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Assessing Apparent Equilibrium Concentrations in Cementation of Trace Pd, Pt, Au, and Rh from Nitrate Solutions Using Mg, Al, Fe, and Zn

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Abstract: This study explores the impact of nitrate ions on the efficiency of cementing noble metals from diluted waste solutions at a temperature of 30 °C. The research involved measuring the effectiveness of different cementing metals (such as Zn, Al, Mg, and Fe) in the presence of nitrate ions by assessing the change in metal ion concentrations before and after the cementation process using spectrometric analysis. Initial concentrations of noble metals were Pt = 5 ppm, Au = 7.5 ppm, Pd = 5 ppm, and Rh = 1 ppm. Kinetic studies revealed that 24 h is adequate to achieve apparent equilibrium in solutions with pH 2 and 1 M nitrate ion content. The study identified significant recovery losses for gold and platinum in nitrate solutions, underlining the necessity of nitrate-free solutions in recycling. Zinc and magnesium were effective in cementing Pd and Rh, while aluminum was efficient for Pt reduction in each condition. Complete removal of Au was not achieved with any tested metal, indicating a need for alternative methods.

Keywords: cementation; noble metals; apparent equilibrium concentration; nitrate ions; recycling



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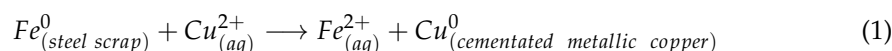


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1. Introduction

In the modern industry, noble metals have a broad spectrum of possible applications. However, considering the high prices [1,2] and low abundance [3] of these metals, there is a strong need to recycle them so they can be used multiple times.

A very common process applied for the recovery of noble metals is cementation [4,5]. It allows noble metals to be retrieved from various materials after leaching them from a solid phase. Cementation is a straightforward process which depends on redox reactions between ions of different metals. The metal used for cementation is lower in galvanic series than the cemented metal (noble metal or heavy metal, for instance). Thus, adding cementing metal to a solution containing noble metal results in a precipitate of the noble metal's particles and a solution of cementing metal ions being obtained. A good example of such a process is a reaction between Cu and Fe, which was once widely used for obtaining copper on an industrial scale [6]:



Another example of cementation is a Merrill–Crowe process, which involves gold recovery with a zinc ion solution [7]. Cementation is applied in the automotive industry as well. Kim and co-workers performed a series of cementations to recover noble metals from spent car exhaust catalysts with the use of Al, Mg, and Zn powders [8]. Cementation is also applied for recovering valuable metals from electronic components and catalytic systems. Mahapatra et al. used cementation with Fe powder to recover Cu after microwave sintering of E-waste and leaching it with HCl [9]. As for the founding industry, Aboody et al. developed a three-step method of Ni recovery from a catalyst used for sponge iron

production, which consists of acidic extraction of metal, Al-based cementation, and alkaline leaching for purification [10]. An example of a process strictly targeting noble metals is a work by Barzyk et al. which consists of Ag and Au recovery using non-stoichiometric cuprous sulfide grains [11] and a study by Patcharawit et al. focused on Ag recovery from electroplating solutions with the use of Zn [12].

Cementation has many assets—it is a quick, safe, and simple process with a relatively low cost (assuming the process is conducted without additional heating of the solution). Ranchev et al. showed these advantages in their study on silver recovery, achieving a silver yield exceeding 94% with the use of cheap iron powder, acidic thiourea solution as a leaching agent, and simple laboratory equipment [13]. We can see a similar approach in a study by Goc and co-workers, in which they cemented noble metals from concentrates with Zn powder [14]. Successful results can also be observed in a study by Rabah and co-workers, involving Mo and Co recovery from spent hydrogenation catalyst [15]. These advantages make cementation a technique of choice for noble metals retrieval from large-scale industrial waste as well [16].

Unfortunately, cementation also has some flaws—for example, during cementation, precipitate losses may occur [12]. Another disadvantage is high consumption of metal used for cementation (especially during precipitation from low-pH solution), low selectivity, and additional material losses for neutralization of acid (which is necessary due to poor kinetics in acidic conditions [17]). However, the biggest disadvantage of cementation is its limited efficiency, which comes from the reaction's balance [18,19]. As a result, in the post-reaction solution, a large amount of non-reduced noble metals' ions often remains. This means an additional yield reduction, which is highly undesired considering the high cost of noble metals.

There are many factors determining the kinetics of cementation: the influence of solution's ionic composition [17], pH [20], temperature [21–23], cementation time, and stirring speed [6]. Also, the nature of ions in solution has a great influence on cementation efficiency [23], as well as the particle size of the metal used for cementation [24]. Kim et al. investigated the influence of ultrasounds on cementation effectiveness and achieved a 92% yield of Ir [25]. Sulka et al. showed that acid concentration can affect the morphology of Ag deposits obtained through cementation [26]. Kuntzy et al. who used cyanide solutions for Au cementation with Mg, observed that the Au yield is strongly connected to the concentration of CN^- ions in solution and reaches 80% at optimal concentration (0.001–0.005 M $[\text{Au}(\text{CN})_2]^-$), but when supported with ultrasounds, this increases to 95% [27]. Elshazly proved that even the orientation of metal plates and their oscillation speed are significant factors determining the effectiveness of heavy metal cementation [28].

Cementation can be coupled with various techniques, such as adsorption, ion exchange, or solvent extraction [29]. It can be also supported electrochemically by the use of a conductor or semiconductor [30]. Ion exchange can be used to overcome the low selectivity of cementation, just like in the study by Xing et al. [31]. Gros et al. used a rotating disc electrode to enhance their cementation performance [32], as did Makhoulfi and co-workers, who used this technique to improve lead ion removal from acidic aqueous solution [33].

Currently, the cementation process of noble metals has been employed in recycling processes, particularly in small-scale operations. In these cases, aqua regia, a mixture of nitric and hydrochloric acids, is typically used to leach materials containing noble metals [34,35]. Our industrial experience indicates that, in solutions resulting from the leaching of noble metals with solutions containing high concentrations of nitrate ions, the cementation process occurs with limited efficiency. This leads to losses in the yield of noble metal recycling. Given the high value of noble metals and the large scale of their global processing [36,37], even minor losses in their recovery can result in significant economic impact. Therefore, it is crucial to minimize these losses by optimizing the parameters of the recovery process, including the cementation process.

