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Precipitation of Precious Metals Concentrates from Post-Elution Solutions from Ion-Exchange Processes

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Abstract: Precious metals have long been considered as critical raw materials in many countries. There is a growing emphasis on recovering these metals from secondary sources such as automotive catalysts or WEEE (waste of electrical and electronic equipment). During the leaching process of these materials, solutions with low concentrations of precious metals are obtained, which necessitates the use of ion-exchange methods. Following sorption and elution, a post-elution solution called eluate is produced, containing precious metals and no impurities. This eluate must undergo further processing to obtain pure metals or its compounds. The objective of this study was to explore the feasibility of recovering precious metals from post-elution solutions through cementation, reduction, precipitation, or refining techniques. The analysis of the research results indicated that metallic zinc powder is the most effective cementing agent for platinum, palladium, rhodium, and gold. Metallic aluminum and copper powders can selectively cement gold and palladium, separating them from platinum and rhodium. Aqueous hydrazine hydrate solution is the best-reducing agent for precious metals, while an aqueous hydrogen peroxide solution can selectively reduce platinum and palladium, separating them from gold and rhodium.

Keywords: precious metals; critical raw materials; ion-exchange method; recovery of metals from post-elution solutions; elution

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1. Introduction

Precious metals, including platinum, palladium, rhodium, and gold, have been recognized by the European Union as critical materials for many years; therefore, the recovery of these metals is very important for the sustainable development of the European and global economy [1–5]. Nowadays, technologies for obtaining precious metals increasingly use waste as base raw materials. This is caused by decreasing resources of primary raw materials and their centralized occurrence in South Africa, Russia, and China [6–11]. Automotive catalysts or WEEE (waste of electrical and electronic equipment) are the most often used secondary raw materials to recycle and recover precious metals [11–13]. The main part of every recovery technology is leaching, which dictates the future steps of the process. In terms of precious metals, solutions of chlorides are used, especially for multi-component materials, due to the high efficiency of leaching of platinum, palladium, rhodium, and gold [14–18]. The solutions obtained after the leaching of waste materials contain low concentrations of precious metals (<100 mg/dm^3) and often high concentrations of other metals (e.g., Cu, Zn, Fe, Co, Ni, Al) [19]. In such cases, the use of ion-exchange methods may be the only economic and technologically viable solution for the selective recovery of precious metals, when compared to other techniques like precipitation or solvent extraction, which use solutions with high concentrations of precious metals (often >1 g/dm^3) [20–22].

Ion-exchange consists of three stages, between which, a resin is washed with water:

- Conditioning—performed only at the beginning of the bed operation; this process is replaced by regeneration at a later time;
- Sorption;
- Elution/regeneration.

During the elution, a resin is washed with a solution of a specific eluting agent (called eluent). Many eluents were already tested in the publications concerning the recovery of Pt, Pd, Rh, and/or Au, e.g., HCl [23–28], thiourea [26,27,29,30], thiourea in H_2SO_4 [23,24,28], thiourea in KOH [23,24], thiourea in HCl [25,28,29,31–33], thiourea in NaOH [25,28], NH_4SCN [23,24], NaOH [29], NH_4Cl [29], NaCl [26,27,29,30], HNO_3 [29], Na_2CO_3 [26,27,29,30], NaSCN [25], acetone in HCl [34], $NaClO_4$ [26,27], sodium citrate [26,27], $NaHSO_3$ [26,27], and Na_3PO_4 [26,27]. In many cases, thiourea is considered the best eluting agent, as it has a high affinity toward precious metals, thanks to sulfur, which is part of its chemical structure. Many publications focus on the sorption and elution aspects of the ion-exchange method, attempting to selectively recover precious metals from a multi-component solution. And it is indeed very important; however, almost no publications focus on processing solutions after elution, known as eluates. Obtaining a product with a high market value is the core goal of every technology, which allows researchers to determine whether it can be further implemented in the industry or not.

One possible method for recovering precious metals from eluates is cementation. Cementation, or contact replacement, is the process of replacing (displacing) metals from their salt solutions with other metals having a lower standard electrode potential. It is a process that is very often used in metallurgy to refine solutions. It occurs at a solid metallic interface (cementing agent), resulting in the reduction of ions to their zero-valence state, which can be described by the following equation:

$$\mathrm{PM^{n+}}_{(aq)} + \mathrm{CA}_{(s)} \rightarrow \mathrm{PM}_{(s)} + \mathrm{CA^{n+}}_{(aq)}$$

where PM refers to precious metal and CA refers to the cementing agent.

In precious metals chemistry, metals like zinc, aluminum, or iron are often used as cementing agents [35–37].

Other methods that are often used to process post-elution solutions are reduction (using hydrazine hydrate, sodium borohydride, ascorbic acid, oxalic acid, and formic acid as reducing agents [38–40]), and precipitation (using NaOH, NH_3, and NH_4Cl as precipitating agents [41,42]). Refining processes often combine different methods (extraction, reduction, cementation, precipitation) to obtain high-purity compounds of specific precious metals.

Therefore, the aim of this research is to determine the possibility of recovery and/or separation of platinum, palladium, rhodium, and gold, contained in the post-elution solutions by precipitating them in the form of concentrates and/or compounds, which would help assess the possibility of implementation of this process in the industry. An attempt was also made to check if a refining process applies to this type of solution. A solution containing thiourea in hydrochloric acid, obtained during the elution of precious metals from three different commercial resins, was used during the experiments. To our knowledge, such extensive experiments on processing post-elution solutions containing precious metals have not been researched and published to date.

2. Materials and Methods

2.1. Materials

Puromet MTS9200 and Puromet MTS9850 were provided by Purolite (King of Prussia, PA, USA), and Lewatit MonoPlus MP 600 was provided by LANXESS Energizing Chemistry (Cologne, Germany). The resins after sorption tests with different concentrations of platinum, palladium, rhodium, and gold, were used. The characteristics of the resins are shown in Table 1.

Table 1. Characteristic of the ion-exchange resins.

Name	Type	Functional Group	Ionic Form	Matrix	Company
Puromet MTS9200	Weak base	Isothiouronium	H+	Polystyrenic cross-linked with divinylbenzene	Purolite
Puromet MTS9850	Weak base	Polyamine	FB	Polyacrylic cross-linked with divinylbenzene	Purolite
Lewatit MonoPlus MP 600	Strong base	Quaternary ammonium type 2	Cl-	Polystyrenic	LANXESS

Hydrochloric acid (35%–38%, AR, Avantor, Gliwice, Poland) and thiourea (CP, Avantor, Gliwice, Poland) were used for the elution experiments. The following materials were used for the cementation experiments: metallic zinc powder (industrial—ZGH "Bolesław", Bukowno, Poland; and commercial—CP, Chempur, Piekary Śląskie, Poland), metallic aluminum powder (CP, Avantor, Gliwice, Poland), metallic magnesium powder (99.9%, Avantor, Gliwice, Poland), metallic cobalt powder (99%, Avantor, Gliwice, Poland), metallic nickel powder (99.4%, Avantor, Gliwice, Poland), and metallic copper powder (CP, Avantor, Gliwice, Poland). In the reduction and precipitation tests, the following reagents were used: hydrazine hydrate (40%, CP, Chempur, Piekary Śląskie, Poland), formic acid (80%, CP, Chempur, Piekary Śląskie, Poland), ammonia (25%, AR, Avantor, Gliwice, Poland), oxalic acid (dihydrate, 98%, Avantor, Gliwice, Poland), and hydrogen peroxide (30%, AR, Chempur, Piekary Silesia, Poland). In the precious metal-refining experiments, the following materials were used: for gold extraction—Carbitol (diethylene glycol dibutyl ether, 99%, Dow, Midland, MI, USA); for palladium extraction—dioctyl sulfide (97%, Thermo Fisher Scientific, Waltham, MA, USA); for palladium re-extraction—aqueous ammonia solution; for the palladium precipitation—hydrochloric acid; for the platinum precipitation—ammonium chloride (99.5%; Honeywell Fluka, Charlotte, NC, USA) and aqueous ammonia solution; and toluene was used for diluting extractants (AR, Chempur, Piekary Śląskie, Poland). Solid sodium hydroxide (AR, Chempur, Piekary Śląskie, Poland) was used to adjust the pH. Demineralized water with an electrolytic conductivity of <2 µS/cm was used in the experiments.

