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Open System Leaching of Sphalerite in Butanoic Acid Solution and Empirical Analysis of Zinc Extraction Based on Initial Solution pH, Leaching Time and Ore Mass-input

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Abstract

This paper presents an open system leaching of sphalerite in butanoic acid solution. Empirical analysis of extracted zinc concentration based on constant leaching time and sphalerite mass-input as well as varying initial solution pH was carried out. The three factorial derived model: $\beta = \left[\alpha^{-1}\left(\alpha^{0.91} + 1.55\ \mathrm{lin}\theta + 0.3\gamma^{2}\right)\right]^{3}$ *shows that the extracted zinc concentration increases with decrease in the initial solution pH even at constant leaching time and ore mass-input. This is attributed to the fact that at lower solution pH, the concentration of* H^+ *(which is the principal attacking species) in the solution increases and so increases the rate of interaction between* H^+ *and* S^{2-} *to form* H_2S *and metallic zinc. The validity of the derived model is shown by the expression* $\alpha\ \sqrt[3]{\beta} = \alpha^{0.91} + 1.55\ \ln\theta + 0.3\gamma^{2}$ *where both sides of the expression are approximately equal. Computational analysis of results of extracted zinc concentration show that the average extracted zinc concentration per unit minute of leaching as obtained from experiment, derived model and regression model are 0.5627, 0.5669 and 0.5627 mg/kg* min^{-1} *respectively. Similarly, average extracted zinc concentration per unit leaching solution pH as obtained from experiment, derived model and regression model are 14.5413, 14.6586 and 14.5413 mg/kg respectively. Also, average extracted zinc concentration per unit ore mass-input as obtained from experiment, derived model and regression model are 13.5047, 13.6041 and 13.5047 mg/kg* g^{-1} *respectively. Statistical analysis of results of extracted zinc concentration indicates that the standard error in predicting the extracted zinc concentration (using results from derived model, regression model and experiment) for each value of the initial solution pH are 0.2378,* 4×10^{-5}*, and 1.4677 % respectively. The maximum deviation of the model from experimental values is less than 4.5% which implies 95.5% operational confidence level.*

Keywords: Sphalerite, leaching, zinc extraction, butanoic acid solution, leaching time, ore mass-input.

Introduction

Applicability of zinc has been widely accepted in furtherance of science and technology. In corrosion protection it is used as protection coatings on steel, as an alloying metal with copper to make brass, as diecastings and as chemical compounds in rubber, ceramics, paints, and agriculture. For proper growth and development of humans, animals, and plants zinc is an essential element[1]. In nature, wurtzite, sphalerite and marttite are polymorphs (having many shapes). This implies that apart from having different structures which translates into different shapes, they have the same chemical composition with Zn, Fe, and S as the major composition[2]. Studies have shown that sphalerite is the more common mineral of the three.

It has been reported[3] that problems such as high energy cost, shortage of high grade ores, processing of lean and complex ores and exploitation of smaller deposits necessitated the development of low temperature hydrometallurgical processes for the extraction of base metals from their sulphide ores and concentrates. Conventionally, hydrometallurgical processes for the extraction of a base metal from a sulphide concentrate involve catalytic sulphating, roast, leaching of the metallic values, solvent extraction and stripping. Roasting can be eliminated from the extraction of a base metal from a sulphide concentrate with the production of elemental sulphur instead of sulphur dioxide. High rate of extraction of the metals is realizable as insoluble low entropy phases are not always formed[4]. However, for the dissolution of sulphides a high oxidation potential is required[5]. Hydrogen peroxide has a standard redox potential of 1.77V in acidic medium [6], and this makes easy the oxidation of sulphide to sulphur since redox potential of sulphur / metal sulphide pair is less than that of hydrogen peroxide[7].

Leaching of powdered sphalerite using hydrogen peroxide and nitric acid has been studied[8]. The effect of parameters such as concentrations of hydrogen peroxide and nitric acid, reaction temperature stirring speed and particle size were investigated. Results of the investigation showed that hydrogen peroxide and nitric acid concentrations, temperature and stirring speed have tremendous effect on the leaching of sphalerite while sphalerite leaching was found to be inversely proportional to the particle size of the ore. The use of hydrogen peroxide as an oxidant for the leaching of zinc and copper from a complex sulphide ore using sulphuric acid showed that zinc and copper concentrations decreased while, sulphur, silica, iron and lead contents increased[9].

