Iranian Journal of Chemical Engineering

Journal Homepage: www.ijche.com

pISSN: 1735-5397
eISSN: 2008-2355

Regular Article

Effect of the Particle Size of Zinc Powder on the Efficiency of the Cementation of Ni-Cd in the Cold Purification Reactor

P. Abbasi, K. Shayesteh*, V. VahidFard, M.-J. Khani

Department of Chemical Engineering, University of Mohaghegh Ardabili, Ardabil, Iran.

ARTICLE INFO

Article history:
Received: 2023-02-03
Accepted: 2023-11-30
Available online: 2023-12-31

Keywords:
Zinc powder size,
Ni-Cd removal,
Cementation,
Cold purification,
Zinc manufacturing process

ABSTRACT

The cementation reaction of Ni-Cd occurs on the surface of zinc powder, and the Ni-Cd ions in the zinc sulfate solution (make-up) change into a solid metal deposit during the process. The primary purpose of this study is to evaluate the effect of the particle size of zinc powder on the operational parameters of cementation, such as the quantity of the zinc powder used, the reaction temperature, and the contact time. These parameters are influential on cost reduction as well as the manufacturing rate of zinc ingot. Results indicated that providing that the zinc powder, -325 mesh, is used, the consumption of zinc powder used in the industry can be reduced by an average of 40%. It was also confirmed that the best times for the cementation of Ni-Cd for all studied sizes were 75 and 60 minutes respectively. The Ni and Ca were removed in -325 mesh to the optimal values at 85℃ and 65℃ respectively. By optimizing the evaluated parameters, the concentrations of Ni and Cd impurities were obtained at the lowest possible and acceptable levels for transferring the make-up solution to the electrolysis stage.

DOI: 10.22034/ijche.2023.384387.1477 URL: https://www.ijche.com/article_186543.html

1. Introduction

Pure zinc metal is manufactured by converting the zinc sulfide concentrate into zinc oxide. The steps include leaching with sulfuric acid, the purification of the leach solution, and finally, electrowinning of zinc from the refined zinc sulfate solution. The leaching process usually consists of an acid leach and a neutral leach in which impurities, such as iron, germanium, silica, etc., are dissolved and removed [1, 2]. The resulting leach solution must still be suitable for the electrowinning stage because some impurities, such as nickel, cadmium, and cobalt, remain in the leach solution. Importing these impurities into the electrowinning stage makes the resulting zinc sheet impure. It causes an increase in the electricity consumption, a decrease in the anode life, and a hole in the zinc sheet [3, 4]. As a result, these impurities are removed from

*Corresponding author: k.shayesteh@uma.ac.ir (K. Shayesteh)

the system in two hot and cold purification stages before the electrowinning stage. In zinc manufacturing factories in Iran, the hot purification process uses potassium permanganate and lime to precipitate the cobalt impurities, while in cold purification, nickel and cadmium pollutants are precipitated by cementation with zinc powder, and they are removed from the system through filtration [5-7].

Cementation means removing or reducing the number of elements of which the chemical potential is higher than the chemical potential of zinc; the removal method is shown in reaction 1 [7-9].

$$Zn^0 + M^{2+} \longrightarrow Zn^{2+} + M^0 \quad (1)$$

In other words, the mechanism of the Ni-Cd cementation process involves the galvanic corrosion of the anodic and cathodic reactions on the active sites of the zinc powder surface. This means that zinc metal tends to oxidize and release electrons spontaneously. Nickel and cadmium ions also tend to receive the electrons emitted from zinc and to be reduced [9, 10]. Therefore, if the mixing process is performed well, nickel and cadmium metal ions will reach the zinc surface and become neutral by taking electrons from the zinc powder and gradually depositing them. The zinc powder becomes a Zn^{2+} ion and disappears. Therefore, the finer the used zinc powder particles, by creating a larger surface per unit mass of zinc powder, the higher the nickel and cadmium cementation rate will be [11, 12]. The Ni-Cd cementation reaction follows the first-order kinetics. Consequently, the concentrations of Ni-Cd can be predicted from equation 2.

$$\mathrm{Ln}\left[\frac{C(t)}{C0}\right] = \frac{-KAt}{V} \quad (2)$$

$$K = A/V\, e^{-\frac{Ea}{RT}} \quad (3)$$

K is the reaction rate constant calculated according to equation (3). C(t) is the concentration of nickel or cadmium at any time, C_0 is the initial concentration of nickel or cadmium, and t is the reaction time. Furthermore, A is the surface of the zinc powder, and V is the volume of the solution. Ea is the activation energy, R is the gas constant, and T is the absolute temperature. [13].

From equations 2 and 3, it can be concluded that to achieve specific concentrations of nickel and cadmium, the process must be performed at a lower time and temperature as the surface increases. Therefore, studying and investigating the effect of the particle size of the zinc powder used in the Ni-Cd cementation in the cold purification stage can confirm or reject the claim that it affects the efficiency of the process [13].

It can be expected that the cementation reaction develops further by using finer particles of zinc powder; this, in addition to increasing the concentration of Zn^{2+} cations in the solution, will also improve the process efficiency of the removal of Ni-Cd. Another advantage of the small size of zinc powder is the low rate of the deposition of zinc powder. The sedimentation rate will also increase with an increase in the size or diameter of the zinc particles. Hence, coarser particles are expected to appear more intact in the sediment, increasing the consumption of zinc powder. One of the disadvantages of using finer zinc powder is the reversibility of the sedimentation of impurities in the solution, which can reduce the removal efficiency. Bockman et al. reported the more significant reversibility of cobalt when less than 36 µm zinc powder is used. Notably, the size of coarse zinc powder is usually between 100-200 µm, while the size of fine zinc powder is between 15-40 µm. The industrial powders used worldwide to remove nickel and cadmium usually vary from 50 to 75 µm in size with an average surface area of 1.74 g/m^2 [14-18].

