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DETERMINATION OF EFFECTIVE PARAMETERS IN PILOT PLANT SCALE DIRECT LEACHING OF A ZINC SULFIDE CONCENTRATE

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Abstract: Several studies have been conducted on direct leaching of zinc sulfide concentrate, in the recent years, though the results of these studies are not in balance with the industrial condition. Hence, the aim of the current investigation was to study direct leaching of the Angouran zinc sulfide concentrate using a tubular reactor on a pilot scale. The volume and height of the reactor were 440 dm^3 and 9 m, respectively and sphalerite was dissolved under hydrostatic pressure of the reactor. The ferrous sulfate concentration of the solution plays a key role in the process and sphalerite oxidation by regenerated ferric sulfate has been proposed as main dissolution mechanism in the direct leaching process. The working parameters such as ferrous sulfate, sulfuric acid and air flow rate, zinc sulfate initial concentration and particle size were analyzed in this study. Due to the scale effect and higher rate and volume of reactor in comparison with laboratory-scale experiments, reached data are more reliable to use in industrial applications. The zinc conversion percent increased as the ferric sulfate and sulfuric acid concentration was increased, but the criterion was decreased with an increscent of zinc sulfate initial concentration and the particle size. About 86% of zinc was recovered at temperature 368 K (95 °C), 0.4 mol dm^{-3} ferrous sulfate concentrations, 0.25 mol dm^{-3} sulfuric acid, and air flow rate of 0.41 $dm^3_{air}\ dm^{-3}_{slu}\ min^{-1}$.

Keywords: *direct leaching, sphalerite concentrate, effective parameters, pilot scale*

Introduction

Angouran lead and zinc mine was established in the Zanjan province (Iran) that produce massive amount of sulfide minerals including sphalerite and lead. Therefore, extraction and recovery of zinc from sulfide resource seems necessary. In recent years, direct leaching of the zinc sulfide concentrate has been interested considerably due to the technical and environmental limitations of the conventional roast-leach-electrowinning process (RLE) (Haakana et al., 2008; Santos et al., 2010). Two alternative processes have been suggested for zinc sulfide leaching in the sulfate

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solutions: high pressure leaching (Xie et al., 2007; Yan et al., 2010) and atmospheric leaching (Aygon, 2006; Salmi et al., 2010; Souza et al., 2006; Xu et al., 2013). Use of high pressure leaching was developed in the 1980s, considerably. In this process sulfuric acid attacks to sulfide ore as follows (1):

$$H_2SO_4 + ZnS_{(s)} \rightarrow ZnSO_{4(aq)} + H_2S_{(g)}. \tag{1}$$

However, the presence of oxygen in the system decreases sulfuric acid attack effect in direct leaching processes (Yan et al., 2010). Sphalerite could be oxidized directly by pressured oxygen and sulfuric acid as follows (2):

$$2ZnS_{(s)} + O_2 + 2H_2SO_4 \rightarrow 2ZnSO_{4(aq)} + 2H_2O + 2S^0_{(s)}. \tag{2}$$

On the other hand, the oxygen would oxidize ferrous sulfate and the solvated ferric sulfate is formed as follows (3):

$$4FeSO_{4\,(aq)} + O_2 + 2H_2SO_4 \rightarrow 2Fe_2(SO_4)_{3(aq)} + 2H_2O. \tag{3}$$

The oxidation rate of Fe^{2+} to Fe^{3+} increased quadratically with increasing ferrous sulfate concentration (Dreisinger and Peters, 1989; Xie et al., 2007). The regenerated ferric sulfate can oxidize ZnS. Then, the solvated zinc sulfate and elemental sulfurs are released which can be seen in the following reaction (4):

$$Fe_2(SO_4)_3 + ZnS_{\,(s)} \rightarrow ZnSO_4 + 2FeSO_4 + S^0_{(s)}. \tag{4}$$

The Fe^{3+} concentration could has a significant effect on zinc conversion and the order of Fe^{3+} in ZnS dissolution was reported 0.35 (Souza et al., 2007) and 1 (Dutrizac, 2006). The atmospheric leaching is performed under normal pressure condition (Dutrizac, 2006) and the added ferric sulfate oxidizes zinc sulfide (Eq. 4). Also, adding other chemical oxidant caused oxidization of the ferrous sulfate and regeneration of ferric sulfate (Aydogan, 2006; Sokic et al., 2012, Agacayak et al., 2014). Among chemical oxidizers, the addition of oxygen as an oxidizing agent of atmospheric leaching was a little more desirable option. The most important advantage of oxygen gas, compared to other chemical oxidants (such as nitric acid, sodium nitrate and etc.), is that it has no harmful effects on the environment. In this regard, Santos et al. (2010) studied ferric ion formation, without adding sulfide concentrate, by oxygen gas injection in solution. They reported that it was so slow, so that lower than 10% of ferrous ions converted to ferric ions after 10 hours. The ferric ion formation rate was accelerated by increasing the dissolved oxygen concentration (Holmes and Crundwell, 2000). The retention time and partial pressure of oxygen bubbles can be increased in order to increase dissolved oxygen (Kaskiala, 2005).

