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Analysis of the Final Solution pH Relative to Dissolved Concentrations of Lead and Zinc during Leaching of Galena in Butanoic Acid *(pp. 89-100)*

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Abstract: A model was developed for evaluation and predictive analysis of the final solution pH relative to dissolved concentrations of lead and zinc during leaching of galena in butanoic acid solution. The established model shows that the final leaching solution pH is dependent on the initial solution pH and dissolved concentrations of lead and zinc. The validity of the model was rooted in the expression of this study where both sides of the expression were approximately equal to 1. The maximum deviation from the corresponding experimental value was less than 4% which is quite within the acceptable deviation limit of experimental results. The standard deviation and variance evaluated from model-predicted and experimental values of the final solution pH are 0.3194 and 0.1020 and 0.2571 and 0.0661 respectively indicating proximate agreement and validity for the model.

Key words: model, final pH, galena leaching, butanoic acid solution

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1 INTRODUCTION

There has been for long, a wide scale application of pyrometallurgical route as a conventional means of lead extraction from galena. Basically, two main processes have accounted for world's production of lead; the hearth smelting and the blast furnace smelting of roasted ores. The applicability of pyrometallurgical treatment of lead ores has shown that though these routes have effectively recovered both lead and other associated precious metals, they have not really been widely accepted due to emission of poisonous gases during the associated operations. This invariably has become a set back to the much orchestrated need for environmental-friendly industrial operations in lead producing industries. Studies by Dutrizac and Chen (1990) and Flaskett et al (1982) have shown that the application of hydrometallurgy in lead extraction prevents SO_2 formation by recovering elemental sulphur. This no doubt reduces air pollution.

An attempt has been made in the past (Dutrizac, 1986) to leach galena concentrate using ferric chloride brine. The results of the investigation reveal that ferric chloride exhibits substantially faster dissolution rates for most sulphides, it is regenerated easily by chlorination of ferrous chloride leaching by-products, and it has greater potential for the treatment of complex sulfides. Following a similar work to investigate the thermodynamics and kinetics of the process, Seon-Hyo et al., (1986) discovered that under the prevailing leaching condition of their work, the distribution of the various metal chloro complexes is relatively insensitive to the extent of PbS dissolution.

Dix and Hendrix (1986) carried out further studies to evaluate the kinetics of the process of Cl_2-O_2 leaching of galena flotation concentrate indicate that the rate of gas transfer can be enhanced by increasing the partial pressure of the gas and by using vigorous agitation to increase the surface area of the liquid-gas interface.

In a similar work, Nwoye (2009) derived a model for predicting the initial solution pH at pre-assumed final pH and concentration of dissolved zinc, during leaching of galena in butanoic acid solution has been derived. The model;

$$\alpha = \left(\frac{1.4\gamma}{\ln\left[(Z_n)^{1/3}\right]}\right) \tag{1}$$

shows that the initial pH of the leaching is dependent on the values of the pre-assumed final solution pH and concentration of dissolved zinc. The validity of the model was rooted in the expression $e^{N(\gamma/\alpha)} = \sqrt[3]{Z_n}$ where both sides of the expression were approximately equal to 4. In case, the maximum deviation of the model-predicted initial solution pH value from that of the corresponding experimental value was less than 2%. In both derivations (Nwoye, 2009 and 2010) the initial solution pH was directly proportional to the final solution pH.

Nwoye (2010) derived a model for predicting the initial solution pH at pre-assumed final pH and concentration of dissolved lead, during leaching of galena in butanoic acid solution. The model;

$$\alpha = \left[\frac{1.61\gamma}{\ln\left[(P_b)^{1/3}\right]}\right] \tag{2}$$

shows that the initial pH of the leaching is dependent on the values of the pre-assumed final solution pH and concentration of dissolved lead. The validity of the model was rooted in the expression $e^{N(\gamma/\alpha)} = \sqrt[3]{P_b}$ where both sides of the expression were approximately equal to 5. The maximum deviation of the model-predicted initial solution pH value from that of the corresponding experimental value was less than 3%. Model for assessment and computational analysis of the concentration of zinc dissolved during leaching of sphalerite in butanoic acid solution has been derived (Nwoye and Mbuka, 2010). The model

$$Z_n = \text{Antilog}\left[\left(\exp\{\gamma/\alpha\}\right)^{0.6173}\right] \tag{3}$$

is dependent on the initial and final pH of the leaching solution. The validity of the model was found to be rooted in the expression $(\text{Log } Zn)^{1.62} = \exp(\gamma/\alpha)$ where both sides of the expression are approximately equal to 3. The maximum deviation of the model-predicted concentrations of dissolved zinc from that of the corresponding experimental values is less than 14% which is quite within the acceptable deviation limit of experimental results.