The names "metallic powder" and "dust" were used interchangeably.

2.2. Methods

The scheme of the research process is presented in Figure 1.

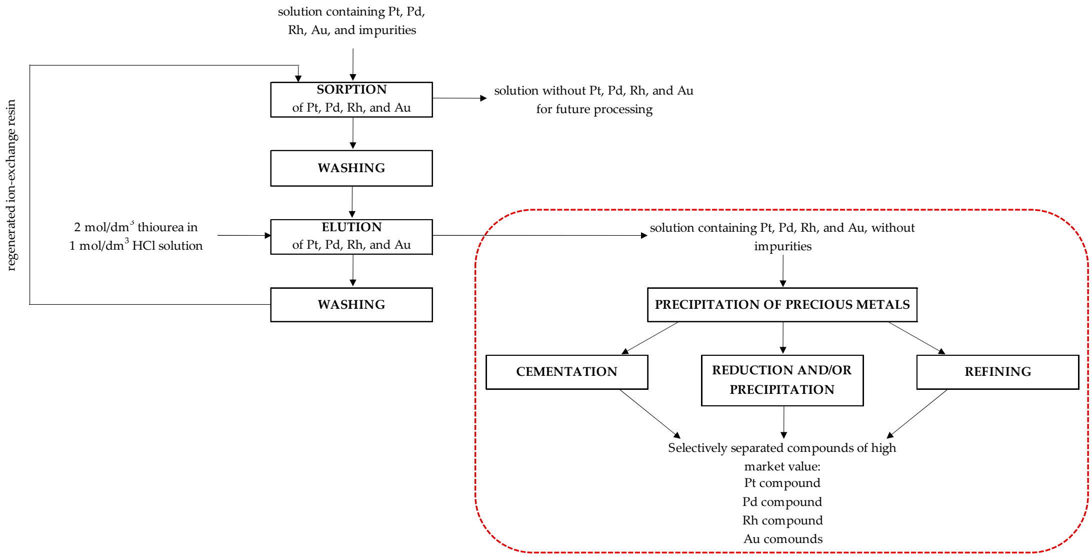


Figure 1. Scheme of the research plan.

The publication covers the steps in red brackets.

2.2.1. Preparation of the Eluate

A mixture of 2 mol/dm^3 of thiourea in 1 mol/dm^3 of HCl was used for the elution process. To obtain a solution with a significant concentration of precious metals, post-sorption resins from the previous works were used [43,44]. The prepared eluent was mixed with the resins using a ratio of V_r:V_e = 1:10 (V_r—resin volume, V_e—eluent volume) for 1 h at room temperature. Subsequently, the solution was filtered. This process was repeated for three ion-exchange resins (Puromet MTS9200, Puromet MTS9850, and Lewatit MonoPlus MP 600) and the obtained solutions were combined. A total volume of 13 dm^3 of post-elution solution consisting of 2 mol/dm^3 of thiourea in 1 mol/dm^3 of HCl was obtained, with the composition shown in Table 2. The pH of the solution was 0.16.

Table 2. Composition of the eluate.

Concentration [mg/dm^3]			
Pt	Pd	Rh	Au
105.0	115.0	4.4	8.0

2.2.2. Cementation Experiments

Tests were conducted to determine the possibility of cementing precious metals from the post-elution solution using various cementing agents. Metallic zinc powder (industrial and commercial), metallic magnesium powder, metallic aluminum powder, metallic copper powder, metallic nickel powder, and metallic cobalt powder were selected for testing. For this purpose, a measured amount of eluate (25 cm^3) was mixed with a specific amount of cementing agent (0.10 g; 0.25 g; 0.50 g; 0.75 g; 1.00 g; 1.50 g) for 1 h, at room temperature. After the given time, the samples were filtered, the pH values of the solutions were measured, and then they were analyzed for the contents of Pt, Pd, Rh, and Au. The solid precipitates were weighed while wet and then again after drying at 100 °C.

2.2.3. Reduction and Precipitation Experiments

Subsequent experiments were performed to determine the possibility of reducing or precipitating precious metals from the post-elution solution. A 40% aqueous hydrazine hydrate solution, 80% aqueous formic acid solution, 25% aqueous ammonia solution, oxalic acid, and 30% aqueous hydrogen peroxide solution were used in the tests. A measured amount of eluate (25 cm^3) was mixed with a specific amount of reducing agent (when using solutions—2.5 cm^3; 3.5 cm^3; 5.0 cm^3; 7.5 cm^3; 10.0 cm^3; 15.0 cm^3; when using solid materials—0.5 g; 1.5 g; 3.5 g; 5.0 g; 7.5 g; 10.0 g) for 1 h, at room temperature. After the given time, the samples were filtered, the pHs of the solutions were measured, and then they were analyzed for the contents of Pt, Pd, Rh, and Au. The solid precipitates were weighed while wet and then again after drying at 100 °C. While using formic acid and oxalic acid solutions, the pH was corrected during the process with solid NaOH.

2.2.4. Refining Experiments

Using the post-elution solution, the precious metal refining test was carried out according to the methodology developed by the Łukasiewicz Research Network—Institute of Non-Ferrous Metals, Centre of Hydroelectrometallurgy. The process consisted of the following steps:

- Concentration of the solution—the eluate was concentrated tenfold to increase the concentration of precious metals. A total of 1000 cm^3 of the concentrated solution was obtained, from which a sample of 20 cm^3 was taken, which was then analyzed for the contents of Pt, Pd, Rh, and Au;
- Au extraction—980 cm^3 of the solution was mixed with 500 cm^3 of a 50% Carbitol solution in toluene (*v*/*v*) at a temperature of about 70 °C for 1 h. After the extraction

process, the phases were separated. The volumes of the organic phase (485 cm^3) and the aqueous phase (970 cm^3) were measured. A sample of 20 cm^3 was taken from the aqueous phase, which was then analyzed for the contents of Pt, Pd, Rh, and Au;

