Evaluation of Manganometry Method Replacement by Cementation Method to Remove of Cobalt from Zinc Sulfate Solution

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Abstract

One of the effective and important steps of the production of Zn in zinc factories is the purification step to remove the general impurities such as cobalt, nickel, and cadmium that can cause the creation of problems in the electrowinning process. In Iran's zinc factories, firstly, at the hot purification step cobalt using the manganometry method, and then at the cold purification step nickel & cadmium using the cementation method with the help of Zn powder removed. In the aim of this study is evaluated the usability of the cementation method instead of the manganometry method. In this paper, important and effective parameters such as temperature, Zn powder dosage, mixing time, amount of trioxide antimony, copper sulfate effect, particle size, zinc ions concentration, mixing speed, and pH of zinc sulfate solution were studied and optimized. The Optimal state is obtained at 85 °C, pH= 4.5, 20 mg/L Sb_2O_3 concentration, 8 g/L zinc dust, 600 rpm mixing speed in 75 minutes. Decreasing the particle size of zinc dust increased the removal efficiency, but increasing the amounts of copper sulfate and zinc ions caused decreasing in efficiency. Results showed that cobalt, nickel, and cadmium removal efficiencies for the manganomery method were 99%, 0%, and 20% and for the cementation method were 99.5%, 99.7%, and 99.9%, respectively. Also, results indicated that the cementation method due to the increase of soluble zinc concentration; not being removes of manganese ions; simultaneous removal of impurities such as cobalt, nickel, and cadmium in a single step; and saving time and cost, has a higher performance rather than to manganometry method.

Keywords

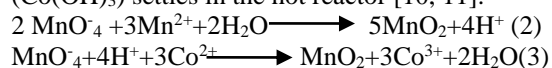Zinc Sulfate Solution; Cobalt Removal; Manganometry Method; Cementation Method; Optimization.

1. INTRODUCTION

Zinc is the fourth most widely used metal in the world and is usually produced from sphalerite, marmatite, calamine, etc. minerals by the hydrometallurgical method. The hydrometallurgical method has four main stages, including dissolution or leaching, purification, electrowinning, and production of zinc ingots. The feed of this process is zinc concentrate, which mainly contains zinc sulfide [1, 2]. In the leaching step, the zinc concentrate is dissolved in concentrated sulfuric acid and dissolved in zinc. In addition to zinc, other impurities, such as cobalt, nickel, cadmium, copper, etc., are dissolved in the leaching solution (solution obtained from the leaching process). These impurities reduce the purity of zinc deposition on the cathode in the electrowinning phase and reverse zinc dissolution by forming Zn-Ni and Zn-Co galvanic cells. They also increase the energy used to make zinc sheets due to overvoltages. For this reason, proper purification of the zinc-containing solution before electrowinning is essential [3-5]. In most zinc production units worldwide, these metal ions are usually removed from the electrolyte solution by cementatio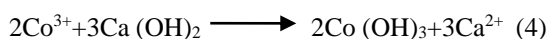n with the help of zinc powder. In this process, the removal of an interfering metal species M^{2+} is done by replacing it with metal on Zn^0 (in the form of zinc powder or zinc metal sheet) and the release of Zn^{2+} ions into the solution [6, 7].

$$Zn^0 + M^{2+} \longrightarrow Zn^{2+} + M^0 \quad (1)$$
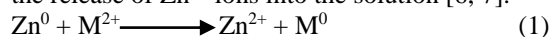
Cobalt, due to higher activation energy (86.6 kJ/mole) than other impurities such as nickel and cadmium, for proper removal, requires higher temperatures and activator ingredients such as arsenic trioxide, antimony trioxide, Potassium antimony tartrate, and copper sulfate. These activators significantly improve the driving force required to remove cobalt [8, 9]. In Iran, arsenic trioxide was initially used to remove cobalt, but due to the production of arsine gas (AsH_3), which is very toxic and deadly, and the inability of Iranian factories to properly ventilate it, the project of using arsenic trioxide Failed. Currently, in Iran, potassium permanganate is used to remove cobalt. In this method, based on the reactions, 2 to 4 permanganate ions (MnO_4^-) are used, and the cobalt (II) ion is oxidized to cobalt (III). By adding some lime, cobalt (III) as cobalt hydroxide ($Co(OH)_3$) settles in the hot reactor [10, 11].

$$2\,MnO_4^- + 3Mn^{2+} + 2H_2O \longrightarrow 5MnO_2 + 4H^+ \quad (2)$$
$$MnO_4^- + 4H^+ + 3Co^{2+} \longrightarrow MnO_2 + 3Co^{3+} + 2H_2O \quad (3)$$

$2Co^{3+}+3Ca\,(OH)_2 \longrightarrow 2Co\,(OH)_3+3Ca^{2+}$ (4)

According to the reactions performed, manganese, which is a beneficial element for the zinc electrolysis step, precipitates in the form of MnO_2 with cobalt. One of the prominent features of manganese is the formation of a layer on the lead anode which prevents corrosion of the anode. In addition to keeping the anode healthy, it also increases the purity of the produced zinc sheet [1, 10, 11]. To compensate for manganese, some manganese sulfate ($MnSO_4$) is added to the solution before the electrolysis step; Of course, its amount does not compensate for the manganese required in electrolysis. Manganese sulfate impurities also cause sludge in electrolysis cells. Due to the problems mentioned in the manganometry method, the need for further research and studies to replace more efficient methods for the cobalt Purification process in the Iranian industry instead of manganometry is fully felt. One of the largest zinc production companies in Iran is Calcimin Company. Dandy Zinc Factory, a branch of this company, is one of the largest producers of zinc ingots in Iran and the Middle East, producing 85 tons per day. This factory is located about 100 km south of Zanjan city and next to the lead factory. Most of the factory's feed is supplied from the Anguran mine, which is located 20 km from the factory [11].

