



Kinetics of sulfuric acid leaching of cadmium from Cd–Ni zinc plant residues

Mohammad Sadegh Safarzadeh^{a,b,*}, Davood Moradkhani^{a,b,c}, Mehdi Ojaghi-Ilkhchi^d

^a Laboratory for Leaching and Purification Processes, R&D Center, Iranian Zinc Mines Development Company (IZMDC), P.O. Box 45195-1134, Zanjan, Iran

^b Research and Engineering Company for Non-ferrous Metals (RECO), P.O. Box 45195-1134, Zanjan, Iran

^c Faculty of Engineering, Zanjan University, Zanjan, Iran

^d Faculty of Materials Engineering, Sahand University of Technology, Tabriz, Iran

ARTICLE INFO

Article history:

Received 31 January 2008

Received in revised form 8 July 2008

Accepted 9 July 2008

Available online 25 July 2008

Keywords:

Cadmium

Nickel

Zinc plant residues

Dissolution

Kinetic model

Diffusion-controlled process

ABSTRACT

Cd–Ni filtercakes are produced continuously at the third purification step in the electrolytic production of zinc in the National Iranian Lead and Zinc Company (NILZ) in northwestern Iran. In this research, the dissolution kinetics of cadmium from Cd–Ni residues produced in NILZ plant has been investigated. Hence, the effects of temperature, sulfuric acid concentration, particle size and stirring speed on the kinetics of cadmium dissolution in sulfuric acid were studied. The dissolution kinetics at 25–55 °C and $t \leq 5$ min was found to follow a shrinking core model, with inter-diffusion of cadmium and sulfate ions through the porous region of alloying layer (Cd_5Ni , $\text{Cd}_2\text{Ni}_{1.9}$ and $\text{Cd}_{10}\text{Cu}_3$) as the rate determining step. This finding is in accordance with the apparent activation energy (E_a) of 13.363 kJ/mol and a linear relationship between the rate constant and the reciprocal of squared particle size. Arrhenius constant was calculated as 6.3942 min^{-1} . The order of reaction with respect to sulfuric acid concentration, solid/liquid ratio and particle size were also achieved. The rate of reaction at first 5 min based on diffusion-controlled process can be expressed by a semi-empirical equation as:

$$\left[1 - \left(\frac{2}{3}\right)X - (1 - X)^{2/3}\right] = k_d t = 997[\text{H}_2\text{SO}_4]^{1.0475} \left(\frac{S}{L}\right)^{-0.5969} r_0^{-2.1819} \exp\left(-\frac{13.363}{RT}\right) t$$

It was determined that the dissolution rate increased with increasing sulfuric acid concentration and decreasing particle size.

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"It's a very funny thought that if bears were bees, they'd build their nest at the bottom of trees, and that being so (if bees were bears), we shouldn't have to climb up all those stairs."

From *Winnie-the-Pooh*, By A.A. Milne

1. Introduction

In spite of their toxicity, cadmium and its compounds are used in different industries such as electroplating, pigments, synthetic chemicals, ceramics, metallurgical and photographic products, electronics and other industries. Industrial applications for cadmium have recently been developed and consequently the direct production of this metal has increased [1].

Located in northwestern province of Zanjan, Iran, in NILZ electrolytic zinc plant, with a capacity of 20,000 t Zn/y, a major amount

of Cd–Ni filtercake has been stockpiled during the years and also about 50 kg of the same residue per ton of produced zinc is added to dumps daily.

Fig. 1 shows a conceptual flow sheet which explains the purification stages and origin of the Cd–Ni filtercake in NILZ plant.

The following items draw our attention to treat Cd–Ni residues:

1. stringent environmental rules;
2. increasing demand for cadmium metal;
3. easy and fast dissolution kinetics of the residue in sulfuric acid;
4. increasing prices of cadmium [2].

Depending on the composition of zinc concentrate, the composition of filtercake may vary. For example, the average composition of such a filter cake in Iranian zinc plants is as follows [2]:

Zn = 40–55%; Cd = 13–16%; Ni = 3.5–4.0%;

Cu = 1.5–2.0%; Pb = 1.0–1.5%; Ca = 2–3%.

The high nickel content of this residue has made it different from similar residues produced in other zinc plants. As a result, the

* Corresponding author at: Laboratory for Leaching and Purification Processes, R&D Center, Iranian Zinc Mines Development Company (IZMDC), P.O. Box 45195-1134, Zanjan, Iran. Tel.: +98 241 4221027; fax: +98 241 4221027.

E-mail address: sadeghsafarzadeh@gmail.com (M.S. Safarzadeh).

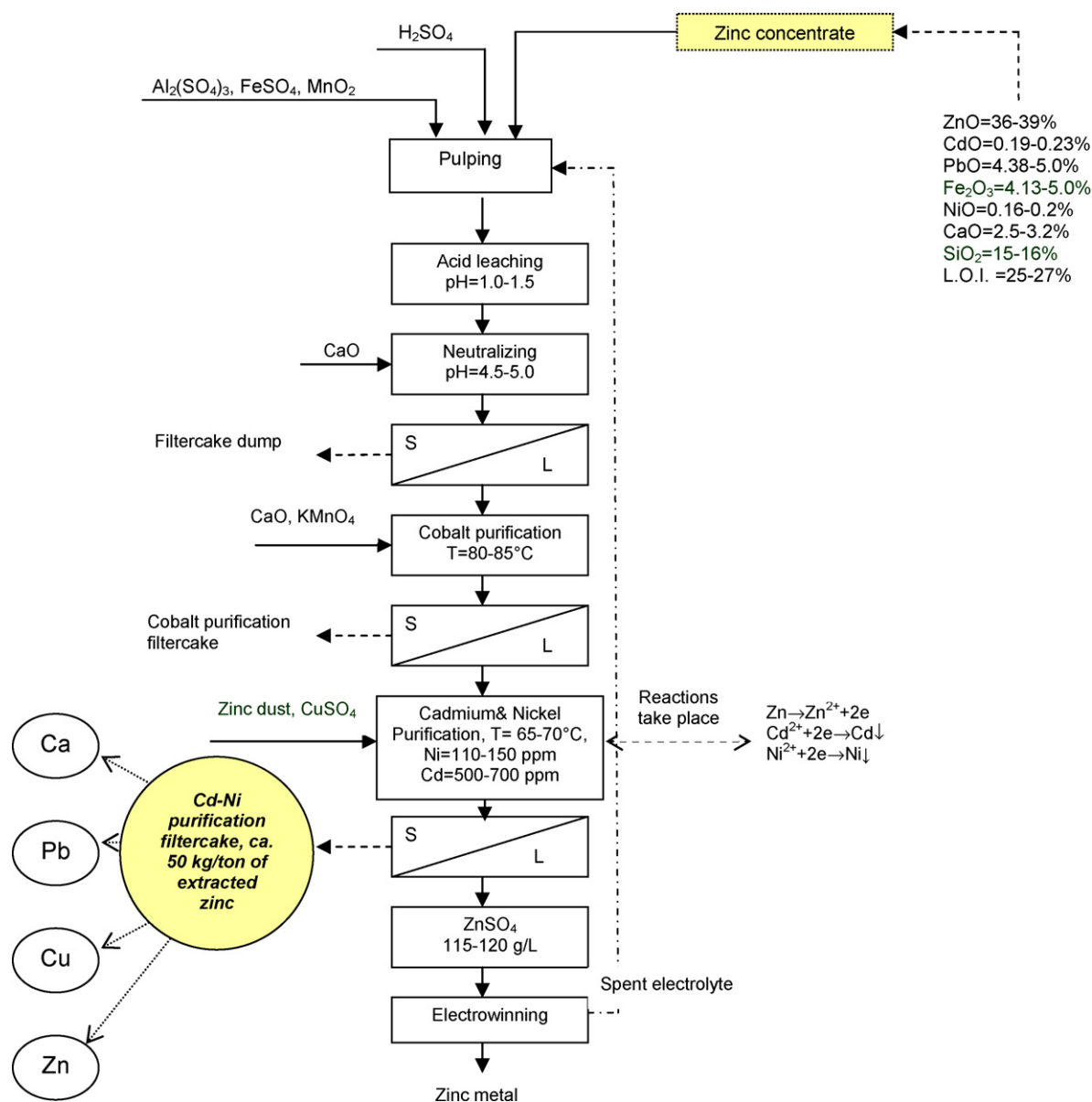


Fig. 1. Conceptual flowsheet of electrolytic zinc production in NILZ plant showing the origin of Cd–Ni purification filtercake [2].

appropriate treatment for this residue has become important from hydrometallurgical and economical points of view [3].