- Pd extraction—the aqueous phase from the previous step (950 cm^3) was mixed with 500 cm^3 of 50% di-n-octyl sulfide solution in toluene (v/v) at room temperature for 1 h. After the palladium extraction process, the phases were separated. The volumes of the organic phase (500 cm^3) and the aqueous phase (945 cm^3) were measured. A sample of 20 cm^3 was taken from the aqueous phase, which was then analyzed for the contents of Pt, Pd, Rh, and Au. The organic phase was then used in the Pd re-extraction process;
- Pd re-extraction—the organic phase from the Pd extraction step (500 cm^3) was mixed with a 25% aqueous ammonia solution (500 cm^3) at room temperature for 1 h. After the process, the phases were separated. The volumes of the organic phase (485 cm^3) and aqueous phase (485 cm^3) were measured. A sample of 25 cm^3 was taken from the aqueous phase, which was then analyzed for the contents of Pt, Pd, Rh, and Au;
- Pd precipitation—the aqueous phase from the Pd re-extraction step was used to precipitate palladium. Concentrated hydrochloric acid (150 cm^3) was added at room temperature to the stirred solution in portions until a slightly brown precipitate was formed. The next day, the solution was filtered, its volume was measured (495 cm^3), and a sample of 25 cm^3 was taken, which was then analyzed for the contents of Pt, Pd, Rh, and Au. The precipitate was weighed while wet (0.4618 g) and then again after drying at 100 °C (0.0820 g);
- Precipitation Pt—the aqueous phase from the Pd extraction step was used for platinum precipitation. A concentrated aqueous solution of ammonium chloride (300 g/dm^3, 200 cm^3) was added at room temperature to the stirred solution in portions. During the process, significant amounts of yellow precipitate were formed, which prevented filtration. We decided to perform the following two tests:
    - ○ Pt precipitation using an aqueous solution of NH_3—for this purpose, 50 cm^3 of a 25% aqueous ammonia solution was added to 100 cm^3 of the heated solution. A brown precipitate formed. The next day, the solution was filtered, its volume was measured (160 cm^3), from which a sample of 20 cm^3 was taken and the contents of Pt, Pd, Rh, and Au were analyzed. The precipitate was weighed while wet (0.7038 g) and then again after drying at 100 °C (0.0948 g);
    - ○ Pt precipitation using an NH_4Cl solution—for this purpose, 200 cm^3 of an aqueous ammonium chloride solution (300 g/dm^3) was added to 100 cm^3 of the heated solution. The next day, the solution was filtered, its volume was measured (280 cm^3), from which a sample of 20 cm^3 was taken and the contents of Pt, Pd, Rh, and Au were analyzed. The precipitate was weighed while wet (0.5039 g) and then again after drying at 100 °C (0.1048 g).

2.2.5. Calculations

The efficiency of cementation, reduction, and refining was calculated according to the following formula:

$$U = \frac{V_i \cdot C_i - V_f \cdot C_f}{V_i \cdot C_i} \cdot 100\% \tag{1}$$

C_i—initial concentration of the metal in the solution [mg/dm^3], C_f—final concentration of the metal in the solution [mg/dm^3], V_i—initial volume of the solution [dm^3], V_f—final volume of the solution [dm^3].

2.2.6. Analytical Methods

The analyses were carried out by the Łukasiewicz Research Network–Institute of Non–Ferrous Metals, Centre of Analytical Chemistry, and Centre of Functional Materials (Gliwice, Poland). The concentrations of platinum, palladium, rhodium, and gold in the collected solution samples were determined by inductively coupled plasma mass spectrometry (ICP-

MS; NexION 300D, PerkinElmer, Waltham, MA, USA). To analyze the composition of the precipitates, a MiniFlex 600 diffractometer (Rigaku, Tokyo, Japan) equipped with a CuKα copper lamp (λ = 1.5406 Å) and a ZSX Primus WDXRF (Rigaku, Tokyo, Japan) were used. The average error of the method was around 5%, depending on the dilution of the samples and the concentration of precious metals.

3. Results and Discussion

3.1. Cementation Experiments

Metallic zinc powder is one of the most common cementing agents for precious metals [36,45,46]. Most of the time, a chemically pure, commercial form of it is used; therefore, the possibility of using an industrial one was researched. Commercial zinc powder is a pure substance without any impurities or unwanted metals. On the other hand, industrial zinc powder, typically a by-product of industrial processes of variable composition, may contain impurities, especially of metals processed in that specific industrial plant. This research was conducted to determine if industrial plants could use their own metallic zinc powder to cement precious metals instead of having to use commercially manufactured zinc powder.

The results of the experiments of the cementation with zinc are shown in Figure 2.

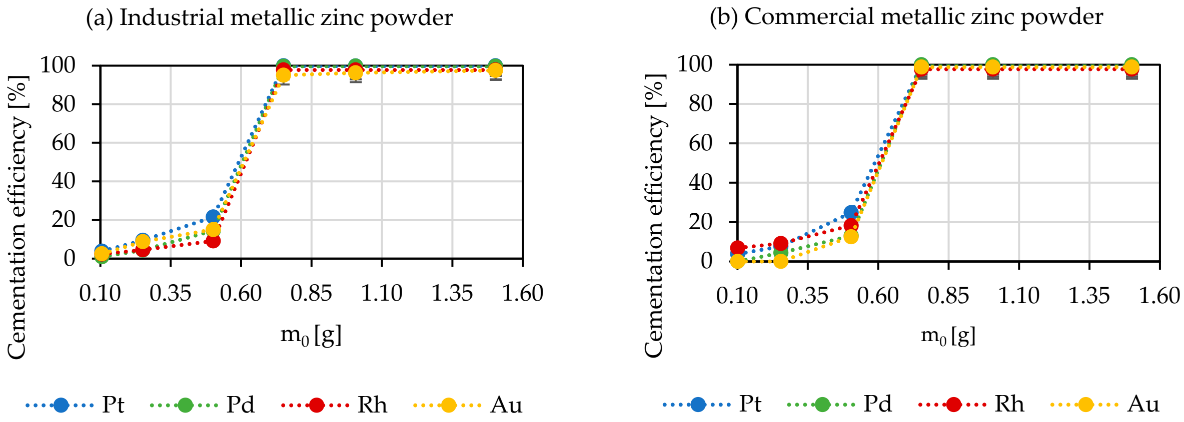


Figure 2. Dependence of the cementation efficiency on the initial amount of added metallic zinc powder (m_0).

Analysis of the data in Figure 2 indicates that the metallic zinc powder can be used for the cementation of platinum, palladium, rhodium, and gold from eluates, as the cementation efficiency of these metals reached results > 99% when adding 0.75 g of Zn. It is important to note that when using cementation, the metal dust first reacts with the free acid and only then with the precious metals. The process becomes even more complicated when the forms in which precious metals occur in solutions are considered. Taking into account only the dominant complexes in the chloride solution, the cementation process can be represented using the following equations:

$$[PtCl_6]^{2-} + 3Zn + 2H^+ \rightarrow Pt + 3Zn^{2+} + 6Cl^- + H_2$$

$$[PdCl_4]^{2-} + 2Zn + 2H^+ \rightarrow Pd + 2Zn^{2+} + 4Cl^- + H_2$$

$$2[RhCl_6]^{3-} + 6Zn + 6H^+ \rightarrow 2Rh + 6Zn^{2+} + 12Cl^- + 3H_2$$

$$2[AuCl_4]^- + 4Zn + 2H^+ \rightarrow 2Au + 4Zn^{2+} + 8Cl^- + H_2$$

However, such a situation would only occur if the eluate contained only dominant forms; in addition, there may also be less popular complexes in chloride solutions, such as $[PtCl_4]^{2-}$, $[Pt(OH)Cl_5]^{2-}$, $[Pt(OH)_2Cl_4]^{2-}$, $[PdCl_6]^{2-}$, $[Pd(H_2O)Cl_3]^-$, $[Rh(H_2O)Cl_5]^{2-}$, $[Rh(H_2O)_2Cl_4]^-$, $[RhCl_6]^{2-}$, $[AuCl_2]^-$, $[Au(OH)Cl_3]^-$, or $[Au(OH)_2Cl_2]^-$.

More importantly, precious metals can also form complexes with thiourea, which due to the high affinity of sulfur to platinum, palladium, rhodium, and gold, can be more dominant and stable complexes than chloride ones. Possible chloride complexes of platinum with thiourea are presented in Figure 3.