Another issue that has increased the sensitivity of the purification process in the Iranian zinc industry is the presence of many impurities in the soil of the Anguran mine compared to other studies. According to Table 1, the number of impurities in different feeds in the studies compared to the Anguran mine shows that with the leaching of Anguran soil, much higher impurities enter the leaching solution [11]. On the other hand, the high concentration of cobalt in the solution makes the purification process more difficult. Also, due to the presence of disturbing ions in the solution, the acidity of the process, and the presence of hydrogen ions, the precipitation of some of the zinc powder intact, the activation of only part of the zinc powder by antimony trioxide, oxidization the some of the zinc powder in the zinc powder production process and the reaction time makes it impossible to predict the zinc powder consumption by stoichiometry; Therefore, the importance of the purification process in the Dandy Zinc Factory plant is much more severe than most zinc Factories in the world [11-14].

According to the above, the purpose of this study is to compare the practical processes of manganometry and cementation with the help of antimony trioxide in the removal of cobalt. By optimizing the parameters affecting two processes on a laboratory scale on the leaching solution of the company on Dandy, the efficiency of the two methods in removing cobalt impurities is compared with each other. Also, the advantages of the cementation method in removing cobalt and other impurities compared to manganometry are carefully examined. Finally, the feasibility of replacing the cementation method with manganometry according to the available facilities is analyzed practically. It should be noted that this research has been done in the Dandy Zinc Smelting Factory, so in all experiments performed in this research, the factory leaching solution has been used.

Table 1. Comparison of the presence of Co, Ni, and Cd impurities in different feeds

Reference	Year of publication	Type and amount of impurities (ppm)		
		Co	Ni	Cd
Guler, et al [15]	2016	4.4	12.3	13.3
Krause, et al [16]	2015	39	-	266
Zaheri [17]	2011	15	-	-
Dib, et al [4]	2006	10	1.5	-
Xu, et al [9]	2006	3.9	1.6	9.4
Dib, et al [18]	2007	2	3	4
Casaroli, et al [19]	2005	50	50	50
Boyanov, et al [20]	2004	13.8	1.1	134
Boyanov, et al [2]	2004	2.6-10	3.8	147.6
Kayin [21]	2003	75	-	-
Friedrich, et al [7]	2002	2.8	2.3	206
Bockman, et al [22]	2000	10	-	200
Raghavan, et al [23]	1999	5	4	360
Nelson [24]	1998	30	-	30
Lu, et al [25]	1997	30	-	-
Singh, et al [26]	1996	10-14	3-4	375-400
Polcaro, et al [27]	1995	10	-	-
Van der pas [28]	1995	30	-	-
Lew [29]	1994	26	-	-
Tozawa, et al [30]	1992	10	-	-
Blaser, et al [31]	1983	5-25	-	-
Present work	2019	110	167	600

2. EXPERIMENTAL

2. 1. Materials

The solution used in this work is the leach filter solution (post-filter solution) of the Dandy Zinc Factory, the chemical analysis of which is presented in Table 2.

Table 2. Chemical analysis of leaching solution

Metal species	Zn	Co	Ni	Cd	Fe	Mn
Concentration (mg/L^{-1})	85000	110	167	600	10	450

In this article, antimony trioxide in industrial grade and zinc powder with a purity of 99.5% was purchased. HELOS Particle Size device (H3050) was used to measure the distribution of zinc powder particles prepared by Zanjan Powder Company. Fig. 1 shows the granulation analysis of zinc powder.
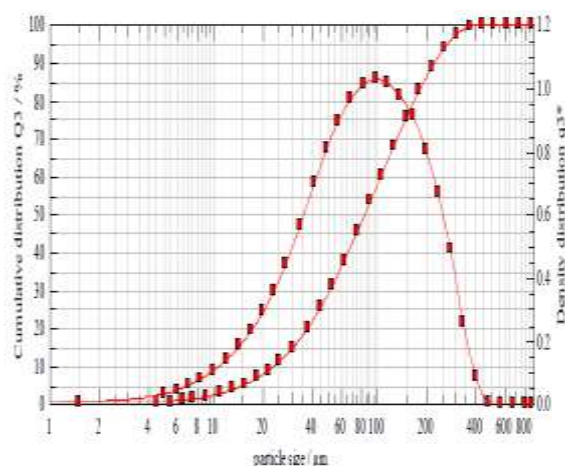

Fig. 1. Diagram of the size distribution of zinc powder used in Dandy Zinc Factory.

Distilled water twice distilled, zinc sulfate, copper sulfate, cobalt sulfate, and cadmium sulfate were used for the solution. Also, sulfuric acid 98% and sodium hydroxide from the German Merck Company were used to adjust the pH.

2. 2. Devices Used

Cementation and manganometry tests were performed in a two-liter glass reactor. A heater stirrer (Heidloph MR 3001 K) was used to create the desired temperature conditions for the experiments. The pH of the leaching solution and its temperature were adjusted by a pH meter (WTW multi 9310 model) and controlled during the experiments. Analysis and measurement of the measured metals were performed with the AA 240 atomic absorption spectrometer (Varian, Australia).

