*Article*

# Recycling of Rhenium from Superalloys and Manganese from Spent Batteries to Produce Manganese(II) Perrhenate Dihydrate

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**Abstract:** This work presents the research results on the development of an innovative, hydrometallurgical technology for the production of manganese(II) perrhenate dihydrate from recycled waste. These wastes are scraps of Ni–based superalloys containing Re and scraps of Li–ion batteries containing Mn—specifically, solutions from the leaching of black mass. This work presents the conditions for the production of $Mn(ReO_4)_2 \cdot 2H_2O$. Thus, to obtain $Mn(ReO_4)_2 \cdot 2H_2O$, manganese(II) oxide was used, precipitated from the solutions obtained after the leaching of black mass from Li–ion batteries scrap and purified from Cu, Fe and Al (pH = 5.2). $MnO_2$ precipitation was carried out at a temperature < 50 °C for 30 min using a stoichiometric amount of $KMnO_4$ in the presence of $H_2O_2$. $MnO_2$ precipitated in this way was purified using a 20% $H_2SO_4$ solution and then $H_2O$. Purified $MnO_2$ was then added alternately with a 30% $H_2O_2$ solution to an aqueous $HReO_4$ solution. The reaction was conducted at room temperature for 30 min to obtain a pH of 6–7. $Mn(ReO_4)_2 \cdot 2H_2O$ precipitated by evaporating the solution to dryness was purified by recrystallization from $H_2O$ with the addition of $H_2O_2$ at least twice. Purified $Mn(ReO_4)_2 \cdot 2H_2O$ was dried at a temperature of 100–110 °C. Using the described procedure, $Mn(ReO_4)_2 \cdot 2H_2O$ was obtained with a purity of >99.0%. This technology is an example of the green transformation method, taking into account the 6R principles.

**Keywords:** batteries; superalloys; rhenium; manganese; metal perrhenates

## 1. Introduction

Rhenium appears extremely rarely in nature, only in a dispersed state, mainly in molybdenite, columbite and copper-bearing shales [1]. Manganese, on the other hand, is the twelfth-most abundant metal in the Earth's crust, occurring mainly in the form of oxides, carbonates and silicates. It is the most common heavy metal after iron [2–4].

The chemical properties of rhenium determine its applications, mainly in the production of superalloys but also in catalysis [5,6]. Rhenium is a heavy metal with a high melting point (>3180 °C), significant density (21.0 $g/cm^3$), high hardness (Mohs 7), high strength, thermal and chemical resistance and can also be easily shaped by plastic processing. It is characterized by the highest modulus of elasticity of all refractory metals, −420 GPa [1,3,7].

Manganese, on the other hand, is a hard, silvery and brittle metal with a pink luster. It is widely used as an additive in steel, lowering its melting point and improving its mechanical properties. It is pyrophoric when crushed. Manganese is in huge demand around the world due to its numerous and diverse applications, mainly in the production of steel and high-capacity batteries [2,8,9].

The world's annual production of rhenium is up to 75 tons, the vast majority of which is recovered from so-called primary raw materials, and only ~8 tons are produced from recycling [1,10,11]. The main manufacturers of rhenium from recycling are countries such as the USA, Canada, Germany, Czechia and Poland [1,12]. Rhenium recycling was much greater in 2014–2015, generating 13 tons/year. Rhenium is manufactured as a side product during the production of other elements both from primary or secondary resources, for example, during the recovery of Co and Ni from superalloys scraps. Consequently, the production of rhenium is influenced by the demand for other metals like cobalt and nickel. Currently, on the metals market, cobalt is considered a critical material in most of the world [13–15]. In contrast, nickel is a strategic material and therefore sought after, mainly due to the development of the battery industry [16,17].

However, the world annual production of manganese is not comparable to rhenium, as it constitutes ~6.2 million tons. South Africa is the world's largest manufacturer of manganese, accounting for 33.5% of its global production. It should also be noted that most of the mining of manganese is concentrated in the Kalahari Desert, which is believed to contain over 70% of the world's resources of this metal. Manganese is recycled mainly from iron and steel scraps; a small amount of it is recycled from aluminum beverage cans. The recycling rate is 37%, and the efficiency is estimated at 53% [18–20].

This publication concerns the preparation of manganese(II) perrhenate dihydrate. Manganese and rhenium share many of the chemical characteristics of transition metals, including multiple valency, the ability to form stable complex ions, paramagnetism and catalytic properties. However, in many aspects, rhenium is chemically more similar to technetium than to manganese [21,22]. For this reason, $Mn(ReO_4)_2 \cdot 2H_2O$ has potential for use in the production of alloys, catalysts or in electrical components [23].

There are not many reports in the literature about the combination of rhenium and manganese and, consequently, about $Mn(ReO_4)_2 \cdot 2H_2O$. There are several reports on the preparation, properties and use of manganese(II) perrhenate and its hydrates.

In 1949, W. T. Smith and G. E. Maxwell described the synthesis of manganese(II) perrhenate dihydrate, which was obtained as a result of the reaction of manganese(II) carbonate or manganese(II) hydroxide with perrhenic acid. This publication also specified the physicochemical properties of the above-mentioned compound, such as solubility, density and freezing point [24].

In 1969, H. G. Mayfield, Jr. and W. E. Bull described the process of forming the complexes of manganese(II) perrhenate with pyridine [25].

However, the synthesis of manganese(II) perrhenate from manganese(IV) oxide, metallic manganese and rhenium(VI) oxide has been patented and described in patent no. US 4027004A. It also explains the properties of the obtained manganese(II) perrhenate, which allows it to be used in electrical components [23].

In 1981, K.V. Ovchinnikov and his team investigated the thermal decomposition of manganese(II) perrhenate in vacuum [26].

In 1997, Charles Torardi and his team presented the magnetic properties of anhydrous manganese(II) perrhenate in a publication. This compound was found to have antiferromagnetic properties. It was also determined that anhydrous manganese(II) perrhenate has trigonal symmetry [27].

A. Butz, G. Miehle, H. Paulus, P. Strauss and H. Fuess, in 1998, researched the crystallographic structure of manganese(II) perrhenate in dihydrate and anhydrous forms and published the results of the dihydrate dehydration process. This compound was obtained as a result of the reaction of manganese(II) carbonate with perrhenic acid. The process was carried out in a temperature range of 50–60 °C in the presence of carbon dioxide [28].

In *Z. Für Krist. -New Cryst. Struct.*, in the same year, an article was published presenting the results of research on the crystallographic structure of $Mn(ReO_4)_2(H_2O)_2$. The compound was obtained as a result of the reaction of manganese(II) carbonate with perrhenic acid [29].

A work about $[Mn(H_2O)_2](ReO_4)_2$ was also published by J. Hetmańczyk and Ł. Hetmańczyk These studies were conducted using spectroscopic methods. The authors presented the dynamics of $H_2O$ ligands and a perrhenate anion in the $[Mn(H_2O)_2](ReO_4)_2$ molecule at the moment of phase transition, as well as the crystallographic structure and thermal properties of the above-mentioned compounds. These compounds were obtained as a result of the reaction of manganese(II) carbonate with perrhenic acid [30].