An electrochemical charge-transfer model has been developed to study the leaching of a sphaleritic flotation concentrate in an acidic ferric sulphate solution[10]. Empirical modelling of dissolved zinc concentration during leaching of sphalerite in butanoic acid solution has been studied[11]. The model is given in equation 1

$$\mathrm{Zn} = \mathrm{Anti\,log}\left\lfloor (\exp(\gamma/\alpha))^{0.6173} \right\rfloor \quad (1)$$

The model shows that the concentration of dissolved zinc depends on initial and final pH of the leaching solution.

The present work is to study an open system leaching of sphalerite in butanoic acid solution and then carry out empirical analysis of zinc extraction based on constant leaching time and sphalerite mass-input as well as varying initial leaching solution pH. The essence of this work is to understand and establish the relationship between extracted zinc concentration and initial leaching solution pH at constant leaching time and ore mass-input. The work is expected to predict the best operating initial leaching solution pH under constant leaching time and ore mass-input.

Material and Methods

100 cm^3 of butanoic acid solution was placed in a 1000cm^3 beaker containing 5g of sphalerite of grain size 150 µm. The initial solution pH was maintained at 4.46. The leaching process was allowed to proceed at a constant temperature of 25^{0}C for 120 after which the leaching solution was filtered. Wet chemical analysis was carried out on the filtrates to determine the extracted zinc concentration after which an average value was taken as the extracted zinc concentration. The experiments were repeated under the same process conditions for initial leaching solution pH: 4.55, 4.6, 4.67, 4.81 and 4.83 at the end of which their corresponding filtrates were analyzed chemically to determine the respective extracted zinc concentrations.

Model Formulation: Data from the experimental work were used for the model formulation. Analysis of these results are presented in table-1 gave rise to table-2 and table-3 [12].

$$\alpha\sqrt[3]{\beta} = \alpha^{K} + N\,\mathrm{lin}\theta + S\gamma^{2}\ \text{(approximately)} \quad (2)$$

Introducing the values of K, N and S into equation (2)

$$\alpha\sqrt[3]{\beta} = \alpha^{0.91} + 1.55\,\mathrm{lin}\theta + 0.3\gamma^{2} \quad (3)$$

$$\sqrt[3]{\beta} = \alpha^{-1}\left(\alpha^{0.91} + 1.55\,\mathrm{lin}\theta + 0.3\gamma^{2}\right) \quad (4)$$

Multiplying the indices of both sides of equation (3) by 3 reduces it to equation (5), the derived model.

$$\beta = \left[\alpha^{-1}\left(\alpha^{0.91} + 1.55\,\mathrm{lin}\theta + 0.3\gamma^{2}\right)\right]^{3} \quad (5)$$

Where, K = 0.91 (equalizing constant), N = 1.55 (equalizing constant), S = 0.3(equalizing constant): (α)= Initial pH of the butanoic acid leaching solution just before the leaching process started. (β)= concentration of dissolved Zn during the leaching process (mg/kg), (γ) = mass-input of sphalerite (g) (θ)= leaching time (mins).

Table-1
Variation of the initial pH of leaching solution with concentration of dissolved Zinc.

(α)	**β (mg/kg)**	**θ (mins)**	**γ (g)**
4.46	71.96	120	5
4.55	71.22	120	5
4.60	68.64	120	5
4.67	64.68	120	5
4.81	64.42	120	5
4.83	64.22	120	5

Boundary and Initial Condition: Sphalerite was placed in a 1000cm^3 beaker containing leaching solution of butanoic acid. Before the commencement of the leaching process, the beaker was taken to be free of bacteria and other microorganisms. Atmospheric oxygen was assumed. The mass of sphalerite used was 5g. The initial solution pH ranged from 4.46-4.83. Leaching temperature of 25°C, leaching time of 2 hrs, butanoic acid concentration at 0.27mol/litre and average ore grain size of 150µm were used.

The boundary conditions are atmospheric oxygen and a zero gradient which was assumed for the liquid scalar at the bottom of the particles and for the gas phase at the top of the particles. The sides of the particles were assumed to be symmetrical.

Results and Discussion

The result of the chemical analysis carried out on the sphalerite used is presented in table-2.

