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PRESSURE ACID LEACHING OF SPHALERITE CONCENTRATE. MODELING AND OPTIMIZATION BY RESPONSE SURFACE METHODOLOGY

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Abstract: The zinc leaching from sphalerite concentrate using oxygen under pressure in sulfuric acid solution was primarily studied and evaluated. The effects of important leaching parameters such as oxygen partial pressure, temperature, solid/liquid ratio and leaching time on leaching efficiency, Zn concentration and Fe extraction were investigated. Response surface methodology based on central composite rotatable design technique was used to optimize the leaching process parameters in order to obtain a suitable leach solution with high Zn leaching efficiency considering further processes such as precipitation of contaminating metal ions and electrolysis. The optimum leaching condition for maximum Zn leaching efficiency and Zn concentration with minimum Fe extraction was determined as follows: oxygen partial pressure of 12 bars, temperature of 150 °C, solid/liquid ratio of 0.20 and leaching time of 89.16 minutes. The achieved experimental results for Zn leaching efficiency, Zn concentration and Fe extraction under the optimum conditions were as 94%, 80 g/dm^3 and 8.1% respectively. The experimental results corresponded well with the predicted results of quadratic polynomial models.

Keywords: *pressure leaching, sphalerite concentrate, optimization, response surface methodology, central composite rotatable design*

Introduction

Zinc sulfide is a predominant form of zinc in the earth crust and sphalerite (ZnS) is the most important mineral among them. Many processes have been developed over decades and at present, nearly 80–85% of total zinc production is carried out by hydrometallurgical processes which include roasting, leaching and electrowinning steps (RLE). In order to prevent the increase in investment and operating costs, zinc sulfide ore is concentrated using froth flotation in practice. Sphalerite concentrates contain approximately 50% Zn. The concentrated sphalerite is roasted to produce zinc oxide followed by leaching with weak sulfuric acid and solution purification from

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other metal impurities using succession of appropriate methods. After this step, high purity metallic zinc is produced by electrolysis.

Roasting stage of the process has some major drawbacks. During calcination, SO_2 is released causing environmental pollution. In addition, iron combines with zinc to form zinc ferrite ($ZnFe_2O_4$) which cannot be leached in weak acid solution. Bypassing the roasting stage for metallic zinc production is mostly preferred from economic and environmental perspective. For this purpose, two alternative processes were proposed in the 1970's and several different leaching studies have been accomplished by many researchers in the course of time: Direct atmospheric leaching in which sphalerite concentrates are leached directly with some oxidizing agents such as acids (Copur, 2002), alkalis (Zhang et al., 2008), ferric salts (Crundwell, 1987; Dutrizac, 1992; Jin et al., 1993; Palencia Perez and Dutrizac, 1991; Santos et al., 2010), hydrogen peroxide (Balaz and Ebert, 1991), oxygen, ammonium, sodium and potassium persulfates (Babu et al., 2002), manganese dioxide (Rao and Paramguru, 1998), and bacteria (da Silva, 2004; Gomez et al., 1997; Haghshenas et al., 2012); and pressure leaching carried out using oxygen under pressure with similarly contributing some oxidizing agents in autoclaves (Baldwin and Demopoulos, 1995; Dehghan et al., 2008; Gu et al., 2010; Harvey et al., 1993; Li et al., 2010a; Xie et al., 2007).

The pressure leaching has been commercially used in several zinc ore/concentrate leaching plants (Filippou, 2004; Ozberk et al., 1995). As an environmentally friendly and economical technology, high pressure leaching is an alternative to conventional RLE route. The pressure leaching reaction of sphalerite is shown in Eq. 1:

$$ZnS + H_2SO_4 + ½O_2 \rightarrow ZnSO_4 + H_2O + S^0. \tag{1}$$

Reaction (1) is slow in absence of dissolved iron, which facilitates the oxygen transfer (Au-Yeung and Bolton, 1986; Crundwell, 1998). In order to dissolve sphalerite, which is a semiconductor with a wide band gap, by an oxidative mechanism, electron must be removed from the bonding orbitals by the oxidant in solution (Crundwell, 2013). In the absence of iron species in solution, dissolved oxygen reacts at the mineral surface to form intermediate oxides (e.g. H_2O_2 and HO_2). This results in a relatively slow discharge of oxygen due to the strength of the oxygen-oxygen double bond (Wadsworth, 1972). In case the presence of iron and oxygen in solution, an electrochemical reaction is occurred at the mineral surface. Fe^{3+}/Fe^{2+} redox couple dominates the surface potential of the mineral. During the dissolution reaction ferric iron reduces to form ferrous iron, then ferrous iron is oxidized to ferric iron by dissolved oxygen in solution (Verbaan and Crundwell, 1986).

Despite the reaction mechanism of sphalerite has been investigated in detail (Crundwell, 1987; Verbaan and Crundwell, 1986) and determined that the reaction kinetics depend on the iron content of the crude ore or concentrate of sphalerite (Palencia Perez and Dutrizac, 1991), the influence of experimental parameters and their interactions on the process results are not exactly figured out yet.

Conventionally, the study of the effects of experimental parameters on pressure acid leaching of sphalerite is carried out using an approach where one parameter at a time is varied. The effect of each experimental parameter is evaluated by altering the level of one parameter at a time while keeping the levels of the other parameters constant. However, this approach is very inadequate and does not provide any information about interactions between experimental parameters in a process. These interactions can be easily detected when a factorial design – through the use of methods such as response surface methodology (RSM) – is performed. In addition, factorial design provides more accurate estimation of the effects of the variables than the "one parameter at a time" approach with the same number of experimental runs (Liu et al., 2011). However, only a few cases of RSM application have been introduced in sphalerite leaching process (Dehghan et al., 2008; Haghshenas et al., 2012; Massacci et al., 1998).