In 2021, B.C. Gong, H.C. Yang, J.F. Zhang, K. Liu and Z.Y. Lu conducted research in which they found that manganese(II) perrhenate, which has a wavy layered structure, doped with electrons exhibits ferromagnetic properties. They also determined that this compound can be a so-called van der Walls magnetic material, which means that it can be used for research on magnetism and in spintronics [31].

In 2020, in *OSTI.GOV*, a detailed crystallographic analysis of manganese(II) perrhenate was described. It showed that $Mn(ReO_4)_2$ crystallizes in a trigonal space group and its structure is two-dimensional [32].

The objective of this study was to produce manganese(II) perrhenate dihydrate exclusively from two waste streams that, to the knowledge of the authors, have not been previously reported in the literature. Furthermore, the innovative method involves handling all waste materials, solid and liquid, to eliminate any loss of components and the need for further processing. This waste-free technology enables the production of high-purity manganese(II) perrhenate dihydrate, a valuable material for future novel applications in alloys, catalysts and electrical components. It is also in agreement with the principles of sustainable development and green transformation, and importantly, it meets the 6R principles in all six areas (rethink, refuse, reduce, reuse, repair and recycle) [33].

## 2. Results and Discussion

### 2.1. Recovery of Manganese from Post-Leaching Solutions of Li–ion Battery Scrap and Analysis of the Obtained $MnO_2$

Manganese precipitation tests were carried out using the post-leaching solutions of Li–ion battery scrap. Before the main precipitation of manganese, the solution was purified from Cu and then from Al and Fe. Copper was precipitated using 1 mole of iron in the form of metallic Fe powder for each mole of copper in the solution, which takes around 45 min with filtration. After filtering the precipitate, 30% $H_2O_2$ solution and then aqueous 20% NaOH solution were added over 30 min until the pH 5.2 was obtained. Neutralization was carried out at a temperature not exceeding 50 °C, and after obtaining the desired pH, the reaction was conducted for 30 min in the obtained conditions. After that time, the precipitated aluminum–iron sludge was filtered to obtain a solution that was sent for the manganese recovery tests. Table 1 lists the compositions of all the solutions, and Figure 1 shows (a) losses of valuable metals in the purification processes (Li, Mn, Co and Ni) and (b) efficiency of the precipitation of pollutants (Cu, Fe and Al).

**Table 1.** Composition of the solutions obtained in the purification tests.

| Type of Solution | Volume, dm³ | Concentration, g/dm³ | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Ni | Co | Al | Mn | Li | Fe | Cu |
| after leaching | 10.0 | 8.20 | 25.60 | 2.50 | 6.54 | 2.56 | 1.80 | 2.50 |
| after Cu precipitation (E) | 9.65 | 8.42 | 26.32 | 2.59 | 6.78 | 2.65 | 4.14 | <0.01 |
| after Fe and Al precipitation (F) | 10.12 | 7.91 | 24.74 | <0.01 | 6.45 | 2.51 | <0.01 | <0.01 |

(**a**) losses of valuable metal            (**b**) efficiency of the precipitation
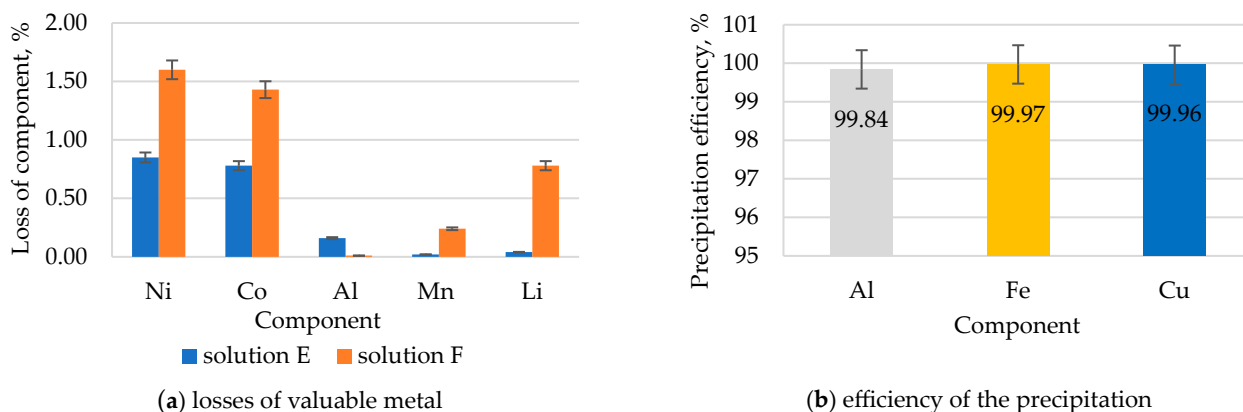
**Figure 1.** Results of the solution purification tests from Cu, Fe and Al.

As can be seen in Figure 1, the losses of valuable metals (Li, Mn, Co and Ni) did not exceed 2% for each component, while the precipitation efficiencies of impurities, such as Cu, Fe and Al, were 99.84%, 99.97% and 99.96%, respectively.

In the next stage, the purified solution was sent for the manganese precipitation tests. Precipitation was carried out using a stoichiometric amount of $KMnO_4$, and the resulting mixture was intensively stirred for 60 min at room temperature. After this time, the precipitate was vacuum-filtered, washed (with solutions of sulfuric acid and water) and analyzed. The solution from the filtration was directed to the recovery of other metals (Ni, Co and Li).

In this way, manganese(II) oxides were obtained, with the compositions depending on the purification stage listed in Table 2. No significant losses of Ni, Li and Co were observed during the process. Cobalt and nickel losses, associated with $MnO_2$ precipitation, were reduced by proposing a recycling of the solutions resulting from the purification. For the selected manganese(II) oxide, after all purification steps, XRD analysis was performed (Figure 2). During the research, a waste management method was developed (Figure 3). SEM analysis was performed for the purified with 20% $H_2SO_4$ manganese(II) oxide—Figure 4.

**Table 2.** Compositions of the obtained manganese(II) oxides.

| Type of MnO$_2$ | Composition, wt% | | | |
|---|---|---|---|---|
| | **Mn** | **Co** | **Ni** | **Fe** |
| crude | 56.10 | 4.14 | 0.90 | <0.01 |
| purified with 1% H$_2$SO$_4$ | 53.30 | 3.55 | 0.67 | <0.01 |
| purified with 20% H$_2$SO$_4$ | 55.90 | 0.20 | 0.16 | <0.01 |

The purification of $MnO_2$ with 20% $H_2SO_4$ solution allowed to reduce the level of impurities below 0.20 wt% of each metal. Thus, $MnO_2$ was obtained, in which the amount of individual impurities such as Co, Ni, and Fe was (wt%): 0.20, 0.16 and <0.01, respectively (Table 2).

As can be seen in Figure 2, XRD analysis confirmed the possibility of producing $MnO_2$ using the described conditions, as the obtained diffractogram shows only the crystalline form of $MnO_2$. The form of the diffractogram indicates a large amount of the amorphous phase.