Table-2
Result of chemical analysis of sphalerite used

Element/Compound	PbS	Al_2O_3	ZnS	Fe_2O_3	K_2O	Wa_2O	MgO	CaO	SiO_2
Unit (%)	21.8	3.65	59.8	2.18	14.52	1.26	0.775	0.11	1.09

Effects of leaching time, ore mass-input and initial solution pH on the concentration of extracted zinc: Results from the leaching process (figure-1 and table-1) show that the concentration of extracted zinc increases with decrease in the initial solution pH and vice versa even when the leaching time and ore mass-input are both constant. This is attributed to the fact that at lower solution pH, the concentration of H^+ (which is the principal attacking species) in the solution increases and so increases the rate of interaction between H^+ and S^{2-} to form H_2S and metallic zinc. As H^+ is fast depleting in the leaching solution due to increased rate of interaction between H^+ and S^{2-}, the final solution pH is expected to be higher depending on the quantity of H_2S dissolving in the solution. Increased dissolution of H_2S in the solution is expected to lower its pH.

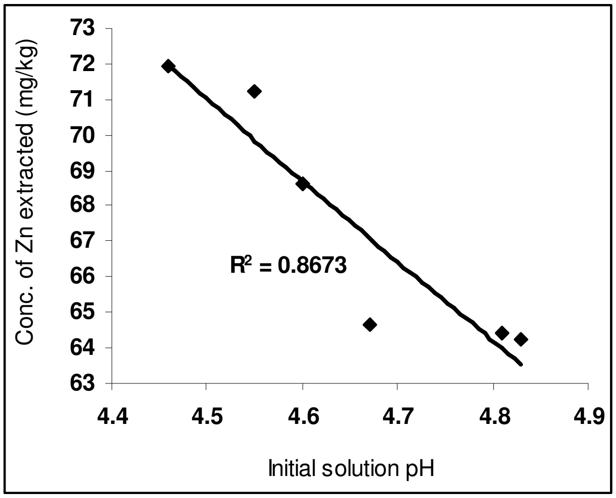

Figure-1
Coefficient of determination between extracted zinc concentrations and initial leaching solution pH as obtained from experiment

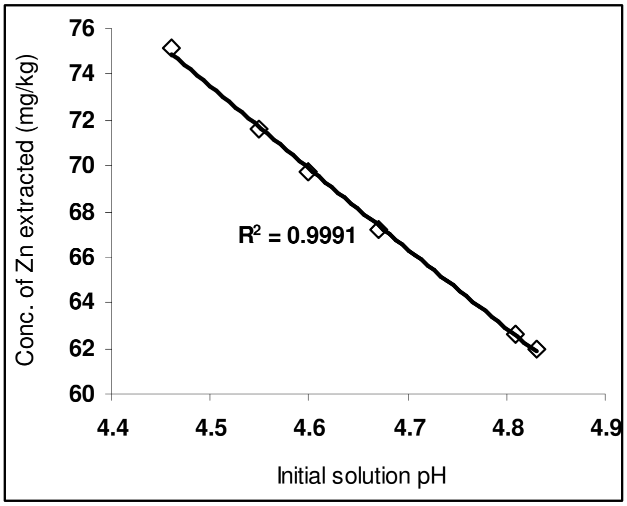

Figure-2
Coefficient of determination between extracted zinc concentrations and initial leaching solution pH as obtained from derived model

Empirical predictive analysis of extracted zinc concentration based on leaching time, ore mass-input and initial solution Ph: A three factorial model; $\beta = \alpha^{-1}(\alpha^{0.91} + 1.55 \ln\theta + 0.3 \gamma^2)^3$ (equation (5)) was derived and used as a tool for empirical predictive analysis of extracted zinc concentration based on leaching time, ore mass-input and solution pH. Tables 4-6 and figures 1-3 indicate that the derived model (MoD), regression model (ReG) and experiment predicted maximum zinc extractions; 75.1263, 71.8923 and 71.96 mg/kg at a pH value: 4.46, constant leaching time; 120min. and sphalerite mass-input: 5g respectively. This is a clear indication that predictions from these models are in agreement with results from the experiment.