A reactor was invented that is suitable for the atmospheric direct leaching of zinc sulfide concentrate (Filippou, 2004). The reactor was constructed from a straight tube equipped with an oxygen inlet in the bottom and stirred with a helical turbine. This design was effective in increasing the oxygen partial pressure and retention time of its bubbles in the reactor. In this case, the redox potential of the solution is rapidly increased by oxygen blowing. In this field, several studies (Haakana et al., 2007; Lampinen et al., 2015) were carried out in laboratory scale to estimate ZnS conversion. The aim of these researches was to identify and predict zinc dissolution in an industrial process.

Lampinen et al. (2015) carried out their experiments in the autoclave under fixed pressure of the reactor. Whereas the pressure varies according to the height of slurry in an industrial process (Filippou, 2004). So, their reactor design (Lampinen et al., 2015) has major differences with an industrial process and the results are in appropriate for investigation of the effective factors. On the other hand, some of the studies (Haakana, 2007; Lampinen, 2010) attempted to clarify the mechanism of direct leaching at larger scale. But the above process was only introduced in a fixed condition and the effect of different parameters (e.g. Fe and H_2SO_4 concentration, particle size and etc.) on zinc extraction has not been presented. Hence, the results were not applicable for practical factor influencing zinc extraction in an industrial process. In the industrial processes, the leaching circuit usually consisted of a high acid leaching step (HAL) and a low acid leaching step (LAL) in an industrial process (Haakana et al., 2008). The sphalerite concentrate was fed to LAL, and the leach residue contains a considerable amount of the undissolved zinc. Therefore, the residue from LAL was fed to HAL.

In this study, direct leaching of zinc concentrate was carried out in tubular reactor and effect of parameters including sulfuric acid, zinc and iron concentration, air flow rate and particle size was studied on Zn conversion in pilot scale. It should be noted that nature and kinetics of leaching reaction may be affected by scale up process (Kolaczkowski et al., 1999). Obtained results of current study could be valid to be used in the industrial processes due to large-scale experiments. Changing the leaching parameters in the working condition, the effective parameters were identified and process optimization was facilitated, consequently. Moreover, the dissolution reaction mechanism was defined based on kinetics of process.

Materials and methods

Materials

The zinc sulfide concentrate of Angouran mine was used in all leaching experiments. Preparation, grinding and grading processes of the zinc sulfide ore were carried out at the Aria mineral processing company at Zanjan, Iran. The size of the particles (d_{80}) along with chemical analysis of the concentrate can be observed in Table 1. As can be seen, the iron content was less than 2.5% in all samples. The X-ray diffraction (XRD) pattern was used for identification of present minerals phase. As shown in Fig. 1, sphalerite is a dominant phase in the sulfide concentrate. In addition to sphalerite, other minerals such as wurtzite (ZnS), smithsonite ($ZnCO_3$), quartz (SiO_2) and otavite ($CdCO_3$) can also be seen. Adjusting acidity and iron concentration of the solution was carried out by industrial grade sulfuric acid (98.5%) and crystalline ferrous sulfate ($FeSO_4{\cdot}5H_2O$).

Analysis Methods

The concentration of metallic ions (Zn, Fe, Cu, Ni, and Cd) in the sample solutions obtained from the leaching experiments was analyzed by atomic absorption spectroscopy (Varian, AA240). The Fe(II) and Fe(III) concentrations were analyzed by cerium(IV) sulfate with phenanthroline indicator and EDTA with the salicylic acid indicator, respectively. The sulfuric acid concentration was determined by sodium hydroxide and methyl yellow indicator. To determine zinc carbonate concentration, first, the concentrate was dissolved in 5.5 M ammonium chloride + 3.5 M ammonium acetate solution and then zinc concentration in the solution was analyzed by atomic absorption spectroscopy (AAS).

Leaching tests

A tubular reactor was designed to do experiments of sphalerite direct leaching. A scheme of the experimental setup is shown in Fig. 2. The volume of tubular reactor and the height of slurry were 440 dm^3 and 9 m, respectively. The acidity, iron and zinc concentration, and the desired temperature of solution were made in primary tank. Then the slurry was pumped into a tubular reactor and the first sample was taken at that time. After filling the reactor with slurry, the valves of the primary tank was closed and the pulp was being circulated from bottom of the tube to the top, for agitation of slurry. The circulation rate of slurry inside the reactor was 80 $dm^3\ min^{-1}$ in all tests and the air flow was fed from the bottom of the reactor. The air flow rate was defined as the volume of the air transferred into the reactor per volume of slurry in a minute ($dm^3_{air}\ dm^{-3}_{slu}\ min^{-1}$). The temperature of the slurry was adjusted indirectly by the hot steam coil. Air flow rate and bottom of the reactors pressure was controlled by gas mass flow controller and manometer, respectively.