2. 3. Methods

One liter of leaching solution from the Dandy Zinc Factory heat purification unit with initial pH of 4.5 was poured into a glass reactor and heated by a heater to reach a specific temperature. The specific amounts of zinc powder and antimony trioxide (in the cementation method) and potassium permanganate and lime (in the manganometry method) were added to the solution. The mixture was mixed by stirring at a specified speed. After the processing time and proper mixing, the mixture was smoothed with ordinary filter paper. Then, the solution under the strainer was sampled, and the amounts of impurities were determined by atomic absorption spectrometry. Also, the sediment on top of the filter paper first dried utterly. Then XRF analysis was performed on the dried sediment. In this paper, the parameters of temperature, mixing time, amount of zinc powder, the concentration of antimony trioxide, mixing speed, and pH of the solution was investigated. The best conditions were determined by examining the test results. To ensure the data, each experiment was repeated three times, and their average was reported.

3. RESULT AND DISCUSSION

3. 1. Effect of temperature on cobalt removal rate

The cobalt cementation reaction follows the first-order kinetics. Therefore, cobalt concentration can be predicted by Eq. 5 [21].

$$Ln[\frac{C(t)}{C0}] = \frac{-KAt}{V} \qquad (5)$$

Where K is the reaction rate constant, which is calculated according to Eq. 6:

$$K=A/V \ e^{-\frac{Ea}{RT}} \qquad (6)$$

$C_{(t)}$ is the concentration of nickel or cadmium at any given time, C_0 is the initial concentration of nickel or cadmium, and t is the reaction time. In addition, A is the practical level of zinc powder to perform the cementation reaction, and V is the volume of the solution. E_a is the activation energy, R is the gas constant, and T is the absolute temperature. According to Equation 6, with increasing temperature, the reaction rate constant of cobalt cementation increases, leading to an increase in reaction speed. Fig. 2 shows the effect of temperature on the cobalt removal rate. As expected, the cobalt removal rate increases sharply with increasing temperature to 85° C; But then, due to the nearness of cobalt removal percent at 90 to 85° C, the slope of the curve becomes almost uniform; At 85° C, the removal rate of cobalt reaches over 99%, and further temperature increase can't have a significant effect on the removal process. Due to the high activation energy of the cobalt removal reaction, at low temperatures, fewer reactive molecules find enough energy to cross the energy barrier, which

slows down the cobalt removal cementation. According to Fig. 2, it is well known that the reaction of cobalt cementation with zinc powder at temperatures between 65° C and 80° C is much more sensitive to temperature than temperatures above 80° C. In other words, a slight change in temperature at lower temperatures causes drastic changes in velocity constant and dramatically increases the reaction rate of cobalt cementation, which is well illustrated in Fig. 2 from 65 to 80 °C. It is obvious. Then, at 80 to 85 °C, the changes in the cementation reaction rate decrease with increasing temperature, so increasing the temperature at temperatures above 85 ° C has little effect on the constant changes in rate. Although the rate of cobalt removal has reached its maximum at 90° C, due to energy and cost savings as well as the proximity of the removal percentage between 85 and 90 °C, the temperature of 85 °C was selected as the optimum temperature for removal of cobalt and was used in the rest of the work. Vanderpas et al. also studied the effect of temperature on the stock solution with an initial cobalt concentration of 30 mg/L. They obtained the optimum temperature for cobalt cementation of 85° C, and at higher temperatures, it was observed that the cobalt removal efficiency decreased. Although this decreasing trend was not observed in this study [11, 28].
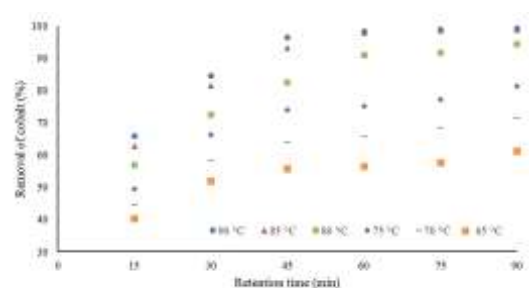

Fig. 2. Investigation of the effect of temperature on zinc removal rate; Test conditions: Mixing time 90 min, the concentration of zinc powder 8 g/L, the concentration of antimony trioxide additive 20 mg/ lit and pH=4.5.

3. 2. Effect of zinc powder on cobalt removal rate
The cementation process removes the metal impurities in the zinc sulfate solution by reducing the metal ions in the leaching solution and adhering to the surface of the zinc powder. Cobalt cementation occurs at active sites of zinc powder generated by antimony trioxide (Zn-Sb). Parameter A in Eq. 5 indicates the area of the active sites of the zinc powder surface, which is a function of time. The higher the level of available zinc powder, the more active sites are expected to form, and the better the metal impurity cementation reaction will be. The A/V parameter in Eq. 6 is the ratio of the effective surface area of