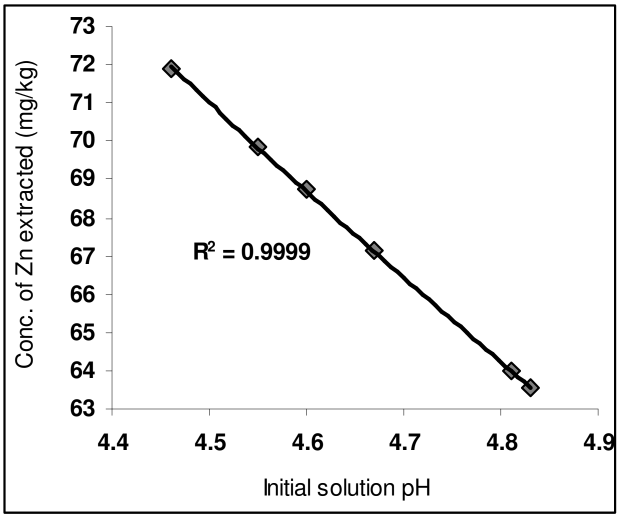

Figure-3
Coefficient of determination between extracted zinc concentrations and initial leaching solution pH as obtained from regression model

Model Validation: The validity of the model is expressed in equation (3) where both sides of the equation are approximately equal. Table-3 also agrees with equation (3) following the values of $\alpha\ \sqrt[3]{Zn} = \alpha^{0.91} + 1.55 \ln t + 0.3\gamma^2$ evaluated from experimental results in table-1.

Table-3
Variation of $\alpha\ \sqrt[3]{Zn}$ with $\alpha^{0.91} + 1.55 \ln t + 0.3\gamma^2$

$\alpha\ \sqrt[3]{Zn}$	$\alpha^{0.91} + 1.55 \ln t + 0.3\gamma^2$
18.5509	18.8191
18.8602	18.8906
18.8343	18.9303
18.7459	18.9858
19.2820	19.0965
19.3421	19.1123

Furthermore, the derived model was validated by comparing the extracted zinc concentration predicted by the model and that obtained from the experiment. This was done using various evaluative techniques such as computational, statistical, graphical and deviational analysis.

Computational Analysis: Computational analysis of extracted zinc concentrations from regression model, derived model, experiment, were carried out and compared to ascertain the degree of validity of the derived model. This was done by comparing extracted zinc concentration per minute of leaching and extracted zinc concentration per unit solution pH and extracted zinc concentration per unit ore mass-input evaluated from regression model, derived model predicted and experimental results.

Extracted zinc concentration per unit minute of leaching β^{θ} (mg/kg) min^{-1} was calculated from the equation (6)

$$\beta^{\theta} = \beta/\theta \tag{6}$$

Substitution of values of extracted zinc concentration β from figures 1-3 (for experimental, derived model and regression model predicted results) and corresponding constant leaching times (as in table -1) in equation (6) evaluates the zinc extraction rate as shown in table -3. The average extracted zinc concentration per unit minute of leaching as obtained from experiment β_{exp}/θ, derived model β_{MoD}/θ, and regression model-predicted results β_{ReG}/θ are 0.5627, 0.5669 and 0.5627 mg/kg min^{-1} respectively.

Table-4
Computed extracted zinc concentration per minute of leaching as obtained from regression model, derived model predicted and experimental results

β_{ReG}/θ	β_{MoD}/θ	β_{exp}/θ
0.5991	0.6261	0.5997
0.5822	0.5964	0.5935
0.5727	0.5808	0.572
0.5596	0.56	0.539
0.5332	0.5215	0.5368
0.5294	0.5163	0.5352

Extracted zinc concentration per unit solution pH β^{α} mg/kg was calculated from the equation (7)

$$\beta^{\alpha} = \beta/\alpha \tag{7}$$

Similarly, substituting values of extracted zinc concentration β from figures 1-3 (for experimental, derived model and regression model predicted results) and corresponding solution pH values (as in table -1) in equation (7) evaluates the extracted zinc concentration per unit solution pH as shown in table-4. The average extracted zinc concentration per unit solution pH as obtained from experiment β_{exp}/α, derived model β_{MoD}/α, and regression model-predicted results β_{ReG}/α are 14.5413, 14.6586 and 14.5413 mg/kg respectively.