It might be useful to review the process in which Cd–Ni is attained. As seen in Fig. 1, the Cd–Ni filtercake is produced through cementation of impurities which accompany zinc sulfate solution using zinc powder and as a result all impurities are reduced on zinc particles. The reaction that occurs, however with excess of zinc much higher than the stoichiometric amount needed. The cementation reaction is a galvanic one in nature, therefore not only cadmium, nickel and copper are cemented on zinc, but also copper and nickel can cement on cadmium. Therefore it is expected that some other metallic compounds be present in the residue which will affect the subsequent leaching process in order to recover the metals [2].

To the best of our knowledge, no experimental report exists on the leaching kinetics of Cd–Ni filtercake in the relevant literature. Safarzadeh et al. [4] have determined the optimum conditions for the leaching of Cd–Ni zinc plant residues using Taguchi experimental plan, with no kinetic evaluation. In this paper, we aim the

dissolution behavior of cadmium in sulfuric acid and also seek a kinetic model to explain its leaching rate.

In this research, the results of leaching of Cd–Ni filtercake with sulfuric acid are presented. The kinetics characterizations of the leaching process were analyzed according to shrinking core model (SCM) [5] and the best fitted equation to the experimental data was determined. A corresponding diffusion model was found suitable to explain the relationship between reaction time and the fraction of cadmium leached and the apparent activation energy of the process was determined. In the leaching experiments, the effects of temperature, acid concentration, stirring speed and solid/liquid ratio on cadmium extraction were investigated.

2. Chemistry of the solution and theoretical behavior of the phases

The leaching of Cd–Ni zinc plant residues deals with the solubilization of Zn, Cd, Ni, Cu and Pb in the form of oxides or elements, present in the filtercake. The behavior of these solid phases under

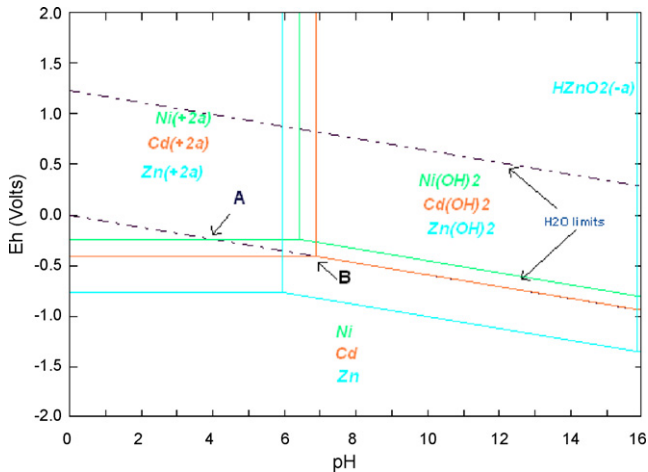
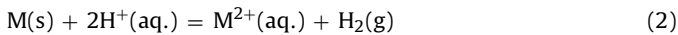
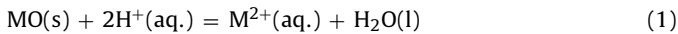


Fig. 2. Superimposed E_h -pH diagrams of Zn, Cd and Ni-H₂O systems at 25 °C, drawn using HSC chemistry software (Outokompu Research, Finland).

sulfuric acid leaching conditions can be predicted from equilibrium data. However, solubilization of metals is a complex phenomenon which cannot be solely predicted with pH-solubility data. Other factors such as redox potential of the system may also have a significant effect on metals leaching [6] and these factors should be integrated into pH-solubility data to improve capability of the model.

In order to simplify the calculations, molar metal ion concentrations can be used instead of activities in all formulations presented. The leaching of metal oxides and metal elements, MO and M, where MO = ZnO, CdO, NiO, CuO and PbO and M = Zn, Cd, Ni, Cu and Pb, can be summarized by the following equilibrium reactions, respectively:



Represented by the respective equilibrium constants, k_1 and k_2 , in which $k_1 = k_2 = [\text{M}^{2+}]/[\text{H}^+]^2$. Since $\text{pH} = -\log[\text{H}^+]$, then

$$\log k = \log[\text{M}^{2+}] + 2\text{pH} \quad (3)$$

Thus the concentration of the metal ion M^{2+} in solution at 25 °C, can be predicted by

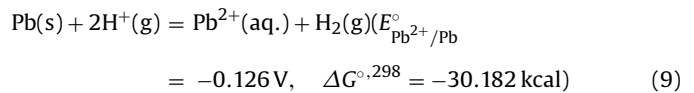
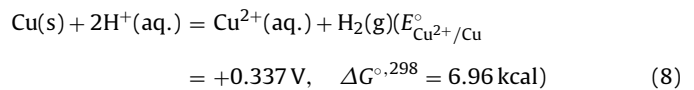
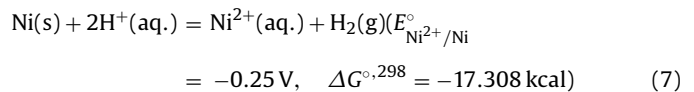
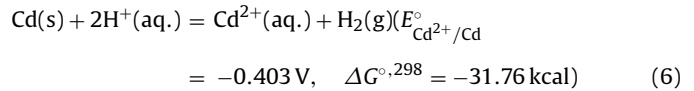
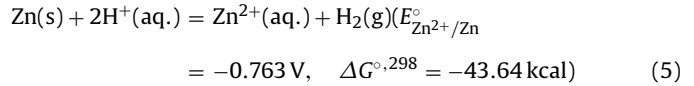
$$[\text{M}^{2+}] = 10^{(\log k - 2\text{pH})} \quad (4)$$

In which k can be calculated from the equation $\Delta G^\circ = -RT \ln k$.

Also, the Cd, Ni, Zn, Cu and Pb sulfates solubility products can be obtained from thermodynamic data. As demonstrated, the equilibrium concentration of M^{2+} resulting from leaching reaction depends on the equilibrium pH of the solution. The utilization of the above methodology should take into account the threshold M^{2+} concentrations given by solubility of metal sulfates. Considering the conditions used in the experiments ($S/L = 125 \text{ g/L}$) and taking into consideration the composition of the filtercake, the metal concentrations in the solution will be far from those limits and therefore the crystallization of MSO_4 species does not to be considered. According to Eq. (4), the proposed leaching conditions are adequate for solubilization of metals [7].

Concerning metal species in elemental form, during leaching experiments oxidation occurs to the divalent state according to reactions (5)–(9) and therefore the solubilization conditions can be predicted from relevant E_h -pH diagrams, as presented in

Figs. 2 and 3.



Please notice that in Figs. 2 and 3, systems are superimposed for a better comparison of solubility areas. Fig. 2 shows that the stability regions of Cd^{2+} , Ni^{2+} and Zn^{2+} are enclosed by the water stability limits, denoting the feasibility of metal oxidation by the acid. However, for pHs lower than 6 for zinc, 6.5 for cadmium (point B) and 4.3 for nickel (point A), the reactions (5)–(7) occur spontaneously.

Also, comparing the areas of solubility regions of the M^{2+} in the diagram indicates that Zn^{2+} , Cd^{2+} and Ni^{2+} have greater solubility areas, respectively. Thus from a strictly thermodynamic viewpoint, it is anticipated that the practical leaching recoveries have the following order: $R_{\text{Zn}} > R_{\text{Cd}} > R_{\text{Ni}}$.