The obtained $MnO_2$ precipitate was contaminated with cobalt and nickel but did not contain iron. After purification with a 20% $H_2SO_4$ solution, a product free of the above-mentioned elements was obtained. It was the substrate for the production of manganese(II) perrhenate.
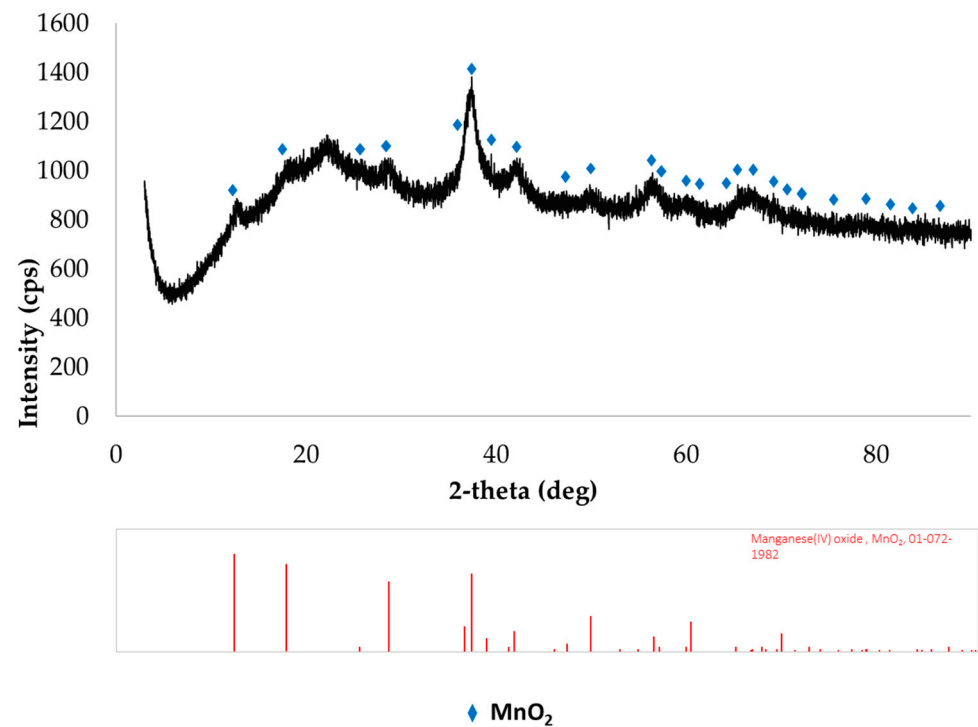
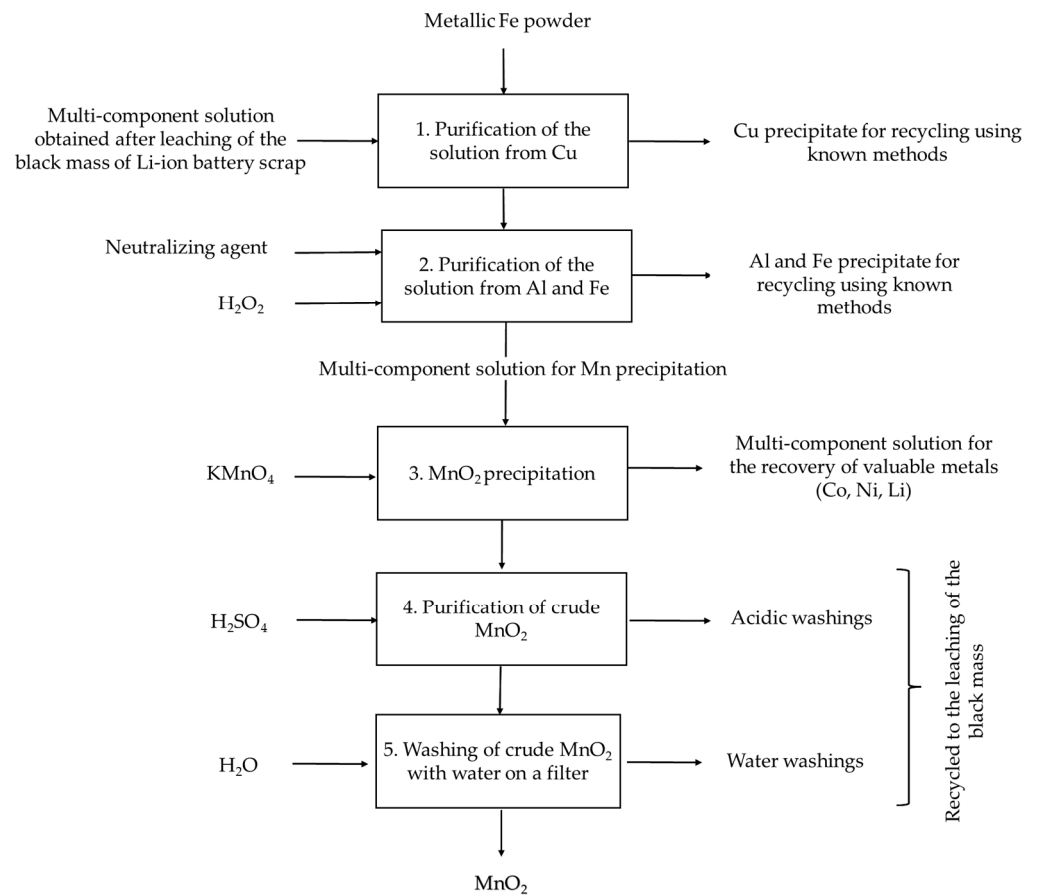**Figure 2.** XRD pattern of the purified $MnO_2$ (purified with 20% $H_2SO_4$).



**Figure 3.** Scheme of $MnO_2$ precipitation from the post-leaching solutions of the black mass from Li–ion batteries.
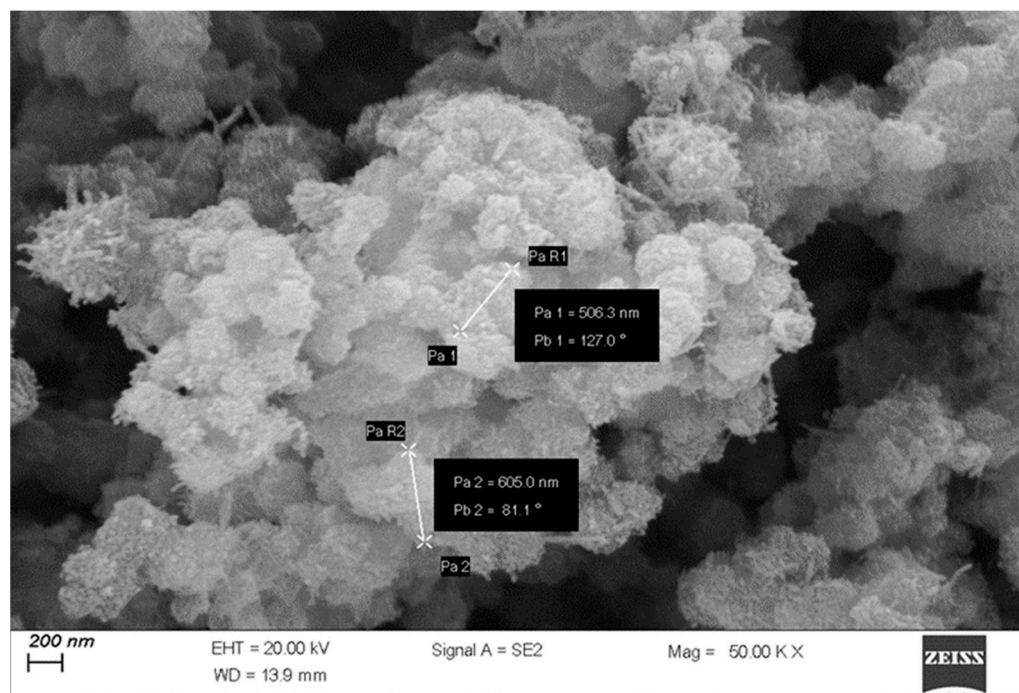
**Figure 4.** SEM analysis of the purified $MnO_2$.