zinc powder to the volume of solution, which increases with increasing the concentration of zinc powder, and due to the constant volume, it leads to a reaction rate constant increase and ultimately increases the rate of cementation reaction. As shown in Fig. 3, increasing the concentration of zinc powder increases the amount of cobalt cementation due to the increase in active sites that can react with cobalt ions. At a concentration of 8 g/L of zinc powder, the removal of impurities reaches its maximum, and there is no need to increase the zinc powder further to remove impurities. Lew et al. determined the optimal amount of zinc powder for cobalt removal to be 4 g/L. The range of industrial consumption of zinc powder worldwide is between 4 to 6 grams per liter. The reason for the difference in the concentration of zinc powder used in this paper is the high concentration of cobalt and other impurities, such as nickel and cadmium, in the feed of Dandy Zinc Factory compared to other studies [11, 29, 32]. According to Table 1, the concentrations of cobalt, nickel, and cadmium in the leaching solution used in the study of Lou et al. were 30, 0 and 0 mg/L, respectively [25]. In contrast, the concentration of cobalt, nickel and, cadmium in the leaching solution used in this study are 110, 160 and, 600 mg/L, respectively.
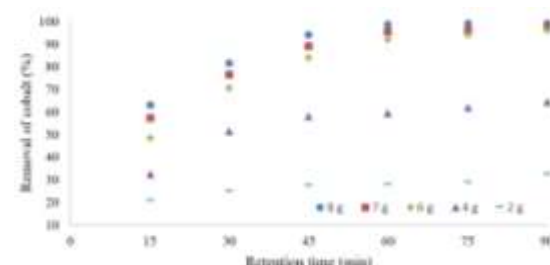

Fig. 3. Investigation of the effect of zinc powder concentration on cobalt removal rate; Test conditions: Mixing time 90 minutes, mixture temperature 85 °C, the concentration of antimony trioxide additive 20 mg/Lit and pH = 4.5)

3. 3. Effect of residence time on cobalt removal rate
The residence time of the leaching solution in the treatment reactor is an effective parameter of the removal rate. As seen in Eq. 5, time is one of the main parameters in the kinetic equation of cobalt cementation. Because the amount of contact affects the interaction of materials. According to Fig. 4, it can be seen that with increasing contact time, the amount of cobalt removal increases and reaches its maximum possible time in 75 minutes. At low contact times, due to spare time for the cementation reaction, a small amount of zinc replaced cobalt in the solution. As the residence time increases, there is enough opportunity for the cobalt ion to interact and replace the zinc ion

provided. The cobalt removal rate from the solution increases. Boyanov et al. investigated the effect of residence time at the KCM, Plovdiv Factory, which operates with an initial cobalt concentration of between 2.6 and 10 mg/L. Their work also showed that the best percentage of cobalt removal occurs in the residence time between 75 to 90 minutes [2, 11].
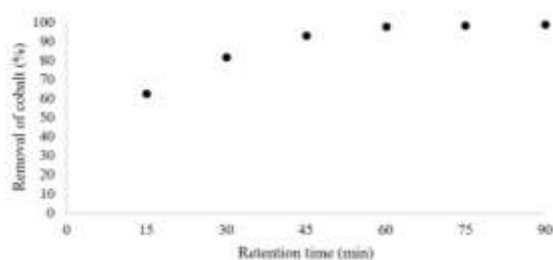

Fig. 4. Effect of contact or mixing time on cobalt removal rate; Test conditions: the concentration of zinc powder 8 g/L, mixture temperature 85 °C, the concentration of antimony trioxide additive 20 mg/L and pH 4.5)

3. 4. Effect of antimony trioxide (Sb₂O₃) additive concentration on cobalt removal rate

According to the oxidation or reduction potentials of -0.28 volts for cobalt and -0.76 volts for zinc, as well as ÄG equal to -93 Kj/mol and the equilibrium constant of $2*10^{16}$ for the cobalt cementation reaction without the presence of an activator, The removal of cobalt by zinc powder is expected to be very rapid, but despite the high thermodynamic driving force, cobalt cannot easily adhere to the zinc powder atomically; In fact, the reaction of cobalt cementation with zinc powder is In terms of thermodynamically easily performed; But kinetically this reaction progresses rapidly. According to Equations 5 and 6, two crucial factors in increasing the reaction rate of cobalt cementation are increasing the temperature and using a catalyst or an activating substance that increases the reaction rate by reducing the activation energy. In this study, antimony trioxide was used as an activator and cobalt removal aid to increase the reaction rate. As shown in Fig. 5, as the concentration of antimony trioxide increases, the reaction rate of cobalt cementation with zinc powder and the percentage of cobalt removal increase. Increasing the antimony trioxide to a concentration of 12 mg/L by forming active Zn-Sb sites,
activates the surface of zinc powder and increases the cementation rate of the reaction of cobalt with zinc; However, values higher than 12 mg/L had a much smaller effect on the cobalt cementation rate and the highest removal percentage was obtained at a concentration of 20 mg/L. It seems that from a concentration of 12 mg/L and above, the maximum

possible amount of active sites is formed on the surface of zinc powder. In most studies, the optimal concentration of antimony trioxide was determined between 1 to 3 mg/L, which due to the difference in the initial concentrations of cobalt in the feed solution of the Dandy Zinc Factory compared to other studies, a significant difference in the concentration of antimony trioxide Consumed oxide is observed [11, 28, 29, 32].
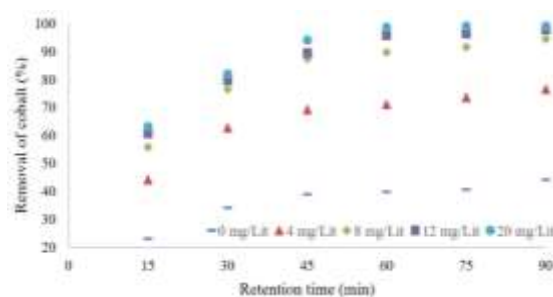