The relevant E_h -pH diagram for Cu and Pb is also given in Fig. 3. The diagram shows that the stability regions of Cu^{2+} and Pb^{2+} are enclosed by the water stability limits as well. However, in the case of Cu and Pb, higher acidities are required for the dissolution reaction, and as can be recognized, the reactions (8) and (9) occur at pH values lower than -6 (point C) and 2 (point D) for Cu and Pb, respectively.

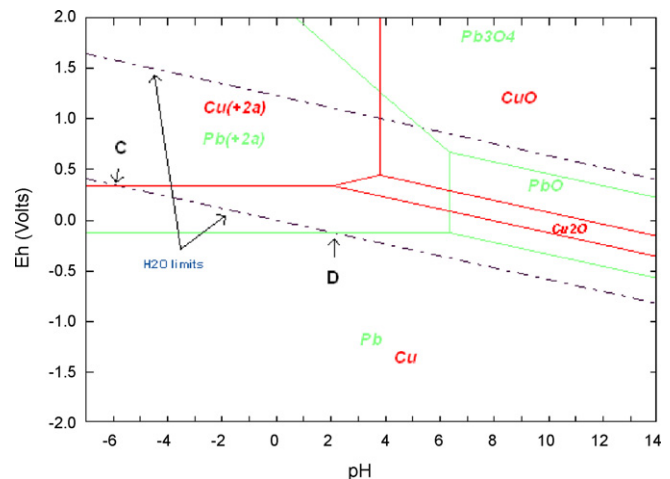


Fig. 3. Superimposed E_h -pH diagrams of Cu and Pb-H₂O systems at 25 °C, drawn using HSC chemistry software (Outokompu Research, Finland).

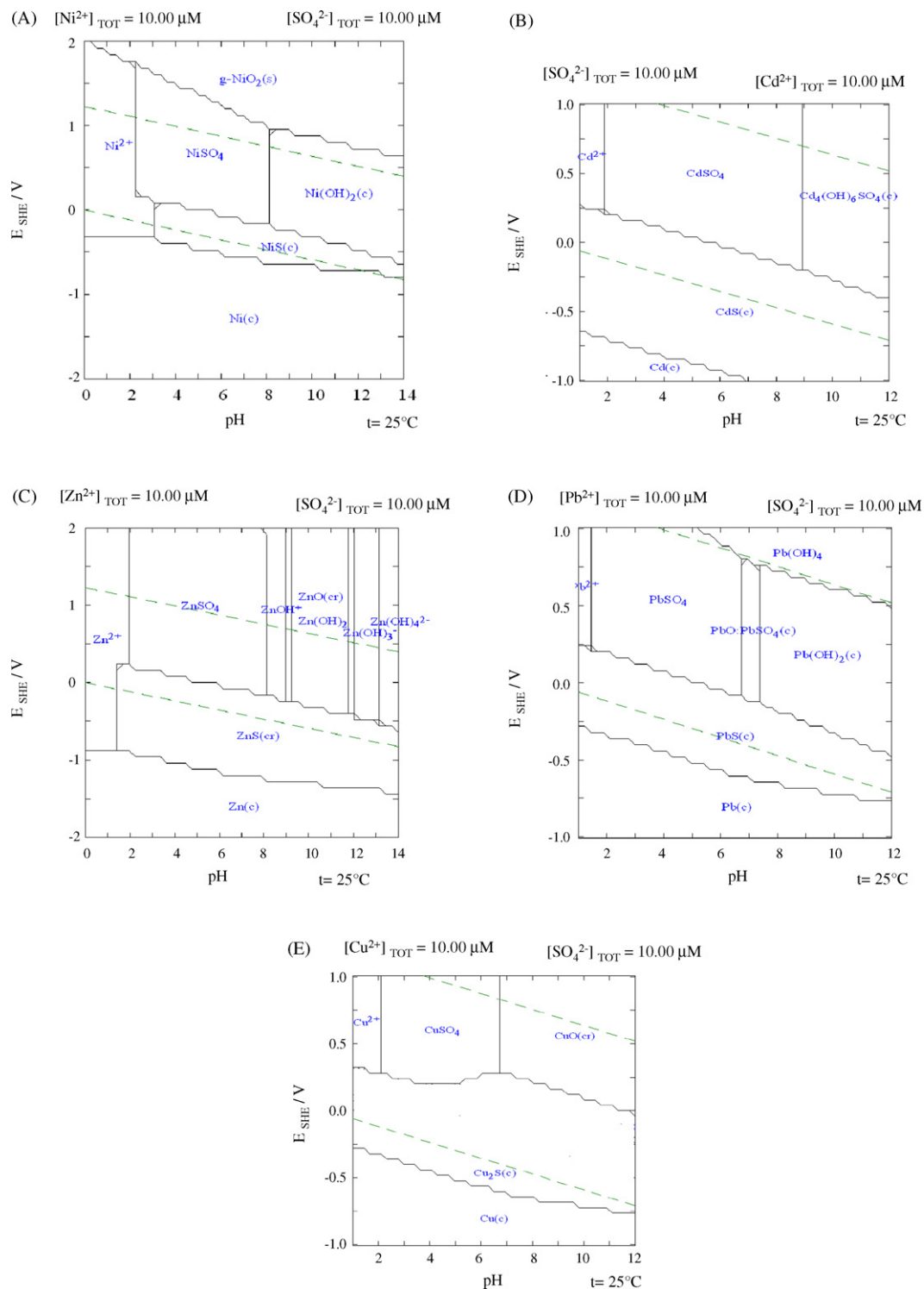
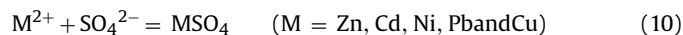


Fig. 4. E_h -pH diagrams of (A) Ni-S-H₂O, (B) Cd-S-H₂O, (C) Zn-S-H₂O, (D) Pb-S-H₂O and (E) Cu-S-H₂O systems at 25 °C, drawn using Medusa software (Royal Institute of Technology, Sweden).

The corresponding E_h -pH diagrams for the sulfate systems are also shown in Fig. 4(A)–(E). From these diagrams, it is established that SO_4^{2-} ions increase the solubility of all metal ions. The following complexation reaction occurs through sulfuric acid leaching:



searching for K_{sp} values for corresponding sulfates, it was found that the K_{sp} for lead(II) sulfate is very low, which means that lead(II)

sulfate is poorly soluble ($K_{sp} = 1.9 \times 10^{-8}$, at 25 °C), as can be seen in the following diagram (Fig. 5) showing addition of SO_4^{2-} to a solution containing 0.1 M of Pb^{2+} at pH of 1.0. Observe that Pb^{2+} solubility drops 10,000-fold as SO_4^{2-} reaches 0.1 M.

Also, Fig. 6 shows the fraction of different ions present in the solution at various SO_4^{2-} concentrations. It is evident from Fig. 6 that as SO_4^{2-} reaches 0.1 M, practically all Pb^{2+} transforms to $\text{PbSO}_4(\text{s})$.

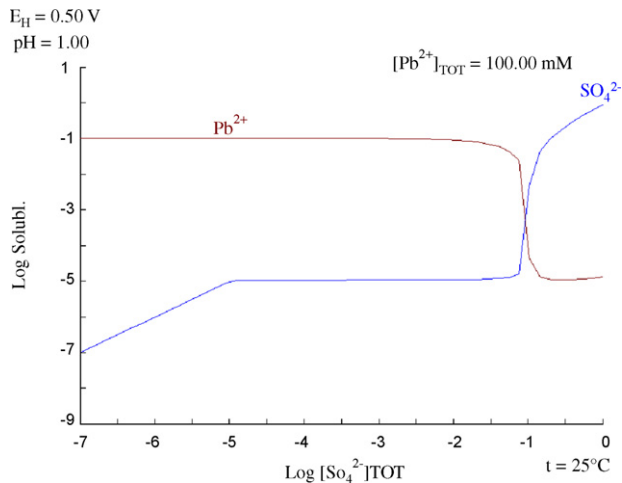


Fig. 5. Plot showing aqueous concentration of dissolved Pb^{2+} as a function of SO_4^{2-} concentration, drawn using Medusa software (Royal Institute of Technology, Sweden).