*2.2. Precipitation and Characterization of the Obtained Manganese(II)Perrhenate Dihydrate*

The production of manganese(II) perrhenate dihydrate was carried out according to the reaction (1)

$$MnO_2 + H_2O_2 + 2HReO_4 = Mn(ReO_4)_2 + 2H_2O + O_2 \tag{1}$$

Purified $MnO_2$ (weighing 10 g) was added alternately with a 30% $H_2O_2$ solution (50 $cm^3$ of hydrogen peroxide for each 10 g of manganese(II) oxide) to the aqueous solutions of perrhenic acid with the concentrations of 18.0 or 295.0 g/$dm^3$ of Re. The tests were carried out at room temperature. In this way, a solution with the pH ranging from 6 to 7 was obtained. After reaching the pH, the solution was stirred for 90 min and successively filtered from the unreacted residue. The resulting solutions were directed to the evaporation to dryness, which was carried out at a temperature < 50 °C with an addition of 30% $H_2O_2$ solution using 15 $cm^3$ of hydrogen peroxide for every 50 g of rhenium. Evaporation tests were also carried out to obtain the first crystals. The crude wet sludge precipitated in this way was combined and sent to the cyclic purification stage. A 30 g portion of crude manganese(II) perrhenate dihydrate was used in the tests. Purification was carried out using recrystallization from water with an addition of 15 $cm^3$ of 30% aqueous $H_2O_2$ solution for every 50 g of Re in the precipitate and successively evaporated to obtain the first crystals. Four purification cycles were carried out. The results of the obtained tests are presented in Tables 3 and 4. Figures 5 and 6 illustrate the influence of the used rhenium concentration on the precipitation efficiency of the obtained manganese(II) perrhenate dihydrate and the influence of purification cycles on the purification efficiency of the obtained compound.

With the use of perrhenic acid with the rhenium concentrations of 18 and 295 g/$dm^3$ both, similar $Mn(ReO_4)_2 \cdot 2H_2O$ precipitation efficiencies were obtained using both precipitation methods. The efficiencies were high, for example, over 92%, while using the evaporation to dryness method. Therefore, the choice of acid concentration for the technology in industry will result from the scale of the production, the amount of waste solutions and the price of energy and will be analyzed at each stage of the technology implementation.
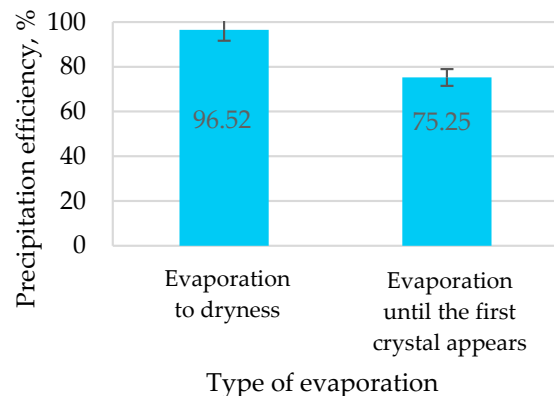
**Table 3.** Results of Mn(ReO$_4$)$_2$·2H$_2$O precipitation.

| Concentration of Re in HReO$_4$, g/dm$^3$ | Volume of HReO$_4$, dm$^3$ | Efficiency of Mn(ReO$_4$)$_2$·2H$_2$O Precipitation, % | Composition in Crude Mn(ReO$_4$)$_2$·2H$_2$O, wt% | | | | |
|---|---|---|---|---|---|---|---|
| | | | Mn | Re | Co | Ni | Fe |
| 18.0 | 2.38 | 92.51 | 9.31 | 62.30 | 0.55 | 0.12 | 0.02 |
| | | 70.56 * | 9.22 | 62.30 | 0.54 | 0.08 | <0.01 |
| 295.0 | 0.15 | 96.52 | 9.54 | 64.30 | 0.51 | 0.13 | <0.01 |
| | | 75.25 * | 9.58 | 64.10 | 0.55 | 0.13 | 0.02 |

\* Research conducted to the precipitation of the first crystals.

**Table 4.** Mn(ReO$_4$)$_2$·2H$_2$O purification results.

| Number of the Cycle | Mass of Mn(ReO$_4$)$_2$·2H$_2$O, g | Precipitation Efficiency of Mn(ReO$_4$)$_2$·2H$_2$O *, % | Composition in Crude Mn(ReO$_4$)$_2$·2H$_2$O, wt% | | | | |
|---|---|---|---|---|---|---|---|
| | | | Mn | Re | Co | Ni | Fe |
| 0 | 30.0 | - | 9.41 | 63.25 | 0.54 | 0.16 | <0.01 |
| I | 24.0 | 80.0 | 9.29 | 62.95 | 0.15 | 0.10 | <0.01 |
| II | 19.6 | 65.3 | 9.29 | 62.95 | 0.10 | 0.10 | <0.01 |
| III | 17.5 | 58.3 | 9.29 | 62.95 | 0.10 | 0.10 | <0.01 |
| IV | 15.2 | 50.7 | 9.29 | 62.95 | 0.10 | 0.10 | <0.01 |

\* Efficiency calculated in relation to the initial mass of crude Mn(ReO$_4$)$_2$·2H$_2$O.
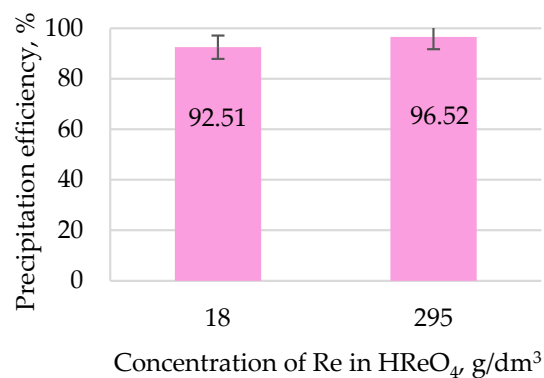


(**a**) evaporation to dryness using different Re concentrations
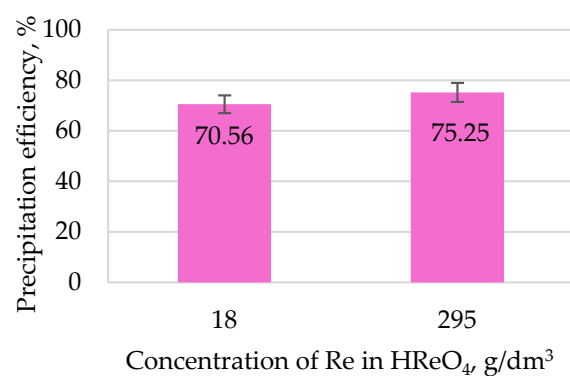
(**b**) evaporation to the precipitation of the first crystals using different Re concentrations
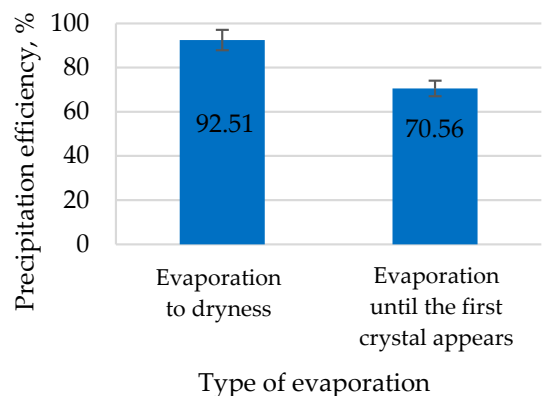
(**c**) different types of evaporation, Re concentration in HReO$_4$—18 g/dm$^3$

