st part)	0.50	0.11	0.60	0.055	0.300	-
	elution (2nd part)	2.50	25.40	395.00	63.500	987.500	97.48
	washings (1st part)	0.90	4.60	21.00	4.140	18.900	-
	washings (2nd part)	1.50	0.60	0.22	0.900	0.330	-

\* it is a mass of Ni sorbed in this cycle + mass of Ni which was not eluted during the previous cycle.



**Figure 6.** Sorption and elution efficiency of nickel (II) ions in six subsequent cycles of ionite C160 work.

As in the case of cobalt and chromium, sorption and elution efficiencies of nickel(II) ions in six subsequent working cycles of C160 ionite were stable and very high. Sorption efficiency was 99.67–99.93%, while elution efficiency was 97.48–99.99%. The degree of ionite saturation with chromium ions was high and equal to ca. 7%. Concentration of chromium in a solution generated during 2<sup>nd</sup> part of elution, directed to neutralization, was high and between 24–32 g/dm<sup>3</sup>.

During investigation of ion-exchange processes, it is important to perform several sorption-elution cycles to determine resin stability. Working parameters of ionite may be also established based on multiple repetitions of the cycles. The results of the first cycle are always subjected to significant errors. The reason for this is that new resin does not achieve equilibrium state during this cycle. For all presented rhenium compounds, including nickel perrhenate, it is assumed that the degree of ionite saturation with metals should be >1%, whereas elution efficiency should be >90%. Therefore, determined efficiencies at the level 96–99% are considered to be very high.

Obtained solutions were combined, neutralized and appropriate compounds (nickel(II) perrhenate and its mixture with cobalt) were separated. Compositions of the prepared substances after drying are shown in Table 21.

**Table 21.** Composition of nickel(II) perrhenate and its mixture with cobalt.

Material/Neutralizing Agent	Re %	Ni %	Co	NH <sub>4</sub> <sup>+</sup> ppm	NO <sub>3</sub> <sup>-</sup> ppm	Cr ppm	Mg ppm	Ca ppm	Na ppm	Zn ppm	Mo ppm	K ppm	Pb ppm
Ni(ReO <sub>4</sub> ) <sub>2</sub> /NiO	66.58	10.51	<10 ppm	<10	<15	<5	<2	3	11	<3	<5	<10	<5
NiReO <sub>4</sub> ) <sub>2</sub> /Ni <sub>met</sub>	66.57	10.51	<10 ppm	<10	<15	<5	<2	<3	<10	<3	<5	<10	<5
mixture/CoO	66.55	3.78	6.78%	<10	<15	<5	<2	<3	<10	<3	<5	<10	<5

In this case the proposed procedure is also allowed to obtain high purity substances fulfilling the requirements for their application in alloy powder production or for electrowinning of Re-Ni alloy.

#### 4. Conclusions

An effective and highly efficient production method of high purity perrhenates of nickel(II), cobalt(II) and chromium(III) as well as their mixtures using ion exchange technique was applied. All developed technologies are characterized by management of waste solutions and low metal loss not exceeding 1%. Obtained products containing rhenium, cobalt, nickel and chromium, are components

suitable for preparation of alloy powder precursors or baths for electrowinning of binary or ternary alloys.

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