The present study intends to assess the effects of parameters such as oxygen partial pressure, temperature, liquid/solid ratio and leaching time to identify the optimum pressure acid leaching conditions of sphalerite with highest Zn leaching efficiency, highest Zn concentration, lowest Fe extraction and quantify interactions between aforementioned parameters through response surface methodology based on the central composite rotatable design (CCRD).

Materials and methods

The concentrate was obtained from a sphalerite flotation plant in Western Turkey. Wet sample was dried at room temperature until it reached a constant weight. Samples were taken from the air-dried concentrate for sieving, chemical, XRD (Rigaku D/Max-2200 model diffractometer using CuKα radiation) and SEM-EDS (Jeol JXA-733 Superprobe) analysis. The chemical and mineralogical composition of the concentrate is presented in Table 1 and Fig. 1 respectively. The main mineralogical phases in sample are sphalerite and small quantities of pyrite, pyrrhotite, galena and quartz.

Table 1. Chemical composition of sphalerite concentrate (mass fraction, %)

Zn	Fe	Pb	Si	Al	Cu	Ca	Cd	Mg	Mn	S
42.71	11.21	2.39	1.01	0.20	0.18	0.18	0.16	0.11	0.10	34.26

The leaching solution was prepared by diluting concentrated sulfuric acid with distilled water in order to obtain a concentration of 1.5 mol·dm^{-3}; then 0.1 g·dm^{-3} of sodium lignin sulfonate was added to the solution as sulfur dispersant. The leaching experiments were conducted in a 1-dm^3 titanium autoclave (Parr Inc., USA). The autoclave was equipped with a heating mantle, a PID temperature controller, a variable speed stirrer operated at 600 rpm, a sampling dip tube and an internally mounted serpentine type cooling coil. Pre-calculated amount of sphalerite concentrate

(-150 μm) was added into 500 cm^3 leaching solution. The reaction vessel was heated up to a pre-set temperature. The oxygen was admitted at the pre-set temperature and the partial pressure of oxygen was adjusted to the desired level and maintained constant during the whole experiment.

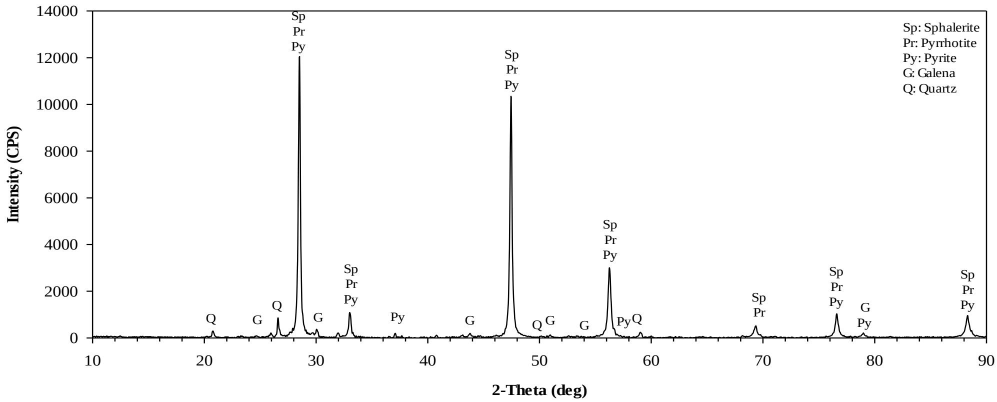

Fig. 1. XRD pattern of sphalerite concentrate

In the experiments, 20–30 cm^3 of slurry was sampled by a sampling dip tube. The slurry was cooled down immediately and filtrated by a 0.45 μm PTFE syringe filter. Metal ions content of the filtrate was analyzed by an ICP-OES (Varian 710-ES).

Representative samples were used in all experiments. All chemicals used were of analytical grade and all solutions were prepared with distilled water.

RSM is a statistical and mathematical technique utilized for multiple regression analysis using quantitative data obtained from properly designed experiments to solve multi-variable equations simultaneously. This method is useful for designing experiments, model building, evaluating the effects of experimental parameters and determining optimum conditions for desirable responses. Central composite rotatable design (CCRD), one of the techniques in RSM, is used extensively in building the second order response surface models (Li et al., 2010b).

A CCRD comprises 2^k factorial points (coded as ±1), augmented by 2k star points (coded as $\pm\alpha$) and n_c center points (coded as 0). The parameter k is the number of controllable experimental parameters and α equals to $(2^k)^{1/4}$.

In this study, the sphalerite concentrate was leached using oxygen pressure leaching. The experiments are designed by varying the leaching parameters using the CCRD. The experimental parameters are (i) x_1, oxygen partial pressure, (ii) x_2, temperature, (iii) x_3, solid/liquid ratio and (iv) x_4, leaching time. The codes and levels of the experimental parameters studied in the experiments are listed in Table 2.

The behavior of the system can be explained by the following second order polynomial equation:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \beta_{ij} x_i x_j + \varepsilon \quad (2)$$

where Y is the predicted response, x_i and x_j are the experimental parameters, β_0 is the intercept term, β_i is the linear effects, β_{ii} is the squared effect, and β_{ij} is the interaction term (Aghaie et al., 2009).