(**d**) different types of evaporation, Re concentration in HReO$_4$—295 g/dm$^3$

**Figure 5.** Results of the influence of the Re concentration in HReO$_4$ and the evaporation method on the efficiency of Mn(ReO$_4$)$_2$·2H$_2$O precipitation.

The use of the second stage of purification allows to obtain $Mn(ReO_4)_2 \cdot 2H_2O$ of satisfactory purity, i.e., 9.29% of Mn, 62.9% of Re, 0.10% of Co and Ni and <0.01% of Fe.

In this way, 15.20 g of wet manganese(II) perrhenate dihydrate was obtained, which was dried at 100–110 °C until a constant weight was reached. Thus, manganese(II) perrhenate dihydrate weighing 14.54 g with a purity > 99% was obtained. XRD analysis was performed for this compound—Figure 7.
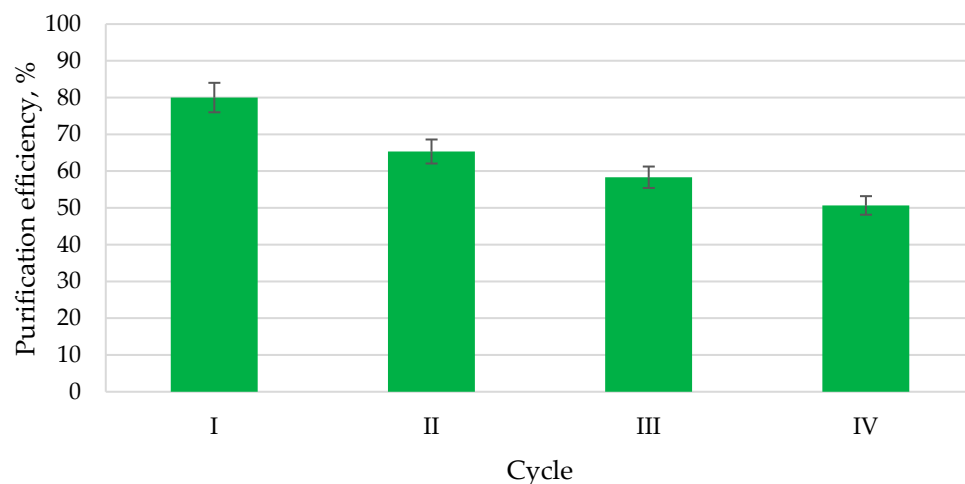


**Figure 6.** Results of the influence of the cyclic purification of $Mn(ReO_4)_2 \cdot 2H_2O$ on the efficiency of the purification of this compound.



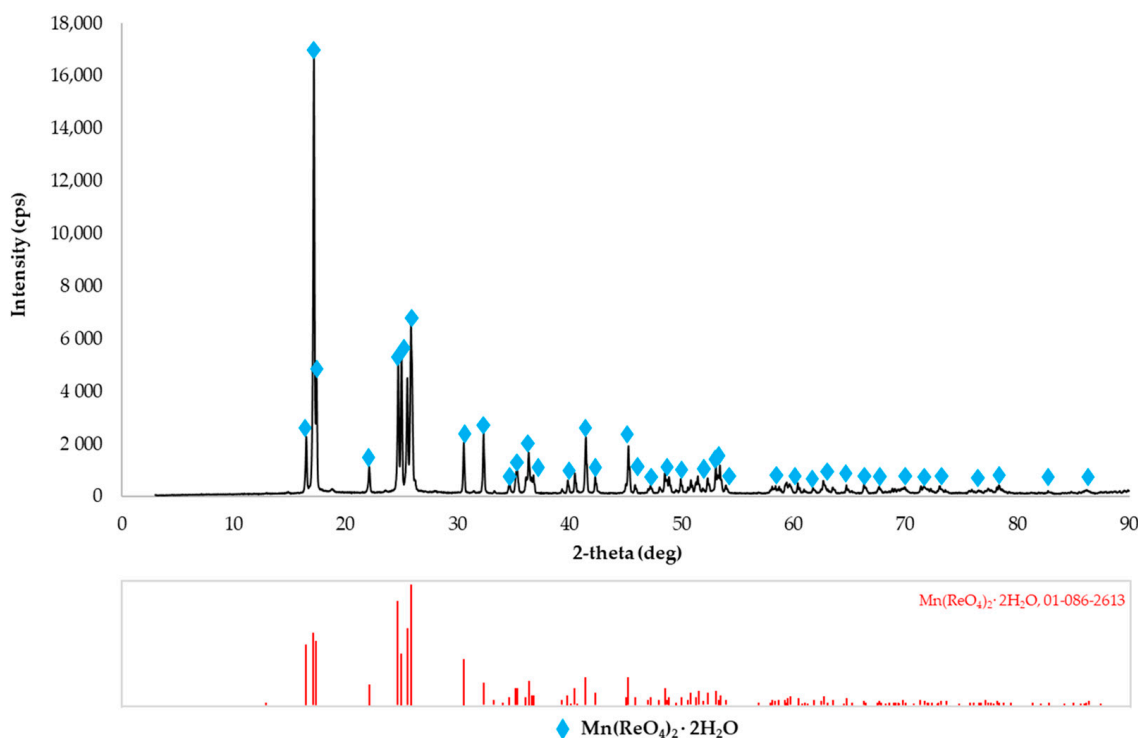**Figure 7.** XRD pattern of $Mn(ReO_4)_2 \cdot 2H_2O$, after four purification cycles.

As can be seen in the diffractogram (Figure 7), a crystalline form of $Mn(ReO_4)_2 \cdot 2H_2O$ was obtained using the described conditions. This diffraction pattern also does not show any amorphous phases and substances.

For this $Mn(ReO_4)_2 \cdot 2H_2O$, its solubility was also determined. The test results are presented in Table 5.

**Table 5.** $Mn(ReO_4)_2 \cdot 2H_2O$ solubility test results.

| Temperature, °C | Solubility of $Mn(ReO_4)_2 \cdot 2H_2O$, % | Standard Deviation |
|---|---|---|
| 0 | 31.5 | 0.09 |
| 10 | 28.2 | 0.10 |
| 20 | 22.7 | 0.22 |
| 30 | 20.5 | 0.16 |

The determined solubilities of $Mn(ReO_4)_2 \cdot 2H_2O$ obtained at various temperature values are consistent with the literature data [24,34]. Each test using the gravimetric method was repeated three times, giving consistent results on the solubility of manganese(II) perrhenate dihydrate. Standard deviations were calculated and are included in Table 5.

