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On the cementation purification of zinc solutions

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Abstract: The article focuses on researching the technology of cementation purification of zinc sulfate solutions from impurities that adversely affect the electrolysis of zinc. The purpose of this work is to explore new approaches for deep cementation purification of solutions, aimed at reducing the consumption of zinc dust and activating additives (antimony and copper compounds) in the technological process, while improving the quality of the purified solution by decreasing the content of cobalt, nickel, and cadmium in the solution supplied for zinc electrolysis. In this study, a new technology for the cementation purification of industrial solutions was developed, which includes the following stages of impurity removal using zinc dust: preliminary purification stage to remove copper to a concentration of 90–110 mg/L; co-precipitation of copper, cadmium, cobalt, and nickel with the addition of antimony trioxide; deep purification of the solutions from all impurities remaining after the first stage. The purification process was conducted under the following conditions: the preliminary deposition took place at a temperature of 50 °C, with a duration of 30 min and a zinc dust consumption of 0.2–0.4 g/L; the first purification stage occurred at a temperature of 80 °C, for a duration of 1 h, with a zinc dust consumption of 2–3 g/L, and an antimony dosage of 3–6 mg/L; the second purification stage was carried out at a temperature of 75–80 °C, for a duration of 1 h, with a zinc dust consumption of 2–3 g/L, and dosages of copper sulfate and antimony at 50 mg/L and 2–3 mg/L, respectively.

Keywords: cementation, cobalt, cadmium, nickel, copper, zinc dust, antimony trioxide, temperature, solution purified for electrolysis.

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К вопросу цементационной очистки цинковых растворов

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Аннотация: Статья посвящена исследованиям технологии цементационной очистки сульфатных цинковых растворов от примесей, отрицательно влияющих на электролиз цинка. Цель работы – поиск новых вариантов глубокой цементационной очистки растворов, позволяющих сократить расходы цинковой пыли и активирующих добавок (соединений сурьмы и меди) в технологическом процессе и улучшить качество очищенного раствора (снижением в нем содержаний кобальта, никеля, кадмия), подаваемого на электролиз цинка. Разработана новая технология цементационной очистки промышленных растворов, включающая следующие три стадии цементации примесей цинковой пылью: предварительная – очистка растворов от меди до концентрации 90–110 мг/л; первая – совместное осаждение меди, кадмия, кобальта, никеля с добавкой триоксида сурьмы; вторая – глубокая очистка растворов от всех оставшихся после 1-й стадии примесей. Эти стадии осуществлялись при следующих режимах: предварительное осаждение протекало при температуре $t = 50$ °C, продолжительности $\tau = 30$ мин и расходе цинковой пыли $m = 0{,}2\div0{,}4$ г/л; 1-я стадия очистки – $t = 80$ °C, $\tau = 1$ ч, $m = 2\div3$ г/л, дозировка по сурьме – 3–6 мг/л; 2-я стадия очистки – $t = 75\div80$ °C, $\tau = 1$ ч, $m = 2\div3$ г/л, дозировка медного купороса по меди – 50 мг/л, по сурьме – 2–3 мг/л. Разработанный метод позволяет снизить содержание примесей в исходном растворе до необходимых пределов для электролиза высококачественного цинка марки SHG. При этом расход цинковой пыли на первую и вторую стадии цементации должен уменьшиться до 35 кг/т цинка.

Ключевые слова: цементация, кобальт, кадмий, никель, медь, цинковая пыль, триоксид сурьмы, температура, очищенный для электролиза раствор.

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Introduction

In recent years, there has been an increasing demand for high-quality zinc of the "Special High Grade" (SHG), in which the zinc content is 0.015 wt. % higher compared to the TsOA grade zinc (Table 1).

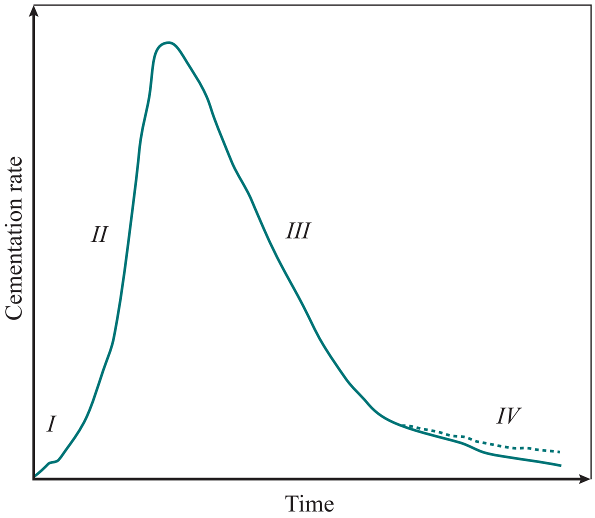
One of the main requirements for producing high-quality zinc is obtaining solutions that are deeply purified from cobalt and nickel. This becomes more challenging at facilities with high levels of organic matter, iron, and other impurities in the electrolytes, which are processed for cementation purification. The operational practices of zinc plants show that cobalt is the primary impurity in zinc solutions, and other trace impurities are highly correlated with it. In 95 cases out of 100, it can be assumed that removing cobalt from the solutions to concentrations of less than 1 mg/L reduces the other impurities to levels acceptable for electrolysis [1; 2].

Analysis of studies on the kinetics of cementation with zinc dust

As a rule, the cementation process proceeds quickly compared to corrosion and cannot be characterized by a single mechanism from start to finish. The entire cementation process, from the moment the cementing metal comes into contact with the solution to the final stage of reaction slowdown, can be divided into several distinct periods, each governed by its own laws [3].