Table 2. Codes and levels of experimental parameters for central composite rotatable design

Parameters	Symbol	Codes and Levels				
		–2	–1	0	+1	+2
Oxygen partial pressure (bar)	x_1	3	6	9	12	15
Temperature (°C)	x_2	105	120	135	150	165
Solid/liquid ratio	x_3	0.05	0.10	0.15	0.20	0.25
Leaching time (min)	x_4	15	40	65	90	115

In order to determine Zn extraction and concentration, and Fe extraction, pregnant leach solution was analyzed using ICP-OES. Metal extractions were calculated using metal concentration values obtained by ICP. In order to estimate the best parameter combination, both Zn extraction and concentration were selected as responses due to the experiments designed for different solid/liquid ratios.

The acid amount was selected by taking into consideration the previous investigations and the results of some pretesting. Xie et al. (2007) reported that Zn leaching rate decreases abnormally with a rise in initial sulfuric acid concentration. If the amount of sulfuric acid added in experiment is over twice the stoichiometric amount, the abnormality occurs. Therefore, the initial acid concentration was adjusted as 1.5 mol dm^{-3} which was between 1.15-fold and 2.30-fold in stoichiometric amount depending on the solid/liquid ratio.

Free acid (H_2SO_4) concentration was analyzed by the method described in the study by Kaya and Topkaya (2011) with the intent of determining the amount of acid remained after reaction in pregnant leach solution. The titration process in the method was conducted using Metrohm 842 Titrando model automatic titrator.

The polynomial equations for the responses were validated by the statistical test known as analysis of variance (ANOVA) for determination of the significance of each term in equations and also to estimate the goodness of fit in each case. Three-dimensional response surface graphs were plotted using Design Expert (version 7.0) software for the experimental results in order to determine the individual and interaction effects of the experimental parameters.

Results and discussion

Process mechanism

The net reaction of sphalerite dissolution (Eq. 1.) is the sum of the three reactions (Eqs 3–5) with the presence of dissolved iron in the acidic sulfate solution (Jan et al., 1976)

$$ZnS + H_2SO_4 \rightarrow ZnSO_4 + H_2S \quad (3)$$

$$2FeSO_4 + H_2SO_4 + \tfrac{1}{2}O_2 \rightarrow Fe_2(SO_4)_3 + H_2O \quad (4)$$

$$H_2S + Fe_2(SO_4)_3 \rightarrow 2FeSO_4 + H_2SO_4 + S^0. \quad (5)$$

According to Eq. 5. there should be Fe^{3+} ions in the leaching solution for the removal of H_2S. In the case when the Fe^{3+}/Fe^{2+} ions are not initially added to the solution, all of the needed Fe^{3+} ions are provided by the iron minerals in the concentrate such as pyrite and pyrrhotite. Dissolution of iron occurs as stated in the reactions listed below in the case of pyrite and pyrrhotite presence in the concentrate

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4 \quad (6)$$

$$FeS + H_2SO_4 + \tfrac{1}{2}O_2 \rightarrow FeSO_4 + H_2O + S^0. \quad (7)$$

Dissolved iron precipitates as jarosite and/or hematite in acidic sulfate solutions due to the hydrolysis of ferric iron at elevated temperature depending on the acidity and the amount of metal sulfate and monovalent cations in the leaching system (Acharya et al., 1992; Yue et al., 2014). Net reactions of the hydronium jarosite and hematite precipitations are stated below

$$2Fe_2(SO_4)_3 + 14H_2O \rightarrow 2H_3OFe_3(SO_4)_2(OH)_6(s) + 5H_2SO_4 \quad (8)$$

$$2FeSO_4 + \tfrac{1}{2}O_2 + 2H_2O \rightarrow Fe_2O_3(s) + 3H_2SO_4. \quad (9)$$

Effects of oxygen pressure, temperature, solid/liquid ratio and leaching time

The CCRD method, which is very popular design for fitting second-order response surfaces, was applied in 30 leaching tests with appropriate combinations of the four parameters (oxygen partial pressure, temperature, solid/liquid ratio and leaching time). Experimental design matrix for CCRD with experimental responses is given in Table 3. The relative standard deviation of the experimental responses was calculated as below 3.66% with 6 replications at central levels of parameters.

The highest zinc extraction (> 94%) was achieved at 90 minutes with highest levels of oxygen partial pressure, temperature and solid/liquid ratio (Exp. 16).

By performing multiple regression analyses on the experimental responses, the experimental results of the CCRD designs were fitted with second-order polynomial equations for each response group. Thus, according to Eq. 2., the predicted models for Zn leaching efficiency, Zn concentrate in leach solution and Fe extraction are described in the following equations in terms of coded factors (between –2 and +2), respectively:

$$\text{Zn Leaching Efficiency (\%)} = 78.02 + 4.34x_1 + 13.11x_2 + 6.47x_3 + 11.12x_4 - 1.41x_1x_2 + 1.43x_1x_3 - 1.68x_1x_4 + 1.21x_2x_3 - 4.74x_2x_4 + 0.35x_3x_4 - 1.96x_1^2 - 5.48x_2^2 - 1.99x_3^2 - 4.34x_4^2 \quad (10)$$

$$\text{Zn Concentration (g dm}^{-3}) = 49.98 + 2.98x_1 + 8.57x_2 + 18.28x_3 + 7.18x_4 - 0.92x_1x_2 + 1.75x_1x_3 - 1.15x_1x_4 + 3.67x_2x_3 - 3.03x_2x_4 + 2.41x_3x_4 - 1.23x_1^2 - 3.49x_2^2 + 0.044x_3^2 - 2.76x_4^2 \quad (11)$$

$$\text{Fe Extraction (\%)} = 75.38 + 1.92x_1 - 4.17x_2 - 16.00x_3 + 2.74x_4 - 1.22x_1x_2 - 2.68x_1x_3 + 0.31x_1x_4 - 13.88x_2x_3 - 3.51x_2x_4 - 4.26x_3x_4 - 2.34x_1^2 - 7.58x_2^2 - 10.29x_3^2 - 6.12x_4^2 \quad (12)$$