The analysis of the conducted research on the precipitation of $Mn(ReO_4)_2 \cdot 2H_2O$ showed that this compound can be obtained using purified $MnO_2$, adding it alternately with the 30% $H_2O_2$ solution (50 cm$^3$ of hydrogen peroxide for each 10 g of manganese(II) oxide) to the aqueous solution of perrhenic acid. The reaction should be carried out at room temperature for 30 min until a pH 6–7 is obtained. $Mn(ReO_4)_2 \cdot 2H_2O$, precipitated by evaporating the solution to dryness, should be purified by recrystallization from water with the addition of $H_2O_2$ at least twice. The purified $Mn(ReO_4)_2 \cdot 2H_2O$ should be dried at 100–110 °C.

Based on the described research, this new, innovative, hydrometallurgical technology was developed for obtaining manganese(II) perrhenate dihydrate that was produced entirely from waste, i.e., superalloy scrap and Li–ion batteries. The next stage of the research will be to find a real application of manganese(II) perrhenate dihydrate in the catalytic, battery and defense industries. Research will be carried out on the possibility of obtaining manganese(II) perrhenate dihydrate with dedicated physicochemical properties, e.g., grain size below 100 nm.

### 3. Materials and Methods

*3.1. Materials*

Perrhenic acid, used in this research, was obtained by leaching the superalloy scrap (Figure 8) with a mixture of acids with an addition of oxidants. The compositions of the materials are shown in Table 6 [35,36]. In this way, a solution was obtained containing 1.1 g/dm$^3$ of Re and mainly nickel but also cobalt, chromium and aluminum. This solution was directed to the sorption of rhenium using a weakly basic ion exchange resin A170 (Purolite, King of Prussia, PA, USA, hydroxide form). The solution obtained after the sorption of rhenium was directed to the recovery of valuable metal components (Ni and Co), while rhenium absorbed in the ion exchange resin was eluted with an aqueous ammonia solution (25%, Chempur, Piekary Śląskie, Poland, p.a.). Ammonium perrhenate was crystallized from the obtained ammonia eluate, which was then dissolved in water and directed to the sorption of ammonium ions using a strongly acidic cation exchange resin C160 (Purolite, USA, hydrogen form) [37,38]. The post-sorption solution, containing perrhenic acid, was sent to the concentration stage, or manganese(II) perrhenate was obtained directly from it. Figure 9 shows the laboratory equipment used in the preparation of perrhenic acid using the method described above. Perrhenic acid used in the conducted research differed in rhenium concentration. The first type came directly from the ion exchange process and was not concentrated. The second type of perrhenic acid was first concentrated and then used to obtain manganese(II) perrhenate dihydrate.
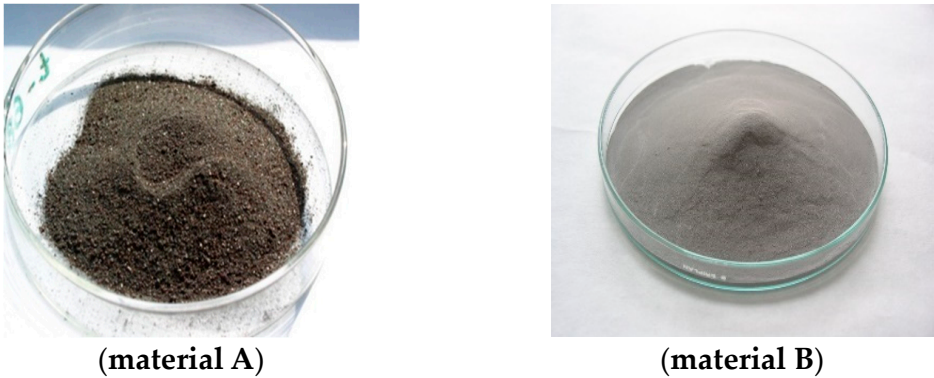
(**material A**)  (**material B**)

**Figure 8.** Pictures of the crushed superalloy scrap used in the research.

**Table 6.** Compositions of the superalloy scrap used in the research.

| Material | Composition, wt% | | | | | |
|---|---|---|---|---|---|---|
| | **Re** | **Ni** | **Co** | **Cr** | **Al** | **Fe** |
| A | 1.78 | 43.32 | 6.50 | 4.70 | 14.50 | 1.30 |
| B | 1.10 | 37.90 | 19.50 | 9.10 | 13.90 | 0.08 |



Leaching of superalloy scrap

Filtration of sludge after leaching of superalloy scrap

Sorption and elution of rhenium

Ammonium perrhenate

Ammonium perrhenate

Ammonium ions sorption

Evaporation of perrhenic acid
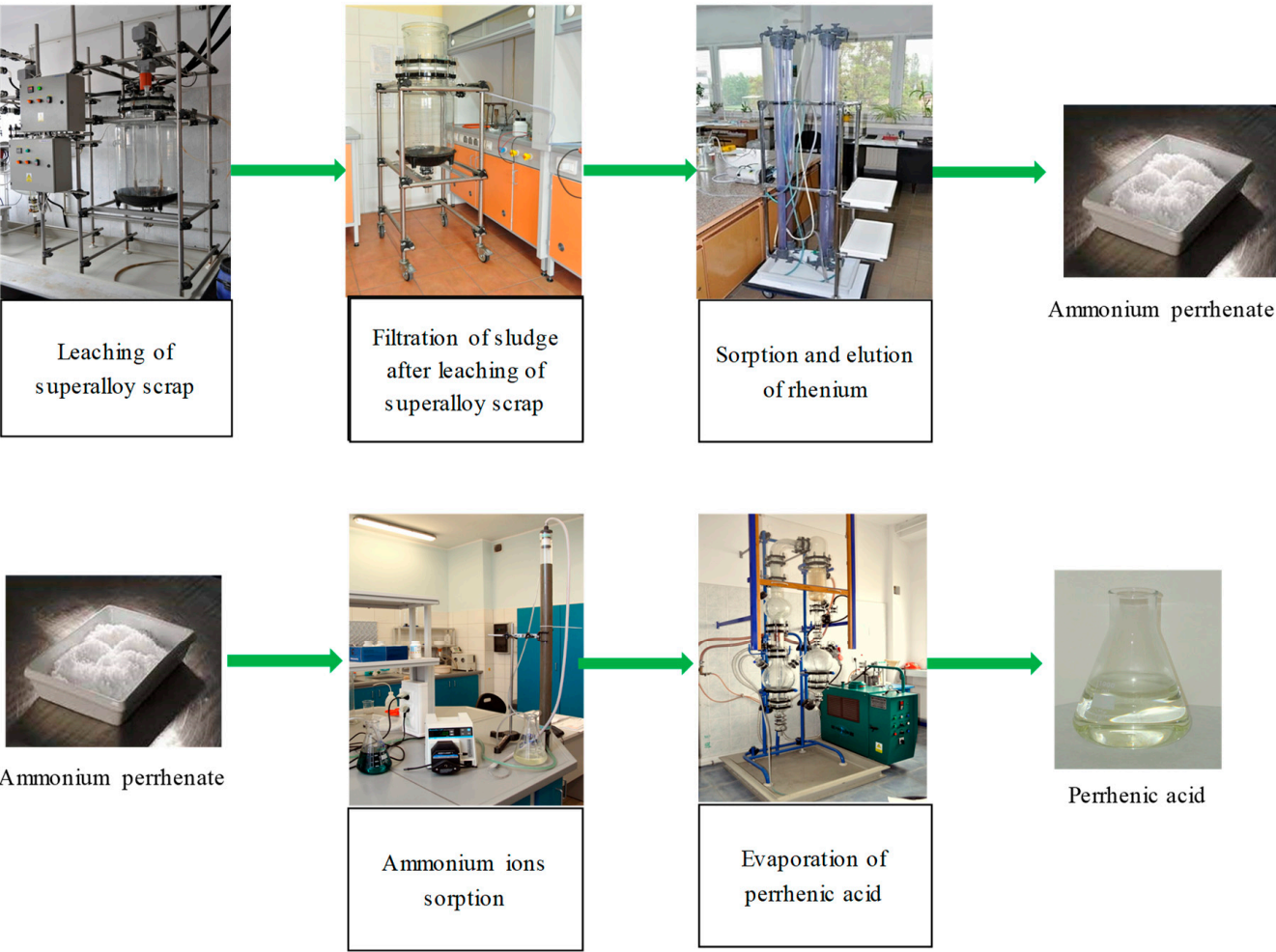
Perrhenic acid