A typical kinetic curve of the cementation process rate is presented in Fig. 1. Its form allows for the identification of four periods in the cementation process. As noted in the study [3], period *I* is observed only when passivating films are present on the surface of the metal and is associated with their removal due to dissolution upon interaction with the electrolyte. However, if the metal surface is in an active state (without passivating films) at the moment of contact with the solution, the surface activation period is absent, and cementation begins immediately after the metal is immersed in the electrolyte, i.e., without an induction period.

According to [3], the second period (*II*) is associated with the process of forming the cathodic surface, which cannot be separated from the process of its growth



Dependence of cementation rate on time
I, *II*, *III*, *IV* – periods of the cementation process

Зависимость скорости цементации от времени
I, *II*, *III*, *IV* – периоды процесса цементации

Table 1. **Chemical compositions (wt. %) of zinc grades TsOA and SHG**

Таблица 1. Химический состав (мас. %) цинка марок ЦОА и SHG

Zinc grade	Zn, not less than	Impurities, not more than					
		Pb	Cd	Fe	Cu	Sn	Al
TsOA	99.98	0.01	0.003	0.003	0.001	0.001	Not standardized
SHG	99.995	0.003	0.003	0.002	0.001	0.001	0.005

in thickness. As soon as the first crystallization centers of the reduced metal appear, the growth of the existing centers begins simultaneously with the formation of new ones.

The third period (*III*) is the main phase of the process, during which the precepitation of the reduced metal primarily grows, and the concentration of its ions in the solution decreases. The rates of side reactions during the main period can generally be neglected.

The fourth period of cementation (*IV*) is the final phase of the reaction's slowdown, which is typically accompanied by a significant increase in the role of side reactions (see the dashed line in Fig. 1). These side reactions often terminate the reduction process long before thermodynamic equilibrium is reached [3].

In the hydrometallurgical production of zinc, the neutral zinc solution (pH = 5.0÷5.2) obtained after the complete dissolution of roasted zinc concentrate in sulfuric acid undergoes cementation purification to remove copper, cadmium, nickel, cobalt, antimony, thallium, and certain uncontrolled trace impurities.

Cementation precipitation of impurity metals (Me^{Z+}) from the solution is carried out using metallic zinc. This process is based on the fact that zinc does not contaminate the zinc solution and is more electro-negative than the precipitated impurities, which is why it acts as a reducing agent for impurity cations. The impurities precipitated on the zinc during cementation form the following decreasing series in terms of cementation rate at temperatures ≤ 70 °C: Cu > Cd > Ni > Co, while Fe^{2+} does not precipitate. At temperatures above 80 °C, as noted in the literature, cadmium precipitates less than nickel and cobalt. This order is typical for the impurity concentrations encountered in zinc production.

The tasks of cementation purification of zinc solutions from impurities include the following:

— improving the degree of solution purification;

— increasing the cadmium content in the cementation precipitates (a raw material for cadmium production);

— reducing the specific consumption of the cementing agent (zinc dust).

The factors influencing the cementation process include temperature, pH level, the quantity and ratio of precipitated impurities, the mass of solid suspended particles in the initial solution, the duration of the operations, and the methods for separating the cementation precipitates from the solution [1].

The degree of cementation purification of the neutral solution effectively increases only during a limited contact time between the zinc dust and the solution (20—30 min). After that, the oxidation of the reduced cadmium begins to dominate over the precipitation of impurities, and the purification performance no longer improves, and may even worsen if "fresh" cementing agent is not added [1].

Thus, the intensification of cementation, as shown in the aforementioned studies, is achieved by the following methods:

— increasing the specific consumption and dispersity of the zinc dust;

— using activators for zinc dust;

— increasing the temperature to the optimal level;

— increasing the stirring rate of the solution;

— avoiding prolonged contact between the solution and the cementing agent.

In the initial stages of cementation purification, copper and cadmium are usually removed. Copper is relatively easily removed from the solution with a stoichiometric consumption of zinc, while complete removal of cadmium is more challenging, as its cementation precipitate can redissolve. The presence of arsenic, antimony, germanium, and oxidizers like Fe^{3+} in the zinc solution promotes the dissolution of cadmium precipitates [2].

An understanding of which metals can be precipitated from a solution via cementation with zinc can be gained by comparing the standard electrode potentials of the metals. Electrochemical theory suggests that all metals with a standard potential more positive than –0.763 V can be cemented with zinc.

Practical approaches to purifying zinc solutions from impurities that negatively impact zinc electrolysis

Based on data from the information-analytical database [1], we analyzed the technologies and purification parameters used by 32 plants worldwide for cobalt removal, considering both periodic and continuous schemes, the number of purification stages, activators, purification temperatures, and the cobalt content in the purified solutions. The majority of plants use continuous impurity removal processes, typically with two or three stages. In 22 % of the cases, α—β-naphthol is used as an alternative to zinc dust for cobalt removal. The most common temperature range for cobalt purification is 60—70 °C. The level of cobalt removal is relatively consistent, with final concentrations ranging between 0.1 and 2.0 mg/L. Common zinc dust activators include Sb_2O_3, As_2O_3, $CuSO_4$, with Schlippe's salt and potassium tartrate used less frequently.

One zinc plant implemented a two-stage purification process using zinc dust with different particle sizes: +0.063—0.25 mm in the first stage and –0.063 mm in the second. In the second stage, copper sulfate and antimony compounds were added as activators. This stage operated at a temperature of 70—90 °C. The first stage was designed to reduce copper and cadmium concentrations in the solution to less than 1 mg/L (Cu) and 7—10 mg/L (Cd), resulting in a copper-cadmium cake that could be used for cadmium production. The second stage focused on purifying the solution from nickel, cobalt, cadmium, and other impurities to meet the specifications required for SHG zinc electrolysis [1]. However, when the new scheme was introduced, challenges emerged in preparing the solutions for zinc electrolysis. The situation became more complex when the plant processed zinc concentrates and oxidized ores with high cobalt and nickel content, leading to increased levels of these metals in the zinc solutions undergoing cementation purification. This situation necessitated a more thorough investigation of the cementation process for cobalt and nickel.