From these findings, it can be predicted that lead can be easily separated from other metal ions present in the solution.

3. Materials and methods

3.1. Materials

The Cd–Ni filtercake used in the experiments was kindly supplied from NILZ plant. The sample included ca. 22% moisture. The composition of the filtercake was determined as follows (wt%): Zn: 44.32, Cd: 15.17, Ni: 3.94, Cu: 1.44, Pb: 1.08, Fe: 0.09, Mn: 0.08, Ca: 2.27 and S: 8.01. As can be seen, the filtercake is mostly composed of zinc, cadmium and nickel. Mineralogical analysis performed using X-ray diffractometry, indicated that Zn, ZnSO_4 , $\text{ZnSO}_3 \cdot 2.5\text{H}_2\text{O}$, CdO and ZnO were the major mineralogical phases in the filtercake [4]. However, it is noteworthy to mention that the XRD experiment only reveals the most abundant phases, generally more than 3 wt%. Hence there can be other phases neglected by XRD.

In the leaching experiments, sulfuric acid from Merck with a purity of 95–98% and a density of 1.82 was used.

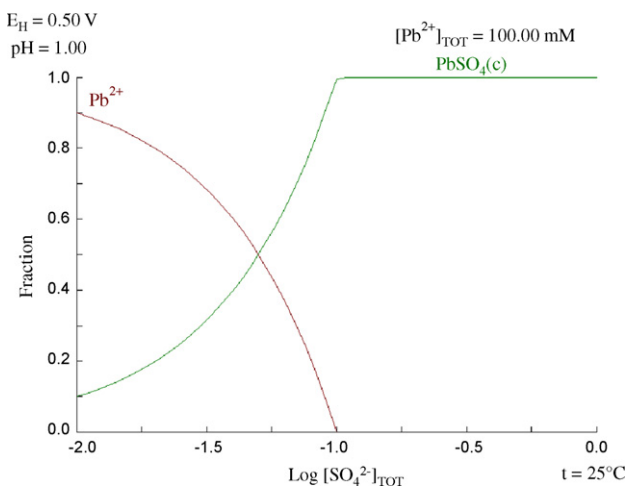


Fig. 6. Plot showing the fraction of Pb^{2+} and PbSO_4 as a function of SO_4^{2-} concentration, drawn using Medusa software (Royal Institute of Technology, Sweden).

Table 1

The parameter values for the leaching of Cd–Ni filtercake in sulfuric acid

Parameter	Value
Temperature ($^{\circ}\text{C}$)	25 ^a , 35, 45, 55
Acid concentration (M)	0.81, 1.0, 1.7 ^a , 2.0
Particle size (μm)	–600 + 500 ^a , –710 + 600, –850 + 710, –1000 + 850
Solid to liquid ratio (g/mL)	1/5, 1/8 ^a , 1/10
Stirring speed (rpm)	0, 100, 200, 300, 400 ^a , 500, 600

^a The constant values used when the effect of other parameters was investigated.

The filtercake was dried at 110 $^{\circ}\text{C}$ for 24 h and then was crushed using a ball mill and sieved into desired particle sizes.

3.2. Experimental procedure

Based on our previous experience in related works and those experimental conditions reported by other researchers for the leaching of similar residues and preliminary tests performed (a) temperature, (b) sulfuric acid concentration, (c) pulp density and (e) stirring speed were chosen as the four variables to be investigated. For each experimental condition, the experiment was repeated twice, and the arithmetic average of the results was used in the plotting of yield curves. The range and values of employed parameters for leaching tests are given in Table 1.

The leaching experiments were performed in a 2 L Pyrex beaker setup in a thermostatically controlled water bath, equipped with a digitally controlled thermometer (within $\pm 0.5^{\circ}\text{C}$). Mechanical stirrer (Heidolf RZR 2020) had a controller unit and its twin-bladed impeller and shaft were coated by Teflon. For minimizing aqueous loss when the system was heated, a reflux condenser mounted on the top of the cell [4]. After adding 1 L of acid with a known concentration to the reaction vessel and setting the temperature at the desired value, a known weight of sample was added to the reactor while stirring the content of the reactor at a certain speed. At desired time intervals, 1 mL of solution was withdrawn from the reactor and the leach solution was diluted with double distilled water. The diluted clear leach solution sample was analyzed for Cd, Zn, Ni, Pb and Cu using an AA-300 PerkinElmer model atomic absorption spectrometer.

In calculating the leaching efficiency of cadmium, a volume correction formula was used; which includes correction factors in itself to account for the volume losses due to sampling [8].

$$X_{M,i} = \frac{(V - \sum_{i=1}^{i-1} v_i)C_{M,i} + \sum_{i=1}^{i-1} v_i C_{M,i}}{m(C_M/100)} \quad (11)$$

where V is the initial volume (mL) of the solution, v_i is the volume (mL) of the sample i withdrawn each time, $C_{M,i}$ is the concentration of M (Cd) in sample i (mg L^{-1}), m is the initial mass of cadmium in g (on a dried basis) added into the reaction vessel and C_M is the concentration of M in the sample (wt% dried solids). Error for each experiment was always below 2%. It must be noted that no copper and lead were dissolved at proposed conditions and hence they were collected at leaching residues. Also, the results for zinc and nickel dissolution will be reported in a separate paper. Nevertheless, the behavior of these metals has been reported in a diagram at the optimum leaching conditions (Fig. 12). The uncertainties of the measurements were estimated with regression analysis procedure.

3.3. Kinetic analysis

Fluid–solid heterogeneous reaction systems have applications in chemical and hydrometallurgical processes. A successful reactor design for these processes depends basically on kinetic data. In the fluid–solid systems, the reaction rate may be generally controlled

by one of the following steps: Diffusion through the fluid film, diffusion through the ash or the chemical reaction at the surface of the core or unreacted material [5].

The rate of the process is controlled by the slowest of these sequential steps.

In order to determine the kinetic parameters and rate controlling step about leaching of cadmium oxide in sulfuric acid solutions, the experimental data were analyzed on the basis of the shrinking core model.

If no ash layer covers the unreacted core as the reaction proceeds, there could be only two controlling steps, namely, fluid film diffusion or chemical reaction.

If the reaction rate is controlled by diffusion through the product layer, it will be an integrated rate equation, as follows [5]:

$$1 - \frac{2}{3}X - (1 - X)^{2/3} = \frac{6bD_{\text{eff}}.[\text{H}_2\text{SO}_4]^n}{\rho_{\text{CdO}}r_0^2}t = k_d t \quad (12)$$

If the reaction is controlled by the surface reaction, Eq. (12) transforms to following equation:

$$1 - (1 - X)^{1/3} = \frac{bk_s[\text{H}_2\text{SO}_4]^n}{\rho_{\text{CdO}}r_0}t = k_r t \quad (13)$$

where, X is the fraction reacted, k_r the kinetic parameter for reaction control, k_d the kinetic parameter for product diffusion control, t reaction time (min), b the stoichiometric coefficient of CdO in leaching reaction (Eq. (15)), k_s the chemical reaction rate constant, $[\text{H}_2\text{SO}_4]$ the sulfuric acid concentration, ρ_{CdO} the molar density of

CdO, r_0 the particle radius, n the order of reaction with respect to H_2SO_4 and D_{eff} the effective diffusion coefficient.

Eq. (12) reveals that if diffusion through the product layer controls the leaching rate, there must be a linear relationship between the left side of the equation and time. The slope of the line is the rate constant k_d and it must be directly proportional to $1/r_0^2$. Also the temperature dependence of the reaction rate constant can be calculated by the Arrhenius equation:

$$k_d = A \exp\left(\frac{-E_a}{RT}\right) \quad (14)$$

where A is frequency factor, E_a is activation energy of the reaction, R is universal gas constant and T is absolute temperature.

4. Results and discussion

Reaction between cadmium oxide and sulfuric acid can be written as follows:



Based on the above reaction, the effects of various parameters were evaluated in the following sections.