Table 3. Experimental design matrix for CCRD with experimental results

Exp. #	O_2 partial pressure (bar)	Temp. (°C)	Solid/ liquid ratio (w/v)	Leaching time (min)	Zn Leaching efficiency (%)	Zn Concentration (g dm^{-3})	Fe Extraction (%)	Free Acid Concentration (mol dm^{-3})
1	6	120	0.10	40	26.65	11.38	43.00	1.186
2	6	120	0.10	90	57.74	24.66	61.73	0.931
3	6	120	0.20	40	32.86	28.07	45.96	0.743
4	6	120	0.20	90	67.33	57.51	57.87	0.174
5	6	150	0.10	40	62.68	26.77	67.47	0.894
6	6	150	0.10	90	76.44	32.65	74.45	0.808
7	6	150	0.20	40	74.69	63.80	26.85	0.160
8	6	150	0.20	90	90.56	77.36	6.45	0.259
9	12	120	0.10	40	36.05	15.40	50.52	1.142
10	12	120	0.10	90	63.63	27.18	71.49	0.884
11	12	120	0.20	40	50.49	43.13	53.45	0.440
12	12	120	0.20	90	77.06	65.82	49.56	0.151
13	12	150	0.10	40	68.65	29.32	72.86	1.132
14	12	150	0.10	90	75.14	32.09	79.94	1.044
15	12	150	0.20	40	86.50	73.89	10.74	0.239
16	12	150	0.20	90	94.18	80.45	8.68	0.276
17	3	135	0.15	65	58.24	37.31	58.40	0.631
18	15	135	0.15	65	78.93	50.57	74.66	0.358
19	9	135	0.15	15	33.18	21.26	44.80	0.966
20	9	135	0.15	115	84.91	54.40	58.00	0.355
21	9	135	0.05	65	56.27	12.02	65.24	1.109
22	9	135	0.25	65	80.62	86.08	4.16	0.096
23	9	105	0.15	65	30.11	19.29	49.08	1.195
24	9	165	0.15	65	78.88	50.53	42.06	0.613
25-30	9	135	0.15	65	78.02±1.99	49.98±1.27	75.38±2.76	0.361±0.009

The ANOVA confirmed that the models for all responses are statistically significant even at confidence level of 99.99% (p-value <0.0001). According to the results of ANOVA for Zn leaching efficiency, all the first and second order terms of independent parameters are significant. The relative significance of these parameters for the Zn leaching efficiency is in the order of temperature, leaching time, solid/liquid ratio and oxygen partial pressure (P_{O_2}). The statistical analysis results of the interaction terms show that there are significant interactions among leaching time with both P_{O_2} and temperature at 95% confidence level (p-value < 0.05). For Zn concentration, all the first and second order terms of independent parameters are significant except the second term of solid/liquid ratio. The relative significance of these parameters is descending orders of solid/liquid ratio, temperature, leaching time and P_{O_2}. For Fe extraction, the exception is the first term of P_{O_2} and descending order of relative significance of parameters is solid/liquid ratio, temperature and leaching time. There are significant interactions for both Zn concentration and Fe extraction among solid/liquid ratio with all other parameters and among temperature with leaching time at 95% confidence level.

The predicted values versus the experimental data for the Zn leaching efficiency, Zn concentration in leach solution and Fe extraction are shown in Fig. 2. The figures indicate that the predicted values are quite proximate to the actual values and Eq. (10), (11) and (12) are well-fitted to the experimental data.

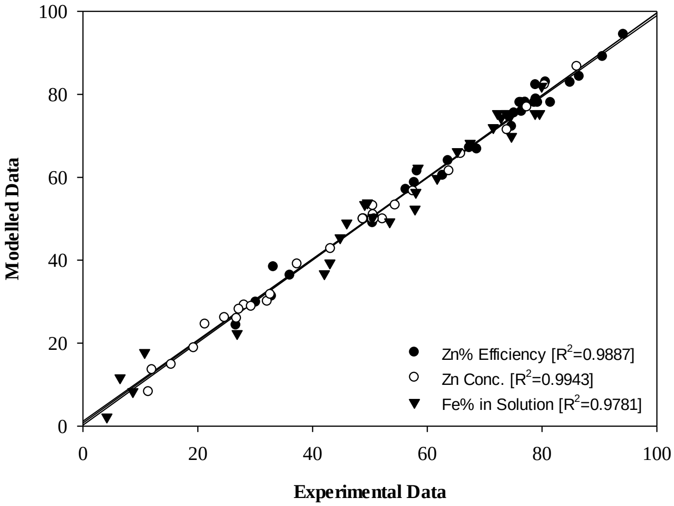

Fig. 2. Experimental vs. modeled data of all responses

The vapor pressures of sulfuric acid solution were determined initially under experimental conditions. Addition of oxygen was performed to obtain the desired level of P_{O_2}. Some increase in Zn efficiency was observed with increasing P_{O_2} under all experimental conditions other than long leaching time, high temperature and low S/L ratio. This exception may occur due to encapsulated particles by molten sulfur at elevated temperature. At low S/L ratio; increasing P_{O_2} results in increasing Fe extraction independently of temperature and leaching time. Fe extraction tends to decrease in the long term in despite of increasing in the short term with increasing P_{O_2} at low temperature and high S/L ratio.