From another perspective, cementation reactions are heterogeneous electrochemical reactions where the cation has the zinc cation released in the solution after reaching the solid surface and taking an electron from the anode; in these electron interactions, a deposit of interfering cations is formed on the anode [13]. Fig. 1 illustrates the mechanism of the cementation metal impurities by zinc powder [8].

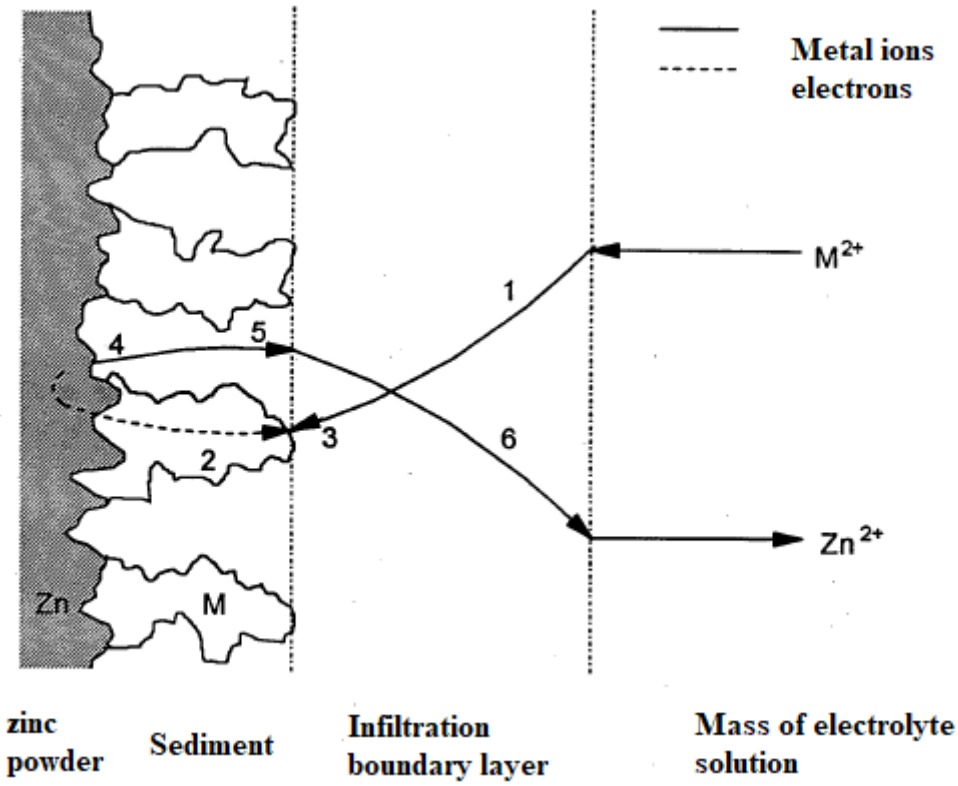

Figure 1. Reaction stages for the cementation of metal impurities by zinc powder [19].

According to Fig 1, The steps of the cementation reaction are as follows.

1- Transfer of M^{2+} metal ions from the mass of the solution to the metal-solution interface through the boundary layer of liquid; 2- Conduction of electrons from the dissolved anodic zinc to the cathodic sites through the adhesion of sediments to each other and the transfer of electrons;

3- Dehydration of metal deposit M and the formation of a crystal network through the connection of atoms of metal deposit M;

4- Diffusion of Zn^{2+} ions from anodic sites and hydration;

5- Transfer of Zn^{2+} ions to the solution through the sediment layer;

6- Transfer of Zn^{2+} ions to the mass of the solution through the boundary layer of the liquid [19].

The kinetic model proposed for the cementation reaction of metal impurities in the zinc sulfate solution is a shrinking core model confirmed by Zhang et al., Younesi et al., Pal et al., Karavasteva, and Zakeri. As you can see in Fig. 2, the reaction first occurs on the outer surface of the zinc powder core in this model. Then, the zinc powder core reacts with metal impurities over time, forming a layer of metal impurities on the zinc powder core. As more time passes, the formed layers become denser and denser, and the zinc powder core becomes finer and finer [8, 20-23].

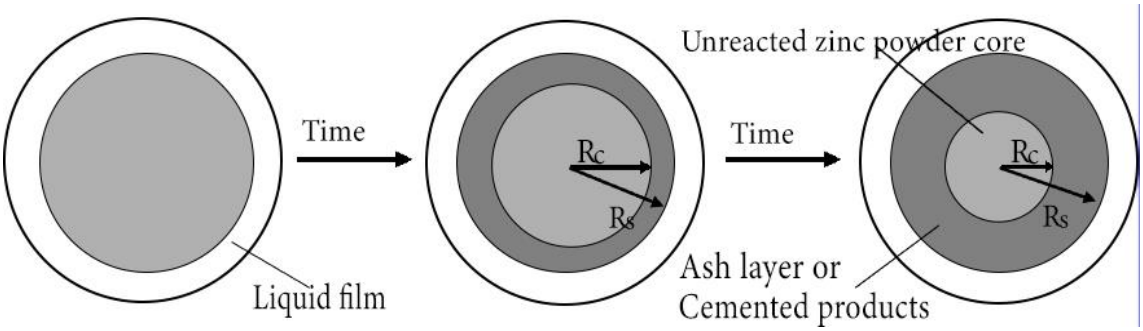

Figure 2. Schematic presentation of the shrinking core model [8].

However, Vahid Fard stated that the nickel and cadmium cementation mechanism cannot follow the shrinking core model. Figures 3, a and b show that due to the cementation of nickel, cobalt, and cadmium, the smooth surface of the powder becomes scaly. According to Figure 3, the cemented metals are observed on the surface of the zinc powder, and the zinc powder is flaked. This is versus the shrinking core model [17].