4.1. Effect of temperature

The temperature effect was examined in the range of 25–55 °C under the conditions of 1.7 M acid concentration, –600 + 500 μm

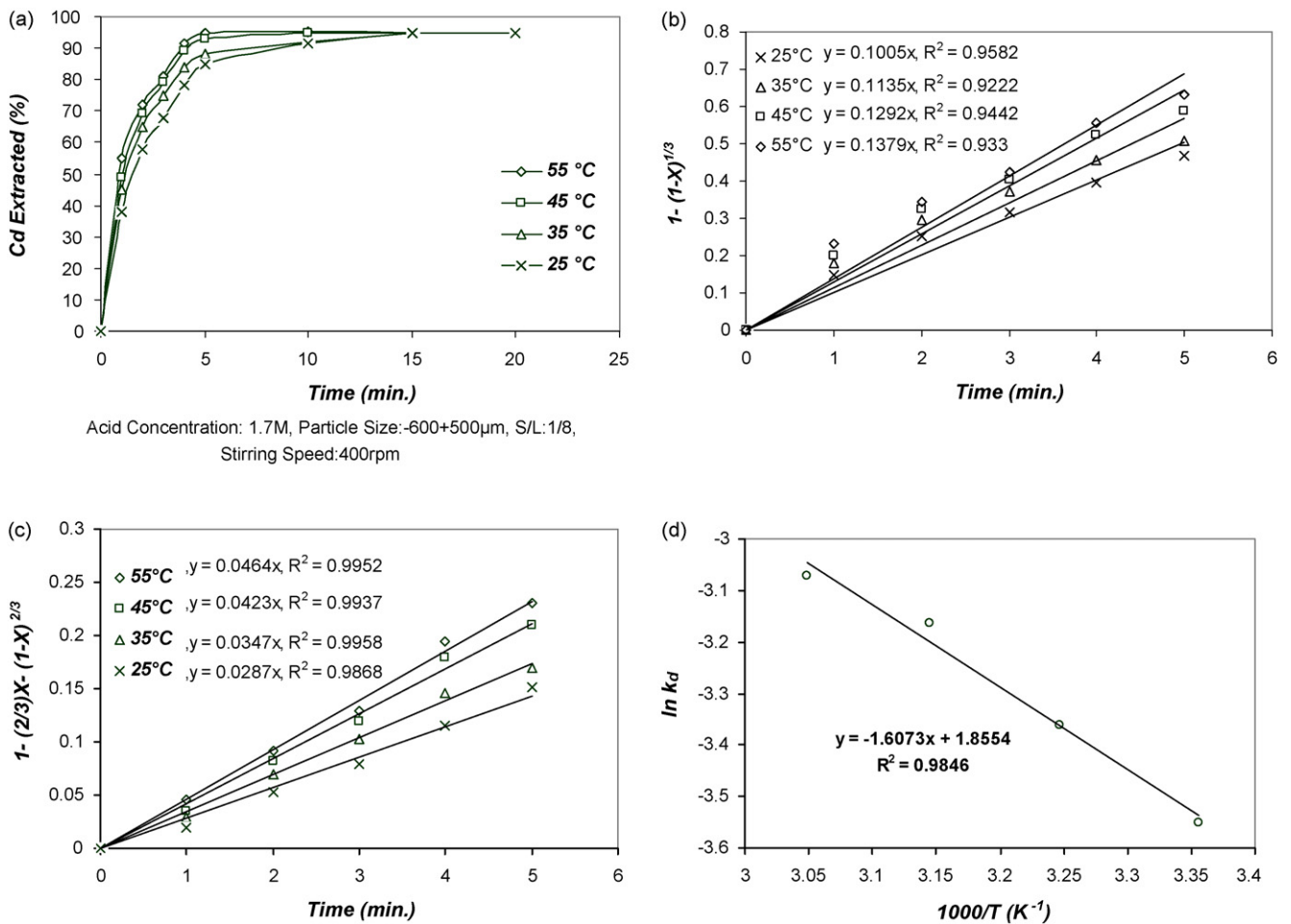


Fig. 7. (a) The effect of temperature on the dissolution of cadmium at proposed experimental conditions. (b) The variation of $1 - (1 - X)^{1/3}$ with time at various temperatures, (c) The variation of $1 - (2/3)X - (1 - X)^{2/3}$ with time at various temperatures and (d) Arrhenius plot of reaction rate against reciprocal temperature.

particle size, solid/liquid ratio of 1/8 and 400 rpm stirring speed. As seen from Fig. 7(a), the cadmium recovery increased as the temperature was increased. The recovery after 5 min reached 95%, 93%, 88% and 85% for 55, 45, 35 and 25 °C, respectively.

However, the cadmium dissolution hardly increased after a rapid dissolution in 5 min. Despite the beneficial effect of temperature on the reaction rate, cadmium dissolution in our study was considered to be fast in nature and hence at room temperature, a maximum dissolution is achieved in a convincingly short time of about 15 min.

Eqs. (12) and (13) were applied for the results obtained from each temperature values. Fig. 7(b) presents the data plot according to chemical reaction control. Also Fig. 7(c) shows the data plot according to diffusion control process. The results reveal that the values for the correlation coefficient (R^2) in Fig. 7(c) are closer to 1 than those in Fig. 7(b). So Eq. (12) was found to fit the data best. Such results indicate that the linear relationship between $1 - (2/3)X - (1 - X)^{2/3}$ and leaching time (t) is significant and suggest that the leaching rate of cadmium is controlled by diffusion through the product layer. The apparent rate constants (k_d) were calculated as slopes of the straight lines. Using the apparent rate constants obtained by application of Eq. (12), the Arrhenius plot ($\ln k_d$ vs $1/T$) was obtained (Fig. 7(d)) and the activation energy was calculated as 13.360 kJ/mol. This value clearly confirms that this process is most likely controlled by diffusion of ions through product layer.

4.2. Effect of acid concentration

The stoichiometric acid concentration for a total dissolution of filtercake was calculated to be about 2 M. Thus the effect of acid concentration in the range of 0.81–2.0 M was studied at 25 °C with a stirring speed of 400 rpm for $-600 + 500 \mu\text{m}$ particle size and pulp density of 1/8. As seen in Fig. 8(a), the increase in acid concentration increased the dissolution rate of cadmium. For 0.81 and 1.0 M concentrations, there is virtually an acid deficiency effect. Nevertheless, it was observed that there was no beneficial effect of increasing acid concentration more than 1.7 M. However, after elapsing a certain time, namely 15 min, the efficiency practically remains constant. This behavior could be explained by the fact that as the acid concentration in the medium increases, the apparent rate of product increases and as the product reaches the saturation value near the solid particle; it forms a difficult soluble solid film layer around the particle. Consequently, the dissolution process slows down [9].

The cadmium extraction efficiencies after 15 min leaching at 0.81 and 1.7 M sulfuric acid were found to be 63% and 95%, respectively.

The effect of leaching time on the dissolution of cadmium is also evident in Fig. 8(a). Obviously, the cadmium recovery increased with increasing leaching time with the initial dissolution of cadmium being very rapid. For 1.7 M concentration, after 5 min, 85% cadmium recovery was achieved and this increased to 95% after 15 min. Thus 15 min of leaching time was found to be optimum.

Also, the results for the effect of sulfuric acid concentration were applied to this kinetic model and k_d values for each sulfuric acid concentration were determined. From the k_d and sulfuric acid concentration values, a plot of $\ln k_d$ versus $\ln[\text{H}_2\text{SO}_4]$ was obtained (Fig. 8(b)). As seen in Fig. 8(b), the order of the reaction with respect to sulfuric acid was proportional to a 1.047 power ($[\text{H}_2\text{SO}_4]^{1.047}$) with a correlation coefficient of 0.9859.