It is well established [1; 2] that the most common method for purifying zinc solutions from cobalt is cementation with zinc dust, along with the addition of activators, most frequently arsenic and antimony in the form of salts, oxides, or elemental substances. Zinc dust activation is typically enhanced when antimony and arsenic are introduced into the solution along with copper ions. Some studies have demonstrated the advantages of using pentavalent antimony as an activator for the removal of Co^{2+} and Ni^{2+} at concentrations of 0.25—0.4 mg/L [4].

Zinc dust containing inclusions of lead, aluminum, copper, and antimony is also employed for the cementation of Co^{2+} and Ni^{2+} [5—7]. In one study [5], it was proposed to purify zinc sulfate solutions from impurities using zinc dust with the following composition, in %: 0.001—0.03 Al, 0.05—1.0 Pb, and occasionally 0.02—0.1 Cu. The alloy for producing zinc dust is prepared by adding lead and zinc to a zinc-aluminum alloy [5—7]. The purification process with zinc dust is conducted in two stages, following a counter-current principle. Zinc dust containing these impurities is added in excess during the second stage of cementation, where cobalt and nickel are removed from the solution. At least part of the cementation precipitate, along with excess zinc dust, is directed back to the first stage of cementation to precipitate cadmium and copper from the solution.

The authors of study [8] examined the effect of PbO and oxides formed during the first stage of the Harris process, which represents a mixture of lead and antimony oxides. Their findings showed that lead oxides in the solution promote more complete precipitation of cobalt and nickel during cementation with zinc dust. To enhance nickel precipitation efficiency, it was suggested to introduce zinc cakes, as well as lead and zinc sulfides [1]. Another study [9] proposed that in addition to antimony, the purification process could benefit from the addition of lead salts (20—100 mg/L), sulfur (100—5000 mg/L), activated carbon, bentonite, and limestone.

The Debari zinc-electrolyte plant in India was commissioned in 1967 [10], and its production capacity was expanded to 45000 tons in 1976. During this expansion, an electrolyte purification process was introduced, which involved the addition of K—Sb-tartrate to zinc dust for cementation of impurities. Initially, the zinc dust consumption was 62 kg per ton of zinc, but starting in 1977, the specific consumption steadily increased, reaching 80 kg per ton due to the declining quality of zinc sulfide raw materials. Based on studies aimed at reducing zinc dust consumption, a two-stage purification scheme was developed. The first stage involved a reduced amount of zinc dust, and the resulting copper-cadmium cake was removed from the process. In the second stage, additional zinc dust was introduced, and the cake separated by a hydrocyclone was returned to the first purification stage. The implementation of this two-stage method reduced zinc dust consumption to 35—40 kg per ton.

In study [11], a three-stage purification process is described. In the first stage, recycled zinc dust from the second and third stages is introduced, and at a temperature of 70—75 °C, copper and cadmium are completely precipitated, along with a significant portion of cobalt. The precipitate is separated in two thickeners, each 9 meters in diameter. The overflow is heated to 95 °C and sent to the second stage (a cascade of four tanks). Here, the remaining cobalt is removed by adding Sb_2O_3 powder to the first tank and zinc dust to the first, third, and fourth tanks. The excess zinc dust, together with the cobalt precipitate, is separated from the solution in hydrocyclones and returned to the first purification stage. The hydrocyclone overflow is sent to the third stage, which serves as the final purification and acts as a buffer before the solution is sent for filtration. A small amount of zinc dust is added in the third stage to prevent cobalt, cadmium, and copper from re-dissolving into the solution. The pH of the solution is maintained at 3.6—3.8 for better filterability. Filtration is carried out using filter presses with polypropylene fabric and kraft paper. The filtered solution is then sent to electrolysis.

Several studies have demonstrated the effectiveness of removing cobalt from solutions using butyl xanthate and other organic substances such as hydroxylamine, ethylenediamine, urea, and water-soluble nitroso compounds, water-soluble salts of nitroso compounds [12; 13], as well as salts of tartaric acid [14]. At the same time, it has been noted [1] that the presence of organic substances significantly slows down the cementation of cobalt due to their adsorption on the cathodic areas of the zinc metal. Therefore, the methods developed for impurity removal [15] are of practical importance not only for wastewater treatment but also for obtaining high-quality solutions for electrolysis.

It has been established [16] that the addition of nonylphenol polyethylene glycol and polyethylene glycol negatively affects the cementation of cobalt, while the addition of dinaphthylmethane-4,4-disulfonic acid does not influence the cementation process. It was shown that copper has a positive effect on cobalt cementation, whereas antimony has a negative effect. It was also noted that at a temperature of 65—85 °C, the cementation reaction of Co^{2+} proceeds in a kinetic regime and follows first-order reaction kinetics. The studied process includes two periods: an initial period (up to 4 min) and a main period (up to 10 min), which is associated with intensive hydrogen evolution.

Publications [17; 18] xplore the effect of surfactants (SAA) on the cementation of nickel using zinc powder with a particle size of 54—74 µm from solutions containing 180 mg/L of nickel and 200 mg/L of copper, respectively. Surfactant additions ranged from 15—30 mg/L. It was found that the presence of surfactants inhibits the nickel cementation process, resulting in smaller grain sizes and lower porosity of the cementation precipitates. As the temperature increases, nickel crystal size and precipitate porosity also increase.