The leaching temperature is a significant thermodynamic factor. In general, rising the leaching temperature increases the leach kinetics. Figure 3. illustrates typical temperature effect on reaction rate of the zinc extraction from the sphalerite concentrate. An increase in the temperature from 105 °C to 165 °C enhanced the initial reaction rate (Fig. 3) and Zn efficiency from 39% to 80% at 90 minutes (Exp.23→Exp.24) (Table 3) as expected. Similarly, Fe extraction increases with increasing temperature at low S/L ratio conditions. But leaching temperature has adverse effect at high S/L ratio conditions, so dissolved iron sharply decreases in the solution (e.g. from 58% to 6.5%) due to precipitation of iron as both jarosite and hematite form with increasing temperature (Exp. 4→Exp. 8) (Table 3).

Effect of S/L ratio on the leaching system should be evaluated from different perspectives such as amount of iron minerals entered to the system, initial acid concentration to concentrate ratio, acid concentration changing during the process, dissolved metal sulfate concentration which influence zinc dissolution rate, zinc sulfate concentration, amounts of both precipitated and remained iron in the solution.

Fe^{3+} ion which is a strong oxidizing agent ($E_{Fe^{3+}/Fe^{2+}}$= 0.771 V) plays a crucial role for dissolution reactions of many sulfide minerals (Yazici and Deveci, 2014). Concordantly, the amount of iron minerals entering the leaching system -the initial solid/liquid ratio- is very significant for dissolution of zinc in case non-existence of dissolved iron initially. In analogy to leaching temperature, increasing S/L ratio enhances Zn leaching efficiency under all experimental conditions. Positive effect of high iron concentration on zinc leaching efficiency and in connection with zinc extraction can be explicitly seen at low temperature where iron precipitation is slower than iron dissolution. Iron extraction shows tendency to stay steady or decrease in percent at low temperature and all P_{O_2} levels, but to increase approximately 2-fold in concentration, with increasing S/L ratio. Hence, Zn leaching efficiency enhances in parallel with increasing iron concentration (e.g. from 0.14 mol dm^{-3} to 0.20 mol dm^{-3}) in the solution (i.e Exp. 10→Exp. 12). Crundwell (1988), also concluded that iron content of the concentrate affects the rate of Zn extraction.

Essentially, a rise in Zn leaching rate is expected by increasing the initial sulfuric acid concentration. However, previous investigations indicate that if the initial sulfuric acid amount is twice over the stoichiometric amount, the reaction given in Eq. 5. will go the left and more H_2S hindering the dissolution of zinc will be produced (Jan et al., 1976; Xie et al., 2007). Xie et al. (2007) concluded in their study that at higher H_2SO_4/concentrate ratios (>4:1), Zn leaching rate decreased with increasing H_2SO_4/concentrate ratio. Figure 4a shows that initial zinc dissolution kinetics enhances with decreasing initial acid concentration even at H_2SO_4/concentrate ratios of <1:1.

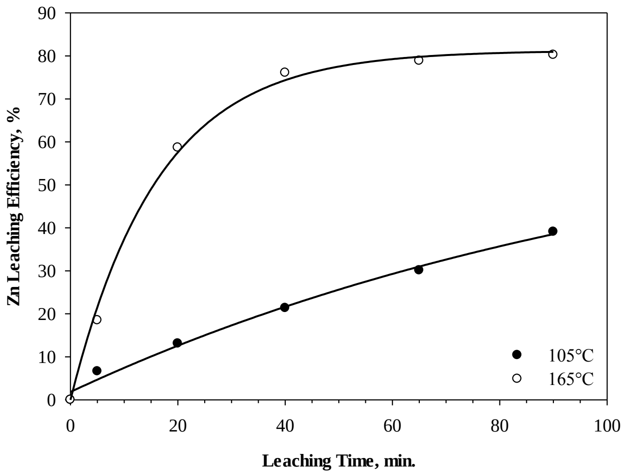

Fig. 3. Dissolution kinetics of zinc from sphalerite concentrate (P_{O_2}: 9 bar, S/L ratio: 0.15 (w/v))

Acid concentration level in the solution is controlled by the dissolution of zinc and iron minerals. Dissolutions of sphalerite and pyrrhotite are acid consuming reactions (Eq. (1) and (7)) where dissolution of pyrite dissolution produces acid (Eq. (6)). Free acid concentration of solution decreases as long as zinc dissolves which ends up with increasing pH. Under all experimental conditions, increasing S/L ratio induces decreasing of free acid concentration in the solution in parallel with increasing Zn concentration (Table 3).

Lack of acid in the system leads to start precipitation of iron. Dutrizac and Jambor (2000) reported that hydronium jarosite formed at pH range between 0.4 to 1.4 and temperature between 100 °C to 160 °C. In addition, ferric sulfates can precipitate as hematite at elevated temperature depending on pH and divalent metal sulfate (such as $ZnSO_4$, $MgSO_4$) concentration (Reid and Papangelakis, 2006; Tozawa and Sasaki, 1986). Increasing S/L ratio paves the way for precipitation of iron due to decreasing of free acidity and increasing $ZnSO_4$ concentration simultaneously. On the other hand, precipitation of iron produces some acid (Eq. (8) and (9)). Thus, acid concentration is stabilized between 0.15-0.25 mol dm^{-3} till all iron in the solution precipitates (Table 3). Figure 4. illustrates the total precipitation of iron after 20 minutes in 0.5/1 H_2SO_4/concentrate ratio which reveals the fact that zinc extraction reduces correspondingly. A similar trend can also be determined for the results gathered for the 0.75/1 H_2SO_4/concentrate ratio. However, a significant amount of iron remaining in the solution occurs for the 1/1 H_2SO_4/concentrate ratio while zinc dissolution proceeds.