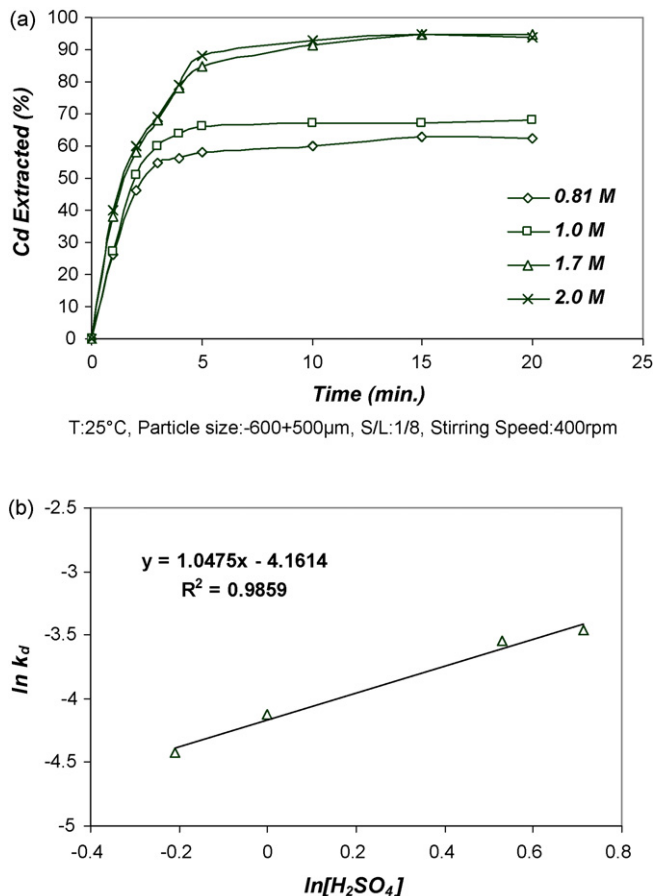


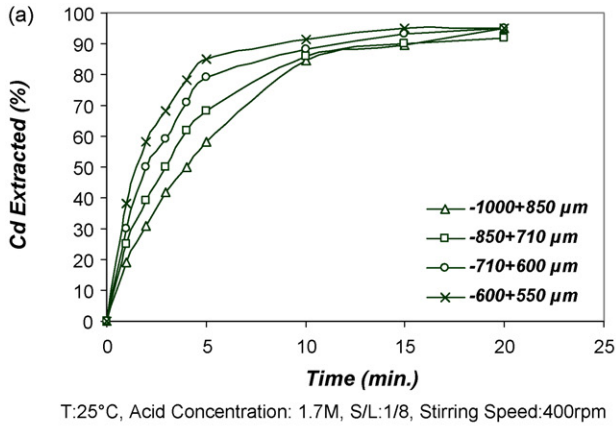
Fig. 8. (a) The effect of sulfuric acid concentration on the dissolution of cadmium at proposed experimental conditions. (b) Plot for the determination of reaction order with respect to $\ln[\text{H}_2\text{SO}_4]$.

4.3. Effect of particle size

Four different particle sizes ($-600 + 500$, $-710 + 600$, $-850 + 710$ and $-1000 + 850 \mu\text{m}$) were used in the experiments with 1.7 M sulfuric acid concentration, 25 °C, 1/8 pulp density and 400 rpm stirring speed. From Fig. 9(a), it is evident that the smaller the particle size, the faster was cadmium dissolution. By decreasing the particle size, the contact area of particles with the fluid increases. The results showed that the particle size had a meaningful effect on the dissolution of cadmium. The cadmium extraction reached 89.5% and 95% after 15 min leaching for $-1000 + 850$ and $-600 + 500 \mu\text{m}$ particle sizes, respectively.

In order to clarify the quantitative relationship between the reaction rate and particle size, the experimental data in Fig. 9(a) were analyzed in terms of Eq. (12), and the rate constants (k_d) for the four sizes were obtained and plotted in Fig. 9(b) against d_0^{-2} (d_0 is the average initial particle diameter). The regression equation is found to have an R square of 0.9867. The directly proportional relationship of rate constants to d_0^{-2} supports the conclusion that the leaching of cadmium in sulfuric acid is diffusion controlled.

From the effects of particle size on cadmium dissolution given in Fig. 9(a), the apparent rate constant was determined. According to $\ln k_d - \ln r_0$ curve shown in Fig. 9(c), the order of reaction with respect to particle size (r_0) was found to be inversely proportional to a 2.1819 power ($r_0^{-2.1819}$).



T:25°C, Acid Concentration: 1.7M, S/L:1/8, Stirring Speed:400rpm

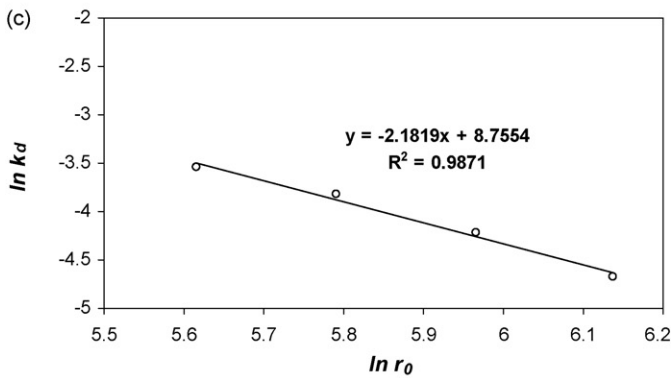
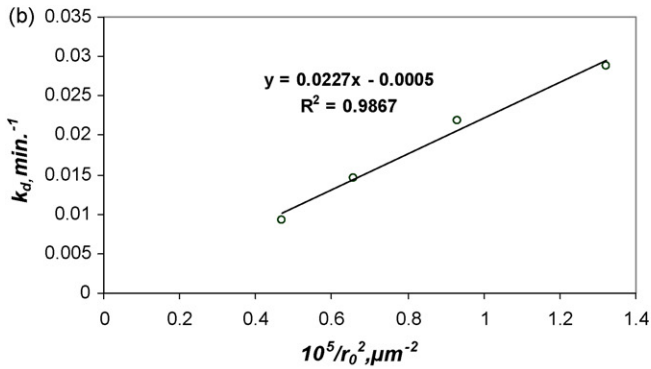
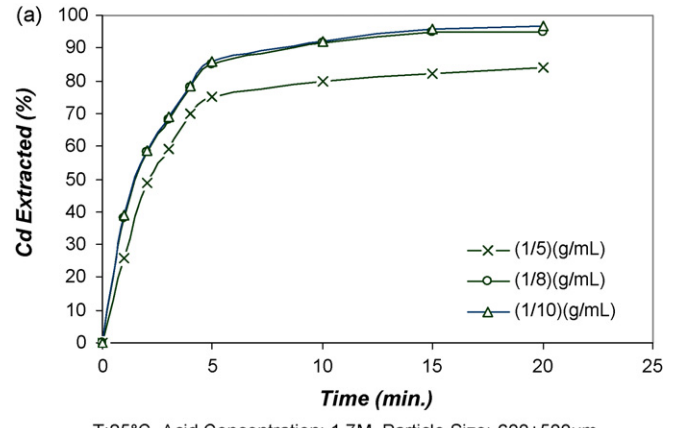


Fig. 9. (a) The effect of particle size on the dissolution of cadmium at proposed experimental conditions. (b) Plot of k_d against $1/r_0^2$ and (c) Plot of $\ln k_d$ against particle size.

4.4. Effect of solid/liquid ratio

Fig. 10(a) gives the cadmium recovery as a function of solid to liquid ratio (weight of solid/volume of liquid) at 25 °C in solutions containing 1.7 M sulfuric acid and particle size of –600 + 500 μm with a stirring speed of 400 rpm. According to experimental results presented in Fig. 10(a), it was found that cadmium recovery increased until the solid/liquid ratio of 1/8, where 95% of cadmium recovery was achieved. Therefore, this quantity was considered optimum for the dissolution of cadmium.

From the effect of solid/liquid ratio on cadmium dissolution given in Fig. 10(a), the apparent rate constant was determined. According to $\ln k_d - \ln(S/L)$ curves shown in Fig. 10(b), the order of reaction with respect to solid/liquid ratio was found to be inversely proportional to a 0.5969 power ($[S/L]^{-0.5969}$).