Extracted zinc concentration per unit mass-input of sphalerite β^{γ} (mg/kg) g^{-1} was calculated from the equation (8)

$$\beta^{\gamma} = \beta/\gamma \tag{8}$$

Table-5
Computed extracted zinc concentration per unit solution pH as obtained from regression model, derived model predicted and experimental results

β_{ReG}/α	β_{MoD}/α	β_{exp}/α
16.1193	16.8445	16.1345
15.3535	15.7289	15.6527
14.941	15.1512	14.9217
14.3783	14.3888	13.8501
13.3021	13.0104	13.3929
13.1534	12.8278	13.2961

Also, on substituting values of extracted zinc concentration β from figures 1-3 (for experimental, derived model and regression model predicted results) and corresponding constant sphalerite mass-input values (as in table -1) in equation (8), the extracted zinc concentration per unit sphalerite mass-input is evaluated as shown in table -5. The average extracted zinc concentration per unit sphalerite mass-input as obtained from experiment β_{exp}/γ, derived model β_{MoD}/γ, and regression model-predicted results β_{ReG}/γ are 13.5047, 13.6041 and 13.5047 mg/kg g^{-1} respectively.

Table-6
Computed extracted zinc concentration per unit mass-input of sphalerite as obtained from regression model, derived model predicted and experimental results

β_{ReG}/γ	β_{MoD}/γ	β_{exp}/γ
14.3785	15.0253	14.392
13.9717	14.3133	14.244
13.7457	13.9391	13.728
13.4293	13.4392	12.936
12.7966	12.516	12.884
12.7062	12.3916	12.844

Statistical Analysis: Statistical analysis of derived, regression model predicted and experimental extracted zinc concentrations were carried out for comparative assessment through evaluation of the standard error (STEYX), correlation (CORREL) and measure of variability (AVEDEV). Table-7 shows that the standard error in predicting the extracted zinc concentration (using results from derived model, regression model and experiment) for each value of the solution pH are 0.2378, 4 x 10^{-5}, and 1.4677 % respectively.

Table-7
Comparison of the standard errors evaluated from derived model (D-Model), regression model (ReG) and experiment (ExD) based on solution pH

Analysis	**Based on solution pH**		
	D-Model	**ReG**	**ExD**
STEYX	0.2378%	4 x 10^{-5}%	1.4677%

Also the correlations between extracted zinc concentration and solution pH as obtained from derived model, regression model and experiment considering the coefficient of determination R^2 from figures 1-3 was calculated using equation (9)

$$R = \sqrt{R^2} \qquad (9)$$

Table-8 shows the highlighted correlations as 0.9995, 0.9999 and 0.9313 respectively. These evaluated results indicate that the derived model predictions are significantly reliable and hence valid considering its proximate agreement with results from regression model and actual experiment.

Table-8
Comparison of the correlations evaluated from derived model (D-Model), regression model (ReG) and experiment (ExD) based on solution pH

Analysis	Based on solution pH		
	D-Model	ReG	ExD
CORREL	0.9995	0.9999	0.9313

Evaluated AVEDEV (table- 9) from experimental, derived model and regression model predicted results show significant proximate agreement between each other. Results from these statistical tools were evaluated using Microsoft Excel version 2003.

Table-9
Comparison of the AVEDEV evaluated from derived model (D-Model), regression model (ReG) and experiment (ExD) based on solution pH

Analysis	Based solution pH		
	D-Model	ReG	ExD
AVEDEV	31.6825	31.435	31.435

Graphical Analysis: Comparative graphical analysis of figure-4 shows very close alignment of the curves from model-predicted extracted zinc concentration (MoD) and that of the experiment (ExD). The closeness of these curves is indicative of agreement between both experimental and model-predicted extracted zinc concentration.

Comparison of derived model with standard model: The validity of the derived model was further verified through application of the regression model (ReG) in predicting the trend of the experimental results. Critical graphical analysis of figure-5 shows very close alignment of the curves from model-predicted extracted zinc concentration (MoD) and that of the experiment (ExD). The degree of alignment of these curves is indicative of the proximate agreement between both experimental and model-predicted extracted zinc concentration. Comparative analysis of curves from figure-5 shows very close alignment of these curves and significantly similar trend of data point's distribution for experimental (ExD), derived model-predicted (MoD) and regression model predicted (ReG) results of extracted zinc concentration.