The aim of this work is to derive a model for evaluation and predictive analysis of the final solution pH relative to the initial solution pH and dissolved concentrations of lead and zinc during butanoic acid leaching of Ishiagu (Nigeria) galena. The proposed work resulted from the need to predict the expected final solution pH, (given the initial solution pH) when lead and zinc dissolve during leaching of galena. It is expected that the model would guide extractive metallurgists in achieving maximum yield through the application of the optimum initial pH on the leaching solution. This derivation is in furtherance of the previous work (Nwoye, 2008).

2 MODELLING

During the leaching process, the ore was assumed to be stationary in the reaction vessel and contains the un-leached lead and zinc as part of reaction remnants. The ore was attacked by hydrogen ions from butanoic acid within the liquid phase, and in the presence of oxygen.

2.1 Model Formulation

Results from experimental work of Nwoye (2008) carried out at SynchroWell Research Laboratory, Enugu were used for the model derivation. These results are as presented in Table 1. Computations with Table 1 data resulted to Table 2 which indicates approximately that;

$$\left({}^{\gamma}/_{\alpha}\right) = \left({}^{P_b}/_{Z_n}\right)^{n} \tag{4}$$

$$\gamma = \alpha\left[\left(P_b/Z_n\right)^{n}\right] \tag{5}$$

Introducing the value of n into equation (5) reduces it to;

$$\gamma = \alpha\left[\left({}^{P_b}/_{Z_n}\right)^{0.02}\right] \tag{6}$$

Where

$n = 0.02$ (Net dissolution factor for lead and zinc dissolved together (in same vessel) in butanoic acid) determined in the experiment (Nwoye,2008).

$\alpha =$ Initial pH of the butanoic acid leaching solution just before the leaching process started.

γ = Final pH of the butanoic acid leaching solution at time t.

Zn = Concentration of dissolved Zn during the leaching process (mg/kg)

Pb = Concentration of dissolved Pb during the leaching process (mg/kg)

Equation (6) is the derived model**.**

Table1: Variation of the initial and final pH of the butanoic acid leaching solution with the concentrations of dissolved lead and Zinc

(γ)	(α)	Zn (mg/kg)	Pb (mg/kg)
3.98	3.80	79.96	140.22
4.25	4.08	77.34	138.42
4.33	4.24	72.24	136.22
4.41	4.36	72.02	136.02
4.50	4.46	71.96	135.86
4.61	4.55	71.22	135.04
4.63	4.60	68.64	133.96
4.72	4.67	64.68	133.34
4.84	4.81	64.42	132.82
4.86	4.83	64.22	132.60

3 BOUNDARY AND INITIAL CONDITIONS

Galena was placed in cylindrical flask 30cm high containing leaching solution of butanoic acid solution. The leaching solution is non flowing (stationary). Before the start of the leaching process, the flask was assumed to be initially free of attached bacteria and other micro organism. Initially, the effect of oxygen on the process was assumed to be atmospheric. In all cases, mass of galena used was 5g. The initial and final pH range of leaching solutions used; 3.80-4.83 and 3.98-4.86 and leaching time of 2 hrs (120 minutes) were used for all samples. A constant leaching temperature of 25^{o}C was used. Butanoic acid concentration at 0.27mol/litre and average ore grain size; 150µm were also used. Details of the experimental technique are as presented in the report (Nwoye,2008).

The leaching process boundary conditions include: atmospheric levels of oxygen (considering that the cylinder was open at the top) at both the top and bottom of the ore particles in the gas and liquid phases respectively. A zero gradient 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 symmetries.

4 MODEL VALIDATION

The formulated model was validated by calculating the deviation of the model-predicted final pH from the corresponding experimental pH values as well as the standard deviation and variance for both data. The deviation recorded is believed to be due to the fact that the surface properties of the ore and the physiochemical interactions between the ore and leaching solution which were found to play vital roles during the leaching process were not considered during the model formulation. It is expected that introduction of correction factor to the predicted final pH, gives exactly the experimental final pH values. Deviation (De) (%) of model-predicted initial pH values from those of the experiment is given by

$$D_e = \frac{M_1 - E_1}{E_1} \times 100 \qquad (7)$$

where M_1 = Model-predicted final pH values
E_1 = Experimental final pH values

Since correction factor (Cv) is the negative of the deviation,

$$C_v = -D_e \qquad (8)$$

Substituting equation (7) into equation (8) for D_e

$$C_v = -100\left[\frac{M_1 - E_1}{E_1}\right] \qquad (9)$$

It was observed that addition of the corresponding values of Cv from equation (9) to the model-predicted final pH gave exactly the corresponding experimental final pH values (Nwoye, 2008). The model was also validated by comparing the values of the variance and standard deviation evaluated from experimental and model-predicted data (Nwosu, 1992). The variance V is established with classical relation as