Iron removal was carried out after leaching process through neutralization of pregnant leach solution (PLS). Hence, leaching experiments were carried out in the low concentration of sulfuric acid (0.15-0.5 mol dm^{-3}) and the concentration of ferrous sulfate in solution was selected 0.02-0.4 mol dm^{-3}. During test time, the temperature, sulfuric acid and iron concentration of the solution were controlled, frequently.

Table 1. Chemical composition of different fractions of complex concentrate

d_{80} (µm)	Zn(%)	Fe(%)	Pb(%)	Cd(%)	Cu(ppm)	Ni(ppm)	Mn(ppm)
62	50.8	2.6	3.6	1.65	910	463	174
75	46.5	2.1	3.3	1.6	827	433	170
88	50.6	2.4	3.1	2.1	870	450	172
125	46.7	2.5	3.46	2.1	911	715	200

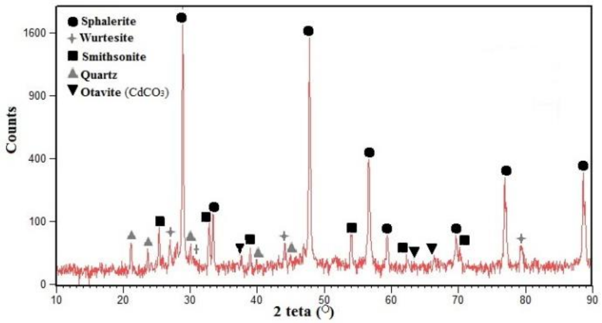

Fig. 1. XRD pattern of zinc sulfide concentrate

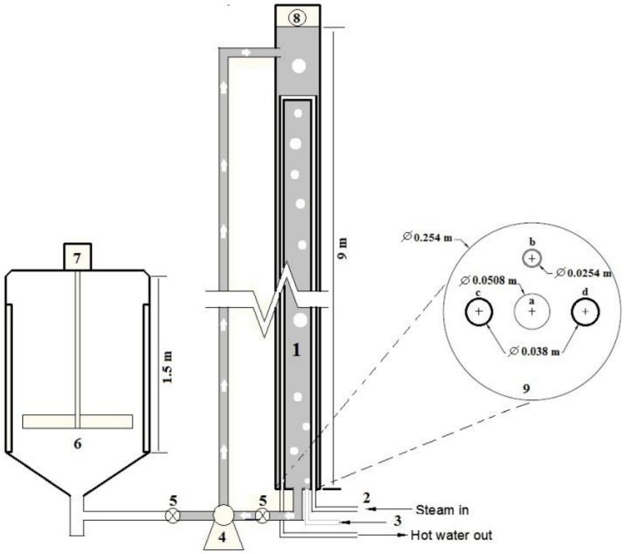

Fig. 2. Schemes of leaching setup 1) tubular reactor 2) steam input 3) air inlet 4) pump 5) tap off 6) primary tank 7) electromotor 8) liquid level float 9) cross section of tube: (a) slurry circulation tube (b) air inlet (c) steam in (d) hot water out

Results and discussion

Effect of acid concentration

The concentration of the sulfuric acid is one of the most important parameters that could affect leaching of zinc sulfide concentrate. The effect of sulfuric acid concentration on the sphalerite leaching was studied at the ranges of 0.15–0.5 mol dm^{-3}. As it can be seen in the Fig. 3, the increase of H_2SO_4 concentration results in the relative increase of zinc extraction. The zinc conversion percent at 0.15, 0.25 and 0.5 mol dm^{-3} are 42%, 47%, 53%, respectively, that the order of H_2SO_4 was calculated approximately 0.25.

Fe^{3+} ion is main oxidation agent in leaching that could attack to ZnS surface. The increasing H_2SO_4 concentration led to the increase the rate Fe^{3+} generation, according to Eq. 3. In fact, H_2SO_4 supplies needed species of SO_4^{2-} in Fe^{2+} to Fe^{3+} oxidation reaction and increasing acid concentration has exhibited a positive effect on the reaction rate (Eq. 3). On the other hand, direct sulfuric acid attack to the surface of the mineral is probable and the hydrogen sulfide (H_2S) gas is released as a result of reaction (Eq. 1) (Yan et al., 2010; Dutrizac, 2006). Moreover, the acid attack reaction was suggested as the main leaching reaction by Corriou et al. (1988) and Xu (2013).

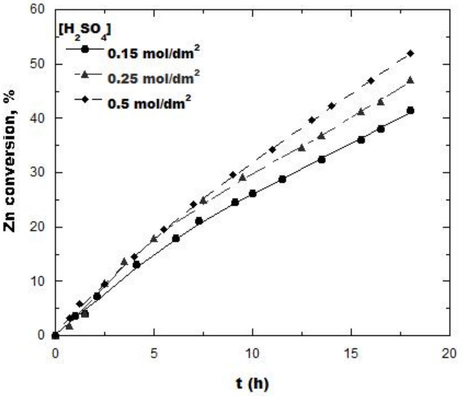

Fig. 3. Effect of sulfuric acid concentration on zinc extraction. T = 360 K (87 °C), 0.025 mol dm^{-3}, $[FeSO_4]$ 0.2 mol dm^{-3}, air flow rate 0.4 $dm^3_{air} \cdot dm^{-3}_{slu}$ min^{-1}, particle diameter 88 μm