Study [18] also investigated the effect of adding nonylphenol polyethylene glycol on cadmium cementation using zinc powder with a particle size of 54—74 µm from solutions containing 202 mg/L Cd^{2+} and 200 mg/L Cu^{2+} at a pH of 4.5. It was found that, unlike the negative effects on nickel cementation observed with all tested surfactants, the cadmium cementation process was accelerated. The rate constant for cadmium cementation in the presence of copper ($K\cdot10^3$, cm/s) decreased in the following order: from 4.2 in the presence of nonylphenol polyethylene glycol, to 3.7 (without additives), to 3.3 with the addition of polyethylene glycol, and to 2.6 in the presence of dinaphthylmethane-4,4-disulfonic acid.

The authors of study [19] noted that in organizing a continuous process for purifying solutions to permissible levels of impurities that negatively affect zinc electrolysis, the presence of surfactants in the initial solution would require an increased consumption of zinc dust to achieve the desired level of purification.

In study [20], Sb_2O_3 powder was used as an activator for cobalt cementation. Optimal conditions were determined for cobalt cementation from zinc sulfate solutions containing 150 000 mg/L $ZnSO_4$ and 24 mg/L cobalt. The Co^{2+} concentration in the solution was reduced to 1 mg/L under the following cementation conditions: zinc dust with a particle size of 120—150 µm was used at a dosage of 5 g/L; Sb_2O_3 was added at 4 mg/L; the pH of the solution was 4.5; and the temperature was 85 °C. The optimal conditions for cobalt removal with antimony (*III*) oxide were established as follows [20]: temperature of 80—85°C, Cu^{2+} concentration of 200—300 mg/L, and Sb to Co ratio of (0.5—2) : 1.

In study [21], a modified method for deep purification of zinc sulfate solutions from cobalt was described. The initial solution contained (in mg/L): 80—180 Cu, 300—450 Cd, 4—8 Co, 4—8 Ni, 5—12 Ti, and 0.1—0.15 As. Under optimal conditions—zinc powder dosage of 3.0—3.5 g/L, potassium antimony tartrate ($K(SbO)C_4H_4O_6$) at 1 mg/L, $CuSO_4$ at a minimum of 25 mg/L, pH = 4.5÷4.8, temperature of 80—85 °C, and a contact time of 3.0—3.5 h a purified solution was obtained, containing 0.1 mg/L Co, less than 0.3 mg/L Ni, and increased levels of copper (0.13—0.15 mg/L), cadmium (1.0 mg/L), and thallium (2.0 mg/L).

Study [22] investigated the conditions for purifying zinc sulfate solutions from cobalt, with zinc concentrations of 154 000 mg/L and impurities (in mg/L) as follows: Cu — 290, Cd — 610, Co — 22, Fe — 3, Ni — 6, Sb — 2. Cementation was carried out in two stages at a temperature of 70 °C, pH = 4.5, with the addition of 20 mg/L Cu^{2+}, 100 mg/L As, and 2 g/L zinc powder. In the first stage, the degree of cobalt purification reached 50 %. After the second stage, cobalt concentrations in the solution were reduced to less than 0.75 mg/L.

Research [23] investigated the impact of metal salt additives (Cu, Cd, Pb, Sb, Sn) on the kinetics of cobalt cementation using zinc powder with particle sizes ranging from 50 to 750 µm and a specific surface area of 1.74 m^2/g. The optimal conditions for cementation were identified as follows: temperature of 85 °C, and additive concentrations (in mg/L) of Cu — 15, Cd — 10, and Sb — 2. The cobalt cementation process was found to follow a first-order kinetic model, with an activation energy of 51 kJ/mol. Significant differences were noted between the cementation behavior of cobalt in industrial and synthetic solutions.

Research conducted in study [24] demonstrated that when Sb_2O_3 is added during cobalt cementation, antimony co-precipitates with cobalt, resulting in a cementation product containing a metallic CoSb compound.

Study [25] explored the cementation of cobalt using zinc powder from a solution containing (in mg/L): 13—28 Co, 3.0 Sb_2O_3, and 150 000 Zn at a pH of 5.0. The optimal cementation conditions, which reduced the cobalt concentration to less than 0.5 mg/L, were determined to be: temperature 85 °C, contact time 90 min, stirring speed of the pulp 300 rpm, and zinc powder consumption (particle size <55 μm) of 1.6 g/L.

Optimal conditions for cobalt and nickel cementation in the presence of $CuSO_4$ and $K(SbO)C_4H_2O_6$ as activators were identified in study [26]: temperature 80 °C, contact time 75 min, and zinc powder consumption of 1500 % of the stoichiometric amount, with an Sb : Co = 1. It was noted that extending the purification time beyond 75 min resulted in partial dissolution of the cementation precipitates. The absence of copper in the solution significantly affected nickel cementation, while the absence of arsenic had a lesser impact.

Study [27] highlighted the negative effect of high zinc concentrations on cobalt cementation. It was noted that at zinc concentrations greater than 50000 mg/L, only a few percent of cobalt was removed from the solution after 3 h. The cementation process was carried out on a rotating zinc disk at 90 °C, with an initial cobalt concentration of 10 mg/L, pH = 3.3, and no activators.

Study [28] examined the mechanism of cobalt removal using zinc dust with the addition of As_2O_3 and Cu in a galvanic cell with a membrane, a zinc anode, and a copper cathode. The cell design was described, and the following cathodic reactions were presented: $2H^+ + 2e^- = H_2\,(г)$, $2Co^{2+} + 2HAsO_2 + 6H^+ + 10e^- = 2CoAs + 4H_2O$. The anodic reaction was: $Zn = Zn^{2+} + 2e$. It was shown that the degree of cobalt removal increased with higher temperatures and the amount of added As_2O_3. The addition of Cu^{2+} accelerated cobalt precipitation, explained by the formation of a galvanic couple between zinc and copper. The pattern of cobalt cementation changed significantly with the addition of activators. Comparative data on cobalt cementation rates (relative units) were provided in studies [28, 29]: 1 (no additives), 1.1 (copper added), 3.0 (antimony added), 18.0 (copper + antimony added) at a temperature of 73 °C, with initial solution concentrations (in mg/L): Co — 30, Cu — 30, Sb — 1.5, and zinc dust consumption of 4 g/L, pH = 3.6.