$$V = \frac{\sum(x - x_a)^2}{\sum n} \qquad (10)$$

Furthermore, standard deviation is given by

$$SD = [V]^{1/2} \qquad (11)$$

Substituting equation (10) into equation (11) reduces it to;

$$SD = \sqrt{\frac{\sum(x - x_a)^2}{\sum n}} \qquad (12)$$

$$x_a = \left(\frac{x_1 + x_2 + x_3 + x_4 \ldots}{\sum n}\right) \qquad (13)$$

where

SD = Standard deviation
V = Variance
x = Variables representing the final solution pH
x_a = Arithmetic mean
n = Number of samples

5 RESULTS AND DISCUSSION

The derived model is equation (6). Computational analysis of experimental data in Table 1 gave rise to Table 2.

Table 2: Variation of (γ/α) with $(Pb/Zn)^n$

(γ/α)	Pb/Zn	$(Pb/Zn)^n$
1.0474	1.7536	1.0113
1.0417	1.7898	1.0117
1.0212	1.8857	1.0128
1.0115	1.8886	1.0128
1.0090	1.8880	1.0128
1.0132	1.8961	1.0129
1.0065	1.9516	1.0135
1.0107	2.0615	1.0146
1.0062	2.0618	1.0146
1.0062	2.0648	1.0146

An ideal comparison of the final solution pH as obtained from experiment and as predicted by the model for the purpose of testing the validity of the model is achieved by considering the R^2 values (coefficient of determination). The values of the correlation coefficient, R calculated from the equation:

$$R = \sqrt{R^2} \qquad (14)$$

using the r-squared values (coefficient of determination) from Figs.1-4 show better correlations (0.9658) and (0.9881) with model-predicted final solution pH than that obtained from experiment (0.9634) and (0.9821) (relative to dissolved concentrations of Zn and Pb respectively). This suggests that the model predicts more accurate, reliable and ideal final solution pH than the actual experiment despite its deviations from the experimental values.

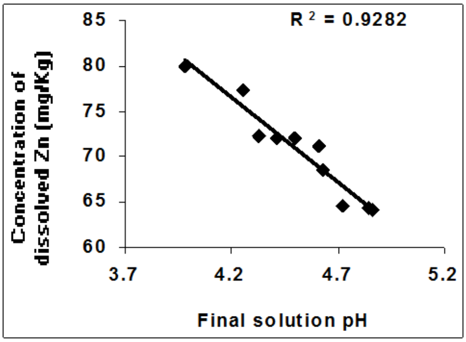

Figure 1: Effect of final solution pH on the concentration of dissolved zinc as obtained from experiment (Nwoye, 2008)

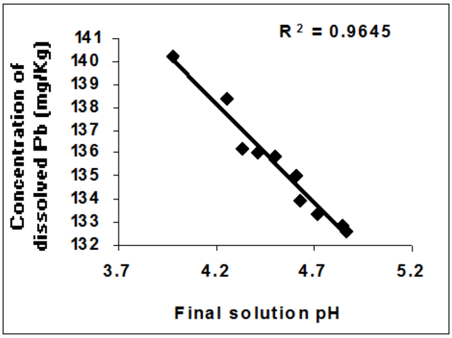

Fig.ure 2: Effect of final solution pH on the concentration of dissolved lead as obtained from experiment (Nwoye, 2008)

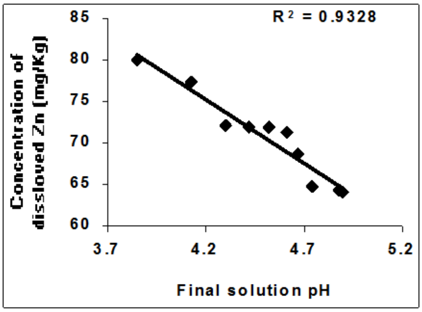

Fig.ure 3: Effect of final solution pH on the concentration of dissolved zinc as predicted by derived model

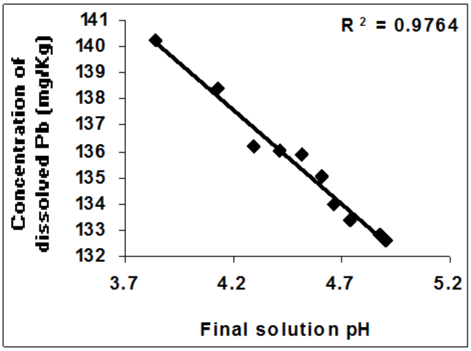

Figure 4: Effect of final solution pH on the concentration of dissolved lead as predicted by derived model

Comparison of Figs. 5 and 6 shows very close alignment of the curves from model-predicted values of the final pH (MoD) and that from the corresponding experimental values(ExD). The degree of alignment of these curves is indicative of the proximate agreement between both experimental and model-predicted final solution pH. The validity of the model is believed to be rooted on equation (6) where both sides of the equation are approximately equal to 1. Table 2 also agrees with equation (6) following the values of (γ/α) and $(Pb/Zn)^n$ evaluated as a result of statistical and computational analysis carried out on the experimental results in Table1.