Among noble metals, gold is of particular interest for recycling due to its relatively high concentration in electronic scrap [38,39], while palladium, platinum, and rhodium are

significant because of their use in automotive catalytic converters [40,41]. As previously noted, zinc is commonly employed for the cementation of these metals. However, iron, aluminum, and magnesium are increasingly being explored due to their differing kinetics [42] and selectivity [43–45] in the cementation process of noble metals. The advantages of these metals as cementing agents include a relatively low price, a high potential difference in relation to precious metals, and, in the case of iron and magnesium, low or practically negligible toxicity. This is particularly important in the management of post-process waste and the costs of its disposal.

In light of current trends in noble metal recycling, this research investigates the cementation of platinum, gold, palladium, and rhodium from dilute nitrate-containing solutions using zinc, magnesium, iron, and aluminum as cementing agents. The primary objective is to identify the most effective cementing agent for recovering these noble metals. This study focuses on determining the apparent equilibrium concentration of noble metal ions in solution following cementation under various processing conditions. Given that the equilibrium state in the cementation process depends on numerous variables, the model reflecting the actual equilibrium state according to thermodynamic theory is likely to differ from the experimentally obtained values. Therefore, in this work, the term “apparent equilibrium” is used to indicate that this value was observed as a result of the experiments conducted.

The effectiveness of a cementing agent is inversely related to the equilibrium concentration of noble metal ions in the solution; a lower apparent equilibrium concentration indicates a more effective cementing agent. The concentrations of precious metals in the studied solutions were Pt = 5 ppm, Au = 7.5 ppm, Pd = 5 ppm, and Rh = 1 ppm, all based on chloride solutions. These conditions simulate real waste solutions from industrial processes involved in recycling precious metals from spent catalysts used in the chemical industry.

2. Materials and Methods

The solution for the cementation process was prepared by dissolving appropriate amounts of RhCl_3 (Acros Organics, p.a., Geel, Belgium), AuCl_3 (Acros Organics, p.a., Geel, Belgium), PtCl_4 (Acros Organics, p.a. Geel, Belgium), and PdCl_2 (Acros Organics, p.a. Geel, Belgium) in 0.01 M hydrochloric acid (Chemland, p.a., Stargard, Poland). Then, 100 cm³ of the prepared solution was measured into 250 cm³ Simax screw-top glass containers. For selected series, the pH was adjusted using 8 M NaOH solution (Chemland, p.a., Stargard, Poland), obtaining values of 1.5, 2, and 3; pH was measured using a pH electrode (Hydromet ERH-11, Syców, Poland). The electrode was calibrated before measurements with five buffer solutions at pH 0, 2, 5, 10, and 12 (POCH, Gliwice, Poland) and a temperature of 25 °C. The measurement accuracy was ± 0.05 pH. The pH values of the solutions after the cementation process were measured using the same pH electrode. Nitrate ion solutions were prepared from a pH 2 stock solution by adding an appropriate amount of NaNO_3 (Chemland, p.a., Stargard, Poland), obtaining concentrations of 0 M, 0.5 M, and 1 M nitrate ions (see Table 1). To the prepared solutions, 0.5 g of cementing metal was added; these were Mg (1 mm chips, Chemland, p.a., Stargard, Poland), Al (5 mm chips, Chemland, p.a., Stargard, Poland), Fe (<50 μm powder, Chemland, p.a., Stargard, Poland), and Zn (<50 μm powder, Chemland, p.a., Stargard, Poland). No pre-treatments were applied to the cementing metals.

The assumed mass of 0.5 g is at least 10 times in excess of the amount required for the process, accounting for losses due to dissolution of the metal in the acidic solution. All experiments (see Table 1) were carried out in parallel for two repetitions over a period of 72 h. The process was conducted in thermostatic laboratory shakers at a temperature of 30 °C. After adding the cementing metal, the reaction containers (Simax bottles) were tightly sealed. The system remained closed throughout the duration of the experiment. After the experiments were completed, no increased pressure was observed in the system.

Table 1. Experimental series of cementation solutions.

	pH	Nitrate Ions Concentration [M]
Cementing metal Mg, Al, Zn, Fe	1.5	0
	2	0
	3	0
	2	0.5
	2	1

It was assumed that the morphology of the cementing metal had no effect on the apparent equilibrium concentration of the cemented noble metals. Cementation kinetics were carried out to confirm this assumption for a period of 24 h. For all experimental work, demineralized water ($>18\text{ M}\Omega$, Polwater, Kraków, Poland) was used.

The efficiency of the cementation process and the ability of individual cementing metals to deeply remove noble metal ions from solutions were determined by measuring the change in the concentration in the solution before and after the process. To analyze the concentrations of the solutions, approximately 3 mL of each tested solution was sampled. For the post-cementation analysis, shaking was halted 4 h prior to sampling to allow the sediment to settle and to collect the solution from above the sediment. The collected samples were then filtered through fine-pore filter paper (for quantitative analysis) and subsequently analyzed directly using MP-AES to determine the concentrations of the precious metals. No dilution of the analyzed solutions was performed.

The concentrations of Rh, Au, Pt, and Pd were measured using an Agilent MP-AES 4200 microwave-induced plasma emission spectrometer (Agilent, Santa Clara, CA, USA). The instrument operated with nitrogen (from a generator) as the carrier gas. The sampling time was 30 s, the rinsing time with the tested sample was 30 s, and the stabilization time was 30 s. Prior to measurement, the device was calibrated using a set of standards with concentrations of 0 ppm, 0.05 ppm, 0.1 ppm, 1 ppm, 5 ppm, and 10 ppm for each of the tested noble metals: Au, Pt, Pd, and Rh. The standards were prepared by diluting commercial calibration solutions (1000 ppm in 10% HCl, PlasmaCAL, Villebon-sur-Yvette, France) in 0.1 M HCl. These calibration solutions are compliant with quality standards [46,47]. Calibration curves were linear, with correlation coefficients of 0.99996 for Pt, 0.99957 for Au, and 1.00000 for both Pd and Rh.

Depending on the analyzed element, the accuracy of the analysis on this device varied. In the case of noble metals, including those analyzed in this work, i.e., platinum, gold, palladium, rhodium, it was possible to analyze the concentration of these ions above 10 ppb. The MP-AES method is a spectrometric technique that determines the total concentration of ions in a solution, irrespective of their oxidation states.

Theoretical calculations of ΔG values were conducted using HSC Chemistry 5.1 software (Outokumpu research center, Helsinki, Finland), which includes a comprehensive thermodynamic database of various chemical species. This software allows for the determination of ΔG values for specific chemical reactions at a given temperature. However, it is important to note that the software does not account for reaction kinetics or non-ideal behavior of solutions, making it impossible to assess the interference caused by factors such as the presence of nitrate ions in the process.