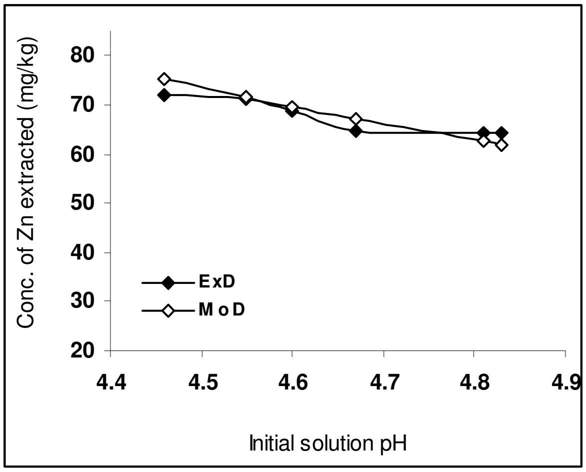

Figure-4
Comparison of the extracted zinc concentrations (relative to initial solution pH) as obtained from experiment and derived model

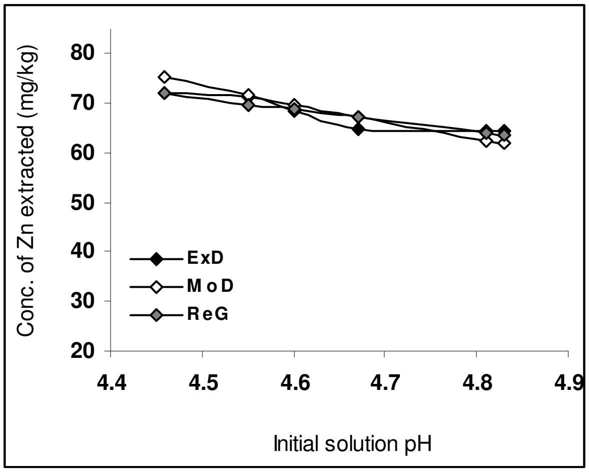

Figure-5
Comparison of the extracted zinc concentration (relative to initial solution pH) as obtained from experiment, derived and regression model

Deviational Analysis: Analysis of extracted zinc concentration from the experiment and derived model revealed deviations of the predicted model values from the actual experimental results. This is attributed to the fact that the surface properties of the sphalerite and the physiochemical interactions between the ore and the leaching solution which were found to have played vital roles during the process were not considered during the model formulation. This resulted to the introduction of correction factor, to bring the predicted model of extracted zinc concentration to those of the corresponding experimental values.

Deviation (Dn) of model-predicted extracted zinc concentration from that of the experiment is given by

$$Dn = \left(\frac{Pz - Ez}{Ez} \right) \times 100 \qquad (10)$$

Where, Pz = Extracted zinc concentration as predicted by derived model, Ez = Extracted zinc concentration as obtained from experiment.

Correction factor (Cr) is the negative of the deviation i.e

$$Cr = -Dn \quad (11)$$

Therefore,

$$Cr = -\left(\frac{Pz - Ez}{Ez}\right)\times 100 \quad (12)$$

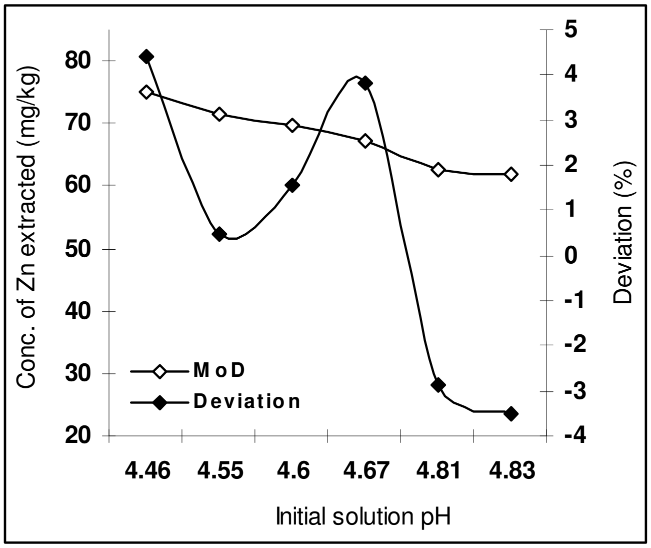

Figure-6
Variation of model-predicted extracted zinc concentration with associated deviation from experimental results (relative to initial solution pH)

Variation of model-predicted concentration of extracted zinc with its associated deviations: Figure-6 shows that the maximum deviation of the model predicted from the corresponding experimental values is less than 4.5%. Comparative analysis of figure-6 shows that the least and highest deviation are +0.49 and + 4.4% respectively. These correspond to dissolved zinc concentration of 71.5664 and 75.1263 mg/kg for initial leaching solution pH of 4.55 and 4.46 respectively.