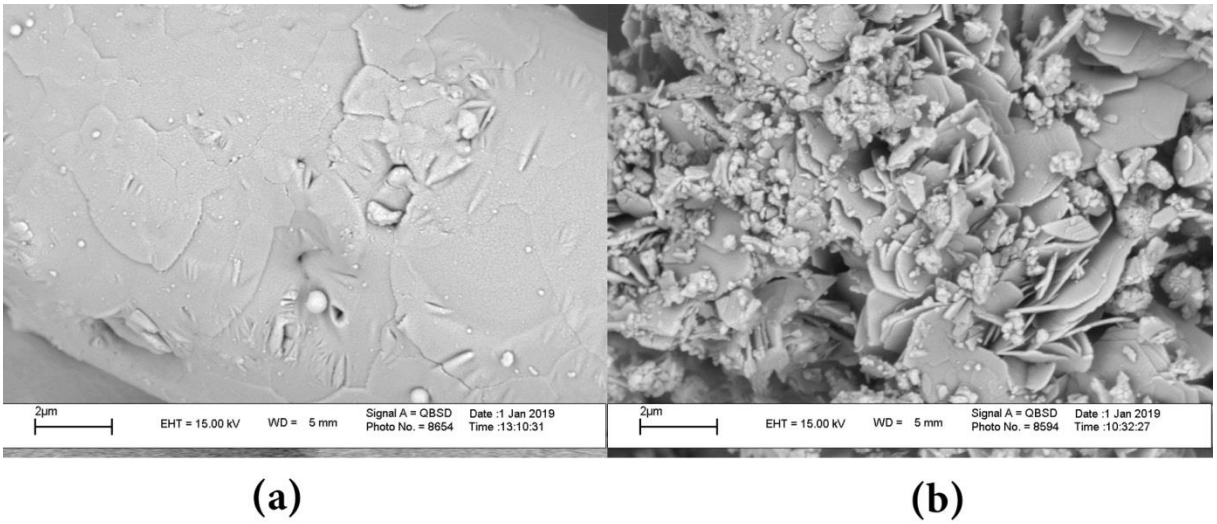

Figure 3. Morphology of the zinc powder surface (a before cementation (b after cementation [17].

With the increased reaction time, the cementation becomes more difficult because of the formation of a deposit of disturbing cations, i.e., nickel and cadmium, on the zinc powder. Therefore, the cementation rate is expected to increase by a size reduction of zinc powder and an increase in the contact surface between the solution and zinc powder [13, 17]. In this article, the effect of the particle size of the zinc powder on the efficiency of the Ni-Cd cementation process is studied. The main objective of this article is to evaluate the effect of the size of zinc powder on the operational parameters of the cementation process, such as the quantity of the consumed zinc powder, the reaction temperature, and the contact time, or, in other words, the time of the cementation reaction. Therefore, specific sizes of zinc powder were provided by granulating the used zinc powder with a shaker and a sieve column. The tests were conducted on the leach solution of Dandi plant of Calcimin Company. Therefore, the achieved results are expected to be applied in other Iranian zinc plants than Dandi zinc plant.

2. Experimental

2.1. Materials

The studied solution was the feed of the cold refinery unit of Dandi Zinc Smelting Plant (Calcimin Company). The chemical analysis of the feed and a sample of the purified solution in a cold treatment reactor is presented in Table 1.

Table 1
Chemical analysis of the feed and product.

Metal	Zn	Co	Ni	Cd	Fe	Mn
Feed (mg/L)	83400	1.1	170	480	1	8
Product (g/L)	85100	0.9	1.5	1.3	<0.1	<0.1

In this article, industrial-grade zinc powder was purchased. A sieve analysis of the zinc powder was also conducted with ashaker and a sieve column. Two-time distilled water was used for solving and diluting. Sulfuric acid and Merck sodium hydroxide were also used to adjust the pH.

2.2. The tools applied

All experiments were conducted in a glass reactor with a 2-liter volume. The optimal temperature conditions to conduct the experiments were provided by a heater-stirrer (Heidolph MR 3001 K). The initial pH of the make-up solution was adjusted by a pH meter (WTW multi 9310 model). Also, the temprature was controlled during the experiments by a glass thermometer. This research analyzed and measured the metals by an atomic absorption spectrometer model AA 240 (Varian, Australia). A particle size device with the HELOS (H3050) model was also applied to measure the distribution of zinc powder particles provided by Zanjan Powder Company. A Sieve model (DAMAVAND-ASTM E:11) with different meshes was used for granulating the zinc powder.

2.3. Methodology of the experiment

First, using a sieve, some of the zinc powder was granulated into 100, 170, 200, +325 and -325 meshes. Then, one liter of the input solution of the cold purification stage in Dandi zinc plant with an initial pH of 5 was poured into a glass reactor and heated by a heater to reach the process temperature. Then, specific quantities of zinc powder with certain particle sizes were added to the solution and mixed with a stirrer as required. After the reaction time, the mixture was filtered with a vacuum pump using the filtration process. Then, the filtered solution was sampled, and the number of metal ions was determined with the atomic absorption device. Influential parameters such as the particle size of the zinc powder, temperature, contact time, stirring rate, and quantity of the used zinc powder were evaluated. It is worth noting that the permissible limit for the electrolysis stage is achieved when the concentration of Cd-Ni reaches below 1.1 mg/L. To ensure the accuracy of data and the reproducibility of the experiments, each experiment was repeated three times, and the average was reported.

3. Results and Discussion

3.1. Effect of the particle size of the zinc powder on the removal rate of Cd-Ni

First, the zinc powder provided by Zanjan Powder Company was analyzed with a particle size analyzer. Fig. (4) illustrates the distribution of particle sizes of the zinc powder.