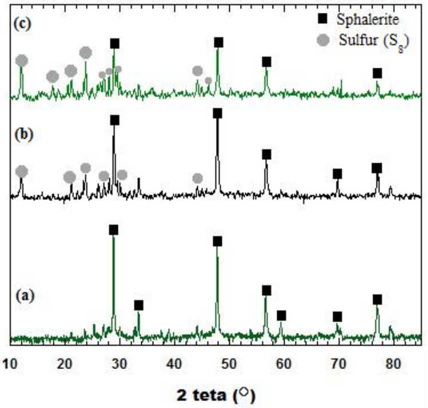

Fig. 4. XRD pattern of leaching residue, (a) beginning of the process (b) after 6 h and (c) after 12 h

Products of leaching could help to recognize the zinc dissolution reaction. So, X-ray diffraction was used to analyze the leach residue and the patterns have been shown in Fig. 4. Doing so, the elemental sulfur (S_8) peaks were formed with a decrease of sphalerite peaks intensity in 6 h and 12 h samples. According to these findings, the elemental sulfur is the main product of the direct leaching reaction of sulfide concentrate.

Crundwell (2013) presented that the dissolution reaction starts with an acid attack on the mineral surface to form H_2S, in the following, H_2S is oxidized by the oxidant in the solution and elemental sulfur is formed. In order to determine the contribution of acid attack reaction, Begar et al. (2015) studied pressure leaching of sphalerite in the absence of oxygen. The zinc extraction below 373 K (100 °C) is less than 25%. They concluded temperature has a major influence on the sphalerite leaching and more than 95% of zinc at 433 K (160 °C) dissolved.

The leaching process without oxygen blowing was surveyed to understand the role of sulfuric acid. The zinc conversion was lower than 4%, whereas this criterion is increased to 75% with air blowing in similar condition (e.g. H_2SO_4, Fe, $ZnSO_4$ concentration, and temperature). Therefore, direct acid attack reaction gives a little participation to the leaching process. Hence, elemental sulfur could be formed by direct oxidation of sphalerite through ferric ions or oxygen (Eq. 2 and 4) and the acid attack reaction has negligible effect in the zinc dissolution process.

Effect of the ferrous sulfate initial concentration

The effect of ferrous sulfate initial concentration on the zinc extraction was demonstrated in Fig. 5. The experiments were carried out at the four different iron concentrations 0.02, 0.1, 0.2 and 0.4 mol dm^{-3}. It can be seen that iron initial concentration has a significant effect on zinc conversion, undoubtedly. Increasing the iron initial concentration increases the zinc conversion in 16 hours, obviously. So that, the Zn recovery percentage is lower than others at 0.02 mol dm^{-3} Fe. Table 2 represents the concentration of ferric ions (Fe^{3+}) at different time intervals of 4, 8, 16 h and different ferrous sulfate initial concentration. As can be seen in Table 2, Fe^{3+} concentration has increased in the early hours, and then remained at constant values. By plotting Fe^{2+} concentration versus Fe^{3+} concentration at these constant values, a straight line (with a slope of 10.07) was formed (Fig. 6.) Therefore, the ratio of ferrous ion to ferric ion (Fe^{2+} / Fe^{3+}) is 10. Based on the Nernst equation, the redox potential of solution could be calculated by Fe^{2+} / Fe^{3+} ratio which specify approximately 690 mV. On the other hand, the solubility of oxygen in sulfuric acid solution has been reported lower than 0.001 mol dm^{-3} (Kaskiala, 2005). Accordingly, due to the very low concentration of oxygen and the significant impact of Fe concentration on Zn conversion, oxygen couldn't directly oxidize sulfide concentrate. The ferric ions oxidize sphalerite concentrate, according to Eq. 4 and the ferric ion plays a critical role in direct leaching of sphalerite in pilot scale. The zinc conversion percent are 6%, 21%, 42, 70% in 0.002, 0.009, 0.018, 0.034 of Fe^{3+} concentration, and the order of Fe^{3+} in ZnS dissolution reaction is approximately 1.

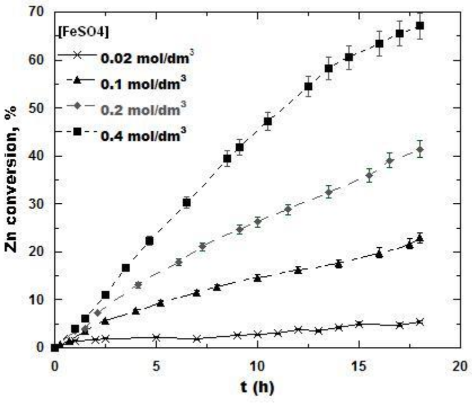

Fig. 5. Effect of ferrous sulfate initial concentration on zinc extraction.
T = 360 K (87 °C), [H_2SO_4] 0.15 mol dm^{-3}, air flow rate 0.4 dm^3·dm^{-3}·min^{-1},
[$ZnSO_4$]$_{initial}$ 0.025 mol·dm^{-3}, mean particle diameter 88 μm