Fig. 5. Investigation of the effect of antimony trioxide concentration on cobalt removal rate, Test conditions: Mixing time 90 minutes, the concentration of zinc powder 8 g/L, mixture temperature 85 °C and pH=4.5)

3. 5. Effect of mixing speed on cobalt removal rate

Stirring or mixing speed is another parameter affecting the kinetics or speed of heterogeneous chemical reactions. Increasing the mixer speed increases the mass transfer rate and the number of effective collisions. On the other hand, cementation reactions are heterogeneous electrochemical reactions in which a cation releases a zinc cation in solution by reaching a solid surface and capturing an electron from the anode. In these electron interactions, a precipitate of an annoying cation is formed on the anode. The prerequisite for the cementation reaction is that the cobalt ions must reach the active sites of the zinc powder. Then, having enough energy, it overcomes the energy barrier and by taking electrons from zinc powder, it precipitates as an element on the surface of zinc powder. Proper mixing increases the probability of cobalt ions colliding with active zinc sites and speeds up the cobalt cementation reaction. Proper mixing also distributes the powder particles evenly in the solution and prevents them from settling, which can have a significant effect on the efficiency and duration of the reaction. As shown in Fig. 6, as the mixing increases, the cobalt removal rate also increases; However, at stirring speeds above 600 rpm, a decrease in process efficiency is observed, so that if the stirring speed reaches 700 rpm, the removal percentage decreases from about 99% to 96%. According to the changes in the removal efficiency by changing the mixing speed, it can be concluded that the mass transfer can control the reaction. Makhloufi and Dib investigated the effect

of various parameters, such as temperature and mixing speed of the solution, on the cobalt and nickel cementation rate constant simultaneously. They observed that the cobalt cementation reaction rate constantly increases significantly with increasing temperature, which is entirely consistent with the present study. While the change in the turbulence of the solution did not cause a significant change in the rate constant, on the other hand, the rate constant of the nickel cementation reaction increased with increasing turbulence. In contrast, the temperature change did not affect it [4, 18].
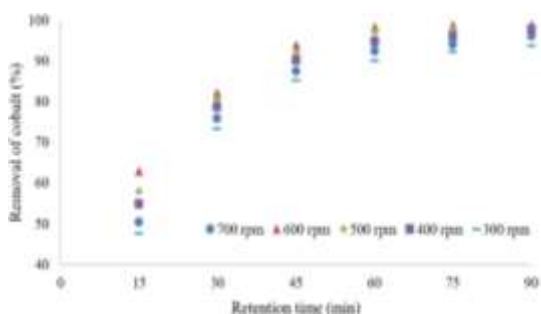

Fig. 6. Investigation of the effect of agitator speed on cobalt removal rate; Test conditions: Mixing time 90 minutes, the concentration of zinc powder 8 g/L, mixture temperature 85 °C, the concentration of antimony trioxide additive 20 mg/L and pH = 4.5.

3. 6. Effect of pH on cobalt removal rate
Thermodynamically, the pH of the solution is a critical parameter in determining the nature and stability of cementation reaction products. The optimum acidity for the cobalt cementation process should be such as to minimize the hydrogen reversibility and the formation of zinc-based compounds ($Zn(OH)_2$, $ZnSO_4$, …) [28]. As shown in Fig. 7, the highest cobalt removal rate was obtained at pH=4.5. At higher pH, cobalt removal decreases due to the formation of zinc hydroxide and zinc sulfate based on the surface of zinc powder and the inactivation of active sites on the surface of zinc powder. Also, in amounts lower than 4.5, more zinc powder reacts with hydrogen and is consumed. For this reason, the available surface area for the cobalt cementation reaction is reduced, which leads to a decrease in the cementation reaction efficiency and a greater risk of cobalt sediment reversibility; Therefore, pH = 4.5 was selected and used as the optimal value. According to a study by Raghavan et al., PH plays an essential role in bringing cobalt to deficient levels. They reported that if the pH <5, the formation of sulfate on the base inactivates the active sites of the zinc powder and reduces the efficiency of the reaction. Also, at pH values below 4, zinc powder consumption increases. Their results showed that the highest removal was performed at pH = 4.5 [23].
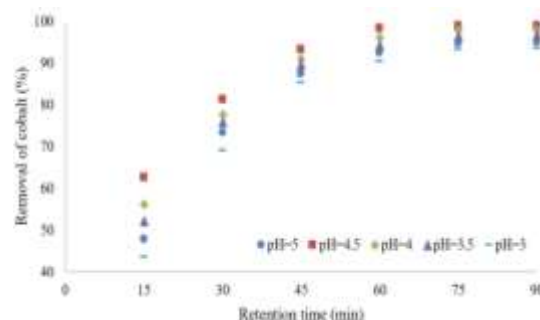

Fig. 7. Investigation of the effect of pH on cobalt removal rate; Test conditions: Mixing time 90 minutes, the concentration of zinc powder 8 g/L, mixture temperature 85 °C, the concentration of antimony trioxide additive concentration 20 mg/L).