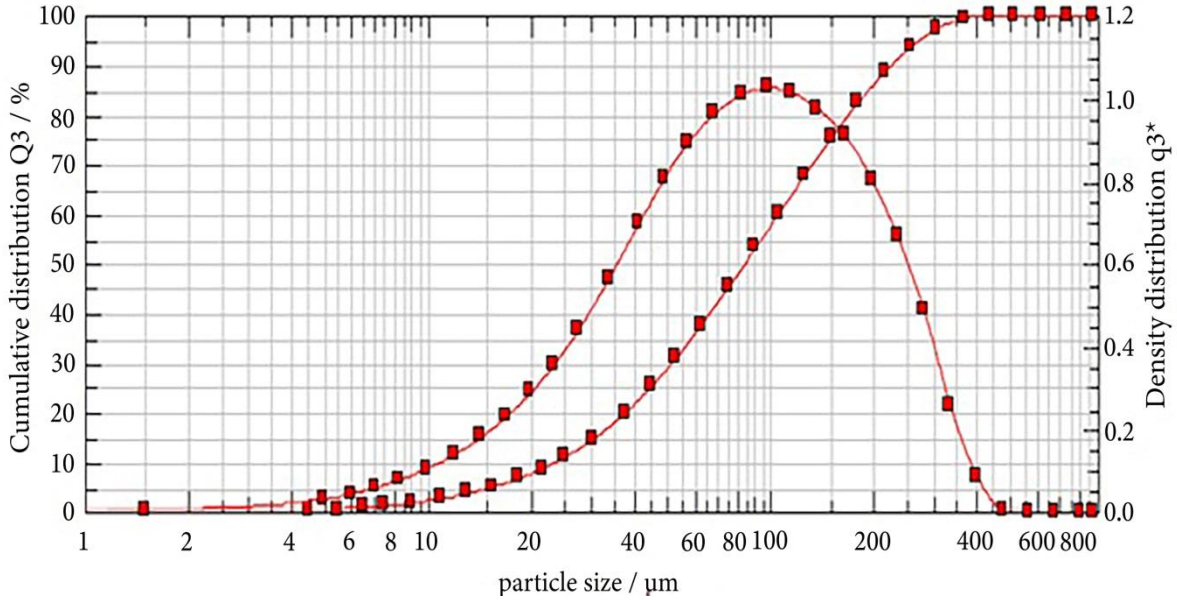

Figure 4. Diagram of the distribution of the particle size of the zinc powder used in Iran's zinc industry.

According to Fig. (4), over 85% of the particle size is below 200 µm, about 30% is between 100-200 µm, and about 20% is below 40 µm. The size of about 15% of the studied zinc powder is between 50-75 µm. Unfortunately, the granulation of zinc powder used in this article, which is almost the same as in the analysis of zinc powder used in Iranian factories, is very different compared to the international standards. In other words, according to Fig. (4), only 15% of the zinc powder used is between 50 and 75 µm (the global standard size of zinc factories) [14-18]. In the production line of Dandi zinc plant, no action is taken regarding the granulation. The zinc powder is used with this size distribution according to Fig. (4). There is between 40-50% zinc in the cake resulted from cold filtration, and one of the main reasons for this is the zinc powder being improperly sized. In this article, as mentioned in the experiment methodology section, zinc powder was first granulated with a shaker and a sieve column with 50, 100, 170, 200, 325, and -325 meshes. This article sampled zinc powder from each mesh to check the impact of size. To carry out the Ni-Cd cementation reaction, the metal ions must reach the surface of the zinc powder and be cemented by capturing electrons. Therefore, increasing the surface of the zinc powder available for the reaction increases the Ni-Cd cementation rate. There are two methods to increase the effective surface for the reaction; in the first method, theamount of the zinc powder is increased, and in the other, the particle size is decreased. Increasing the amount of the zinc powder is improper due to increased production costs. In addition to increasing the reaction rate, using particles with finer sizes can reduce costs. Fig. 5 illustrates the effect of the particle size of zinc powder on the removal of nickel and cadmium by the cementation method. As you can see, the size of the particles does not significantly affect the cadmium cementation reaction; in the nickel cementation reaction, however, the rate of nickel cementation will sharply increase as the particle size reduces with mesh 100 onwards. Then, the slope of the graph becomes milder, and from the mesh 200 onwards, at a concentration of about 2 g/L, the maximum separation takes place in the leach solution in different meshes used for zinc powder. In a study conducted by Cruz, it was stated that the

zinc powder with larger particles was more effective in removing cadmium and copper than cobalt and nickel; this confirms the results of the present study [24-26].

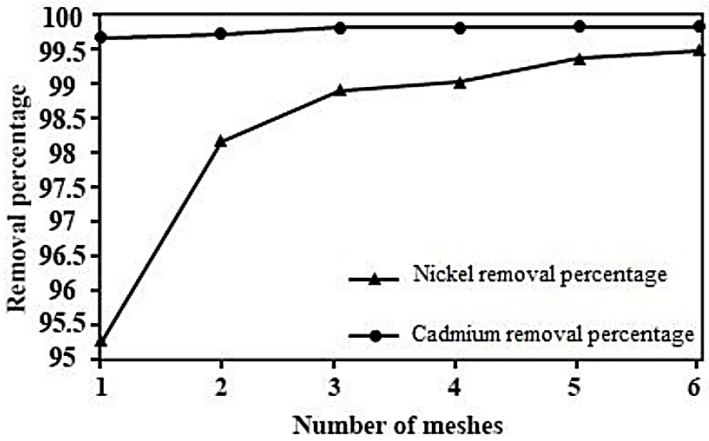

Figure 5. Effect of the particle size on the removal of cadmium and nickel by the cementation method in 1- 50 mesh, 2- 100 mesh, 3- 170 mesh, 4- 200 mesh, 5- +325 mesh, 6-325 mesh Experiments conditions: temperature = 85℃, pH = 5, zinc volume: 2 g/L, retention time: 75 min.