Table 2. Ferric ion concentration in different initial iron and zinc concentrations and passing of time

Initial $FeSO_4$ concentration (mol dm^{-3})	Initial $ZnSO_4$ concentration (mol dm^{-3})	Air flow rate $\frac{dm^3_{air}}{dm^3_{slu.}.min}$	[FeIII] after 4 h (mol dm^{-3})	[FeIII] after 8 h (mol dm^{-3})	[FeIII] after 16 h (mol dm^{-3})
0.02	0.025	0.41	0.0012	0.015	0.002
0.1			0.0055	0.009	0.009
0.2			0.008	0.015	0.018
0.4			0.012	0.026	0.035
0.4	0.025	0.41	0.012	0.026	0.035
	0.5		0.0140	0.03	0.035
	1		0.0155	0.032	0.036
0.2	0.025	0.22	0.0085	0.013	0.017
		0.41	0.008	0.015	0.018
		0.75	0.01	0.015	0.018

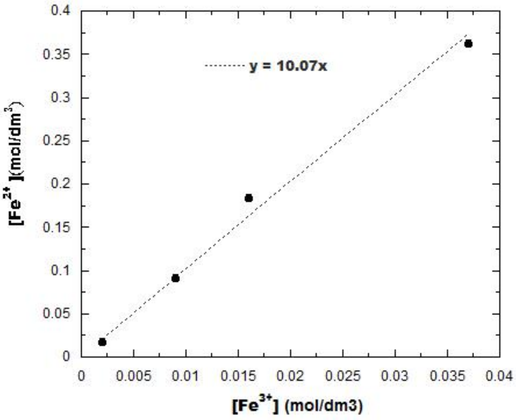

Fig. 6. Fe^{2+} vs. Fe^{3+} concentration at 0.02, 0.1, 0.2, 0.4 mol dm^{-3} initial Fe after 16 hours. T = 360 K (87 °C), [H_2SO_4] 0.15 mol dm^{-3}, air flow rate 0.4 dm^3 dm^{-3} min^{-1}, $[ZnSO_4]_{initial}$ 0.025 mol dm^{-3}, particle diameter 88 μm

Effect of air flow rate

As mentioned, oxygen may influence the Fe^{3+} formation rate. Figure 7 shows the effect of air flow rate on zinc extraction. Zn extraction at a lower flow rate (0.22 dm^3_{air} dm^{-3}_{slu} min^{-1}) is 33% after 16 hours. Increasing the air flow rate led to increase in Zn conversion, so that the Zn conversions at 0.41 and 0.75 dm^3_{air} dm^{-3}_{slu} $min^{\mathbf{-1}}$ are 39% and 42%, respectively. The dissolution of oxygen in solution is directly related to the partial pressure of oxygen (Kaskiala, 2005). Dreisinger and Peters (1989) suggested oxygen gas dissolution in aqueous solution continues by oxidization of Fe^{2+} ions by oxygen molecules and the dissolved oxygen could affect Fe^{3+} concentration. The oxygen pressure regime was defined by the height of slurry in a tubular reactor (Lampinen, 2010). The role of air flow rate at 0.41 and 0.75 $dm^3_{air}\ dm^{-3}_{slu}\ min^{-1}$ is negligible on zinc dissolution due to a similar regime of oxygen pressure. But in another view, oxygen gas transfer to all parts of the reactor is of a great importance. As can be seen in Table 2, the rate the Fe^{2+}oxidation at 0.22 $dm^3_{air}\ dm^{-3}_{slu}\ min^{-1}$ is lower than 0.4 $dm^3_{air}\ dm^{-3}_{slu}\ min^{-1}$. Hence, shortage of oxygen for reaction happens with lower flow rates in direct leaching of sphalerite in pilot scale.

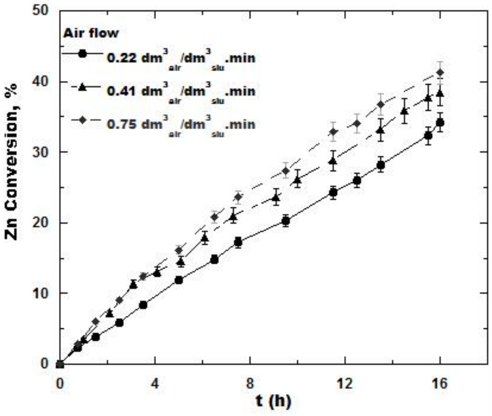

Fig. 7. Effect of air flow rate on zinc extraction.
T = 360 K (87 °C), $[H_2SO_4]$ 0.15 mol dm^{-3}, $[FeSO_4]$ 0.2 mol dm^{-3},
$[ZnSO_4]_{initial}$ 0.025 mol dm^{-3}, mean particle diameter 88 μm