3. Results and Discussion

The concentration of each solution before cementation was measured. Depending on the series (amount of added NaOH and NaNO_3 solution), the concentrations of noble metals in the stock solutions were, on average, Pt = 5 ppm, Au = 7.5 ppm, Pd = 5 ppm, and Rh = 1 ppm.

Theoretical values of the efficiency of the noble metal cementation process using selected cementing metals were determined. Subsequently, the kinetics of the process

were examined to determine the time needed to establish apparent equilibrium. Finally, cementation tests were carried out on the prepared test systems, and the actual values of the process efficiency were determined.

3.1. Thermodynamics of Cementation Reactions

The cementation process is primarily driven by the difference in standard electrode potentials between the metal used for cementation and the metal ion being cemented. This potential difference drives the redox reaction, where the metal with the higher reduction potential is reduced while the metal with the lower reduction potential is oxidized. Cementing metals such as magnesium (Mg), aluminum (Al), zinc (Zn), and iron (Fe) each have distinct standard potentials, influencing their effectiveness in reducing Rh, Au, Pt, and Pd. A thorough understanding of these thermodynamic principles is essential for optimizing cementation processes in industrial applications.

The Gibbs free energy change (ΔG) is a crucial parameter in predicting the feasibility of cementation reactions. A negative ΔG indicates a spontaneous reaction, while a positive ΔG suggests a non-spontaneous process. The value of ΔG is calculated using the standard electrode potentials of the involved metals, as shown in Equation (2):

$$\Delta G = \Delta G^{\circ} + RT \ln K_{eq} \quad (2)$$

where ΔG° is the Gibbs energy change under standard conditions (1 M, 298 K), R is the universal gas constant, T is the temperature, and K_{eq} is the equilibrium constant.

In the cementation process, ΔG° is dependent on the difference in the standard potentials of metals taking part in a cementation process (E°), as shown in Equation (3):

$$\Delta G^{\circ} = -zFE^{\circ} \quad (3)$$

where z is the number of electrons transferred, F is the Faraday constant, and E° is the standard potential difference between the metals.

The conclusion from Equations (2) and (3) is that a greater standard potential difference between the cemented metal and the metal used for cementation results in a more negative ΔG (i.e., a more spontaneous reaction). Therefore, using a metal with a lower standard potential as a cementing metal is thermodynamically favored. This is illustrated by calculating ΔG for different cementing metals using HSC Chemistry software, specifically for the cementation of Pd in the form of chloride complex $[\text{PdCl}_4]^{2-}$, as in this study, cementations are conducted in hydrochloric acid. The results of ΔG calculations and the equilibrium constants (K_{eq}) from HSC database are compiled in Table 2.

Table 2. K_{eq} and ΔG values for Pd cementation by different cementing metals. The assumptions for the calculations were as follows: Pd is present as $[\text{PdCl}_4]^{2-}$, $E^{\circ} = 0.987$ V, Adapted from Ref. [48], and $T = 298.15$ K (25 °C). One mole of each reagent is present in the system, with aqueous solutions having a concentration of 1 M.

Cementing Metal	Standard Potential [V]	K_{eq}	ΔG [kJ/mol]
Mg/Mg ²⁺ [49]	−2.37	1.929×10^{114}	−563.92
Al/Al ³⁺ [50]	−1.66	6.377×10^{98}	−652.28
Zn/Zn ²⁺ [51]	−0.76	1.121×10^{45}	−257.12
Fe/Fe ²⁺ [52]	−0.44	1.930×10^{35}	−201.39

The results in Table 2 indicate that Al was the most thermodynamically favored among the tested cementing metals, as reflected by its more negative Gibbs free energy change. This was despite Mg having a lower standard potential value due to Al's half-reaction involving a higher number of electrons transferred. However, from an industrial perspective, the key consideration is not merely the thermodynamic favorability, but rather the efficiency of recovering noble metals from waste solutions. Reaction efficiency refers to the percentage of

reactants converted into the desired product [53]; thus, in the context of cementation, 100% efficiency would indicate that all noble metal ions were completely reduced to solid metals.

The cementation process is driven by the potential difference between metals. However, it is important to note that the equilibrium potential is dependent on the activities of these metals. Consequently, complete recovery of the cemented metal from the solution is not possible because, as the concentration of the cemented metal becomes sufficiently low, its potential approaches that of the cementing metal. The Nernst equation is a fundamental tool in electrochemistry that relates the cell potential of an electrochemical reaction (E) to the standard electrode potential and the activities (or concentrations) of the chemical species involved, as well as the reaction temperature [54]. This relationship is mathematically expressed in Equation (4):

$$E = E^0 + \frac{RT}{zF} \ln \frac{C_{red}}{C_{ox}} \quad (4)$$

where C_{red} and C_{ox} are the concentrations of the reduced and oxidized species, respectively.

When the cementation reaches equilibrium, the system can be described by transforming the Nernst equation into the form [55] shown in Equation (5):

$$E_{cem}^0 + \frac{RT}{z_{cem}F} \ln C_{eq,cem} = E_{rec}^0 + \frac{RT}{z_{rec}F} \ln C_{eq,rec} \quad (5)$$

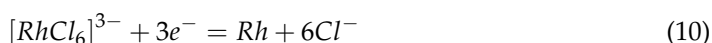
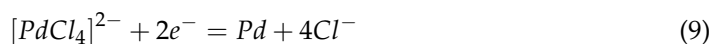
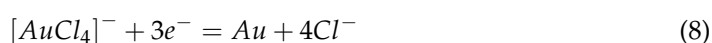
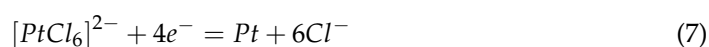
where $C_{eq,cem}$ is the equilibrium concentration of the cementing metal, $C_{eq,rec}$ is the equilibrium concentration of the recovered metal, $C_{eq,rec}$ is the equilibrium concentration of the recovered metal, z_{cem} is the number of electrons transferred in the half-reaction for the cementing metal, and z_{rec} is the number of electrons transferred in the half-reaction of the recovered metal.

If the initial concentration of the cementing metal ($C_{0,cem}$) is equal to zero and we assume that the cementing metal will not be leached so that the only way to increase its concentration in the solution is by means of cementation, then the equilibrium concentration of the cementing metal can be described as Equation (6):

$$C_{eq,cem} = \frac{z_{rec}}{z_{cem}} (C_{0,rec} - C_{eq,rec}) \quad (6)$$

where $C_{0,rec}$ is the initial concentration of the recovered metal.