3. 7. Effect of zinc ions
In this section, the effect of zinc ion concentration (Zn^{2+}) on cobalt removal is investigated. As shown in Fig. 8, as the concentration of zinc ions in the solution increases, the cobalt removal rate decreases. The results show that the best removal efficiency is obtained when the cobalt cementation reaction is performed without the presence of zinc ions in the solution. By adding zinc ions to the solution up to a concentration of 30 g/L, the cobalt removal efficiency is significantly reduced, which indicates that even low concentrations of zinc ions have a significant effect on reducing the reaction rate of cobalt cementation. The results also show that without the presence of zinc ions in the solution, cobalt ions are easily removed by zinc powder and even without the need for antioxidant trioxide. Therefore, it is clear that the main factor in slowing down the removal of cobalt is the presence of zinc ions. Zinc ions appear to inhibit the movement of cobalt ions in the solution toward the zinc powder and make it difficult for the cobalt ions in the solution to reach the surface of the zinc powder. In a study conducted by Nelson on cobalt cementation in zinc sulfate solution, the efficiency of the cobalt cementation process decreased with increasing Zn^{2+} concentration, which confirms the present study [11, 24].
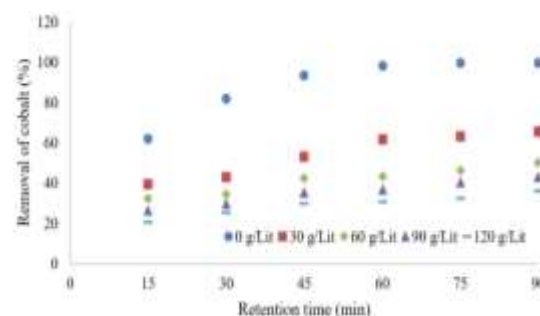

Fig. 8. Investigation of the effect of zinc ions on cobalt removal; Test conditions: mixing time 90 minutes, the concentration of zinc powder 8 g/L, mixture temperature 85 °C, the concentration of antimony trioxide additive concentration 20 mg/L and pH=4.5)

3. 8. Particle size effect

Particle size is another crucial influential parameter considered in this research. Fig. 9 shows the effect of zinc powder particle size on cobalt removal by the cementation method. As shown in Fig. 9, the cobalt cementation reaction rate increases sharply as the particle size decreases. For the cobalt cementation reaction, by reducing the particle size from 100 mesh upwards, the cobalt cementation rate increases sharply, then the slope of the diagram decreases. In this paper, with the help of a system consisting of shakers with columns of sieves with the mesh of 50, 100, 170, 200, 325, and 325, zinc powder was granulated, and to investigate the effect of size, some zinc powder was prepared from each mesh. To perform the cobalt cementation reaction, the metal ions must reach the surface of the zinc powder and be cemented by electron capture. Therefore, increasing the level of zinc powder available for the reaction increases the rate of cobalt cementation. There are usually two ways to increase the effective surface of the reaction. The first method is to increase the zinc powder, and the other method is to reduce the particle size used. Increasing zinc powder is not a suitable method due to rising production costs. However, the use of smaller particles, in addition to speeding up the reaction, also reduces the consumption of zinc powder and, in other words, reduces costs. In a study by Krause, the results showed that zinc powder with finer particles had a much more significant effect on the removal of cobalt and nickel than copper and cadmium, which confirms the present study [11, 33, 37].
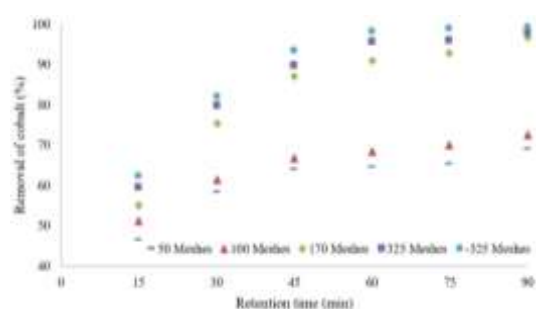

Fig. 9. The effect of particle size on the removal of cobalt by the cementation method; Test conditions: mixing time 90 minutes, the concentration of zinc 8 g/L, mixture temperature 85 °C, the concentration of antimony trioxide additive 20 mg/L and pH=4.5)

3. 9. Effect of adding copper sulfate

In the zinc industry around the world, most mills typically use zinc powder and copper sulfate to remove cobalt impurities in a hot purification reactor. By forming a Cu-Zn alloy, copper is expected to create more active sites for the cobalt cementation reaction and facilitate electron transfer between cobalt and zinc powder. Fig. 10 shows the effect of different amounts of copper on the cobalt cementation reaction efficiency. According to the figure, with increasing the concentration of copper in the solution, the amount of cobalt removal decreases sharply. Studies by Zheng et al. And Yang et al. The removal of cobalt showed that Cd-Zn and Cd-Co alloys are formed in the presence of cadmium, which means that copper sulfate has little effect on the efficiency of the cobalt cementation process. [11, 34, 35]. Copper sulfate can also reduce cobalt deposition and precipitate itself as an element that can harm cobalt removal. The results of this study were confirmed by Zeng et al. And Yang et al. For cobalt. Fig. 11 shows the effect of copper on cobalt cementation without the presence of cadmium ions in the solution [34, 35]. According to Fig 11, it is observed that with increasing copper concentration, the cobalt cementation reaction efficiency increases. Initially, when cadmium and copper are not present in the solution, the removal of cobalt is low. Without the addition of additives, it seems that under no circumstances can it reach the desired concentration for electrowinning of zinc, but by adding 100 mg/L of copper sulfate is observed to cause a significant increase in cobalt removal efficiency. At the concentration of 200 mg/L of copper, the percentage of cobalt removal reaches nearly 99%, and with increasing the concentration of copper sulfate to 600 mg/L, the percentage of cobalt removal reaches 99.5%. This indicates the positive effect of copper sulfate additive on cobalt cementation reaction. Fig. 11 shows well that when cadmium is not present in the solution, the addition of copper is necessary for cobalt cementation. Its catalytic effect significantly increases the cobalt removal efficiency. When cadmium is present in the solution, the addition of copper to the solution causes competition between cadmium and copper to obtain electrons from the zinc powder, and consuming large amounts of zinc powder can even harm process efficiency [11, 34].
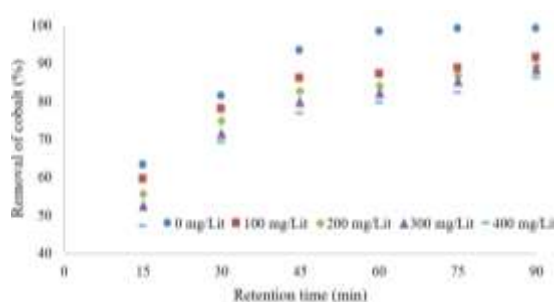