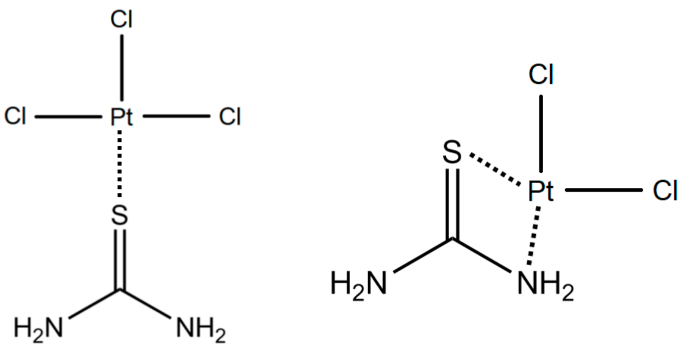


Figure 3. Examples of platinum–thiourea complexes.

This means that it is difficult to calculate how much excess metallic zinc powder was used in a given experiment. However, a good indicator of whether cementation has taken place with full efficiency is the measurement of the pH of the solution on an ongoing basis (Table 2). When using industrial Zn, at the beginning of the process, the pH is within the range of 0.16–0.53, but it increases rapidly to a pH of ~5.3 with the addition of approximately 0.75 g of Zn, which would indicate a complete conversion of free acid. This value may be the limit point for carrying out the cementation process using industrial metallic zinc powder, as an increase in the amount of added Zn is not required. An XRD pattern analysis of the selected precipitate after cementation was performed (with the addition of 0.75 g of Zn).

The data shown in the diffractogram in Figure 4 indicate that the sample contains precious metals such as Pt, Pd, and Rh in an unbounded form. In addition, peaks for Zn are also visible. When using Au, its concentration was probably too low for the signal to be visible in the diffractogram. The shape of the diffractogram and intensities imply that the sample was mostly filled with amorphous material, which makes XRD analysis difficult.

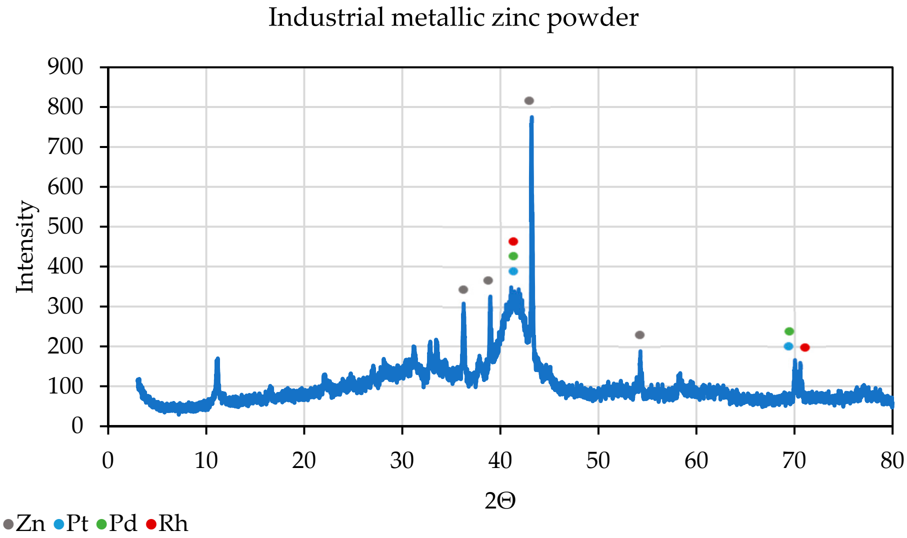
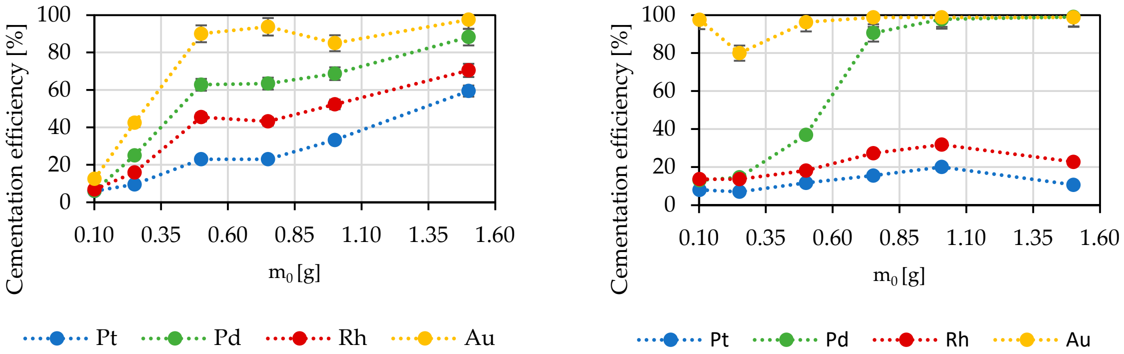
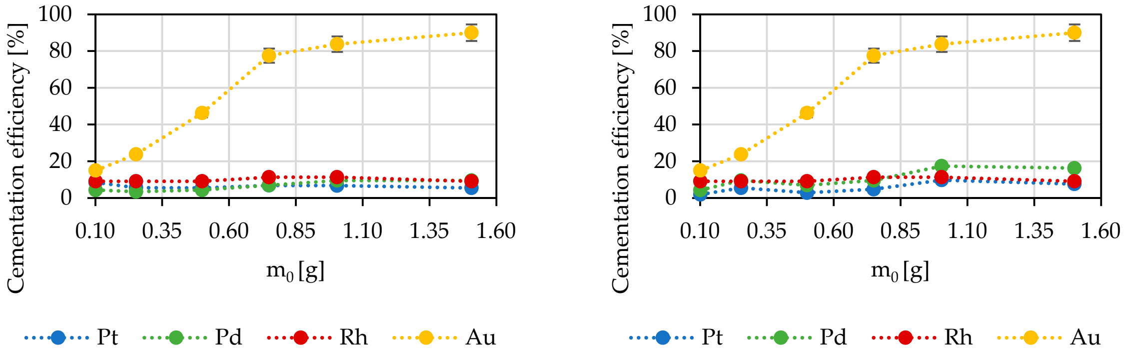


Figure 4. XRD pattern for the sample after cementation with the addition of 0.75 g of metallic Zn powder.

Figure 5 shows the results of the influence of the amount of added metallic magnesium, aluminum, nickel, cobalt, and copper powder on the cementation process.


(a) Metallic magnesium powder (b) Metallic aluminium powder


(c) Metallic nickel powder (d) Metallic cobalt powder

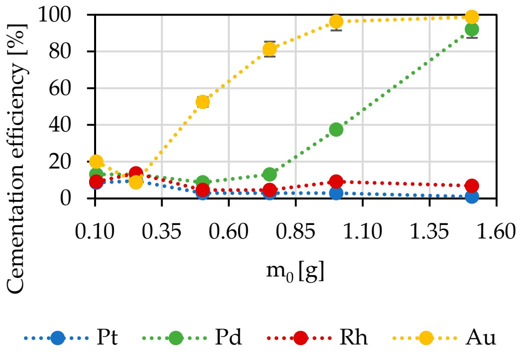

(e) Metallic copper powder

Figure 5. Dependence of the cementation efficiency on the initial amount of added metallic magnesium, aluminum, nickel, cobalt, and copper powder (m_0).

The pH of the solutions after the cementing process and the weights of the precipitates are presented in Table 3.

Table 3. Results of the research on cementing the precious metals from the post-elution solution.