T:25°C, Acid Concentration: 1.7M, Particle Size:-600+500μm, Stirring Speed:400rpm

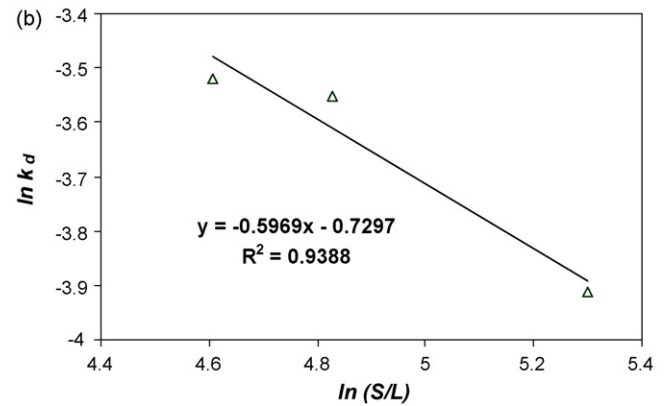
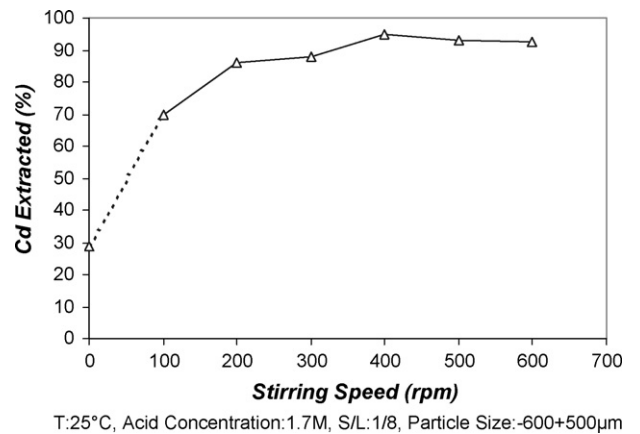


Fig. 10. (a) The effect of solid/liquid ratio on the dissolution of cadmium at proposed experimental conditions and (b) Plot of k_d against pulp density.

4.5. Effect of stirring speed

The effect of stirring speed on the dissolution of cadmium was investigated at various stirring speeds (0 (no agitation), 100, 200, 300, 400, 500 and 600 rpm) at 25 °C in solutions containing 1.7M sulfuric acid and with solid/liquid ratio of 1/8 and particle size of –600 + 500 μm. The duration of each experiment was 15 min.



T:25°C, Acid Concentration:1.7M, S/L:1/8, Particle Size:-600+500μm

Fig. 11. The effect of stirring speed on the dissolution of cadmium at proposed experimental conditions.

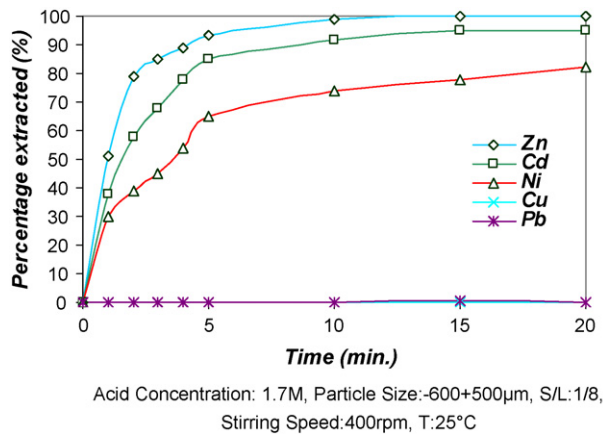


Fig. 12. Dissolution yield curves for Zn, Cd, Ni, Cu and Pb at optimum leaching conditions (temperature: 25 °C, acid concentration: 1.7 M, pulp density: 1/8, stirring speed: 400 rpm, particle size: –600 + 500 µm).

Fig. 11 shows that the stirring speed has a significant effect on the dissolution of cadmium. The cadmium recovery obtained under the same experimental conditions without agitation was 29%, while it was nearly 95% when 400 rpm stirring speed was applied. It can be concluded that this effect occurs by the increased diffusion rate of ions in leaching medium with increasing agitation [10]. However, the results show that the leaching rate of cadmium increases quickly below 400 rpm and remains almost constant beyond this speed. Therefore 400 rpm was chosen as optimum agitation rate.

4.6. The behavior of Zn, Ni, Cu and Pb

The behavior of Zn, Ni, Cu and Pb is shown in Fig. 12 at proposed conditions. The order of leaching efficiency was found to be $Zn > Cd > Ni$ at the optimum leaching conditions (1.7 M acid concentration, –600 + 500 µm particle size, solid/liquid ratio of 1/8, 400 rpm stirring speed and 25 °C temperature). This manner is in complete concordance with theoretical predictions made in Section 2. Also, no copper and lead were dissolved and they were easily separated, as theoretically foreseen. This manner was also reported elsewhere [11–13].

AAS analysis confirmed this observation. Moreover, to ensure the above result, the leaching residue was subjected to XRD analysis, which confirmed the existence of Cu and Pb in the residue. As can be observed from Fig. 13, the residue is composed of Cu_2O ,

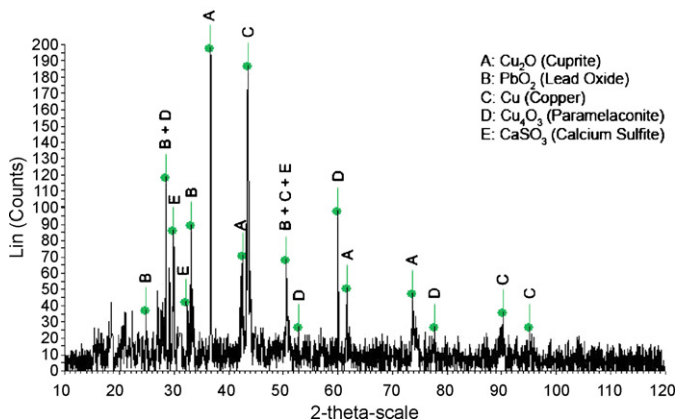


Fig. 13. X-ray diffraction analysis of leaching residue.

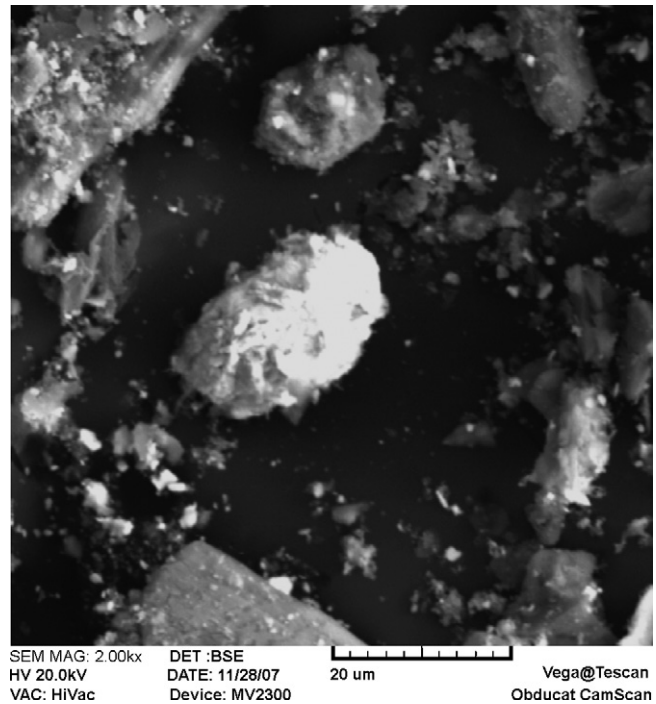


Fig. 14. SEM micrograph of a typical Cd_5Ni aggregate (the white phase in the center).