Studies [2; 9; 30] have noted that the effect of surfactants (SAA) on cementation processes lies in their adsorption on the surface of cementation elements, creating additional resistance in the electrical circuit, which reduces the current. In macroelectrolysis, the desired current can be easily maintained by adjusting the voltage supplied to the bath, but in low-power cementation systems, overcoming this additional resistance would require selecting a galvanic couple with a high electromotive force (EMF). Ultimately, the presence of surfactants in solutions undergoing cementation leads to an increase in the time required to achieve the target residual concentration of the precipitated metal in the solutions [30—34].

An analysis of the literature shows that nearly all plants have implemented a three-stage purification scheme, which includes an intermediate stage for partially removing copper from the process. It is known that for deep purification of solutions from cobalt and nickel, increased consumption of zinc dust with a particle size of less than 55 μm is necessary, along with the mandatory addition of antimony compounds and the presence of copper in the solution. A significant reduction in zinc dust consumption was achieved at the “Zinkgruvan” plant (Kokkola, Finland) by using arsenic trioxide during the cementation stage [1]. Additionally, this plant differs from other known purification schemes in the sequence of operations: after the intermediate stage of partial copper precipitation, the first stage involves deep purification from cobalt and nickel (while at most other plants, the first stage targets copper and cadmium), and the final stage focuses on deep cadmium purification (while other facilities prioritize cobalt and nickel at this stage).

In light of the above, the present study investigated a purification scheme involving deep precipitation of cobalt and nickel in the first stage.

The aim of the study is to explore new approaches for deep cementation purification that would reduce the consumption of zinc dust and activating additives (antimony and copper compounds) in the technological process, while improving the quality of the purified solution lowering the concentrations of cobalt, nickel, and cadmium supplied in the solution used for zinc electrolysis.

Experimental

The following technology for cementation purification of industrial solutions is proposed:

Preliminary stage — cementation purification of the solutions from copper to a concentration of 90—110 mg/L ($t = 50$ °C, $\tau = 30$ min, zinc dust consumption $m = 0.2 \div 0.4$ g/L);

Stage 1 — co-precipitation of copper, cadmium, cobalt, and nickel with the addition of antimony trioxide (t = 80 °C, τ = 1 h, m = 2÷3 g/L, antimony dosage — 3—6 mg/L);

Stage 2 — deep purification of the solutions from all impurities remaining after the first stage (t = 75÷80 °C, τ = 1 h, m = 2÷3 g/L, copper sulfate dosage — 0—50 mg/L, antimony dosage — 2—3 mg/L).

The overall consumption of reagents was as follows: zinc dust — 4.2—6.4 g/L, copper sulfate dosage — 50 mg/L, antimony dosage — 5—9 mg/L. The variation in reagent consumption is due to the differing impurity content in the neutral industrial zinc solution used in the experiments.

The following starting materials were used:

— neutral industrial zinc solutions with the following average composition (in mg/L): Zn — 136 800, Co — 4.09, Cd — 562, Cu — 306, Ni — 3.85, Sb — 0.41, As — 0.35, total Fe — 91.1, Fe^{2+} — 22.9;

— antimony trioxide solution — a suspension with a solid concentration of 800 mg/L;

— copper sulfate solution;

— fine zinc dust.

During the preliminary precipitation stage, copper was cemented from zinc solutions obtained during the leaching of roasted zinc concentrate, using zinc dust (40—60 % fraction size —0.063 mm).

As a result of the preliminary precipitation, filtrates with varying copper concentrations were obtained and used in the first stage of cementation purification:

Filtrate number	1	2	3	4	5	6	7
Cu, mg/L	65	93	100	115	124	200	300

In the first stage of cementation, the starting filtrate with different residual copper concentrations (from 65 to 300 mg/L) after the preliminary precipitation was treated with antimony as a Sb$_2$O$_3$ pulp (with an Sb: (Co + Ni) ratio of 1 : 1), and zinc dust with a particle size of –0.063 mm was added for impurity precipitation (Cu, Cd, Co, and Ni) at a dosage of 2.5 g/L. Cementation at this stage was carried out at 80 °C for 1 h. The parameters (zinc dust consumption, temperature, and duration of the process) were determined through additional experiments using filtrates obtained after preliminary copper precipitation to concentrations of 90—110 mg/L. The effect of copper content in the filtrates after preliminary precipitation on the residual cadmium and cobalt content in the solution after the first stage of cementation was established:

Cu, mg/L	65	93	100	111	124	200	300
Cd, mg/L	0,12	0,13	0,15	0,25	2,6	4,8	104,5
Co, mg/L	0,26	0,21	0,22	0,27	0,30	0,35	2,62

It is clear that the cadmium and cobalt concentrations in the solution after the first stage of purification decrease as the copper content in the solution following the preliminary cementation is reduced. Thus, a preliminary conclusion can be made that to achieve acceptable levels of cadmium and cobalt for zinc electrolysis, the copper concentration in the solution after the preliminary cementation should be between 90 and 110 mg/L.

As mentioned earlier, additional experiments were conducted to establish more accurate purification conditions, determining the temperature, duration, zinc dust dosage, and activating additives. It was also proven that the preliminary stage of copper precipitation to the indicated concentrations (90—110 mg/L) is necessary. The results of the experiments are presented in Table 2.

The data in Table 2 show that increasing the temperature reduces the concentration of certain impurities in the filtrate. However, at 85 °C, after 1 h, cobalt undergoes reverse dissolution, leading to a rise in its concentration. Therefore, a temperature of 80 °C is considered optimal, as the concentrations of other impurities remain within acceptable limits at this level.