Fig. 10. Effect of copper sulfate on cobalt removal; Test conditions: mixing time 90 minutes, the concentration of zinc 8 g/L, mixture temperature 85 °C, the concentration of antimony trioxide additive 20 mg/L and pH=4.5).

Fig. 11. Effect of copper sulfate without cadmium in solution; Test conditions: mixing time 90 minutes, the concentration of zinc 8 g/L, mixture temperature 85 °C, the concentration of antimony trioxide additive 20 mg/L and pH=4.5)
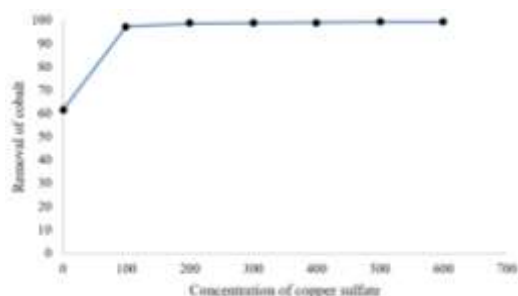
3. 10. Comparison of the efficiency of the cementation method with manganometry method in removing impurities

As stated in the study, all experiments were performed on the leaching solution of Dandy Zinc Factory. Due to the presence of essential elements in the leaching solution, optimization results were presented based on the maximum removal of cobalt. Also, the two processes of cementation and manganometry were optimized in laboratory conditions, which were compared in Table 3 of the optimal conditions of the two processes.

According to Table 3, the manganometry method removes only cobalt impurities, while in the cementation method with zinc powder, in addition to cobalt, nickel and cadmium are also removed. In fact, with the results of this study, it can be hoped that instead of the cold and hot treatment stage in the current production line, the concentration of impurities in the same hot treatment will reach the desired level for electrolysis. This saves much money, such as reducing the cost of purchasing permanganate and manganese sulfate, time, and energy. In addition, in the cementation method, zinc powder is dissolved in the form of Zn^{2+} ions according to reaction 1 in the leaching solution, which increases the concentration of zinc in the solution. The results show that the concentration of zinc increases after cementation. (Zinc concentration changed from 85000 mg/L to 90390 mg/L after the cementation process, which was concentrated at about 5390 mg/L), which is converted back to a zinc sheet during the electrolysis step. In other words, in cementation, it succeeds in removing impurities, and the powder is recovered on consumption. Another feature of

the cementation method is that due to the concentration of zinc ions in the solution, it is possible to produce zinc sheets from a lower grade feed, which is due to the reduction of zinc grade in the feed during recent years have been very important. Also, since manganese is a valuable element for the electrolysis process and can protect the anode in an acidic environment; Therefore, in the manganometry method, due to the removal of manganese ion, its concentration reached less than 10 mg/L, which needs to be added to the make-up solution before the electrolysis process of manganese sulfate to reach the standard concentration of manganese but, this increases the cost of production; But in the cementation method, the manganese concentration remains intact; Therefore, it is not necessary to add manganese sulfate before electrolysis. In the manganometry method for cobalt deposition, some lime must be added to the leaching solution because after converting cobalt ion (II) to cobalt (III) by potassium permanganate, to convert cobalt hydroxide ($Co(OH)_3$), it is necessary to add It is lime. However, in the cementation method, there is no need to add lime at this stage, and the removal operation can be performed at the same pH of the leach filter solution, which was 4.5. Not adding lime in the cementation method also reduces production costs. Many of these points are mentioned in the articles of the authors of this article [11-14, 36-38].

3. 11. XRF fluorescence investigations

The results of sediment analysis for manganometry and cementation methods are given in Table 4. As can be seen, the high amounts of nickel, cadmium, and cobalt in the sedimentation of the cementation method indicate the simultaneous removal of all three impurities in one step. However, with the analysis of sediment in the manganometry method, only the amount of cobalt is high and the amounts of nickel and cadmium are meager. Also, the percentage of manganese in cementation sediment is tiny (about 500 mg/L), while the amount of manganese in manganometry sediment is 82000 mg/L, which indicates high removal of manganese from the leaching solution by manganometry method. Analysis of sediments obtained from cementation and manganometry methods also shows the superiority of the cementation method over manganometry method in removing cobalt, nickel, and cadmium [11].