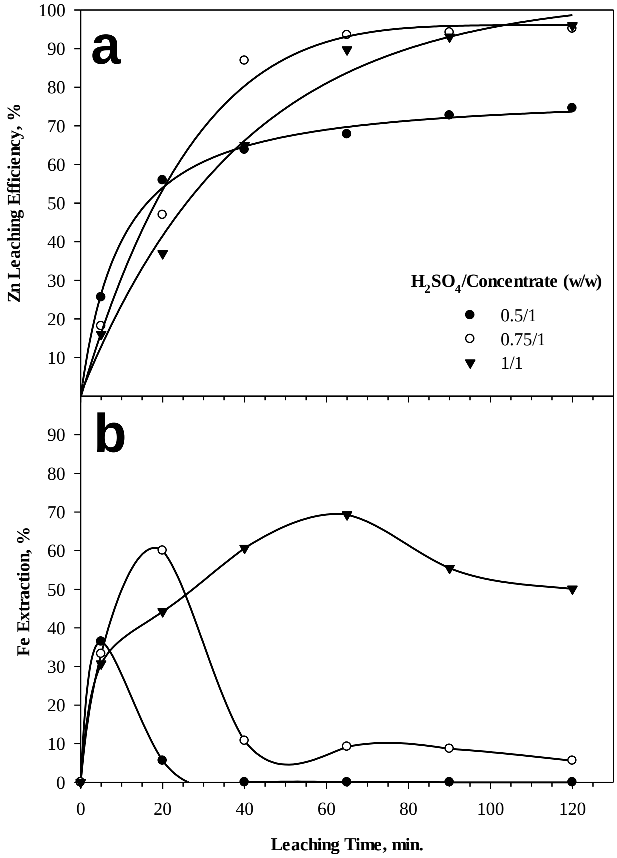

Fig. 4. Effect of initial acid concentration on Zn leaching efficiency (a) and Fe extraction (b) (temp: 150°C, S/L: 0.20 (w/v), P_{O_2}: 12 bar)

In order to comprehend the interaction effects of parameters on Zn leaching efficiency, three-dimensional (3D) graphs for the predicted responses were plotted in Fig. 5 basing on Eq. 10. It can be observed in Fig. 5a that temperature and leaching time have individually and simultaneously important effect on the Zn leaching efficiency. P_{O_2} has limited effect at all levels of leaching time (Fig. 5b.) and temperature (Fig. 5d.) and at low level of the solid/liquid ratio (Fig. 5c.). However, P_{O_2} and the solid/liquid ratio have synergetic effect on the extraction of zinc at their higher levels.

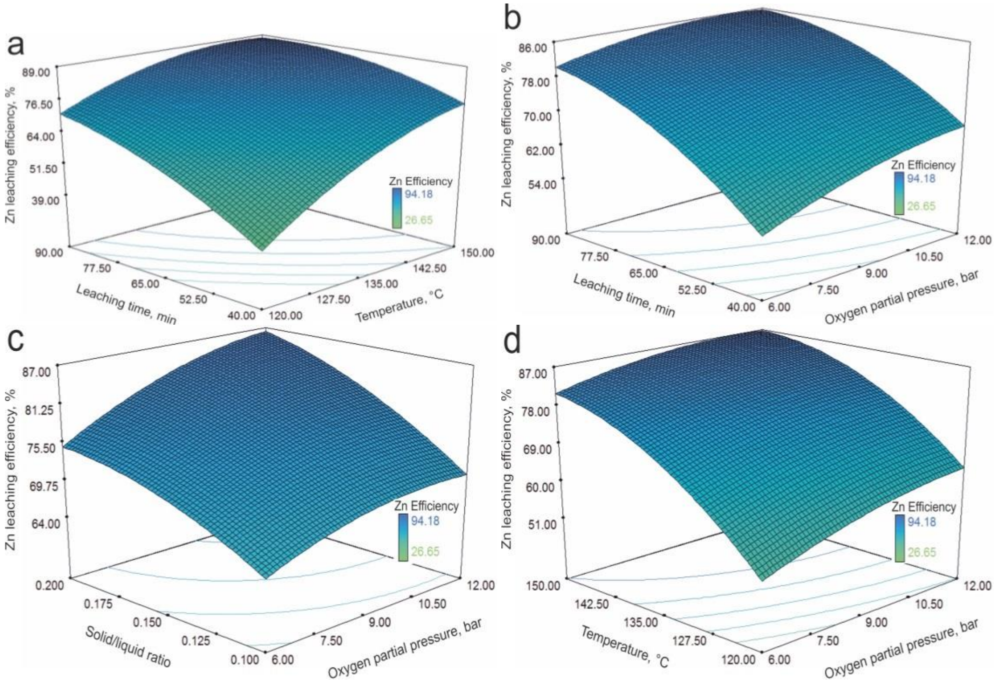

Fig. 5. Response surface plots showing the simultaneous effects of dual parameters on Zn leaching efficiency (other parameters are held at center level), (a) temperature and leaching time, (b) P_{O_2} and leaching time, (c) P_{O_2} and solid/liquid ratio, (d) P_{O_2} and temperature

Optimization of process parameters and confirmation test

One of the main objectives of this research is to determine an optimum leaching process condition with highest Zn leaching efficiency and Zn concentration in the solution and lowest Fe extraction. The optimization of process parameters are not only limited to Zn the leaching efficiency. Hence the amount of Fe dissolved triggers the loss of Zn in the electrolyte during iron precipitation process due to co-precipitation of zinc in iron oxides (Sinclair, 2005). Besides, it is known that the lower the Zn concentration in the electrolyte, the higher becomes the energy consumption during electrolysis (Alfantazi and Dreisinger, 2001; Mahon et al., 2014). The optimum conditions of the pressure acid leaching of sphalerite in two cases were determined using Design Expert software version 7.0 and presented in Table 4.