Combining Equations (5) and (6) allows us to calculate the equilibrium concentrations of recovered metals. Assuming all noble metals are present in form of chloride complexes, which is very likely as experiments are conducted in hydrochloric acid, the following half-Reactions (7)–(10) will take place:



The standard potential values for the above reactions are $E^0 = 0.744$ V [56] for Equation (7), $E^0 = 1.002$ V [48] for Equation (8), $E^0 = 0.591$ V [48] for Equation (9) and $E^0 = 0.431$ V [48] for Equation (10).

Using the initial concentrations of noble metal ions in the solution, which are based on our experimental values (Pt = 5 ppm, Au = 7.5 ppm, Pd = 5 ppm, and Rh = 1 ppm), the equilibrium concentrations for different cementing metals can be determined. The results are shown in Table 3.

Table 3. $C_{eq,rec}$ values for Pt, Au, Pd, and Rh cemented by different cementing metals. The assumptions for the calculations were as follows: $T = 298.15$ K (25°C). All noble metals are presented in their chloride complex form, initial concentrations to experimental ones.

Cementing Metal	$C_{eq,Pt}$ [M]	$C_{eq,Au}$ [M]	$C_{eq,Pd}$ [M]	$C_{eq,Rh}$ [M]
Mg	7.40×10^{-220}	4.37×10^{-178}	3.71×10^{-105}	5.09×10^{-150}
Al	3.17×10^{-169}	3.89×10^{-140}	7.91×10^{-80}	8.97×10^{-112}
Zn	5.34×10^{-111}	1.92×10^{-96}	9.98×10^{-51}	2.24×10^{-68}
Fe	2.31×10^{-89}	3.25×10^{-80}	6.56×10^{-40}	3.78×10^{-52}

The results presented in Table 3 suggest that only very small amounts of noble metal ions should remain in the solution after the cementation process, provided that a stoichiometric amount or excess of cementing metals is used. However, these calculations are simplified, as Equation (5) does not account for factors such as the ionic strength of the solution or interference from other ions, such as nitrates, which are challenging to quantify but could significantly impact the actual equilibrium concentrations.

It is important to note that the MP-AES method used to determine metal concentrations in our studies does not differentiate between oxidation states or complex forms of the analyzed samples. Consequently, even though the initial oxidation states of the noble metals are known (as they correspond to those in the chloride salts used to prepare the analyzed solutions), the oxidation states of the noble metals remaining in the solution cannot be determined. For instance, Pt could be present in either the Pt^{4+} or Pt^{2+} oxidation state.

The cementation process itself likely occurs in stages, with Pt and Au initially being reduced to lower oxidation states (+2 and +1, respectively) before ultimately being reduced to their metallic forms, unlike the simplified reactions shown in Equations (7) and (8). This multi-stage aspect of some cementation reactions should not introduce significant error into our ΔG calculations, as Gibbs free energy is a state function and depends only on the initial and final states, not on the pathway taken [57]. However, when considering equilibrium concentration calculations, accounting for intermediate states in the cementation reactions could lead to some variations in the results. Nonetheless, the simplified calculations were used to illustrate how minuscule the amounts of noble metals theoretically remaining in the solution after cementation should be.

3.2. Cementation Kinetics Studies

The first stage of the research involved conducting kinetic tests for the cementation process from solutions with pH 2 and a nitrate ion content of 1 M. The experiments were conducted for each of the tested cementing metals over 24 h, with 1 cm³ samples taken at specified intervals. Each sample was filtered. This study aimed to determine whether apparent equilibrium had been achieved after the assumed cementation process time. The results of the kinetic studies are presented in the Figure 1 as relative concentrations, which represent the ratio of the final [C] to the initial [C]₀ concentration, expressed as a percentage.

As shown in the graphs in Figure 1a–d, 24 h is sufficient for the system to achieve apparent equilibrium. Depending on the test series, the concentration of the noble metals after cementation either fell below the detection threshold (which is 0.01 ppm of absolute concentration for the tested elements) or remained significantly unchanged over time.

It is noteworthy that in some samples, fluctuations in the concentration of the cemented metal were observed over time (see Figure 1c,d) or an increase in concentration (see Figure 1b) relative to the previous measurement point was noted. This is likely due to the system being in dynamic equilibrium with nitrate ions and a limited amount of dissolved oxygen in the solution. In the research system, at various stages of the cementation process, we assume the presence of ions such as H^+ , Cl^- , NO_3^- , Na^+ , noble metal ions, and cementing metal ions. Additionally, the system contains gases dissolved in the solution, such as hydrogen, oxygen, and nitrogen from the air, as well as noble metals and cementing metals in their zero oxidation states. Under these conditions, a dynamic equilibrium of H^+

ions and NO_3^- can be expected to occur [58]. The redox potential of HNO_3 (in accordance to Equation (11)) is $E^0 = 0.96 \text{ V}$ [59], indicating that it is a strong oxidizing agent.