Effect of zinc initial concentration

The effect of zinc sulfate initial concentration sulfate concentration can be seen in Fig. 8. Increasing zinc sulfate concentration 0.025 to 1 mol dm^{-3} decreases leaching recovery and the order of initial $ZnSO_4$ effect in Zn dissolution is -0.1. Dutrizac (2006) studied the effect of $MgSO_4$ and $ZnSO_4$ concentration on Zn dissolution rate. These sulfate salts had a similar effect on zinc extraction, decreasing the dissolution rate of Sphalerite. He concluded that increasing the sulfate concentrations prevented the leaching reaction rate. On the other hand, too much initial Zn in solution shifts equilibrium to left direction in Zn dissolution reaction based on the Le Chatelier principle. With reference to Table 2, Fe^{3+} analysis shows that the rate of ferric ion formation increased with increasing the zinc sulfate concentration. Therefore, despite the positive effect of sulfate anions on ferrous sulfate oxidation, zinc conversion was decreased in direct leaching of sphalerite.

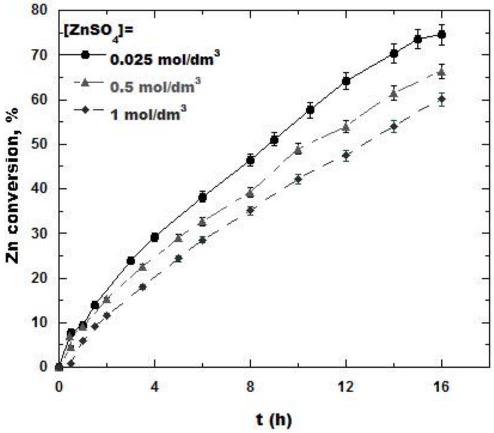

Fig. 8. Effect of zinc sulfate initial concentration on zinc extraction.
T = 360 K (87 °C), [H_2SO_4] 0.15 mol dm^{-3}, [$FeSO_4$] 0.4 mol dm^{-3},
air flow rate 0.4 dm^3_{air} dm^{-3}_{slu} min^{-1}, mean particle diameter 52 μm

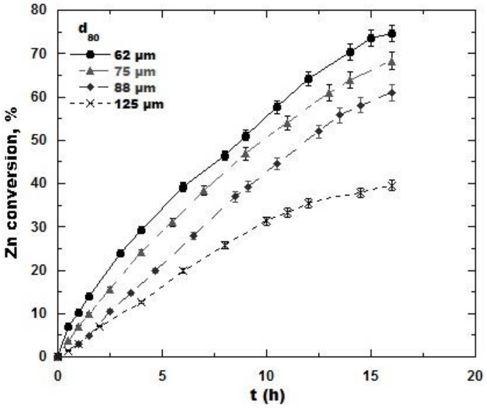

Fig. 9. Effect of mean particle size on zinc extraction.
T = 360 K (87 °C), [H_2SO_4] 0.15 mol dm^{-3}, [$FeSO_4$] 0.4 mol dm^{-3},
air flow rate 0.4 dm^3_{air} dm^{-3}_{slu} min^{-1}, [$ZnSO_4$]$_{initial}$ 0.025 mol.dm^{-3}

Effect of particle size

The effect of solid particle size on the zinc leaching rate is presented in Fig. 9. The zinc conversion of 62, 75, 88 and 125 μm fractions are 40%, 61%, 66% and 75%, respectively. Hence, decrease in particle size (d_{80}) enhances the zinc recovery. The order of particle size on Zn conversion is -0.8. The leaching process is, inherently, a heterogeneous reaction and the reaction happens on the active surface of the area. The active surface area increases when the particle size is decreased. Several studies (Xie et al., 2007; Li et al., 2010), have reported that particle size has a remarkable effect on zinc extraction in pressure leaching process. Also, studies in the field of atmospheric condition (Souza et al., 2007; Dehghan et al., 2008) showed that decrease in the particle size enhances the zinc dissolution.

Efficient Zn recovery and impurities dissolution

The achievement of a satisfactory zinc conversion needs the utilization of high temperatures due to inherently slow dissolution rate of sulfide ore. Hence, some tests were carried out at 368 K (95 °C). The results in Fig. 10 show that temperature has a positive effect on Zn conversion so that the zinc conversion at 368 K after 6, 12 and 18 h is 45%, 70%, 86% respectively, while Zn conversion after 18 h at 360 K (87 °C) is approximately 80%. So, despite higher dissolution rate at 368 K (95 °C), zinc extraction percent has no dramatic increase at 18 hours.