Table 3. Comparison of the efficiency of cementation methods with manganometry method in removing impurities in make-up

Metal ions in solution	Fe^{2+}	Mn^{2+}	Cd^{2+}	Ni^{2+}	Co^{2+}	Zn^{2+}
Initial concentration of elements (mg/L)	10	480	600	167	110	85000
Concentration of elements after removal by manganometry (mg/L)	1	8	480	167	1.1	85000
Concentration of elements after removal by cementation method (mg/L)	0.1<	480	0.6	0.49	0.57	90390

Table 4. Results of sediment analysis for cementation and manganometry methods

Elements	Sb	Pb	Cu	MnO	Cd	Ni	Co
Cement sediment (mg/L)	1069	7200	587	500	33100	12000	6922
Manganometric sediment (mg/L)	34.6	1500	327	82000	1900	600	6262

3. 12. Possibility of replacing the cementation method with manganometry

To perform the cementation process in the Dandy factory production line, there is no need to change the factory production line, and no special equipment and tools are required. In addition, in the hot purification section, potassium permanganate and lime are removed, and by converting two steps into one step, more production is possible. Because manganese is not removed in the cementation process, the addition of manganese sulfate does not occur in the electrolysis section. In terms of economics, due to the removal of potassium permanganate and lime in hot purification as well as manganese sulfate in electrolysis, reducing the processing time, eliminating the cold purification step, and increasing the life of anodes, the cementation process is much more efficient than manganometry. It should be noted that the primary material required for the cementation process is zinc powder, which is produced from factory waste. Also, in the cementation process, a large amount of zinc powder is recovered and returned to the system as a solution. Also, the amount of industrial antimony trioxide used is meager, which will not cost much to prepare. Therefore, the cementation process in the Dandy Zinc Factory is feasible, and in addition to the ability to increase production according to available facilities, production costs are significantly reduced.

CONCLUSION

In this paper, the parameters affecting the cobalt cementation process were investigated and optimized. Optimal parameters were obtained at pH = 4.5, temperature 85 °C, the concentration of 12 mg/L antimony trioxide, zinc powder 8 g/L, and residence time of 75 minutes. During these conditions, cobalt decreased from the initial concentration of 110 mg/L to the secondary concentration of 0.75 mg/L, which removed 99.5% of the primary cobalt during the cementation process. Also, with increasing the concentration of zinc ions and copper sulfate additive, the reaction efficiency decreased; but reducing the particle size increased the reaction rate. It is clear that due to the advantages of the cementation method, replacing it with the manganometry method in the hydrometallurgical process of zinc production has dramatically reduced costs and energy consumption and is a more efficient and cost-effective method to remove metal impurities from

zinc sulfate solution. Also, in terms of time, the process of general purification of zinc, due to the integration of two stages (hot and cold) in one stage, can be done simultaneously faster and in less time, which is another advantage of the cementation method. The use of antimony trioxide as an additive in small amounts significantly removes cobalt. Antimony trioxide has no environmentally destructive effect due to its use in small amounts. In terms of economics, due to the removal of potassium permanganate and lime in hot purification as well as manganese sulfate in electrolysis, reducing the processing time, eliminating the cold purification step, and increasing the life of anodes, it is more economical than the manganometry method. Therefore, investigations on a laboratory scale showed that the cementation method can be used instead of the manganometry method for the purification of cobalt impurity in Iran's zinc production industries.

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ارزیابی جایگزینی روش منگانومتری با روش سمنتاسیون برای حذف کبالت از محلول سولفات‌روی

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چکیده

یکی از مراحل موثر و مهم تولید روی در کارخانجات روی، مرحله تصفیه برای حذف ناخالصی های متداول مانند کبالت، نیکل و کادمیم است که می تواند در فرآیند الکتروووینینگ باعث ایجاد مشکل شود. در کارخانجات روی ایران، ابتدا در مرحله تصفیه گرم کبالت به روش منگانومتری و سپس در مرحله تصفیه سرد، نیکل و کادمیم به روش سمنتاسیون با کمک پودر روی، حذف می شود. هدف از این مطالعه، بررسی قابلیت استفاده از روش سمنتاسیون به جای روش منگانومتری است. در این مقاله، پارامترهای مهم و موثر مانند دما، مقدار پودر روی، زمان اختلاط، مقدار آنتیموان تری اکسید، اثر سولفات مس، اندازه ذرات، غلظت یون روی، سرعت اختلاط و pH محلول سولفات روی مورد مطالعه و بهینه سازی قرار گرفت. حالت بهینه در دمای ۸۵ درجه سانتی گراد، غلظت ۲۰ میلی گرم در لیتر Sb₂O₃، ۸ گرم در لیتر پودر روی، سرعت اختلاط ۶۰۰ دور در دقیقه، در ۷۵ دقیقه به دست آمد. کاهش اندازه ذرات پودر روی راندمان حذف را افزایش داد؛ اما افزایش غلظت سولفات مس و یون روی باعث کاهش راندمان شد. نتایج نشان داد که راندمان حذف کبالت، نیکل و کادمیم برای روش منگانومتری به ترتیب برابر ۹۹، ۰، و ۲۰ درصد و برای روش سمنتاسیون به ترتیب ۹۹/۵، ۹۹/۷ و ۹/ ۹۹ درصد بود. همچنین نتایج نشان داد که روش سمنتاسیون به دلیل افزایش غلظت یون روی محلول، عدم حذف یون منگنز، حذف همزمان ناخالصی هایی مانند کبالت، نیکل و کادمیم در یک مرحله و صرفه جویی در زمان و هزینه، عملکرد بهتری نسبت به روش منگانومتری دارد.

واژه‌های کلیدی

محلول سولفات روی، حذف کبالت، روش منگانومتری، روش سمنتاسیون، بهینه سازی.