3.2. Effect of the particle size on the used amount of zinc powder

Fig. 6 illustrates the effect of the particle size on the consumption of zinc powder for the removal of nickel. According to Fig. 6, as the particle size becomes smaller, the removal of nickel impurities can be increased with lower amounts of zinc powder. The zinc powder with -325 and 325 meshes has the highest removal percentage at a concentration of 2 g/L, bringing the concentration of the nickel impurity to the permissible limit. For 100, 170, and 200 meshes, the highest removal efficiency also occurs at a concentration of 2 g/L. However, these meshes at such a concentration cannot bring the nickel impurity in the solution to the permissible limit. At the concentration of 1.5 g/L of zinc powder, there is a significant difference between the final concentration of nickel in -325 and +325 meshes compared to the same in 100, 170, and 200 meshes due to the larger effective surface they create. This indicates that the consumption of zinc powder can be decreased by using the zinc powder with smaller particle sizes. Fig. 7 illustrates the effect of the size of zinc powder on the consumption of zinc powder to remove cadmium. By evaluating Fig. 7, you can see that the final concentration of cadmium is close to zero for all sizes at a concentration of 2 g/L of zinc powder, and the maximum amount of cadmium is removed. At this concentration, the size of particles has almost no effect on the final disposal of cadmium. The final concentration of cadmium reaches the permissible limit in -325, 325, and 200 meshes at 1.8 g/L of zinc powder. under such a condition, the larger the particle size, the more concentration of zinc powder is required to bring the concentration of cadmium to the optimum level. Finally, an optimum performance will be obtained for 100 and 170 meshes with a concentration of 2 g/L. Regarding that over 3 g/L of zinc powder is used to remove nickel and cadmium at the cold purification stage in Dandi zinc smelting plant, it can be concluded that with lesser amounts of zinc powder, higher removal percentages of nickel and cadmium can be achieved by increasing the surface area through reducing the particle size; therefore, according to the results, it can be predicted that for the particle

sizes below the -325 mesh up to 1 g/L. The optimal amount of zinc powder, depending on the concentration of impurities. Research shows that by increasing the amount of nickel, cadmium, and cobalt impurities, the optimal amount of the used powder is raised [9, 10, 24-30].

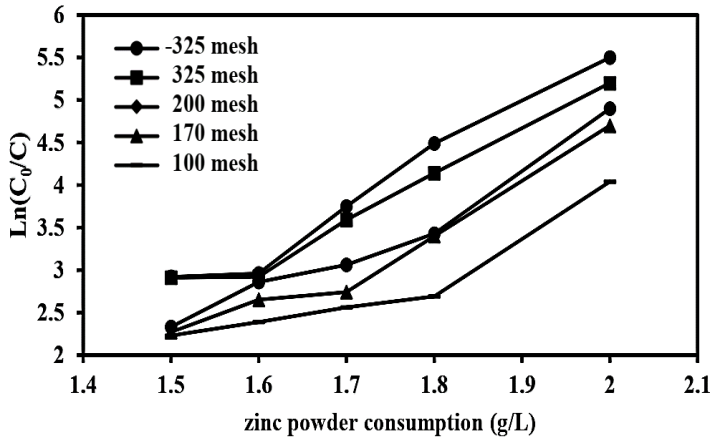

Figure 6. Effect of particle size on the zinc powder consumption for the nickel removal Experiment conditions: temperature = 85℃; pH = 5; retention time: 75 min.

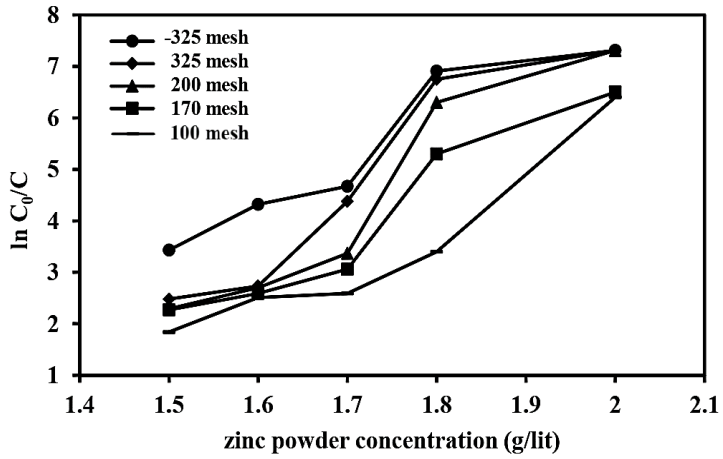

Figure 7. Effect of the particle size on the consumption of zinc powder for the removal of cadmium Experiment conditions: temperature: 85℃; pH: 5; retention time: 75 min.

3.3. Effect of the particle size of zinc powder on the retention time (mixing)

Figures 8 and 9 illustrate the effect of the particle size of zinc powder on the Ni-Cd cementation reaction time. As shown in Fig.s 8 and 9, the reaction rate of Ni-Cd cementation increases with the reduction in the particle size, as expected. In nickel cementation, the lowest concentration of nickel, or in other words, the highest amount of removal, is associated with the mesh of -325 and the lowest amount of reduction is related to the mesh of 100 in the 75 min retention time. For all sizes, the best efficiency of the cementation reaction is observed to be obtained in 75 min. In times longer than 75 min, the pH of the solution increased, and there would be a reduction in the concentration of H^+ . Therefore, according to Le Chatelier's principle, the reversible reaction of nickel to the nickel cation takes place because of the high equilibrium reaction rate of cementation. As a result, the final concentration of nickel in the solution will increase. For particles with -325 and +325