In the first case, the conditions were adjusted according to lower required energy and P_{O_2}, short process time and high capacity intending to achieve the maximum Zn efficiency and concentration with minimum Fe extraction. According to this scenario, the optimum conditions are identified as P_{O_2} at 6 bars, temperature at 139.65 °C, solid/liquid ratio at 0.20 and leaching time at 61.52 minutes. Under these conditions, Zn efficiency of 77.42%, Zn concentration of 64.67 g dm^{-3} and Fe extraction of 41.86% were predicted. On the other hand, to achieve the maximum Zn efficiency and concentration with minimum Fe extraction, the four mentioned parameters were all kept in the range in the second case. As for the second scenario, Zn efficiency of 94.56%, Zn concentration of 82.28 g dm^{-3} and Fe extraction of 8.88% were predicted with the optimum conditions listed in Table 4. By comparison of the cases, the target differentiation in the parameters particularly influenced Zn leaching efficiency and Fe extraction positively for the second case. In addition, there has been observed a slight increase in Zn concentration. Also, the desirability value of Case 2 increased significantly compared to Case 1 (0.669 to 0.971). Accordingly, the optimum experimental conditions for pressure acid leaching of sphalerite were stated as for Case 2.

Table 4. Optimum leaching conditions and predicted results

Parameters/Responses	Case 1		Case 2	
	Target	Optimum Value	Target	Optimum Value
Oxygen Partial Pressure (bar)	Minimize	6	In range	12
Temperature (°C)	Minimize	139.65	In range	150
Solid/liquid ratio	Maximize	0.20	In range	0.20
Leaching time (min)	Minimize	61.52	In range	89.16
Zn leaching efficiency (%)	Maximize	77.42	Maximize	94.56
Zn concentration (g·dm^{-3})	Maximize	64.67	Maximize	82.28
Fe extraction (%)	Minimize	41.86	Minimize	8.88
Desirability	0.669		0.971	

The experimental results of three confirmation tests were gathered by applying the conditions of Case 2 to determine the error margin between predicted and actual results. As shown in Table 5., there are only small differences between the predicted and actual results indicating the successful validation of the proposed models. The relative standard deviation of the confirmation tests data was calculated as below 3.19%.

Table 5. Average results of model validation at optimum leaching conditions

O_2 partial pressure, bar	Temp, °C	Solid/liquid ratio	Leaching time, min.	Zn leaching efficiency, %		Zn concentration, g·dm^{-3}		Fe extraction, %	
				Predicted	Actual	Predicted	Actual	Predicted	Actual
12	150	0.20	89.16	94.56	93.86±1.25	82.28	80.17±1.07	8.88	8.14±0.26

The partial effect of each parameter on zinc efficiency, zinc concentration and iron extraction, based on the equations of the models, was investigated at the optimum levels of other remaining parameters, respectively (Fig. 6). For instance, to determine the partial effect of the S/L ratio, the other three parameters were fixed at their specific optimum levels and so its influence on zinc efficiency, zinc concentration and iron extraction was determined for the three different levels of the S/L ratio, accordingly.

Consequently, Fig. 6. indicates that the most significant parameter affecting the results is the change of S/L ratio by far, followed by temperature at specific optimum levels of other parameters.

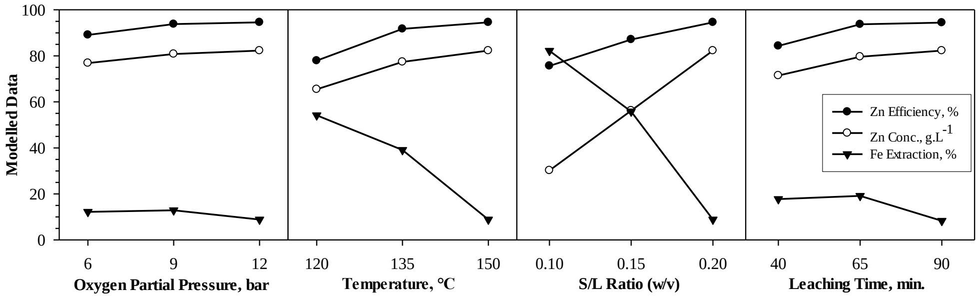

Fig. 6. Effects of parameters on modeled data at optimum conditions

The XRD pattern of the residue obtained after leaching at optimum conditions is shown in Fig. 7. The observed phase formations revealed that elemental sulfur forms as a result of sphalerite and pyrite leaching. The dissolved iron precipitated in the form of hydronium jarosite and hematite where anglesite precipitated from dissolved galena. Quartz and small amount of sphalerite remained as undissolved in the residue. In addition, SEM and EDS analyses conducted on zinc concentrate and leach residue obtained at optimum conditions confirmed the indications reached by XRD analyses (Fig. 8).