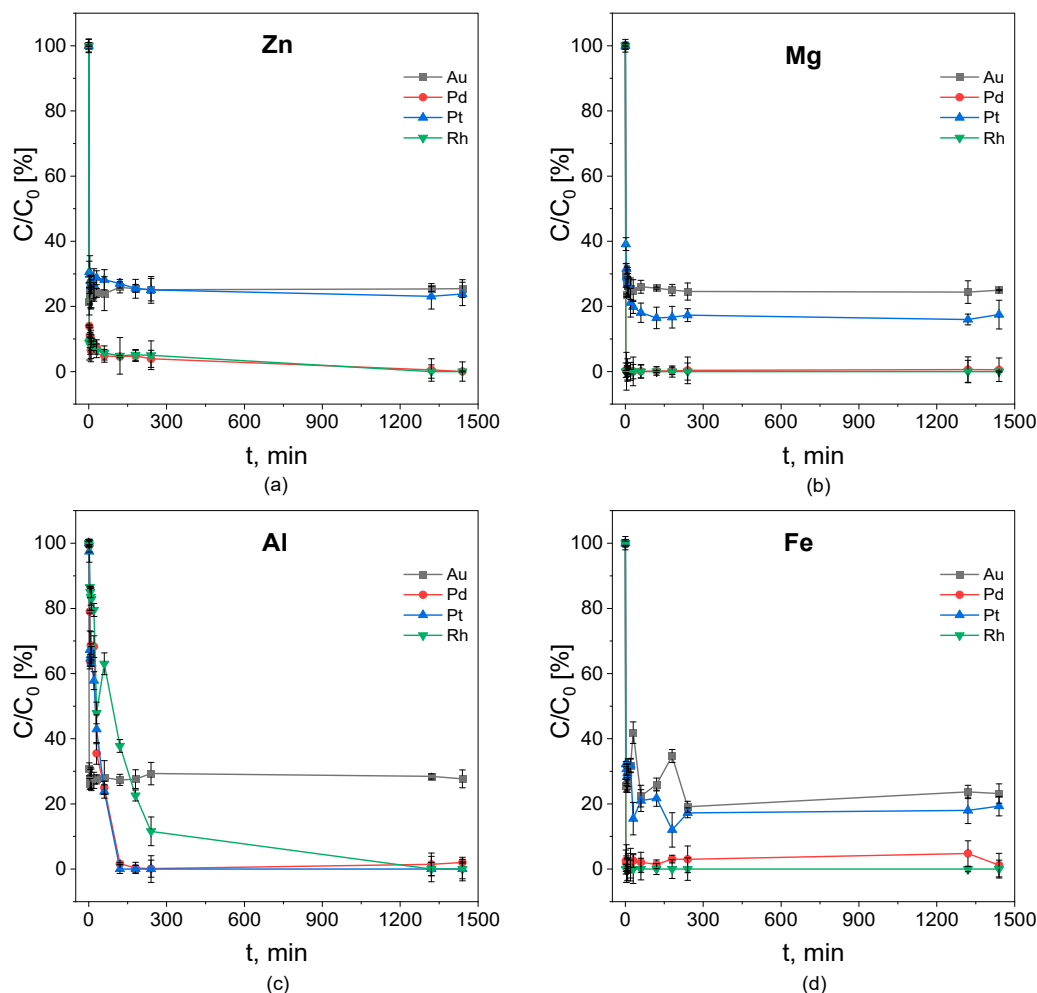
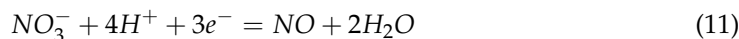


Figure 1. Kinetic curves of the cementation process of Au, Pt, Pd, and Rh using zinc (a), magnesium (b), aluminum (c), and iron (d).

Moreover, at the final stage of the process, we anticipate a dynamic equilibrium involving chloride ions, nitrate ions, and ions of noble metals alongside noble metals in their metallic form [59]. This is characteristic of a classic leaching system for noble metals in aqua regia. However, due to the reduced concentration of hydrogen ions in the final stage of cementation, the equilibrium was strongly shifted towards the metallic form of the noble metal. Nevertheless, it is suspected that this system will remain in dynamic equilibrium with the ionic form of the corresponding noble metal.

The initial rapid decrease in the first stages of the process is associated with the dominant cementation process, during which part of the cementing metal dissolves with the release of hydrogen, causing deoxidation of the solution and creating favorable conditions for the reduction in noble metals. In the subsequent stages, oxygen in the closed system begins to dissolve in the solution, which, combined with oxidizing nitrate ions, causes the deposit of noble metals with a large specific surface area to undergo partial secondary oxidation. Additionally, part of the cementing metal likely remains oxidized according to the above mechanism. The oxidation potential of nitrate ions in the system after the cementation process, as calculated using the Nernst Equation (4), is 0.50 V at a concentration of 0.5 M and 0.51 V at a concentration of 1 M. This calculation assumes a standard potential

$E^{\circ} = 0.96 \text{ V}$ [59] and a H^{+} concentration of 10^{-7} M . This demonstrates that nitrate ions retain oxidizing properties even in systems with low concentrations of H^{+} ions. Therefore, nitrates can effectively act as oxidizing agents or support the oxidation of metals, including noble metals, in neutral or alkaline systems, which is confirmed in the literature [60–62]. The oxidizing effect of oxygen during the leaching of metals under acidic conditions is also well documented in the literature [63,64].

This phenomenon is particularly evident in cementation using Fe (see Figure 1d). The concentrations of Pt and Au undergo abrupt changes within the first 250 min of the process, reaching a relatively stable concentration at about 20% of the initial value only after this period. In this system, the apparent equilibrium is further influenced by the presence of the redox pair Fe(II)/Fe(III).

The above observations are a prelude to further studies on the apparent equilibrium concentration of the cementation process. Furthermore, they confirm that 24 h is sufficient to achieve apparent equilibrium in the tested systems. The cementation processes were carried out for 72 h, which, assuming that 24 h is sufficient, ensured that the system will be in apparent equilibrium after this time.

3.3. Apparent Equilibrium of the Cementation Process

The next step was to carry out cementation. After the process, the samples were left for 24 h to allow sediments to settle. Then, the filtered samples were tested for the content of noble metals remaining in the solutions after cementation. The results of the determinations are presented in Table 4. Each value is the average of two independent measurements performed for each series. The standard deviations for all values obtained did not exceed 5%.

The contents of individual noble metals in the various experimental series showed significant variability. Notably, in nitrate solutions, at least one noble metal remained in the solution. In the case of magnesium cementation (see Table 4), relatively large amounts of Pt and Au and trace amounts of Pd remained in ionic form. In other solutions, where nitrate ions were absent, the system reached apparent equilibrium with concentrations of all metals below the detection threshold of the device. The system without nitrate ions present was consistent with the theoretical calculations. It is significant, however, that nitrate ions affected the apparent equilibrium in the cementation of noble metal ions with magnesium. The observed variation can likely be attributed to changes in ionic strength (I) and, consequently, the ionic activities of the noble metals in solution. Ionic strength can be described using Equation (12):

$$I = \frac{1}{2} \sum_i m_i z_i^2 \quad (12)$$

where I is the ionic strength of the solution and m_i and z_i are the molarity and charge of a given ion, respectively.

Table 4. Apparent equilibrium concentrations ¹ of individual noble metals in solutions after the cementation process conducted at 30 °C for 72 h with zinc, magnesium, aluminum, and iron.

Cementing Metal	pH Before	Nitrate Ions Concentration [M]	Pt [ppm]	Au [ppm]	Pd [ppm]	Rh [ppm]	pH After
Mg	1.5	0	0	0	0	0	8.7
	2	0	0	0	0	0	9.3
	3	0	0	0	0	0	9.6
	2	0.5	0.69	0.61	0.02	0	8.9
	2	1	0.96	0.73	0	0	9.0

Table 4. Cont.