Experiments were also conducted on the cementation of impurities at the first and second stages of purification with varying zinc dust dosages (Table 3), with copper and antimony concentrations of 50 and 2 mg/L, respectively.

As seen from the data (Table 3), acceptable purification results were obtained at the first stage with zinc dust dosages ranging from 2.5 to 4.0 g/L. At the second stage, with high-quality solutions after the first stage, consistently high purification levels for cobalt and cadmium

Table 2. **Chemical analysis of solutions (mg/L) after the first stage of purification from impurities that negatively affect zinc electrolysis**

Таблица 2. Химический анализ растворов (мг/л) после 1-й стадии очистки от примесей, отрицательно влияющих на электролиз цинка

t, °C	Cd	Co	Ni
75	0.15	0.39	0.31
80	0.11	0.22	0.31
85	0.07	0.41	0.21

Table 3. **Concentration of impurities (mg/L) in the solution after purification at different zinc dust dosages (g/L)**

Таблица 3. Концентрация примесей в растворе (мг/л) после очистки при разных дозировках цинковой пыли (г/л)

Stage I				Stage II			
Zinc dust	Cd	Co	Ni	Zinc dust	Cd	Co	Ni
2.5	0.24	0.20	0.29	1.5	0.105	0.233	0.218
3.0	0.23	0.19	0.23	2.0	0.103	0.209	0.162
4.0	0.22	0.13	0.19				

Table 4. **Impurity content in the solution after purification with zinc dust when varying the dosage of activating additives at the second stage of cementation (τ = 1 h, t = 80 °C, zinc dust consumption 2.5 g/L)**

Таблица 4. Содержание примесей в растворе после очистки цинковой пылью при изменении дозировки активирующих добавок на 2-й стадии цементации (τ = 1 ч, t = 80 °С, расход цинковой пыли 2,5 г/л)

Dosage of reagents at the second stage of cementation (mg/L)		Cd, mg/L		Co, mg/L	
Cu	Sb	Solution after the first stage of cementation	Purified solution after the second stage	Solution after the first stage of cementation	Purified solution after the second stage
0	2	0.32	0.11	0.37	0.33
50	2	0.20	0.10	0.35	0.14
50	0	0.15	0.10	0.26	0.28
50	4	0.35	2.59	0.45	0.43

were achieved (at 0.2 and 0.1 mg/L, respectively) with a zinc dust dosage of 1.5 g/L.

Experiments were conducted using different reagent additives as cementation catalysts, specifically with a copper sulfate solution (50 mg/L Cu) and antimony in the form of Sb_2O_3 pulp (6—7 mg/L Sb) at the second stage of purification. The results are shown in Table 4.

The data in Table 4 show that at the second stage of cementation, the introduction of 50 mg/L copper and 2 mg/L antimony minimizes the impurity content in the purified solution. However, increasing the antimony dosage to 4 mg/L, along with the additional introduction of 50 mg/L copper ions during the second stage of purification, worsens the solution quality. In the purified solution, the cadmium content increases to 2.59 mg/L, and cobalt to 0.43 mg/L.

Table 5 provides data on the effect of cementation duration during the first stage on the quality of the obtained solution. The zinc dust consumption was 2.5 g/L. During the first stage of cementation, the solution used came from the leaching of roasted zinc concentrates without the preliminary copper precipitation stage, and its copper content was 300 mg/L.

Table 5. Cobalt and cadmium content (mg/L) at the first stage of purification with increasing process duration

Таблица 5. **Содержание кобальта и кадмия (мг/л) на 1-й стадии очистки при увеличении продолжительности процесса**

τ, min	Cd	Co
0	516	3.54
30	15.5	1.41
60	15.8	0.73
90	59.3	1.64
120	104.5	2.62

According to Table 5, the lowest impurity content is observed after 60 minutes of the first stage, while increasing the duration results in higher cadmium and cobalt concentrations, indicating their reverse dissolution. The data in Table 5 further confirm the necessity of preliminary copper cementation in the solution to a concentration of 90—110 mg/L.

Table 6 presents comparative data on cementation purification of solutions according to the known [1] and developed technologies.

Table 6. **Comparative data of the known and developed technologies**

Таблица 6. Сравнительные данные известной и разработанной технологий

№	Known technology	Developed technology
1	Partial cementation purification from copper	Preliminary stage of cementation purification from copper to a concentration of 90–110 mg/L in the solution
2	First stage of cementation – copper-cadmium purification	First stage of cementation – purification from impurities: Co, Ni, Cd, Cu, etc.
3	Second stage of cementation – purification from Co, Ni, and other cementation impurities	Second stage of cementation – deep purification from cementation impurities remaining in the filtrate after the first stage
4	Total consumption of zinc dust (particle size –0.63 mm) for the 1st and 2nd stages – 75 kg/ton	Total consumption of zinc dust (particle size –0.63 mm) for the 1st and 2nd stages – 35 kg/ton
5	Purified solution content (mg/L): Co – 0.28; Cd – 0.53; Ni – 0.31; Sb – 0.12; Cu – 0.18	Purified solution content (mg/L): Co – 0.1; Cd – 0.1; Ni – 0.2; Sb – 0.015; Cu – 0.069

Conclusions

1. A new scheme for cementation purification of zinc solutions has been proposed, which includes:

— preliminary cementation of impurities using zinc dust in solutions after the leaching stage of roasted products, reducing copper concentrations to 90—110 mg/L;

— conducting the first stage of cementation for cobalt, nickel, and other impurities using zinc dust with a particle size of –0.063 mm at 80 °C, with the addition of antimony compounds;

— carrying out the second stage of cementation for cadmium and other impurities using zinc dust with a particle size of –0.063 mm at 80 °C, with the addition of copper and antimony compounds.