meshes, the final concentration of nickel reaches the optimal level for the following process, i.e., electrolysis, in 75 min. However, for the particle sizes with 100, 200, and 170 meshes, because of the need for making a proper surface for the cementation reaction, favorable conditions are not provided for adequately removing nickel and bringing its concentration to the optimal level in the reactor. According to Fig. 9, in the first 30 min, two +325 and -325 meshes can have the final concentration of cadmium in the solution reach the permissible limit. In a mesh of 200, the final concentration of cadmium reaches the optimal level within the first 45 min. After about 60 min, the removal of cadmium in all meshes reaches its maximum level. At this moment, the concentration of cadmium in the solution reached the values of lower than 0.5 mg/L for all meshes except 100 mesh. For 100 mesh, the concentration of cadmium in the solution reached 0.7 mg/L, which is within the permissible range. At the times longer than 60 min, the reversible reaction of the cadmium cementation also occurs inside the reactor, which can lead to a slight increase in the final concentration of cadmium. Using the proper particle size of zinc powder in the cold purification unit can significantly reduce the operating time of this stage. Hence, the particle size of the used zinc powder is a critical and influential parameter in the Ni-Cd cementation reaction. Many other researchers have confirmed these results [7, 26-31].

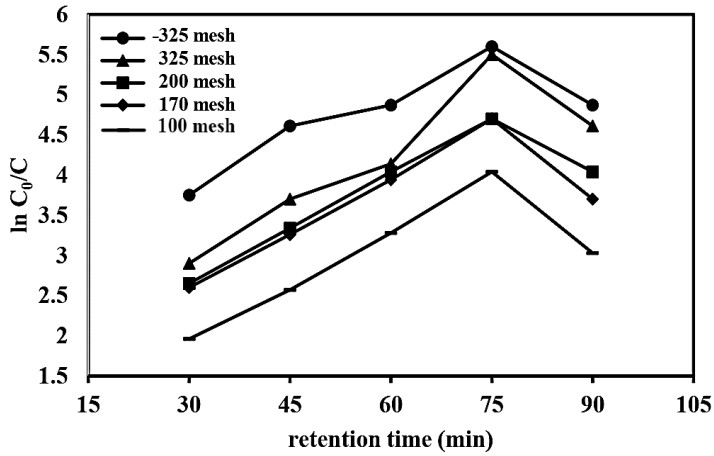

Figure 8. Effect of the particle sizes of zinc powder on the retention time in the removl of nickel
Experiment conditions: temprature: 85℃; pH: 5; zinc quantity: 2g/L.

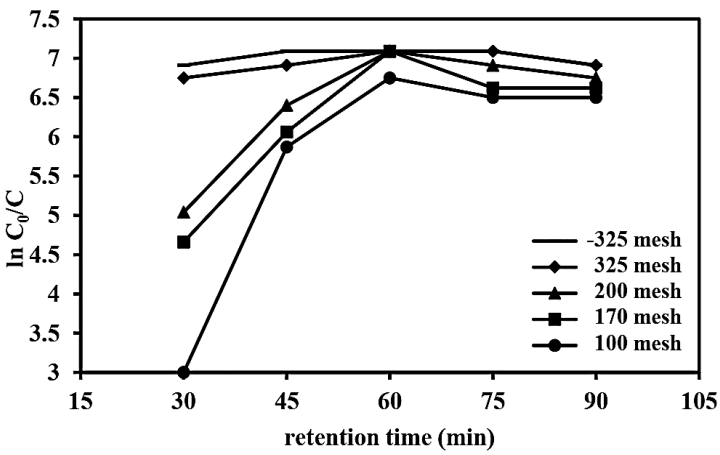

Figure 9. Effect of the particle sizes of zinc powder on the retention time in the removal of cadmium
Experiment conditions: temprature: 85℃; pH: 5; zinc quantity: 2g/L

3.4. Effect of the particle size of zinc powder on the removal temperature of nickel and cadmium

Another significant parameter in the zinc industry is the amount of energy consumption. As long as this process can be performed with less energy consumption and without reducing the removal efficiency, this process will commonly be economical, and there will be more demands for it from an industrial aspect. Fig. 10 illustrates the removal of the nickel impurity in the zinc production process versus temperature with various particle sizes of zinc powder. According to Fig. 10, for every temperature, the secondary concentration of nickel will decrease as the particle size reduces. In other words, the removal of nickel will increase at a specific temperature by reducing the particle size and enhancing the surface area available for the cementation reaction. The maximum removal of nickel for all particle sizes of zinc powder occurs at the temperature of 85℃. The particle size with -325 mesh has the highest removal amount. For -325 and 325 meshes, the concentration of the nickel impurity can reach the permissible level in the make-up solution for the electrolysis stage at 85℃. While the 100, 170, and 200 meshes cannot have the final concentration of nickel reach the permissible level even at a temperature of 85℃ with a concentration of 2 g/L of zinc powder. Fig. 11 also represents the removal degree of the cadmium impurity in terms of temperature for various particle sizes of zinc powder. According to this Figure, as the temperature increases, the performance of different particle sizes to remove cadmium becomes more similar. The concentration of cadmium reaches its lowest level at 85℃ for all sizes, and approximately an identical removal can be seen for all sizes. In other words, the particle size of the zinc powder does not have much effect on the cadmium cementation reaction at a temperature of 85°C. In contrast, the impact of the particle size is quite evident at lower temperatures, so that at a temperature of 65°C, simply the -325 mesh of the zinc powder can have the concentration of cadmium reach the permissible level for the make-up solution. This indicates that when finer particles of zinc powder are used in the cadmium cementation process, the cadmium cementation reaction can be performed with high efficiency at lower temperatures. The results also indicate that, compared to the nickel cementation reaction, the cadmium cementation reaction is more straightforward to achieve and is less affected by variables; this can be attributed to the lower activation energy of the cadmium cementation reaction. Cadmium can also be cemented at low temperatures and with larger particle sizes; it takes place, however, only if the nickel can be removed at high temperatures and with finer particle sizes. These results have been confirmed by Abbasi, Krause, and Boyanov [7, 26,32].