Industrial Metallic Zn Powder				
Amount of the Added Cementing Agent [g]	**Final pH of the Solution**	**Wet Mass of the Precipitate [g]**	**Dry Mass of the Precipitate [g]**	**Semi-Quantitative Analysis of the Precipitate after the Addition of 0.75 g of Dust [%]**
0.10	0.24	1.9032	0.3002	S–30.50, Cl–30.10, Zn–25.50, Pb–9.11, Pt–2.75, Pd–1.52, Cu–0.35, Fe–0.10, Ni–0.05
0.25	0.31	1.9189	0.3139	
0.50	0.53	1.9448	0.3578	
0.75	5.33	2.1503	0.2863	
1.00	5.54	2.2143	0.4822	
1.50	5.65	2.9403	0.9789	

Table 3. *Cont.*

Commercial metallic Zn powder				
Amount of the added cementing agent [g]	**Final pH of the solution**	**Wet mass of the precipitate [g]**	**Dry mass of the precipitate [g]**	**Semi-quantitative analysis of the precipitate after the addition of 0.75 g of dust [%]**
0.10	0.29	1.6627	0.1542	Zn–49.70, Pb–24.50, Pt–13.90, Pd–10.10, Au–0.82, Cu–0.47, Rh–0.37, S–0.22
0.25	0.38	1.7483	0.1201	
0.50	0.64	1.5040	0.2016	
0.75	5.45	2.1197	0.1836	
1.00	5.54	2.7020	0.4424	
1.50	5.51	3.2429	0.9447	
Metallic Mg powder				
Amount of the added cementing agent [g]	**Final pH of the solution**	**Wet mass of the precipitate [g]**	**Dry mass of the precipitate [g]**	**Semi-quantitative analysis of the precipitate after the addition of 1.50 g of dust [%]**
0.10	0.46	1.9622	0.2210	O–53.90, Mg–40.60, C–1.95, Cl–1.90, S–1.43, Al–0.04, Pt–0.04, Pd–0.03, Si–0.02, Fe–0.02
0.25	1.01	1.9519	0.2978	
0.50	9.50	3.2159	0.9205	
0.75	9.36	4.1450	1.5106	
1.00	9.33	5.4689	2.2172	
1.50	9.35	7.9101	3.5238	
Metallic Al powder				
Amount of the added cementing agent [g]	**Final pH of the solution**	**Wet mass of the precipitate [g]**	**Dry mass of the precipitate [g]**	**Semi-quantitative analysis of the precipitate after the addition of 1.00 g of dust [%]**
0.10	0.42	2.2803	0.2205	Al–88.10, O–7.47, C–1.61, Cl–1.17, S–0.92, Fe–0.26, Si–0.18, Pd–0.09, Zn–0.03, Pt–0.02, Au–0.02, Cu–0.02, Ga–0.01, Ca–0.01
0.25	0.49	2.7741	0.2903	
0.50	0.88	3.2110	0.4327	
0.75	3.31	4.4653	0.5936	
1.00	3.35	5.0249	0.9938	
1.50	3.42	7.3790	1.3342	
Metallic Ni powder				
Amount of the added cementing agent [g]	**Final pH of the solution**	**Wet mass of the precipitate [g]**	**Dry mass of the precipitate [g]**	**Semi-quantitative analysis of the precipitate after the addition of 1.50 g of dust [%]**
0.10	0.39	2.3738	0.2691	Ni–83.3, O–11.2, C–3.25, Cl–1.30, S–0.88, Fe–0.06, Co–0.06
0.25	0.39	2.4048	0.4057	
0.50	0.33	2.5790	0.6359	
0.75	0.34	3.1557	0.8771	
1.00	0.28	3.3097	1.0823	
1.50	0.31	3.8497	1.6121	
Metallic Co powder				
Amount of the added cementing agent [g]	**Final pH of the solution**	**Wet mass of the precipitate [g]**	**Dry mass of the precipitate [g]**	**Semi-quantitative analysis of the precipitate after the addition of 1.50 g of dust [%]**
0.10	0.29	2.2294	0.2560	Co–75.10, O–17.8, F–3.37, C–1.77, S–0.96, Cl–0.44, Ni–0.37, Al–0.06, Pd–0.03, W–0.03, Cu–0.03, Fe–0.02, Zn–0.01
0.25	0.31	2.6720	0.4006	
0.50	0.29	3.1806	0.6100	
0.75	0.29	3.6182	0.8726	
1.00	0.37	4.0892	1.1347	
1.50	0.40	4.9818	1.6192	
Metallic Cu powder				
Amount of the added cementing agent [g]	**Final pH of the solution**	**Wet mass of the precipitate [g]**	**Dry mass of the precipitate [g]**	**Semi-quantitative analysis of the precipitate after the addition of 1.50 g of dust [%]**
0.10	0.30	1.8092	0.2866	Cu–45.70, S–32.40, Cl–13.10, C–6.80, O–1.80, Pd–0.11, P–0.03, Al–0.03, Co–0.02, Rh–0.01, Ni–0.01, Fe–0.01, Cr–0.01
0.25	0.33	1.8039	0.2937	
0.50	0.37	3.3004	1.0594	
0.75	0.47	5.0787	2.2757	
1.00	0.62	6.3091	3.2792	
1.50	0.70	7.2591	3.4911	

Figure 5a shows the changes in the cementation efficiencies of precious metals depending on the amount of added magnesium dust. An increasing trend is visible for each precious metal tested. However, it can be concluded that the highest cementing efficiencies were obtained for gold and the lowest for platinum. When adding zinc dust, the pH of the solution also changed during the process. The pH reached a value of approximately 9.50 after adding 0.5 g of Mg, which correlates with a visible increase in the efficiency of gold and palladium cementation. Although magnesium has a lower standard electrode potential (Mg | Mg^{2+} −2.37 V) compared to zinc (Zn | Zn^{2+} −0.76 V), it is less effective as a reductant for precipitating precious metals from the acidic thiourea solution. This could be attributed to the elevated final pH of the solution, causing magnesium to precipitate in various complex forms, thereby diminishing its ability to cement precious metals. This can be observed by the increased amount of non-precious metal precipitate formed at higher pH levels (>9.0) after the process, indicating the presence of additional complexes. The precipitate obtained after cementation contains a significant amount of oxygen, suggesting the formation of hydroxides or oxides.

When the metallic aluminum powder is used as the cementing agent (Figure 5b), there is a visible tendency to selectively precipitate gold and palladium in the form of a concentrate. Additionally, in this case, there was a shift in the pH solution to a level of approximately 3.31 (with the addition of 0.75 g of Al). This is the point at which the efficiency of gold and palladium cementation is practically the highest and the addition of more aluminum dust is not required. This metal can be used to selectively separate Au and Pd in the form of their combined concentrate from Pt and Rh by leaving them in the solution. Similarly, when using magnesium, at a pH > 3 additional amounts of precipitate were formed. However, this did not appear to hinder the cementation of Pd and Au. This could be attributed to the lower pH of the solution. The presence of unneutralized H^+ ions in the solution was likely crucial for the cementation reaction of various complexes of precious metals, as can be seen in the cementation equations with Zn.

Analyzing the data in Figure 5c, it can be concluded that nickel dust does not cement precious metals such as platinum, palladium, and rhodium. However, this metal can be used to recover gold from eluates. An additional important aspect of the process is the magnetic nature of the metallic nickel powder. The concentrate can be easily separated from the solution by using a magnet—this allows us to omit the traditional filtration processes.