**Figure 9.** Scheme of obtaining perrhenic acid from the superalloy scrap.

In this way, two types of perrhenic acid were obtained, containing (1) 18.0 g/dm$^3$ of Re and <0.0001% of Ca, K, Mg, Cu, Na, Mo, Ni, Pb, Fe, NH$_4$$^+$, Bi, Zn, W, As and Al each and (2) 295.0 g/dm$^3$ of Re; <0.0005% of K; <0.0002% of NH$_4$$^+$; and <0.0001% of Ca, Mg, Cu, Na, Mo, Ni, Pb, Fe, Bi, Zn, W, As and Al each [38].

The solutions obtained after the leaching of the black mass from Li–ion batteries were used as the source of manganese—Table 7. Battery masses for the leaching process were obtained as a result of using the technology developed and patented by Łukasiewicz-IMN [39,40].

**Table 7.** Compositions of the black mass from Li–ion batteries used in the research.

| Material | Composition, wt% | | | | | | |
|---|---|---|---|---|---|---|---|
| | **Ni** | **Co** | **Al** | **Mn** | **Li** | **Fe** | **Cu** |
| C | 6.50 | 32.00 | 2.00 | 5.45 | 2.50 | 1.90 | 2.03 |
| D | 12.70 | 17.00 | 2.79 | 10.02 | 2.70 | 2.10 | 1.78 |

After leaching, a solution with the composition of 2.50 g/dm$^3$ of Al, 25.60 g/dm$^3$ of Co, 2.56 g/dm$^3$ of Li, 6.54 g/dm$^3$ of Mn, 2.50 g/dm$^3$ of Cu, 8.20 g/dm$^3$ of Ni and 1.80 g/dm$^3$ of Fe was obtained, which was directed to the MnO$_2$ precipitation tests.

The following materials and reagents were used in this research: sulfuric acid (95%, Chempur, Piekary Śląskie, Poland, p.a.), aqueous solution of hydrogen peroxide (30%, P.P.H. Stanlab, Lublin, Poland, p.a.), demineralized water (<2 µS/cm, Łukasiewicz-IMN, Gliwice, Poland), sodium hydroxide (>98% Stanlab, Poland, p.a.), KMnO$_4$ (99% P.P.H. Stanlab, Lublin, Poland, p.a.) and Fe dust (>98%, Chempur, Piekary Śląskie, Poland, p.a.).

*3.2. Analyses*

All analyses were performed at the Łukasiewicz Research Network—Institute of Non-Ferrous Metals, mainly at the Centre for Analytical Chemistry (Gliwice, Poland).

The rhenium content in manganese(II) perrhenate and perrhenic acid was determined by thin-layer X-ray fluorescence spectrometry using an X-ray fluorescence spectrometer (ZSX Primus, Rigaku, Tokyo, Japan).

Ammonium ions in the aqueous solutions of perrhenic acid were determined by a distillation method with titration after distillation—the Nessler method.

The following instrumental techniques were used to determine the concentrations of Mn, Li, Cu, Mo, Pb, Bi, Zn, W, As, Al, Mg, Ca, K, Mg, Na, Fe, Co and Ni: GFAAS (graphite furnace atomic absorption spectroscopy; Z-2000, HITACHI, Tokyo, Japan), ICP-OES (inductively coupled plasma-optical emission spectroscopy; ULTI-MA 2, HORIBA Jobin-Ivon, Kyoto, Japan), ICP-MS (inductively coupled plasma-mass spectroscopy; Nexion, PerkinElmer, Waltham, MA, USA), FAAS, (flame atomic absorption spectrometry; THERMO SOLAAR S4, Thermo Fisher Scientific, Waltham, MA, USA, equipped with a flame module—deuterium background and correction) and ICP-OES (Optima 5300V, Perkin Elmer, Waltham, MA, USA).

XRD analyses were also performed at the Łukasiewicz Research Network—Institute of Non-Ferrous Metals, Centre of Functional Materials (Gliwice, Poland). The diffraction patterns were prepared using a Rigaku MiniFlex 600 XRD diffractometer equipped with an X-ray tube with a wavelength of 1.5406 Å, a D/TeX silicon strip detector and a Soller slit with a high resolution of 2.5″ on the primary and scattered beam, calibrated using NIST SRM (Standard Reference Material) 640d Si powder.

SEM analyses were also performed at the Łukasiewicz Research Network—Institute of Non-Ferrous Metals, Centre of Advanced Materials Technologies, using a high-resolution Zeiss Gemini 1525 scanning electron microscope, equipped with a Quantax xFlash$^®$6 Bruker Nano X-ray spectrometer.

For the precipitated and purified manganese(II) perrhenate dihydrate, its solubility was measured using a gravimetric method. Figure 10 shows the used laboratory equipment. The excess amount of salt was dissolved in water with a conductivity of 0.06 μS in a thermostated reactor with a heating jacket with a working capacity of $0.5 \times 10^{-3}$ m$^3$. The saturated solution was stirred for 4 h using a magnetic stirrer at a constant temperature. The temperature was controlled using a Huber Ministat CC-K6 thermostat (accuracy $+/-0.02$ °C). After stabilization, a sample of the saturated solution was taken using a syringe equipped with a filter with a pore diameter of 0.22 μm. In order to avoid crystallization during sample collection, the filter and syringe were heated to a temperature 5 °C higher than the solution temperature. The sample was dried in a laboratory dryer at 30 °C. The solubility of manganese(II) perrhenate was calculated based on the mass difference. The experiments were carried out for four temperature values, i.e., 0 °C, 10 °C, 20 °C and 30 °C. Each measurement was repeated three times.
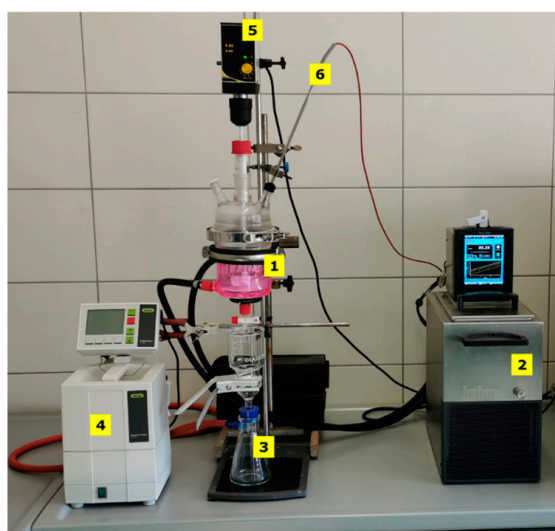


**Figure 10.** The equipment for determining the solubility of $Mn(ReO_4)_2 \cdot 2H_2O$: (1) reactor with the heating jacket; (2) heating and cooling thermostat; (3) vacuum filtration kit; (4) vacuum pump; (5) mechanical stirrer; (6) thermocouple.