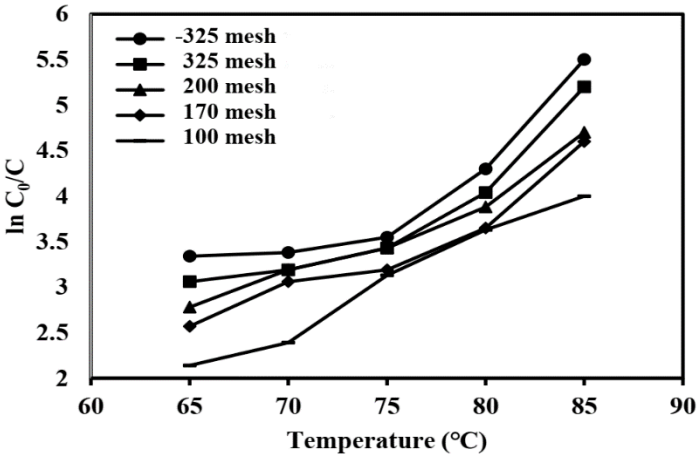

Figure 10. Effect of the particle size of zinc powder on the removal temperature of nickel Experiment conditions: pH: 5; zinc quantity: 2g/L; retention time: 75 min.

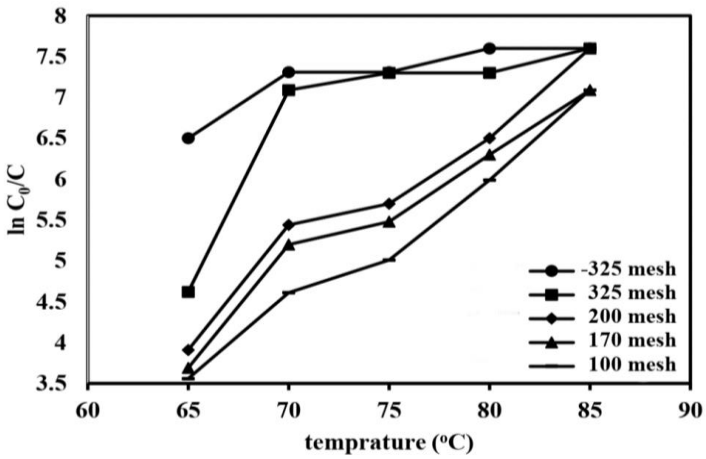

Figure 11. Effect of the particle sizes of zinc powder on the removal temperature of cadmium Experiment conditions: pH: 5; zinc quantity: 2g/L; retention time: 75 min

4. Conclusion

The results indicated that using zinc powder with smaller particles would require a lower temperature, a reduction of the reaction's retention time, and a reduction of the quantity of the zinc powder consumed during the Ni-Cd cementation process. Results show that in -325 mesh, with 1.8 g/L of the zinc powder, an operating temperature of 85℃ and a retention time of 75 min, the cementation reaction can reduce the solution to concentrations of less than 1 mg/L for nickel and less than 0.5 mg/L for cadmium. After filtration, this solution is called a make-up solution. Therefore, the resulting solution is quite proper for the electrolysis process. The quantity of the zinc powder used in Dandi zinc plant is about 100 kg in 30000 l tanks. In other words, in Dandi zinc factory and the cold purification unit, 3.3 g/L of the zinc powder is used. The results showed that using the zinc powder with particles smaller than 44 μm or -325 mesh can reduce the consumption of zinc powder to an amount of 1.5 g/L and make the cementation process in the cold purification unit much more economical. A remarkable result was that the effect of particle size on the nickel cementation reaction was much more than of the same on the cadmium cementation reaction. Cadmium cementation with zinc powder with larger particle sizes can also be performed well, and the particle size of zinc powder does not

significantly affect its removal rate. However, since nickel and cadmium impurities usually appear together and the same process is performed to remove both, it is suggested to use zinc powder with small particles. As a general result, it can be said that the particle size of zinc powder is a significant factor in the cementation reaction in the cold refinery reactor. Still, unfortunately, this very crucial factor is not paid any attention in the Iranian zinc industry.

References

[1] Behnajady, B. and Moghaddam, J., "Statistical evaluation and optimization of zinc electrolyte hot purification process by Taguchi method", *J. Cent. South Univ*., **22** (6), 2066 (2015).

[2] Boyanov, B.S., Konareva, V.V. and Kolev, N.K., "Purification of zinc sulfate solutions from cobalt and nickel through activated cementation", *Hydrometallurgy*., **73** (1), 163 (2004).

[3] Behnajady, B., Balesini, A. and Moghaddam, J., "A new approach to the optimization of zinc electrolyte cold purification process by Taguchi's method", *Can. Metall. Q.*, **53** (3), 333 (2014).

[4] Dib, A. and Makhloufi, L., "Mass transfer correlation of simultaneous removal by cementation of nickel and cobalt from sulfate industrial solution containing copper: Part I: Onto rotating zinc electrode disc", *Chem. Eng. J.*, **130** (1), 39 (2006).

[5] Bae, E. and Yoo, K., "Leaching behavior of valuable metals from by-product generated during purification of zinc electrolyte" *Geosystem Eng.*, **19** (6), 312 (2016).

[6] Huang, Y., Zhang, Z., Cao, Y., Han, G., Peng, W., Zhu, X., Zhang, T.A. and Dou, Z., "Overview of cobalt resources and comprehensive analysis of cobalt recovery from zinc plant purification residue-a review", *Hydrometallurgy*., **193** (1), 105 (2020).