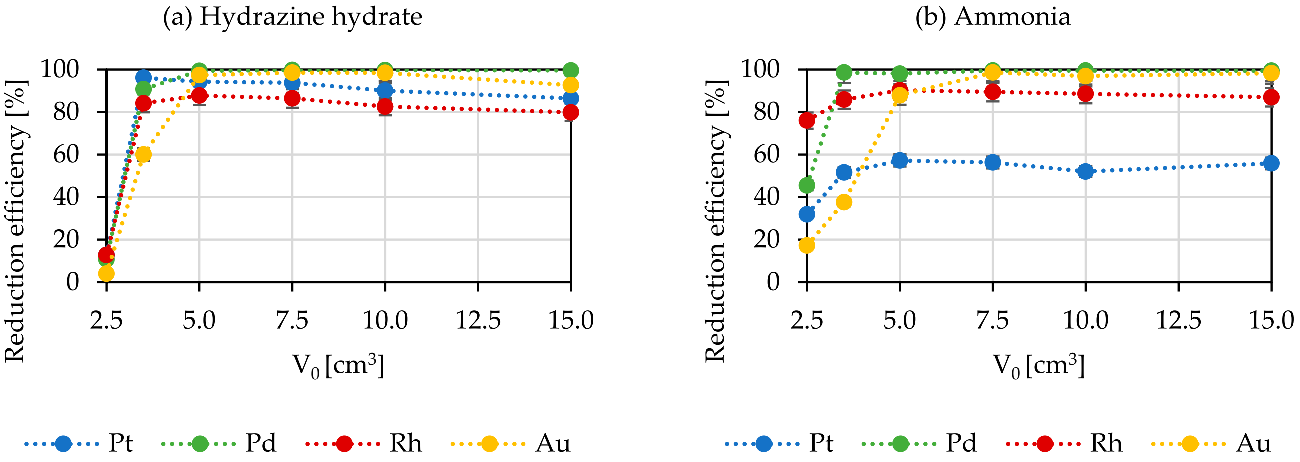
The graph for cobalt (Figure 5d) looks very similar to the graph for nickel. This means that the metallic cobalt powder can also be used to selectively cement gold and, thus, separate it from the rest of the precious metals.

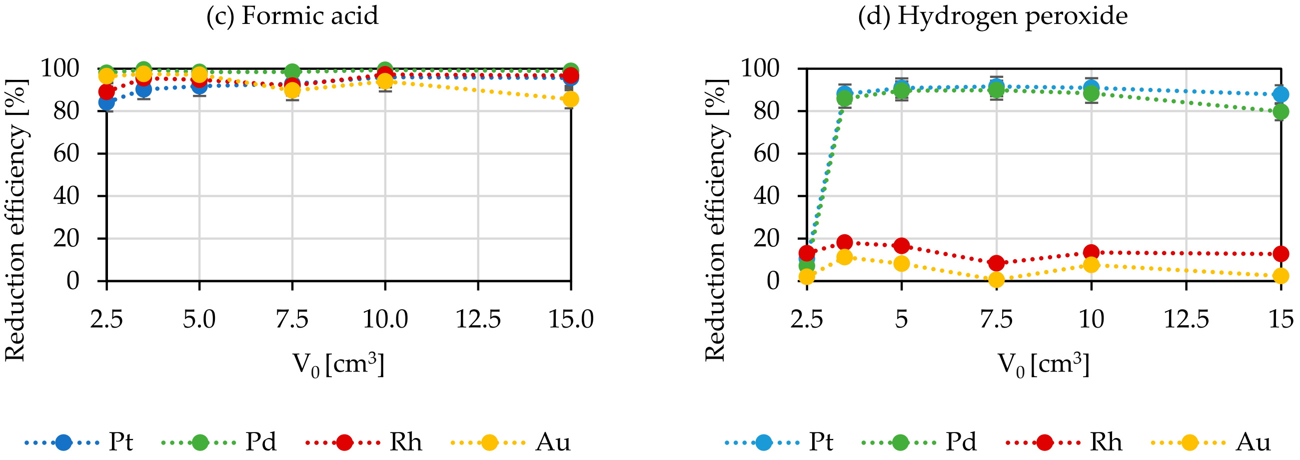
Both cobalt and nickel have higher standard electrode potentials compared to other metals used as cementing agents (Ni | Ni^{2+} −0.257 V and Co | Co^{2+} −0.28 V), resulting in the lowest efficiencies of cementing platinum, palladium, and rhodium. Despite this, the pH of the solution remained unchanged (<0.4 for both nickel and cobalt), indicating that free acid was not completely neutralized. It is conceivable that these metals could precipitate precious metals at higher pH levels. However, the quantity required to neutralize the solution economically would not be feasible for industrial-scale processes.

Copper is often used in metallurgy, although it is more often recovered from solutions through cementation than being actively used in them. However, for example, it can be used to recover silver from acidic solutions. Figure 5e also shows the possibilities of using copper dust for cementing precious metals. The data indicate that the addition of excess dust (minimum 1.5 g of Cu per sample of 25 cm^3) can be used to selectively separate Au and Pd from Pt and Rh by separating them in the form of a concentrate. When using copper, the formation of additional precipitate can be seen. Copper has a strong affinity to sulfur found in thiourea, causing it to precipitate from the solution as thiourea complexes. These complexes were unable to efficiently reduce precious metals to their solid state, resulting in low cementation efficiencies. At higher concentrations of copper, unbound copper likely began to precipitate precious metals, leading to a gradual change in the pH from 0.3 to 0.7.

3.2. Reduction and Precipitation Experiments

The results of testing the influence of the added amount of reducing or precipitating agents on the process are shown in Figure 6.


(a) Hydrazine hydrate (b) Ammonia


(c) Formic acid (d) Hydrogen peroxide

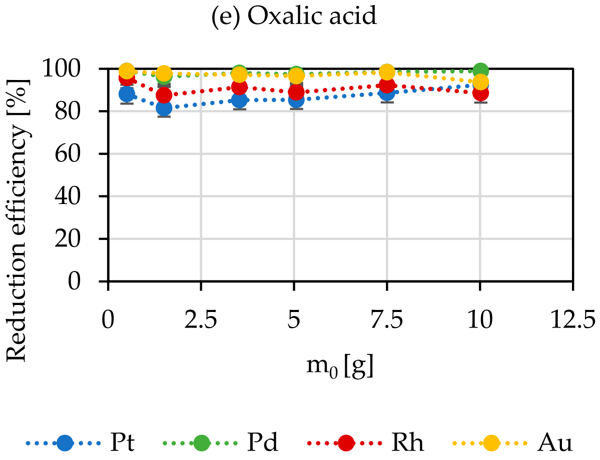

(e) Oxalic acid

Figure 6. Dependence of the reduction efficiency on the initial amount of added aqueous hydrazine hydrate solution, aqueous ammonia solution, aqueous formic acid solution, aqueous hydrogen peroxide solution (V_0), and oxalic acid (m_0).

The pH of the solutions after the reduction process and the weights of the precipitates are presented in Table 4.

Table 4. Results of the research on reducing and precipitating the precious metals from the post-elution solution.