## 4. Conclusions

This work showed that with the use of manganese(II) oxide, precipitated from the post-leaching solutions of the black mass from Li–ion batteries, after prior purification from Cu, Fe, and Al (pH = 5.2)—respectively, steps 1 and 2—$Mn(ReO_4)_2 \cdot 2H_2O$ can be obtained. $MnO_2$ precipitation should be carried out at a temperature not exceeding 50 °C for 30 min using a stoichiometric amount of $KMnO_4$—step 3. The precipitated $MnO_2$ should be washed using a 20% solution of sulfuric acid and then water—steps 4 and 5. Purified $MnO_2$ should be added alternately with a 30% $H_2O_2$ solution (50 cm$^3$ of hydrogen peroxide for each 10 g of manganese(II) oxide) to an aqueous solution of perrhenic acid. The reaction should be carried out at room temperature for 30 min to obtain a pH of 6–7—step 6. $Mn(ReO_4)_2 \cdot 2H_2O$ precipitated by evaporating the solution to dryness—step 7—should be purified by recrystallization from water with the addition of $H_2O_2$ a minimum of two times—step 8. The purified Mn described $(ReO_4)_2 \cdot 2H_2O$ should be dried at a temperature of 100–110 °C—step 9. Using the described procedure, $Mn(ReO_4)_2 \cdot 2H_2O$ with a purity > 99.0% and with a good precipitation efficiency can be obtained. A complete diagram of the entire developed technology is shown in Figure 11.

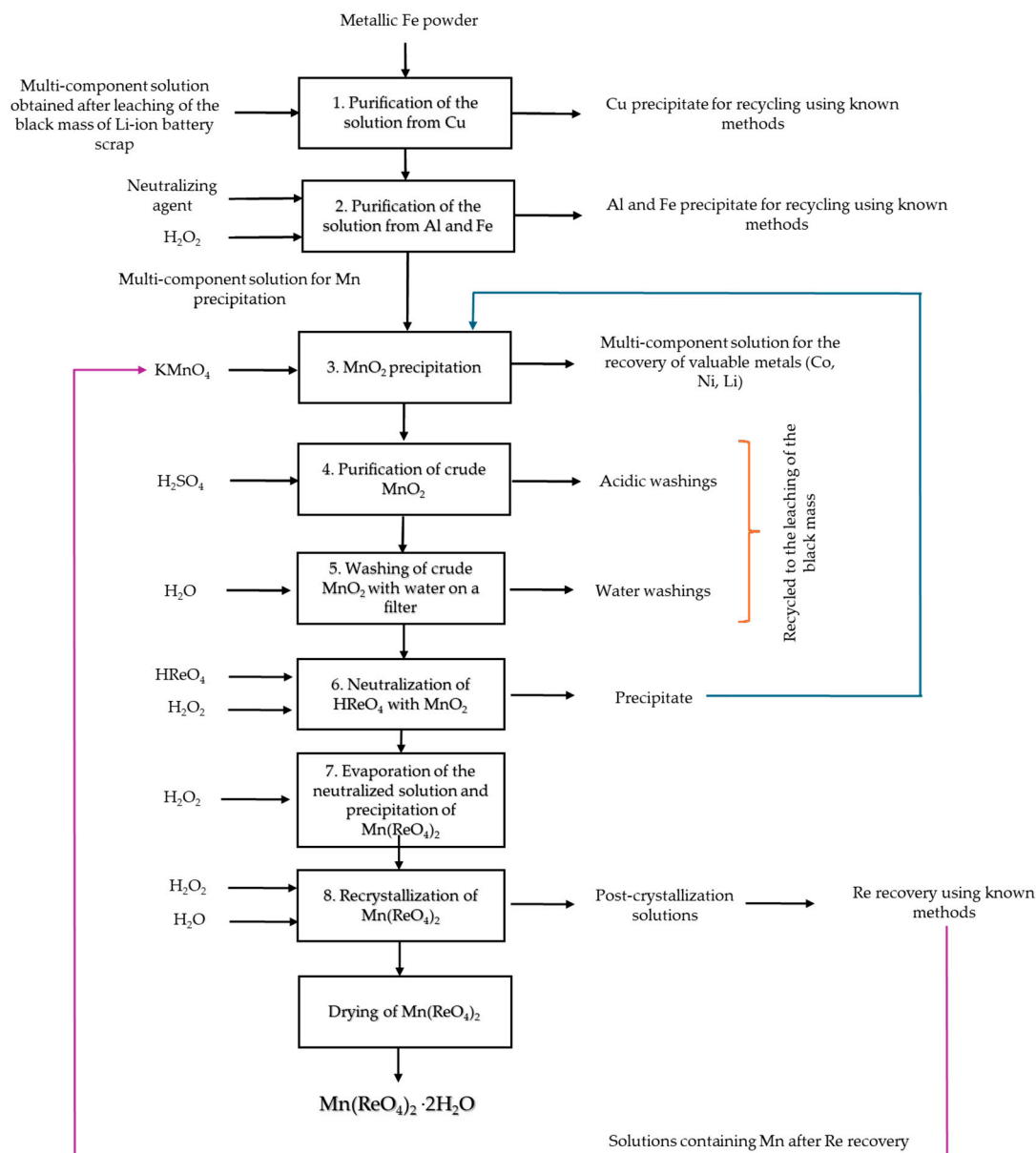**Figure 11.** Diagram of the entire $Mn(ReO_4)_2 \cdot 2H_2O$ production technology from waste.

Figure 11 shows the diagram of the developed method in its entirety, with all the recirculation possibilities and indication of the so-called auxiliary operations. The blue line shows the recycling of sludge formed after the neutralization of perrhenic acid to prevent the loss of manganese and rhenium. The purple line represents the recirculation of the solutions resulting from the purification of $Mn(ReO_4)_2 \cdot 2H_2O$ to minimize the losses of rhenium and manganese. The orange line shows the recycling of the solutions from $MnO_2$ purification to minimize the manganese loss.

## 5. Patents

Part of the results of the work presented in this publication is the material submitted for patenting in the Patent Office of the Republic of Poland on 22 March 2024 entitled Sposób otrzymywania dwuwodnego renianu(VII) manganu(II) z roztworów pochodzących z ługowania masy czarnej baterii Li–ion (English title: Method of obtaining manganese(II) perrhenate dihydrate from the post-leaching solutions of the black mass from Li–ion batteries).

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