2. The necessity of preliminary copper precipitation from leaching solutions to concentrations of 90—110 mg/L before the first purification stage has been experimentally proven, which significantly improves the performance of cementation purification.

3. The developed method allows for reducing the impurity content in the initial solution to the levels required for the electrolysis of high-quality SHG zinc. At the same time, the zinc dust consumption for the first and second stages can be reduced to 35 kg per ton of zinc.

References

1. Kolesnikov A.V. Research and development of processes for producing high-quality zinc from raw materials with a high content of cobalt and nickel: Diss. ... Dr. Sci. (Eng.). Ekaterinburg: UGTU–UPI, 2007. (In Russ.).
   Колесников А.В. Исследование и разработка процессов получения высококачественного цинка из сырья с повышенным содержанием кобальта и никеля: Дис. ... докт. техн. наук. Екатеринбург: УГТУ—УПИ, 2007.
2. Alkatsev M.I. Cementation processes in non-ferrous metallurgy. Moskow: Metallurgiya, 1981. 113 p. (In Russ.).
   Алкацев М.И. Процессы цементации в цветной металлургии. М.: Метал-лургия, 1981. 113 с.
3. Rotinyan A.L., Tikhonov K.I., Shoshina I.A. Theoretical electrochemistry. Leningrad: Khimiya, 1981. 424 p. (In Russ.).
   Ротинян А.Л., Тихонов К.И., Шошина И.А. Теоретическая электрохимия. Л.: Химия, 1981. 424 с.
4. Voldman G.M., Zelikman A.N. Theory of hydrometallurgical processes. Moskow: Intermet Inzhiniring, 2003. 462 p. (In Russ.).
   Вольдман Г.М., Зеликман А.Н. Теория гидрометаллургических процессов. М.: Интермет Инжиниринг, 2003. 462 с.
5. Ageenko E.I., Kolesnikov A.V., Pavlovsky D.A. Study of the kinetics of cadmium cementation in the presence of a flocculant. *Journal of the Siberian Federal University. Chemistry*. 2023;16(2):287—299. (In Russ.).
   Агеенко Е.И., Колесников А.В., Павловский Д.А. Исследование кинетики цементации кадмия в присутствии флокулянта. *Журнал Сибирского федерального университета. Химия.* 2023;16(2):287—299.
6. Danuta K. Cementation purification of industrial solutions of zinc sulfate. *Rud Imetaleniezel*.1979;24(2):65—75.
7. Quathers R. The method of purification of the electrolyte in hydrometallurgy of zinc. *Metallurgie*. 1976;16(3): 164—166.

8. Abrasheva B., Karoleva V. The influence of lead oxide on the deposition of cobalt and nickel from zinc sulfate solutions by zinc dust. Study of the conditions for using oxides of the first stage according to Harris as an activating additive. *Godishn. Institute of Nonferrous Metallurgy.* 1977;15:19—39.
9. Alkatsev V.M., Alkatseva M.I. The influence of PAA glue on the processes of cementation of copper, cadmium and cobalt. *Izvestiya. Non-Ferrous Metallurgy.* 1991;(2):119—120. (In Russ.).
   Алкацев В.М., Алкацева М.И. Влияние ПАА клея на процессы цементации меди, кадмия и кобальта. *Известия вузов. Цветная металлургия*. 1991;(2):119—120.
10. Ageenko E.I., Kolesnikov A.V., Pavlovsky D.A. Investigation of cadmium cementation kinetics in the presence of surfactants. *Bulletin of the South Ural State University. Ser. Chemistry.* 2023;15(2):107—115. (In Russ.). https://doi.org/10.14529/chem230210
    Агеенко Е.И., Колесников А.В., Павловский Д.А. Исследование кинетики цементации кадмия в присутствии ПАВ. *Вестник ЮУрГУ. Сер. Химия.* 2023;15(2):107—115.
11. Kolesnikov A.V. On the issue of cleaning solutions from cobalt with zinc dust. *Non-Ferrous Metallurgy.* 2012;(1):42—47. (In Russ.).
    Колесников А.В. К вопросу очистки растворов от кобальта цинковой пылью. *Цветная металлургия.* 2012;(1):42—47.
12. Polyakov M.L., Polyakova E.M., Polyakova O.M. Method for purifying zinc sulfate solutions from nickel and cobalt. Author's certificate 358271 (USSR). 1985. (In Russ.).
    Поляков М.Л., Полякова Е.М., Полякова О.М. Способ очистки сульфатных цинковых растворов от никеля и кобальта. Авт. св-во 358271 (СССР). 1985.
13. Kolesnikov A.V. Reduction of copper by metallic zinc in aqueous solutions in the presence of high molecular weight surfactants. *Condensed Matter and Interphases.* 2016;18(1):46—55. (In Russ.).
    Колесников А.В. Восстановление меди металлическим цинком в водных растворах в присутствии высокомолекулярных ПАВ. *Конденсированные среды и межфазные границы.* 2016;18(1):46—55.
14. Bockman O., Ostvold T. The effect of tartaric acid salts on the cementation of cobalt from a solution of zinc sulfate on a rotating zinc disk. *Hydrometallurgy.* 2000;55(1):107—112. https://doi.org/10.1016/S0304-386X(99)00079-1
15. Palant A.A., Bryukvin V.A. Purification of hydrometallurgical solutions from organic impurities. *Non-Ferrous Metals.* 2001;(1):87—89 (In Russ.).
    Палант А.А., Брюквин В.А. Очистка гидрометаллургических растворов от органических примесей. *Цветные металлы*. 2001;(1):87—89.
16. Karavasteva M. The effect of certain surfactants on the cementation of cobalt from zinc sulphate solutions by suspended zinc particles in the presence of copper or antimony. *Canadian Metallurgical Quarterly.* 2001;40(2):179—184. https://doi.org/10.1179/000844301794388416
17. Karavasteva M. Effect of surfactants on the cementation of nickel with zinc powder from zinc sulfate solutions in the presence of copper. *Canadian Metallurgical Quarterly.* 1999;38(3):207—209. https://doi.org/10.1179/cmq.1999.38.3.207
18. Karavasteva M. The influence of copper on the effect of certain surfactants during the cementation of cadmium by suspended zinc particles. *Hydrometallurgy.* 1998;48(3):361—366. https://doi.org/10.1016/S0304-386X(98)00009-7
19. Wang T., Lin G., Gu L., Hu T., Xie T., Qu H., Wang S., Zhang L., Cheng S., Liu J. Role of organics on the purification process of zinc sulfate solution and inhibition mechanism. *Materials Research Express.* 2019;6(10):106588. https://doi.org/10.1088/2053-1591/ab3dc5
20. Dai J., Wang D., Q. Jiang L., Jin M. Removal of cobalt from zinc sulfate solutions using the addition of antimony trioxide. *Transactions of Nonferrous Metals Society of China*. 2002;12(6):1172—1175.
21. Ragyavan R., Mohanan P.K., Verma S.K. Modified zinc sulphate solution purification technique to obtain low levels of cobalt for the zinc electrowinning process. *Hydrometallurgy.* 1999;51(2):187—206. https://doi.org/10.1016/S0304-386X(98)00076-0
22. Jiang L., Wang D., Dai J., Jin M., Wei X. Zinc powder consumption decrease in cobalt removal from zinc leaching solution with arsenic oxide. *Nonferrous Metals (China).* 2003;55(1):90—95.
23. Dreher T.M., Nelson A., Demopoulos G.P., Filippou D. The kinetics of cobalt removal by cementation from an industrial zinc electrolyte in the presence of Cu, Cd, Pb, Sb and Sn additives. *Hydrometallurgy.* 2001;60(2):105—116. https://doi.org/10.1016/S0304-386X(00)00152-3
24. Guo Zhang-cheng, Yan Jiang-fend, Yang Xian-wan. Mechanism of Sb_2O_3 in removal of cobalt in zinc sulfate solutions. *The Chinese Journal of Nonferrous Metals.* 2000;10(5):697—700.
25. Liu Z., Tang C., Zhang D., Guo X., Chen H. Study on the purifying processes for zinc leach solutions with antimony trioxides. *Journal of Central South University of Technology (China).* 2000;31(3):225—227.
26. Boyanov B.S., Konareva V.V., Kolev N.K. Purification of zinc sulfate solutions from cobalt and nickel through activated cementation. *Hydrometallurgy.* 2004;73(1-2):163—168. https://doi.org/10.1016/j.hydromet.2003.09.002
27. Tozawa K., Nishimura T., Akahori M., Malaga M.A. Comparison between purification processes for zinc leach