Aqueous Hydrazine Hydrate Solution				
Amount of the Added Reducing Agent [cm^3]	**Final pH of the Solution**	**Wet Mass of the Precipitate [g]**	**Dry Mass of the Precipitate [g]**	**Semi-Quantitative Analysis of the Precipitate after the Addition of 5.0 cm^3 of the Agent [%]**
2.5	0.99	1.8478	0.3931	S–57.60, Cl–38.60, Pt–2.96, Pd–0.49, Au–0.21, Pb–0.06, Cu–0.02, Zn–0.02
3.5	7.00	2.1046	0.5745	
5.0	8.05	2.2642	0.6226	
7.5	8.67	2.0990	0.2689	
10.0	8.57	2.1470	0.2155	
15.0	8.95	2.0778	0.1958	
Aqueous ammonia solution				
Amount of the added precipitating agent [cm^3]	**Final pH of the solution**	**Wet mass of the precipitate [g]**	**Dry mass of the precipitate [g]**	**Semi-quantitative analysis of the precipitate after the addition of 7.5 cm^3 of the agent [%]**
2.5	8.56	2.1341	0.4759	S–68.60, Cl–25.30, Pt–2.91, Pd–1.48, Au–0.58, Fe–0.48, Cu–0.13, Zn–0.12, Cr–0.10, Mn–0.09, Si–0.06, Pb–0.05, Ni–0.05, Rh–0.05
3.5	9.08	2.0681	0.3633	
5.0	9.35	2.2240	0.3018	
7.5	9.65	2.1142	0.3532	
10.0	9.74	2.0710	0.3805	
15.0	9.98	2.1483	0.3071	
Aqueous formic acid solution				
Amount of the added reducing agent [cm^3]	**Final pH of the solution**	**Wet mass of the precipitate [g]**	**Dry mass of the precipitate [g]**	**Semi-quantitative analysis of the precipitate after the addition of 2.5 cm^3 of the agent [%]**
2.5	11.73	2.2678	0.4397	S–77.60, Cl–13.20, Pt–5.28, Pd–1.60, Na–0.77, Au–0.56, Cu–0.56, Fe–0.21, Zn–0.14, Rh–0.07
3.5	11.27	1.7669	0.3149	
5.0	11.89	1.6819	0.4201	
7.5	11.96	5.4388	2.9569	
10.0	11.77	7.5992	4.2114	
15.0	11.90	14.5464	10.2673	
Aqueous hydrogen peroxide solution				
Amount of the added reducing agent [cm^3]	**Final pH of the solution**	**Wet mass of the precipitate [g]**	**Dry mass of the precipitate [g]**	**Semi-quantitative analysis of the precipitate after the addition of 3.5 cm^3 of the agent [%]**
2.5	0.60	2.0913	0.6429	S–99.9, Al–0.13, Ca–0.02, Pt–0.05, Pd–0.03
3.5	0.57	1.8771	0.6699	
5.0	0.64	2.3900	0.9439	
7.5	0.71	3.0994	1.1964	
10.0	0.54	2.9022	1.1962	
15.0	0.48	2.9403	1.0526	
Oxalic acid				
Amount of the added reducing agent [g]	**Final pH of the solution**	**Wet mass of the precipitate [g]**	**Dry mass of the precipitate [g]**	**Semi-quantitative analysis of the precipitate after the addition of 0.5 g of the agent [%]**
0.5	11.20	1.6645	0.1794	S–81.60, Pt–7.90, Cl–3.98, Pd–2.51, Na–2.18, Au–0.79, Cu–0.50, Si–0.18, Zn–0.12, Rh–0.11, Ag–0.10
1.5	11.78	3.7638	1.2657	
3.5	11.68	8.1747	3.6805	
5.0	12.11	13.4003	5.8148	
7.5	11.71	17.6464	8.5139	
10.0	12.22	23.5409	12.0732	

Based on the data in Figure 6a, it can be concluded that an aqueous hydrazine hydrate solution can be used to reduce precious metals from eluates. Hydrazine hydrate can reduce precious metals (PM) according to Equation [47]:

$$4PM^{m+} + mN_2H_4 \rightarrow 4PM_{(s)} + mN_2 + 4mH^+$$

Practically, the addition of 3.5 cm^3 to 25 cm^3 of eluate allowed reducing metals with a high efficiency (>90% for Pt, >99% for Pd, >90 for Au, and >80% for Rh). At this point, a significant increase in the pH was also visible (from approximately 0.99 to 7.00). This means that the pH could be an indicator to assess at what point the reduction process occurs with optimal efficiency; above which, adding excess hydrazine hydrate is not advisable. This would be in accordance with hydrazine hydrate-reducing precious metals in alkaline conditions. For example, the equation for platinum would look like [47], as follows:

$$2Pt^{4+} + 5N_2H_4 + 8OH^- \rightarrow 2Pt + 3N_2 + 4NH_3 + 8H_2O$$

According to the equation, hydrazine hydrate can reduce precious metals in the presence of OH^- ions with better efficiency and, therefore, at a higher pH of the solution, which happened in this case.

XRD pattern analysis of the precipitate after adding 5 cm^3 of aqueous hydrazine hydrate solution was also performed and is shown in Figure 7.

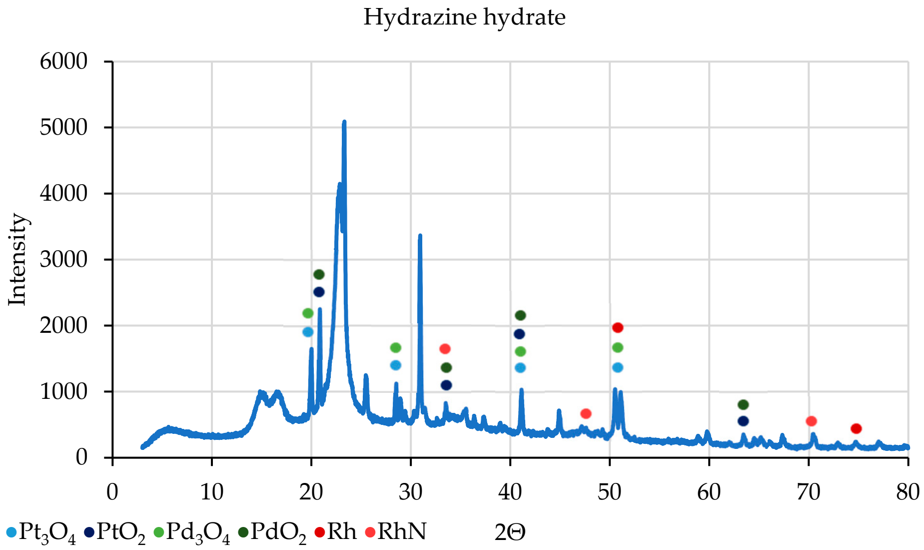


Figure 7. XRD patterns for the sample following reduction with the addition of 5 cm^3 of aqueous hydrazine hydrate solution.

Analysis of the data in the diffractogram in Figure 6 indicates that Pt and Pd compounds are formed in the sample following reduction with hydrazine hydrate, mainly oxides such as Pt_3O_4, Pd_3O_4, PtO_2, and PdO_2. In addition, rhodium is visible in the precipitate, unbound and bound to nitrogen from hydrazine hydrate, forming RhN. When using Au, its amount was probably too low for the signal to be visible in the diffractogram.

Based on the data in Figure 6b, it can be concluded that selective precipitation of gold, palladium, and rhodium is possible while using an aqueous ammonia solution as the precipitating agent. Practically, even a small addition of the ammonia solution causes a high pH increase (>8); however, only after reaching a pH above 9 is the recovery of precious metals carried out with high efficiencies (>98% for Pd, >87 for Au and >86% for Rh). The platinum reduction efficiency remains virtually unchanged throughout the entire process (50–60%). Ammonia solution is very often added to the refining process of precious metals, especially in the presence of chloride ions, as it can precipitate precious metals in the forms of: $Pt(NH_3)_4Cl_2 \cdot xH_2O$, $[Pt(NH_3)_6]Cl_4$, $Pt(NH_3)_4(OH)_2 \cdot xH_2O$, $Pd(NH_3)_4Cl_2 \cdot H_2O$,

$[Pd(NH_3)_4](OH)_2$, or $(NH_4)_3RhCl_6$. The semi-quantitative analysis results showed that in addition to the mentioned complexes, other sulfur-containing compounds were also precipitated due to the strong affinity between nitrogen and sulfur. A combination of amino–chloro–thiourea complexes was likely formed during the precipitation.