[7] Abbasi, P., Investigation of effective parameters on nickel and cadmium removal from ZnSO4 solution at mixed reactor and modeling of reactor performance, MS Thesis. University of Mohaghegh Ardabili, (2019).

[8] Zhang, B. Yang, C. Zhu, H. Li, Y. and Gui, W., "Kinetic modeling and parameter estimation for competing reactions in copper removal process from zinc sulfate solution", *Ind. Eng. Chem. Res*., **52,** 17074 (2013).

[9] Nelson, A., Novel activators in cobalt removal from zinc electrolyte by cementation, MS Thesis. McGill University Montreal, Montreal, (1998).

[10] Lu, J., Dreisinger, D. and Rees, K., "Simultaneous removal of Co, Cu, Cd and Ni from zinc sulfate solution by zinc dust cementation", *Hydrometallurgy*., **197** (1), 105 (2020)

[11] Laatikainen, K., Lahtinen, M., Laatikainen, M. and Paatero, E., "Copper removal by chelating adsorption in solution purification of hydrometallurgical zinc production", *Hydrometallurgy*., **104** (1), 9 (2010).

[12] Karlsson, T., Cao, Y., Colombus, Y. and Steenari, BM., "Investigation of the kinetics and the morphology of cementation products formed during purification of a synthetic zinc sulfate electrolyte", *Hydrometallurgy*., **181** (1), 169 (2018).

[13] Lew, R.W., The removal of cobalt from zinc sulphate electrolytes using the copper-antimoney process, MS Thesis. University of British Columbia, (1994).

[14] Wang, L.Y., Gui, W.H., Teo, K.L., Loxton, R. and Yang, Ch.H., "Optimal

control problems arising in the zinc sulfate electrolyte purification process", *J. Glob Optim.*, **54** (2), 307 (2012).

[15] Xu, R., Ma, K. and Guo, Z., "Activation mechanism of Sb2O3 during removal of cobalt from zinc sulfate solution", *Hydrometallurgy*, **82** (3), 150 (2006).

[16] Halli, P., Agarwal, V., Partinen, J. and Lundström, M., "Recovery of Pb and Zn from a citrate leach liquor of a roasted EAF dust using precipitation and solvent extraction", *Sep. Purif. Technol.*, **236** (1), 116 (2020).

[17] Vahidfard, V., "In study alternative cementation process with using manganometry for removing Cobalt from ZnSO4 solution". MS Thesis. University of Mohaghegh Ardabili (2019).

[18] Bøckman, O., Østvold, T., Voyiatzis, G. A. and Papatheodorou, G. N., "Raman spectroscopy of cemented cobalt on zinc substrates", *Hydrometallurgy*., **55**, 93 (2000).

[19] Shayesteh, K., Abbasi, P., Vahid Fard, V. and Shahedi Asl, M., "Simultaneous removal of nickel and cadmium during the cold purification of zinc sulfate solution", *Arab. J. Sci. Eng.*, **45** (2), 587 (2020).

[20] Younesi, S.R., Alimadadi, H., Keshavarz Alamdari, E. and Marashi S.P.H., "Kinetic mechanisms of cementation of cadmium ions by zinc powder from sulphate solutions", *Hydrometallurgy*., **84**, 155 (2006).

[21] Pal, P., Nazim, M., Dutta, B. K. and AlShoaibi A., "Copper deposition and formation of nano-particles", *Sep. Sci. Technol.*, **49**, 2728 (2014).

[22] Karavasteva, M., "The effect of magnesium and zinc on indium cementation kinetics and deposit morphology in the presence of and without nonylphenylpolyethylene glycol", *Hydrometallurgy*, **150**, 47 (2014).

[23] Zakeri, A., Bafghi, M. Sh. and Shahriari, Sh., "Dissolution kinetics of manganese dioxide ore in sulfuric acid in the presence of ferrous ion", *Iran. J. Mater. Sci. Eng.*, **4** (3-4), 22 (2007).

[24] Krause, B. and Sandenbergh, R., "Optimization of cobalt removal from an aqueous sulfate zinc leach solution for zinc electrowinning", *Hydrometallurgy*, **155,** 132 (2015).

[25] Zaheri, S., "High temperature and high pressure cobalt cementation onto zinc dust". MS Thesis. University of British Columbia (2015).

[26] Krause B. J., Optimization of the purification process of a zinc sulfate leach solution for zinc Electrowinning, MS Thesis, University of Pretoria, (2014).

[27] Abbasi, P., Shayesteh, K., Vahid Fard, V. and Hosseini, M., "Optimization of the nickel removal process from zinc sulfate solution using central composite design of experiments", *Iran. J. Anal. Chem.*, **81**, 17 (2021).

[28] Shayesteh, K., Abbasi, P., Vahid Fard, V. and Hosseini, M., "Providing practical instruction for solving environmental problems from residue (cake) of cold purification process in zinc production process", *J. Environ. Sci. Technol.*, **23** (1), 53 (2021).

[29] Abbasi, P., Shayesteh, K., Vahid Fard, V. and Hosseini, M., "Optimization and comparison of ni and cd removal using zinc powder with the response surface methodology", *Iran. J. Chem. Eng.*, **17** (4), 3 (2020).

[30] Güler, E. and Seyrankaya, A., "Precipitation of impurity ions from zinc leach solutions with high iron contents-A special emphasis on cobalt precipitation", *Hydrometallurgy*, **164**, 118 (2016).

[31] Van der Pas V., A fundamental study of cobalt cementation with zinc dust in the

presence of copper and antimony additives, MS Thesis, University of British Columbia, (1995).

[32] Boyanov, B.S., Konareva, V.V. and Kolev, N.K., "Purification of zinc sulfate solutions from cobalt and nickel through activated cementation", *Hydrometallurgy*, **73** (1), 163 (2004).