solutions with arsenic and antimony trioxides. *Hydrometallurgy.* 1992;30(1-3):445—461.
https://doi.org/10.1016/0304-386X(92)90099-L

28. Bøckman O., Østvold T., Voyiatzis G.A., Papatheodorou G.N. Raman spectroscopy of cemented cobalt on zinc substrates. *Hydrometallurgy.* 2000;55(1):93—105.
https://doi.org/10.1016/S0304-386X(99)00080-8
29. Bagaev A.S. Optimal content of copper ions and the degree of cobalt extraction during cementation cleaning of zinc solutions. *Izvestiya. Non-Ferrous Metallurgy.* 1981;(4):57—58. (In Russ.).
Багаев А.С. Оптимальное содержание ионов меди и степень извлечения кобальта при цементационной очистке цинковых растворов. *Известия вузов. Цветная металлургия*. 1981;(4):57—58.
30. Kolesnikov A.V., Tsyganova I.V. Investigation of flocculant influence on the kinetic parameters of copper recovery in aqueous solution with metal zinc. *Izvestiya. Non-Ferrous Metallurgy.* 2019;(3):4—11. (In Russ.).
https://doi.org/10.17073/0021-3438-2019-3-4-11
Колесников А.В., Цыганова И.В. Исследование влияния флокулянтов на кинетические параметры восстановления меди в водном растворе металлическим цинком. *Известия вузов. Цветная металлургия.* 2019;(3):4—11.
https://doi.org/10.17073/0021-3438-2019-3-4-11
31. Zahmati F., Shayesteh K., Vahidfard V. Removal of cadmium in process of nickel production out of cold purification waste of zinc factories. *Journal of The Institution of Engineers (India): Series D.* 2024:1—10.
https://doi.org/10.1007/s40033-023-00617-0
32. Abbasi P., Shayesteh K., Vahidfard V., Jangara H. Removal of cadmium in the cold purification step by semibatch process. *Chemical Review and Letters.* 2023;6(4): 449—460.
https://doi.org/10.22034/crl.2023.408052.1234
33. Granata G., Tsendorj U., Liu W., Tokoro C. Direct recovery of copper nanoparticles from leach pad drainage by surfactant-assisted cementation with iron powder. *Colloids and Surfaces A: Physicochemical and Engineering Aspects.* 2019;580:123719.
https://doi.org/10.1016/j.colsurfa.2019.123719
34. Kolesnikov A.V., Pratskova S.E. Theory and practice of cleaning solutions with zinc dust in hydrometallurgy. Experimental and theoretical data. Riga: Palmarium Academic Publishing, 2017. 130 p. (In Russ.).
Колесников А.В., Працкова С.Е. Теория и практика очистки растворов цинковой пылью в гидрометаллургии. Экспериментальные и теоретические данные. Рига: Palmarium Academic Publishing, 2017. 130 с.

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