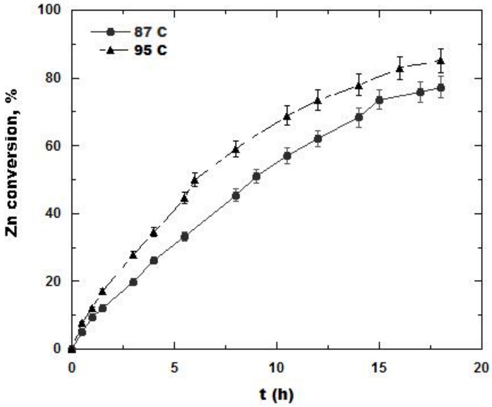

Fig. 10. Zinc extraction at 360 K (87 °C) and 368 K (95°C).
$[H_2SO_4]$ 0.25 mol dm^{-3}, $[FeSO_4]$ 0.4 mol dm^{-3},
air flow rate 0.4 dm$^{3}_{air}$ dm$^{-3}_{slu}$ min^{-1}, $[ZnSO_4]_{initial}$ 0.025 mol dm^{-3}

In addition to the zinc conversion, the dissolution of impurities e.g. Fe, Ni, Cu and etc. is an important factor that affects leaching response. As can be seen in Fig. 11 a, dissolution of iron (as impurity) and cadmium occur in the early hours, which represent dissolution of non-sulfide minerals, such as Otavite ($CdCO_3$) and Siderite ($FeCO_3$). It is noteworthy that the concentration of dissolved Fe decreased with the passage of time. Dissolved iron precipitates as hydroxide $Fe(OH)_3$ and/or goethite FeOOH in acidic sulfate solutions due to the hydrolysis of ferric iron at elevated temperature and low acidity of the leaching system (Lottermoser, 2010). On the other hand, dissolution of nickel and copper are lower. As the nickel and copper concentration in the final solution is less than 70 ppm. Also, the impurities dissolution at 368 K (95 °C) was illustrated in Fig. 11 b. Cd dissolution percent reached 70 % in 18 hours. However, the dissolution of the other elements (Ni, Cu, and Fe) is approximately similar to their dissolution at 360 K (87 °C). The results of this investigation show that the present method could be suitable for separation of zinc from some of the impurities, such as Cu and Ni, but Cd dissolution is remarkable in the system. It should eliminate in the subsequent processes. The elemental analysis of leach residue at 368 K (95 °C) is demonstrated in Table 3. The iron and zinc content in the residue is 8.4% and lower than 12%, respectively.

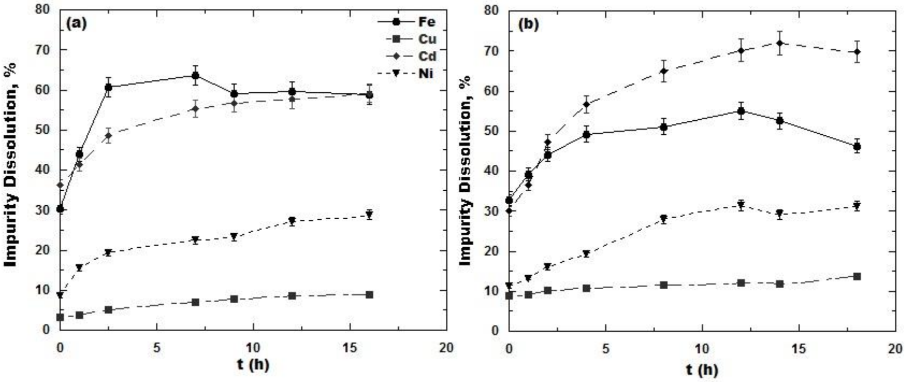

Fig. 11. Dissolution of impurities (Fe, Cu, Cd and Ni) in solution at (a) 360 K (87 °C) and (b) 368 K (95°C). $[H_2SO_4]$ 0.25 mol dm^{-3}, $[FeSO_4]$ 0.4 mol dm^{-3}, air flow rate 0.4 dm$^{3}_{air}$ dm$^{-3}_{slu}$ min^{-1}, $[ZnSO_4]_{initial}$ 0.025 mol dm^{-3}

Table 3. The analysis of leach residue at 360 K (87 °C)

Leach Residue	Zn(%)	Fe(%)	Pb(%)	Cd(%)	Cu(%)	Ni(%)
	11.8	8.4	6.5	0.44	0.86	0.35

Table 4. Rate equations for pseudo homogeneous model and shrinking core model

Kinetic Model	Characterize	rate equations
pseudo homogeneous	First order (H1)	$F(X) = -\ln(1 - X) = kt$
	Second order (H2)	$F(X) = 1/(1 - X) = kt$
shrinking core model	Diffusion control through product layer control (S_d)	$F(X) = 1 - 3(1 - X)^{2/3} + 2(1 - X) = kt$
	Surface chemical reaction control (S_c)	$F(X) = 1 - (1 - X)^{1/3} = kt$

Dissolution kinetic of direct leaching

The leaching reactions between solid and liquid are heterogeneous, which can be represented using heterogeneous and homogeneous control models. The shrinking core model (SCM) supposed that the dissolution rate could be controlled by diffusion through a fluid film or diffusion through the product layer and/or a surface chemical reaction (Dickinson and Heal, 1999). However, the film diffusion control regime usually not considered in the agitated reactors. In the pseudo-homogeneous model, the solids are treated as a pseudo-homogeneous phase and local average particle size in the reactor is calculated from the zinc conversion (Aycan, 2015). The rate equations for each of the models are been presented in Table 4.