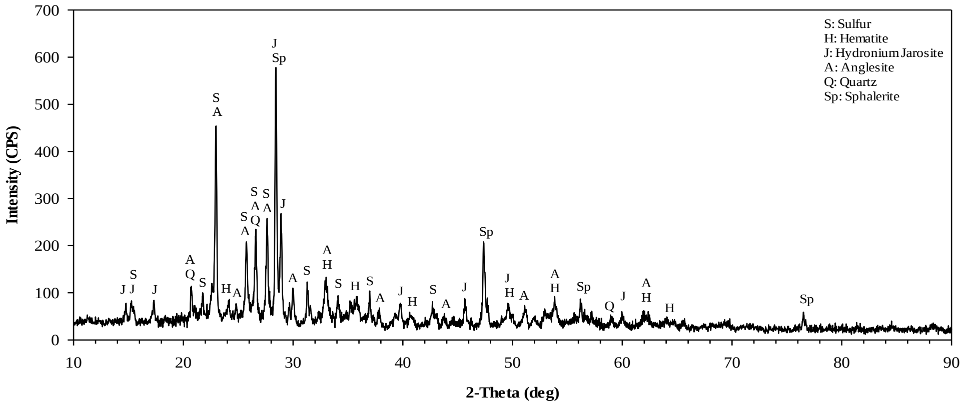

Fig. 7. XRD pattern of the residue obtained after leaching at optimum conditions

Response surface interpolation is a significant method due to facilitating the minimization of parameters which affect input cost, efficiency maximization and product quality that will influence further processes costs. Hence, the parameters of obtaining high quality product with high efficiency and lowest cost can be optimized by this method.

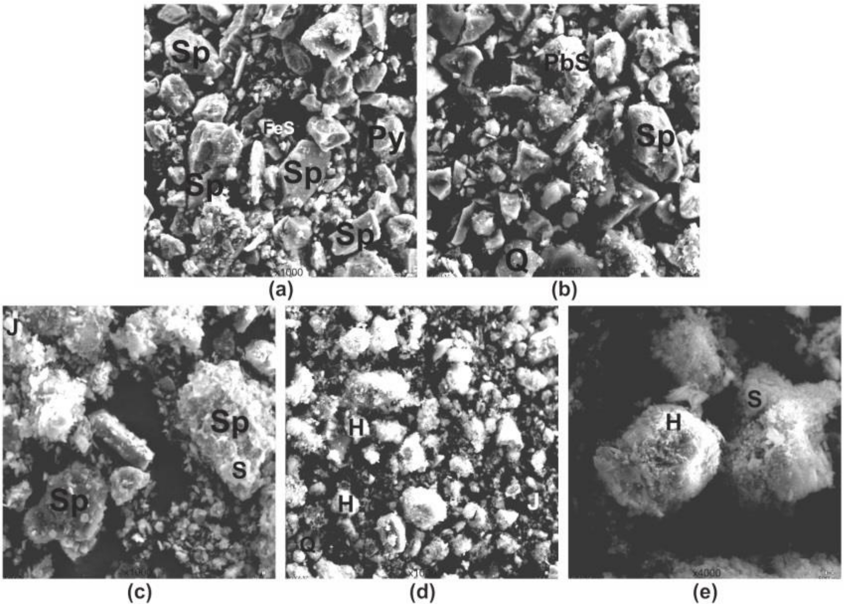

Fig. 8. SEM photographs of sphalerite concentrate and leach residues: (a) and (b) concentrate, (c) residue at 120 °C, (d) and (e) residue at optimum conditions, (Sp: sphalerite, Py: pyrite, FeS: pyrrhotite, Q: quartz, PbS: galena, H: hematite, J: jarosite, S: sulfur).

Variation of the concentrate or ore feed is one of the most important problems in mineral processing and hydrometallurgy plants. In such a case, there is a possibility of the process economics to be affected negatively whereas the efficiency and product quality may be reduced due to variable process conditions. Response surface method may be also facilitated to optimize process parameters when the concentrate or ore feed composition changes. Thus, reduction in efficiency and product quality can be prevented by responding to the process parameters.

Conclusions

The following results may be drawn from the presented study.

1. The four experimental parameters affecting Zn leaching efficiency in the pressure acid leaching process of sphalerite concentrate were all (temperature, leaching time, solid/liquid ratio and P_{O_2}) revealed as statistically significant (in descending significance order). Increasing the level of these parameters enhanced the zinc efficiency and concentrations and also precipitation of dissolved iron.

2. Dissolution of zinc is a fast reaction when dissolved iron and oxygen are present in the solution at elevated temperature.

3. Solid/liquid ratio was determined as the most crucial parameter affecting the amount of iron entering the system, free acid concentration level during the process and dissolved metal sulfate concentration. In order to obtain selective zinc electrolyte with high efficiency and concentration, initial acid/concentrate ratio should be adjusted properly.

4. The most significant interaction terms on Zn leaching efficiency were determined as leaching time vs. temperature and leaching time vs. P_{O_2}.

5. The optimum level of P_{O_2} during the leaching process was identified to be dependent on all the levels of temperature, solid/liquid ratio and leaching time. The increases in temperature, solid/liquid ratio and leaching time levels simultaneously diminished the importance of P_{O_2} control during the leaching process.

6. The indicated optimum leaching conditions for sphalerite concentrate were P_{O_2} of 12 bars, temperature of 150 ºC, solid/liquid ratio of 0.20 and leaching time of 89.16 minutes. The achieved Zn leaching efficiency, Zn concentration and Fe extraction were 94.56%, 82.28 g· dm^{-3} and 8.88%, respectively.

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