Cementing Metal	pH Before	Nitrate Ions Concentration [M]	Pt [ppm]	Au [ppm]	Pd [ppm]	Rh [ppm]	pH After
Al	1.5	0	0	0	0.05	0.02	4.1
	2	0	0	0	0.06	0.02	5.9
	3	0	0	0.46	0.28	0.07	6.1
	2	0.5	0	0.45	0.10	0	6.1
	2	1	0	0.54	0	0	6.0
Zn	1.5	0	0	0	0	0	5.5
	2	0	0	0	0	0	5.8
	3	0	0	0	0	0	6.1
	2	0.5	0.80	0.52	0	0	5.4
	2	1	1.15	0.67	0	0	5.5
Fe	1.5	0	0	0	0.19	0	6.8
	2	0	0	0	0.07	0	6.8
	3	0	0	0	0	0	7.2
	2	0.5	0.80	0.48	0.17	0	6.7
	2	1	0.97	0.56	0.27	0	6.5

¹ Mean value of two measurements performed for each experiment. The deviation between the results did not exceed 5%.

As the concentrations of noble metals, hydrochloric acid, and NaNO₃ in the systems are known, we can easily calculate the I values. The results are presented in Table 5.

Table 5. Ionic strength values for noble metals in solutions calculated for systems without added nitrate ions, with 0.5 M nitrate ions and 1 M nitrate ions.

0 M NO ₃ [−]	Ionic Strength [M]	
	0.5 M NO ₃ [−]	1 M NO ₃ [−]
0.010425	0.510425	1.010425

The ionic strength of the solution is crucial for calculating ionic activities, which represent the effective concentrations of ions [65]. The ionic activity a_i can be described by Equation (13):

$$a_i = C_i \gamma_i \quad (13)$$

where a_i , C_i , and γ_i are the activity, concentration, and activity coefficient of a given ion, respectively.

The activity coefficients of ions can be calculated using the Debye–Hückel law, presented in Equation (14):

$$\ln \gamma_i = -z_i^2 \frac{A\sqrt{I}}{1 + B\sqrt{I}} \quad (14)$$

where A and B are temperature-dependent parameters (for water at 30 °C, they are equal to approximately 0.509 L^{1/2}mol^{−1/2} and 0.238 L^{1/2}mol^{−1/2}nm, respectively) and l is the distance of closest approach of ions.

Since the mean values of l cannot be accurately determined [66], we employed an estimation method. First, we gathered data on the distances between the central metal and chloride ions in various metal chloride complexes. The data available in the literature are as follows:

- $[\text{PtCl}_6]^{2-}$, Pt-Cl ≈ 2.3 Å [67]
- $[\text{AuCl}_4]^-$, Au-Cl ≈ 2.4 Å [68]
- $[\text{PdCl}_4]^{2-}$, Pd-Cl ≈ 2.3 Å [69]
- $[\text{RhCl}_6]^{3-}$, Rh-Cl ≈ 2.3 Å [70]

As is evident from the data, the distances between the central metals and chloride ions in these complexes are remarkably consistent. However, when considering the distance of closest approach for ions, their hydrated states must be taken into account [71]. The key value of interest is the distance between the central metal and the oxygen atom from H_2O in the surrounding water molecules ($\text{Me}\cdots\text{O}$). Doubling this distance provides an approximate effective diameter for the ion, which can be considered as the distance of closest approach for the complexes of interest. While data on this distance for chloride complexes are limited in the literature, we found relevant information for the hydrated $[\text{PtCl}_6]^{2-}$ complex when the mentioned distance was approximately 4.5 Å [72]. Assuming similar distances for other complexes, we then calculated the activity coefficients for the chloride complexes present in the solution by substituting 0.9 nm (9 Å) for the value of l . The results are compiled in Table 6.

Table 6. Activity coefficients for chloride complexes in solutions calculated for systems without added nitrate ions, with 0.5 M nitrate ions and 1 M nitrate ions.

Chloride Complex	Activity Coefficients		
	0 M NO_3^-	0.5 M NO_3^-	1 M NO_3^-
$[\text{PtCl}_6]^{2-}$	0.6260	0.0548	0.0207
$[\text{AuCl}_4]^-$	0.8895	0.4837	0.3793
$[\text{PdCl}_4]^{2-}$	0.6260	0.0548	0.0207
$[\text{RhCl}_6]^{3-}$	0.3486	0.0015	0.0002

The results from Table 6 indicate that the effective concentrations of noble metal complexes in the solutions are significantly reduced in systems containing nitrate ions. This outcome is expected, as increased ionic strength generally leads to reduced ion activity. However, the extent of this reduction is notable, particularly in the case of 1 M NO_3^- . Since activity coefficients depend on the charge of the ions, the $[\text{RhCl}_6]^{3-}$ complex exhibited the lowest activity coefficients. Theoretically, the activity coefficient of 0.0002 for Rh in 1 M NO_3^- system suggests that most of the Rh would not be chemically active, and thus would remain in the solution after the cementation process. However, this does not align with our experimental results. The discrepancy is likely due to the high complexity of the system, which is influenced by numerous factors that we recognize, but which are difficult to quantify with our current experimental data.

The first aspect to analyze is the extended Debye–Hückel law, which is used to calculate activity coefficients (see Equation (15)). This equation is widely used by researchers to characterize electrolytes; however, at higher ionic strengths, it fails to accurately predict the actual activities of ions [73]. For this reason, a more accurate version of the equation, sometimes referred to as the “full” Debye–Hückel equation [74], is often employed to precisely determine ionic activities. This equation is presented in Equation (15):

$$\ln \gamma_i = -z_i^2 \frac{A\sqrt{I}}{1 + Bl\sqrt{I}} + bI \quad (15)$$

where b is the fitting parameter, dependent on the temperature and ions in the solution.

Since parameter b differs for different ions, it must be estimated experimentally. As a result, the “full” Debye–Hückel equation has limited applicability in simplified theoretical calculations.

There are also other factors that contribute to the discrepancies between our experimental data and the theoretical calculations. Furthermore, as noted during the cementation kinetics measurements, nitrate ions, along with dissolved oxygen, likely shift the apparent

equilibrium through secondary oxidation of the cemented noble metals, which, due to their highly developed surfaces, are more susceptible to secondary oxidation [75]. This theory is confirmed by the fact that Rh cementation in almost every series leads to the complete precipitation of the metal from the solution. This is because Rh(0) is the most resistant to oxidants among the noble metals tested. The resistance of Rh(0) to aqua regia, and, thus, to nitrate ions responsible for metal oxidation during leaching, is the greatest among the tested metals. The redox potential of the half-reaction of rhodium chloride complex formation (10) suggests that rhodium should exhibit a lower degree of resistance to the oxidizing action of aqua regia than Au(0), Pd(0), and Pt(0). However, this theoretical prediction does not align with practical observations. This discrepancy indicates that basic computational models cannot fully explain the phenomenon. The relatively high resistance of rhodium to aqua regia is well documented in the literature [76–78] and corroborated by our own experimental findings. It is assumed that the resistance is attributed to the formation of a passive oxide layer on the metal's surface, which effectively protects it. The oxidizing potential required to dissolve this oxide layer is significantly higher than that needed to dissolve metallic rhodium [79].