The shrinking core model is usually used as the kinetic model of Sphalerite leaching (Aydogan, 2006; Souza et al., 2006), but Lampinen et al. (2010) have used a pseudo-homogeneous model for the direct leaching of sphalerite concentrate. So, the kinetics of zinc sulfide concentrate leaching was analyzed using these models. As can be seen in Fig. 12, the leaching kinetics of the Sphalerite doesn`t fit in the second order of pseudo-homogeneous model. The result of the first order in the pseudo-homogeneous model is more acceptable. Also, the regression coefficient for surface chemical reaction control in shrinking core model is remarkable, while the data could not fit according to diffusion control through product layer equation. For an accurate examination of the dissolution kinetics, the rate constant according to chemical reaction control (Sc) and first order (H1) models for different Fe3+, air flow rate and H2SO4 concentration was calculated in Table 5. As can be seen, the regression correlation coefficient (R2) of chemical reaction control is very close to 1 and it is known as the controlling regime in direct leaching of Sphalerite in pilot scale. Thus, according to XRD diffractograms (Fig. 4), a sulfur layer was formed on the particle surface and lixiviant was subjected to leaching reaction through sulfur layer pores, but this layer did not hinder diffusion. Furthermore, sulfuric acid, ferric sulfate, and oxygen were considered as sphalerite leaching reactants (Eq. 1-4) and the effect of these factors was investigated in Table 5. As is also represented in Fig. 7, air flow rate hasn't tangible effect on leaching kinetics in higher flow rate; however the rate constant at 0.22 $dm^3_{air}\ dm^{-3}_{slu}\ min^{-1}$ decreased slightly. Sulfuric acid concentration has a limited effect on reaction rate so that the kinetic constant of reaction changes 0.0092 to 0.012 when H_2SO_4 concentration increases 0.15 to 0.5 mol $dm^{-3.}$

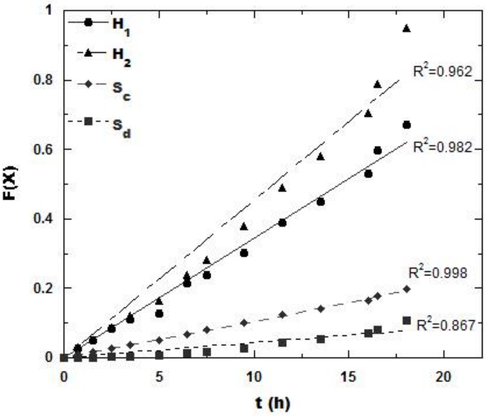

Fig. 12. Direct leaching kinetic trough pseudo-homogeneous model and shrinking core model in 360 K, $[H_2SO_4]$ 0.25 mol dm^{-3}, $[FeSO_4]$ 0.4 mol dm^{-3}, air flow 0.4 $dm^3_{air}\ dm^{-3}_{slu}\ min^{-1}$, $[ZnSO_4]_{initial}$ 0.025 mol dm^{-3}

Table 5. Kinetic constant and correlation coefficient in pseudo homogeneous and shrinking core models

$[Fe_2(SO_4)_3]$ mol dm^{-3}	$[H_2SO_4]$ mol dm^{-3}	Air flow $m^3_{air}\ dm^{-3}_{slu}\ min^{-1}$	S_c		H_1	
			k_{sc}	R^2	k_1	R^2
0.018	0.15	0.22	0.0079	0.998	0.0249	0.984
0.018	0.15	0.41	0.0092	0.992	0.0295	0.969
0.018	0.15	0.75	0.0095	0.998	0.0306	0.991
0.018	0.25	0.41	0.0107	0.995	0.0347	0.968
0.018	0.5	0.41	0.0119	0.999	0.0391	0.990
0.009	0.15	0.41	0.0046	0.988	0.0135	0.962
0.018	0.15	0.41	0.0092	0.992	0.0295	0.969
0.035	0.15	0.41	0.0178	0.997	0.0619	0.980

Conclusions

Direct leaching of zinc sulfide concentrate was studied at low concentrations of sulfuric acid and large scale tubular reactor. The experimental conditions showed a good balance with industrial conditions. By adding crystalline ferrous sulfate and sulfuric acid to the slurry and blowing air to the reactor, zinc sulfide concentrate was dissolved. Due to low effect of acid concentration on zinc conversion and dissolution rate, the acid attack reaction cannot be recognized as the main leaching reaction under such condition. Furthermore, investigation of leach residue through X-ray pattern indicated that elemental sulfur was formed and this is another product of the process instead of hydrogen sulfide (H_2S) gas.

Ferric sulfate concentration has an effective role in zinc extraction and the effect of zinc sulfate initial concentration is more limited. Besides, particle size and sulfuric acid concentration are other effective parameters in the process. The order of $Fe_2(SO_4)_3$, H_2SO_4 and $ZnSO_4$ concentration, particle size and air flow rate was 1, 0.25, -0.1, 0.2 and -0.8 on Zn dissolution, respectively. The kinetic of direct leaching of sphalerite follows a shrinking core model that controls by the surface chemical reaction. Also, impurities (Ni and Cu) conversion is lower than zinc and it is feasible to separate impurities.

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