The use of formic acid (Figure 6c) enables the recovery of all precious metals with a very high efficiency (>80%), with only a small amount of reducing agent added. However, the formation of excess precipitate is visible when the concentration of formic acid and sodium hydroxide exceeds a certain threshold. It is probably a mixture of hydroxide, formic acid, and thiourea complexes. This means that when formic acid is used, special attention must be paid to the reaction balance, which, unfortunately, is not indicated by a change in the pH of the solution throughout the process, as NaOH had to be added to keep the reaction at high efficiency. It is possible that the solid form of precious metals, once precipitated, could potentially oxidize formic acid, leading to the production of more compounds and a significant increase in the amount of precipitate.

Application of the aqueous solution of hydrogen peroxide (Figure 6d) for reduction allows the recovery of platinum and palladium at a high level (with the efficiencies being >90% for Pt and >89% for Pd), selectively separating them from gold and rhodium. The pH change is also not very visible in this case, as it remains <1 throughout the process. Nevertheless, the addition of approximately 3.5 cm^3 of hydrogen peroxide to 25 cm^3 of eluate enables reducing high amounts of Pt and Pd. In this case, a significant amount of sulfur was present in the precipitate, likely forming compounds with precious metals. It is conceivable that instead of pure precious metals, various sulfides were produced.

The data in Figure 6e indicate that precious metals can be recovered with high efficiencies (over 80% for each metal) using oxalic acid. It should be noted that in this case, a large amount of additional precipitate is formed, which is not a compound made entirely of precious metals, but is likely a mixture of hydroxide, oxalic acid, and thiourea complexes, although the precipitation of precious metal oxalates is also possible. Also, the pH in this case cannot be an indicator that determines the maximum reduction efficiencies of Pt, Pd, Rh, and Au as NaOH had to be added to the process to obtain high efficiencies of the precipitation of precious metals.

3.3. Refining Experiment

The results of the precious metal-refining tests are presented in Table 5.

Table 5. Results of the research on refining the precious metals from the post-elution solution.

Metal	Initial Concentration in the Solution [mg/dm^3]	
Pt	562.0	
Pd	585.0	
Rh	18.9	
Au	39.4	
	Au extraction	
Metal	**Final concentration in the solution [mg/dm^3]**	**Recovery efficiency [%]**
Pt	442.0	22.2
Pd	451.0	23.7
Rh	14.8	22.5
Au	28.6	28.2
	Pd extraction	
Metal	**Final concentration in the solution [mg/dm^3]**	**Recovery efficiency [%]**
Pt	403.0	9.3
Pd	445.0	1.8
Rh	12.7	14.6
Au	26.5	7.8

Table 5. *Cont.*

Pd re-extraction		
Metal	**Final concentration in the solution [mg/dm^3]**	**Recovery efficiency [%]**
Pt	0.3	0.4
Pd	0.3	1.8
Rh	0.1	2.4
Au	0.1	2.3
Pd precipitation		
Metal	**Final concentration in the solution [mg/dm^3]**	**Recovery efficiency [%]**
Pt	0.3	0.0
Pd	0.2	32.0
Rh	0.1	0.0
Au	0.1	0.0
Pt precipitation with NH_4Cl		
Metal	**Final concentration in the solution [mg/dm^3]**	**Recovery efficiency [%]**
Pt	84.8	12.7
Pd	94.8	11.6
Rh	3.3	0.0
Au	6.9	0.0
Pt precipitation with NH_3 (aq)		
Metal	**Final concentration in the solution [mg/dm^3]**	**Recovery efficiency [%]**
Pt	88.9	47.7
Pd	44.3	76.4
Rh	1.9	64.5
Au	4.8	57.1

The results presented in Table 5 indicate that it is not possible to carry out this type of precious metal-refining process to obtain pure compounds. The reason for low recovery efficiencies is probably the greater affinity of precious metals for thiourea than for extractants and precipitating agents. This means that the use of solvent extraction techniques is not possible and applications of different selective precipitation techniques will be required.

4. Conclusions

During the research, various tests were performed to extract precious metals from the post-elution solutions. Different methods such as cementation, reduction, precipitation, and refining were used to achieve this objective. The study examined the potential of using metallic powders like zinc, copper, aluminum, magnesium, nickel, and cobalt to cement platinum, palladium, rhodium, and gold. Additionally, the effectiveness of using aqueous hydrazine hydrate solution, aqueous hydrogen peroxide solution, aqueous ammonia solution, aqueous formic acid solution, and oxalic acid in reducing and precipitating precious metals was also investigated. The test results are summarized in Table 6, which shows what agents can be used to precipitate specific precious metals.

Table 6. Summary of the test results, + means cementation/reduction/precipitation is possible, − means cementation/reduction/precipitation is not possible, +/− means cementation/reduction/precipitation is possible, but the use of other agents is recommended.

Cementing/Reducing/Precipitating Agent	Pt	Pd	Rh	Au
Industrial metallic zinc powder	+	+	+	+
Commercial metallic zinc powder	+	+	+	+
Metallic aluminum powder	−	+	−	+
Metallic magnesium powder	+/−	+	+/−	+
Metallic nickel powder	−	−	−	+
Metallic cobalt powder	−	−	−	+

Table 6. *Cont.*

Cementing/Reducing/Precipitating Agent	Pt	Pd	Rh	Au
Metallic copper powder	−	+	−	+
Hydrazine hydrate	+	+	+	+
Aqueous ammonia solution	+/−	+	+	+
Oxalic acid	+	+	+	+
Formic acid	+	+	+	+
Aqueous hydrogen peroxide solution	+	+	−	−

Based on the conducted research, the following additional conclusions can be drawn:

- The best cementing agent for platinum, palladium, rhodium, and gold is metallic zinc powder, whereas commercial metallic zinc powder can be replaced with an industrial one;
- Metallic aluminum and copper powders can be used to selectively cement gold and palladium from the post-elution solutions of thiourea and HCl, separating them from platinum and rhodium;
- Gold can be cemented with metallic powders of zinc, magnesium, aluminum, copper, nickel, and cobalt;
- The best-reducing agent for platinum, palladium, rhodium, and gold is an aqueous solution of hydrazine hydrate;
- Aqueous hydrogen peroxide solution can be used to selectively reduce Pt and Pd from the post-elution solutions of thiourea and HCl, separating them from Au and Rh.
- The research findings suggest that it is possible to selectively precipitate precious metals from thiourea post-elution solutions by using a combination of various cementing, reducing, and precipitating agents in a specific combination.

5. Patents

Part of the results of the work presented in this publication has been submitted for patenting to the Patent Office of the Republic of Poland (patent application number—P.448742), in May 2024, entitled: Sposób rozdziału metali szlachetnych z roztworów tiomocznika z kwasem chlorowodorowym (English title: Method of separating precious metals from solutions of thiourea and hydrochloric acid).

Author Contributions: Conceptualization, K.G.; methodology, K.G. and G.B.; investigation, K.G., J.M., and K.P.; writing—original draft preparation, K.G.; writing—review and editing, K.G., J.K., and G.B.; visualization, K.G.; supervision, G.B., J.K., and K.L.-S. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

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