Au(0) and Pt(0) are susceptible to dissolution in aqua regia at room temperature. Pt(0) dissolution, however, requires heating the mixture. Elevated temperatures increase the oxidation potential of aqua regia [80], thereby enhancing the dissolution kinetics of Pt(0).

However, Rh(0) in reaction with aqua regia dissolves with very low efficiency. Thus, in cementation, the freshly precipitated Rh(0) is probably resistant to secondary oxidation, allowing for the complete, permanent removal of Rh from the solution.

Traces of Rh remained in the solution after cementation with aluminum (see Table 4). Notably, Rh, Au, and Pd remained in the solution after cementation with aluminum metal from solutions that did not contain nitrate ions. This was probably due to the pH of the solutions. A higher pH of solution results in more metal ions remaining in the solution after cementation (see Table 4). It should be noted that, during cementation in acidic solutions, a competitive reaction of the cementing metal with H^+ ions takes place in parallel. In this reaction, the metal dissolves, and the H^+ ions are reduced to hydrogen (H_2). The standard potential of the $H_2/2H^+$ is 0 V, which is higher than that of any of the tested metals (see Table 2). Theoretically, at a higher pH, such as pH 3, the equilibrium concentration after cementation should be lower than that at pH 1. As presented in the theoretical section, the equilibrium concentration is dependent on the redox potential, which is calculated using the Nernst equation. The graph dependence of redox potential and pH, known as a Pourbaix diagram, allows for the determination of thermodynamic equilibrium states. According to the Pourbaix diagrams [59,81] for the systems studied, at a constant redox potential, the preference for the metallic form increases with higher pH. This observation aligns with results seen in real systems during the cementation of simple ions [82,83].

However, the formation of aqua and hydroxy complexes of Au [84,85], Pt [86], Pd [86], and Rh [86] complicates this system. The equilibria of these complexes are strongly pH-dependent [87–90] and change dynamically during cementation, impacting the kinetics and degree of cementation. This occurs because the redox potential varies for the different complex forms of the cemented metals. The calculations presented in Table 3 indicate that the equilibrium concentration of Pd after reaction with aluminum should be orders of magnitude lower than the concentration obtained in the experiment. This discrepancy is attributed to the factors discussed above, including the influence of ionic strength, the presence of nitrate ions in the solution, the presence of oxygen, and the formation of different Pd complexes than those assumed in the calculations.

Cementation with aluminum is also sensitive to the presence of nitrate ions for Au cementation. Significant amounts of Au remained in the solution after the process for both concentrations of nitrate ions. Interestingly, Pt and Rh were completely removed from nitrate solutions.

Zinc showed full effectiveness in cementing Rh and Pd in each tested solution (see Table 4). However, in the presence of nitrate ions, large amounts of Pt and Au remained in

apparent equilibrium in the solution. Considering that zinc is one of the most frequently chosen cementing agents [18,43,91,92], this could lead to substantial losses of these metals in industrial-scale processes. The lower efficiency in cementing noble metals using zinc compared to magnesium or aluminum is also confirmed by theoretical calculations (see Table 3).

Iron, which forms a Fe(II)/Fe(III) redox pair during cementation, significantly increases the system's sensitivity to oxidants, including oxygen and nitrate ions present in the solutions. This results in poor cementing efficiency of Pt, Au, and Pd in these solutions (see Table 4). In the case of Pd, some amounts remain in the solution even at lower pH levels. This is likely due to palladium's weakest resistance to corrosive factors among the cemented noble metals. The secondary oxidation of metallic palladium to its ionic form occurs readily in the presence of chloride ions and an oxidant such as dissolved oxygen [79,93] or Fe(III) [94]. Additionally, iron has the highest standard potential among the selected cementing metals (see Table 2). Iron shows a smaller potential difference in the cementing system than magnesium, aluminum, or zinc, resulting in the lowest driving force for the process.

It should also be noted that, after the apparent equilibrium constant was established, a significant change in pH was observed, suggesting the potential involvement of hydrolysis in the process. The hydrolysis phenomenon has a non-negligible effect on both the kinetics and the apparent equilibrium of cementation. It is well known that the cementing metal ions used in this study, including Mg, Al, Zn, and Fe, undergo hydrolysis at their characteristic pH values [95–97]. Hydrolysis products, such as hydroxides or oxides of these metals, can deposit on the surface of the cementing metal, forming a passive layer. This layer may inhibit further reaction between the cementing metal and the precious metal ions, thereby affecting the reaction kinetics and potentially altering the apparent equilibrium of cementation. Furthermore, hydrolysis can lead to the formation of complex ions of cemented metals (Pt [98,99], Au [100–102], Pd [103,104], and Rh [105,106]) that might not participate in the cementation reaction according to the expected reaction path. These can shift the apparent equilibrium by either removing metal ions from the reactive pool or by introducing new equilibria involving the hydrolyzed compounds. The overall impact depends on factors such as pH, metal ion concentration, and the specific metals involved. In systems where hydrolysis plays a significant role, the experimentally observed equilibrium (apparent equilibrium) may differ considerably from the theoretical equilibrium predicted by models that do not account for hydrolysis.

The relative content of noble metals in relation to the initial content is presented in the graphs in Figure 2. The efficiency and selectivity of the cementation process under the given conditions provide valuable information from an industrial perspective. The graphs clearly demonstrate that the cementation process in nitrate solutions can lead to significant losses in the recovery of noble metals from diluted solutions, particularly for Au and Pt. Therefore, it is essential to consider nitrate-free solutions when designing recycling technology. Notably, higher concentrations of nitrate ions result in greater losses in the recovery of noble metals.

Using zinc or magnesium, it is possible to completely cement Rh and Pd, even in the presence of nitrate ions (see Figure 2a,b). For the recovery of Pt from nitrate solutions, aluminum is recommended, as it is the only tested cementing metal that showed complete efficiency in Pt reduction under all given conditions (see Figure 2c).