Variation of model-predicted concentration of dissolved zinc with its associated correction factors: Comparison of figures 6 and 7 show that the curve of figure-7 is opposite and negative to deviation curves in figure-6 implying that correction factors to the model-predicted concentrations of dissolved zinc indicate similar values as in the deviation but of opposite sign. This is in agreement with equations (11) and (12). It is seen that the correction factor takes care of the effects of the surface properties of the ore and the physiochemical interaction between the ore and the leaching solution which (affected experimental results) were not considered during the model formulation.

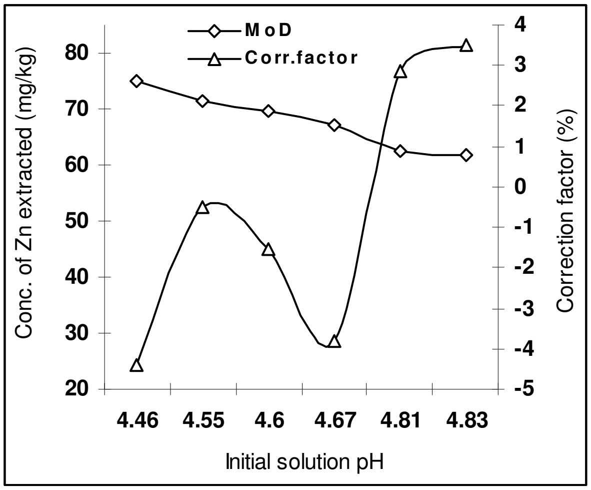

Figure-7
Variation of model-predicted extracted zinc concentration with associated correction factor (relative to initial solution pH)

Consequently, the least and highest correction factor to the model-predicted concentration of extracted zinc are - 0.497% and - 4.4%. These also correspond to the zinc concentration of 71.5664 and 75.1263 mg/kg for initial leaching solution pH of 4.55 and 4.46 respectively. It is pertinent to state that the actual deviations and correction factors are just the modulus of the values. The role of the sign attached to the values is just to show when the deviation is surplus or deficit.

Conclusion

Following open system leaching of sphalerite in butanoic acid solution and empirical analysis of extracted zinc concentration based on constant leaching time and sphalerite mass-input as well as varying initial solution pH, it was concluded that extracted zinc concentration increases with decrease in the initial solution pH even at constant leaching time and ore mass-input. At lower solution pH, the concentration of H^+ (which is the principal attacking species) in the solution increases and so increases the rate of interaction between H^+ and S^{2-} to form H_2S and metallic zinc. The validity of the derived model applied for the empirical analysis is rooted in the core expression $\alpha\, {}^{3}\sqrt{\beta} = \alpha^{0.91} + 1.55 \ln \theta + 0.3\, \gamma^2$ where both sides of the expression are approximately equal. Computational analysis of results of extracted zinc concentration show that the average extracted zinc concentration per unit minute of leaching as obtained from experiment, derived model and regression model are 0.5627, 0.5669 and 0.5627 mg/kg min^{-1} respectively. Similarly, average extracted zinc concentration per unit leaching solution pH as obtained from experiment, derived model and regression model are 14.5413, 14.6586 and 14.5413 mg/kg respectively. Also, average extracted zinc concentration per unit ore mass-input as obtained from experiment, derived model and regression model are 13.5047, 13.6041 and 13.5047 mg/kg g^{-1} respectively. Statistical analysis of results of extracted zinc concentration indicates that the standard error in predicting the extracted zinc concentration (using results from derived model, regression model and experiment) for each value of the initial solution pH are 0.2378, 4 x 10^{-5}, and 1.4677 % respectively. The maximum deviation of the predicted model from that of the corresponding experimental values is less than 4.5% which implies 95.5% operational confidence level.

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