PbO_2 , Cu, Cu_4O_3 and $CaSO_3$. However, no lead sulfate was detected in the residue. This gives rise to the assumption that lead is present as either lead metal or lead oxide in the beginning material. Note that inasmuch as lead content in the residue was as low as 1.08 wt%, which is below detection limit of XRD, at first it was assumed as metal or metal oxide. Also SEM analysis supported this idea, since no lead sulfate was detected through SEM analysis. That lead dioxide is very insoluble in sulfuric acid has been well established. It means that lead is present as PbO_2 in the filtercake and remains unchanged through sulfuric acid leaching and is simply separated.

According to the reactions, there could be two insoluble products, i.e. $PbSO_4$ and copper or nickel, probably cemented on cadmium. The former assumption was rejected due to the previous findings. However, to check the validity of the above discussions, a solid sample was taken from the leaching vessel at $t=2$ min and analyzed using both XRD and SEM. The XRD showed alloying phases, Cd_5Ni , $Cd_2Ni_{1.9}$ and $Cd_{10}Cu_3$. Our attempt to find an insoluble layer on cadmium using SEM had no results, however, a porous aggregate of Cd_5Ni was observed. Fig. 14 represents a typical Cd_5Ni aggregate. With that said, the inter-diffusion of cadmium and sulfate ions through the porous region of the insoluble alloying layer was probably the main resistance to the dissolving process. Reactions (6) and (15) require SO_4^{2-}/Cd^{2+} ion transport between the reaction site and the bulk liquid phase. Therefore, D_{eff} can be replaced by D_e which is defined as coefficient of inter-diffusion of Cd^{2+} and SO_4^{2-} ions through the porous metallic layer. Reactant and product ions, i.e. SO_4^{2-} and Cd^{2+} must diffuse throughout the pores in order to obtain a continuing reaction. D_e is the inter-diffusion coefficient of SO_4^{2-} and Cd^{2+} ions indicating ion transfer within the porous region.

The reaction between cadmium and sulfuric acid is of electrochemical nature. Because of considerable conductivity of the metallic layer, there is no resistance to charge transfer through the solid region. The only remaining resistance is thus related to transfer of ions through the aqueous electrolyte that fills the porous region of the solid phase. This resistance is considered by the inter-diffusion coefficient D_e in the present system.

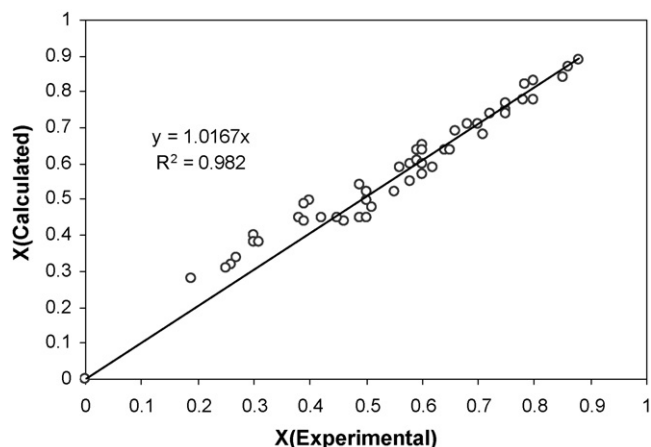


Fig. 15. Comparison of experimental and calculated dissolution fraction of cadmium in sulfuric acid.

5. Process rate equation

Calculations show that activation energy and the order of reaction values with respect to H_2SO_4 concentration, solid/liquid ratio and particle size confirm to the shrinking core model for a diffusion-controlled process. Thus the leaching of Cd–Ni filtercake can be clearly presented by Eq. (16).

$$\left[1 - \left(\frac{2}{3}\right)X - (1 - X)^{2/3}\right] = k_d t = k_0 [\text{H}_2\text{SO}_4]^{1.0475} \left(\frac{S}{L}\right)^{-0.5969} \times r_0^{-2.1819} \exp\left(\frac{-13.363}{RT}\right) t \quad (16)$$

Plotting of $1 - (2/3)X - (1 - X)^{2/3}$ against $[\text{H}_2\text{SO}_4]^{1.0475} (S/L)^{-0.5969} r_0^{-2.1819} \exp(-13.363/RT)t$ gives a k_0 amount of 997 with a regression coefficient of 0.996. To test the agreement between the experimental conversion values and the values calculated from the empirical equation, the plot of X (experimental) versus X (calculated) was drawn. As seen in Fig. 15, the agreement between experimental and calculated values is very good, with relative mean squares of errors of 0.0891 calculated by Eq. (17) and with a regression coefficient of 0.982.

$$E.R. = \left[\frac{1}{N} \sum_{i=1}^N \frac{(X_{\text{cal.}} - X_{\text{exp.}})^2}{(X_{\text{cal.}})^2} \right]^{1/2} \quad (17)$$

where $X_{\text{cal.}}$ is the calculated conversion value, $X_{\text{exp.}}$ is the experimental conversion value, and N is the number of experimental data [14], which is 72.

6. Conclusions

Sulfuric acid leaching, the first chemical step of an integrated process for recovering cadmium from Cd–Ni zinc plant residues was tested. Taking into account the parameters used in the experiments, temperature, acid concentration, pulp density (solid/liquid ratio), particle size and stirring speed and their levels, a kinetic model has been assigned to the dissolution of cadmium present in Cd–Ni zinc plant residues within first 5 min of reaction.

Based on the results obtained in this research, the following conclusions could be drawn:

- It was observed that the reaction rate was not sensitive to temperature in the range of 25–55 °C. However, a minor raise in

dissolution efficiency was evident due to increase in temperature.

- In terms of acid concentration, it was shown that the dissolution rate increased up to 1.7 M, however, increasing concentration did not enhance the dissolution reaction. Also, the dissolution rate increased with decreasing particle size.
- The dissolution of Cd–Ni residues with sulfuric acid solution was found to be controlled by shrinking core model for diffusion-controlled process within first 5 min of the dissolution reaction. The activation energy was calculated as 13.363 kJ/mol for the temperature range of 25–55 °C.
- Dissolution rate could be expressed by Eq. (16), which is a semi-empirical mathematical model symbolizing the process. This expression can estimate the fraction reacted with relative mean squares of errors of 0.0891. Furthermore, the agreement between the $X_{\text{cal.}}$ and $X_{\text{exp.}}$ is linear with a regression coefficient of 0.982.
- As presented by the model, the reaction rate is inversely proportional to the squared particle size.
- The order of the reaction with respect to H_2SO_4 concentration, particle size and solid/liquid ratio were found to be 1.0475, –2.1819 and –0.5969, respectively.
- The optimum leaching conditions were determined as: 1.7 M H_2SO_4 , 25 °C, 125 g/L solid/liquid ratio and 400 rpm. By using a particle size of –600 + 500 μm , 85% of cadmium was extracted after 5 min; however, a slight raise took place in extraction percent in excess of time. A maximum cadmium recovery of 95% was obtained by leaching with 1.7 M sulfuric acid for 15 min at 25 °C with 1/8 solid/liquid ratio agitated at 400 rpm.
- The results showed that it is possible to separate copper and lead from Cd–Ni zinc plant residues through selective leaching. This residue may be stockpiled for the recovery of associated copper and lead, which requires a separate process design.
- Inasmuch as the Cd–Ni filtercake contains heavy metals which cause adverse environmental effects and despite the fact that almost all cadmium present in the filtercake is transferred into the solution, the environmental concerns over heavy metals still stands, since part of cadmium is transferred into the leach residue along with copper and lead, which all are heavy metals. In the view of this fact, the overall process design should take this fact into account and recycle the secondary leach residue as well. One recommendation can be the mixing of secondary residue, left after copper and lead recovery, with primary Cd–Ni filtercakes, which is the subject of our next work. The cadmium bearing solution which is the beginning aqueous for the extraction of cadmium can be used for the separation of cadmium metal through SX-EW or cementation, depending on the impurities present in the solution.

Acknowledgments

This work was financially and scientifically sponsored by R&D center of Iranian Zinc Mines Development Company under the Grant no. IZMDC-RD/07/45-LCd. Thanks are due to Ms. Mashayekhi, R&D center, for performing chemical analyses and also to anonymous reviewers of this paper. M.S.S. is individually indebted to *Songül Karlı*, “büyük sevdam”.

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