Complete removal of Au from nitrate solutions was not achieved with any of the tested cementing metals (see Figure 2a–d). This may be due to Au existing in chloride solutions as the very stable complex ion $(\text{AuCl}_4)^-$ [107]. For this purpose, it is recommended to use other reducing agents, such as ascorbic acid, oxalic acid, or additional intermediate operations such as solvent extraction or adsorption processes, on activated carbon or ion exchange resins. It is recommended to carry out the process in solutions that do not contain nitrate ions. In these conditions, it is possible to completely remove Au from the solution by cementation with each of the tested metals. However, it is particularly reasonable to

use iron (see Figure 2d) in this case, not only for economic reasons, but also for very good kinetics. This is influenced by an additional reducing factor, which is Fe^{2+} ions present in the solution, which allow for deep removal of Au, even from diluted solutions [89]. It should also be noted that removing nitrate ions from an aqueous solution is not technologically feasible under industrial conditions because of low kinetics and complexity [108–110].

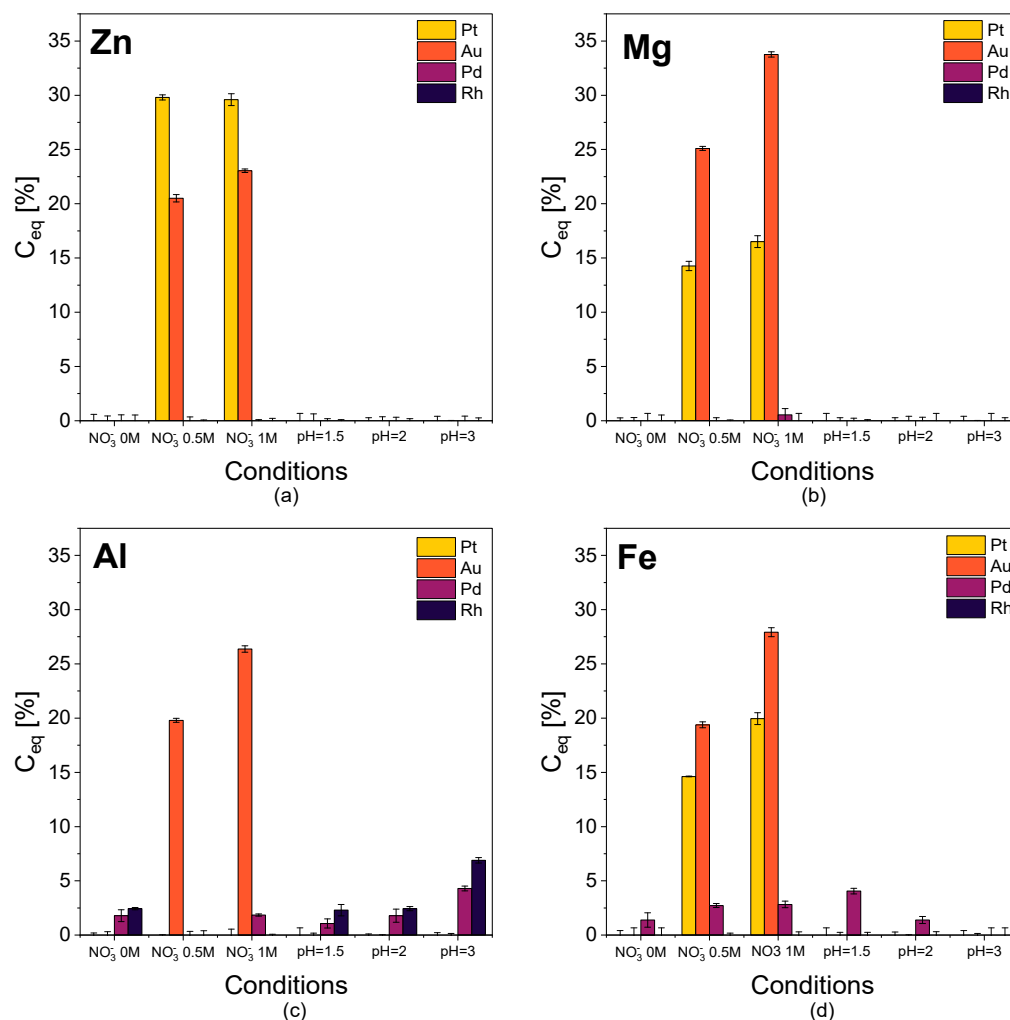


Figure 2. Equilibrium content of noble metals in solutions after the cementation process using zinc (a), magnesium (b), aluminum (c), and iron (d), related to the initial contents. The contents of all metals are marked with an error bar on each of the graphs presented, in the same order. No visible bar for a given metal means that the value for that metal is close to zero.

The profitability of these procedures must, of course, be economically justified. The current prices of selected noble metals and cementing metals, as well as potential metal losses in recycling processes, should be taken into account. For example, cementing with zinc powder from solutions containing 1 M nitrate ions results in Pt and Au losses of 1.15 ppm and 0.67 ppm, respectively. The ppm unit is converted to 1 mg/L, meaning this process results in a loss of 1.15 mg of platinum and 0.67 mg of gold per liter of waste solution. For every 1 m³ of waste solution, this leads to a loss of 1.15 g of platinum and 0.67 g of gold. At the foreign exchange rates of metals [111,112], this equates to a loss of USD 40.48 for platinum and USD 51.18 for gold. The use of an aluminum additive (price \$2.22/kg [112]) can reduce losses by the value of gold.

These considerations should be taken into account when optimizing noble metal recycling processes tailored individually for each company. Given the amount of noble

metals processed, there is a good chance that this will increase the overall profitability of the technology.

4. Conclusions

The initial kinetic studies indicated that 24 h is sufficient for the cementation process to achieve apparent equilibrium for the tested metals in a solution with a pH of 2 and a nitrate ion content of 1 M. The results showed that in most cases, the relative concentration of the cemented metal fell below the detection threshold (which is 0.01 ppm of absolute concentration for the tested elements) or remained stable, indicating effective cementation. Fluctuations in metal concentration over time suggest dynamic equilibrium influenced by nitrate ions and dissolved oxygen, particularly evident in the cementation using iron. The study confirms that a 72 h cementation process ensures apparent equilibrium, providing a robust basis for further investigation into optimizing cementation conditions for industrial applications.

The cementation process in nitrate solutions showed significant losses in Au and Pt recovery, highlighting the need to consider nitrate-free solutions in recycling technology. Zinc and magnesium were effective in completely cementing Rh and Pd even in the presence of nitrate ions, whereas aluminum was uniquely effective in reducing Pt under all tested conditions. Au could not be completely removed from nitrate solutions with any tested cementing metal, suggesting the need for alternative reducing agents such as Na₂SO₃ [113] or additional processes such as solvent extraction [114] or adsorption [115]. The economic feasibility of these procedures must be carefully evaluated, as significant metal losses were observed during cementation with zinc in nitrate solutions, and the use of aluminum could mitigate Pt losses.

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