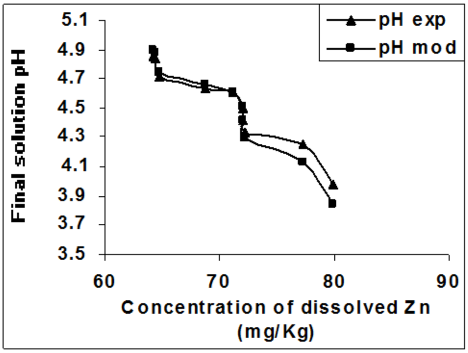

Figure 5: Comparison of the final solution pH resulting from dissolution of zinc in the butanoic acid

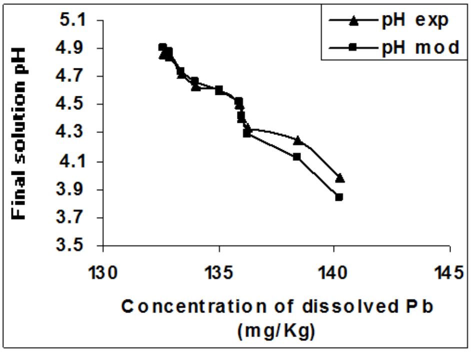

Figure 6: Comparison of the final solution pH resulting from dissolution of lead in the butanoic acid

It was also shown in Fig.7 that the maximum deviation of the model-predicted final pH values from those of the experiment were less than 4% which is quite within the acceptable deviation limit of experimental results. The positive and negative deviations (of the model-predicted final pH) from the actual experimental values show undulating relationship (as in Fig.7) with the model-predicted final pH.

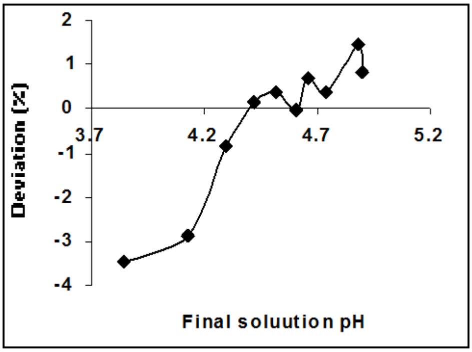

Figure 7: Variation of model-predicted final solution pH with its associated deviation from experimental values (Nwoye, 2008)

The least and highest magnitude of deviation of the model-predicted final solution pH (from the corresponding experimental values) are -0.03 and -3.44% which correspond to final solution pH 4.61 and 3.98 respectively. Correction factor for the model-predicted final solution pH (shown in Fig.8) similarly shows an undulating relationship with model-predicted solution pH. However, the orientation of this curve is opposite that of the deviation values of model-predicted final pH (Fig.7). This is because correction factor is the negative of the deviation as shown in eqns. (8) and (9). It is believed 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.

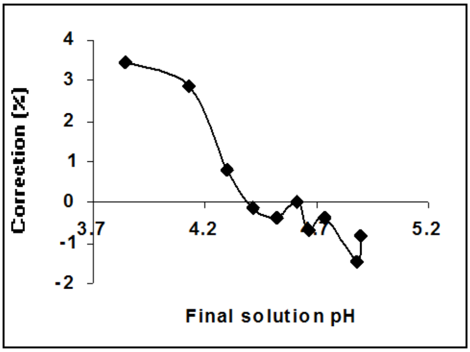

Figure 8: Variation of model-predicted final solution pH with its associated correction factor

Based on the foregoing, Fig.8 indicates that a correction factor of +0.03 and +3.44% make up for the least and highest deviation of -0.03 and -3.44% resulting from final solution pH 4.61 and 3.98 respectively. It is pertinent to state that the actual deviations 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. Comparison of the standard deviation and variance as obtained from experimental data and model-predicted data are made with the following tables.

Table 3: Variance Data for Experimental Values of Final Solution pH

n	$x - x_a$	$(x - x_a)^2$
1	-0.533	0.2841
1	-0.263	0.0692
1	-0.183	0.0033
1	-0.103	0.0106
1	-0.013	0.0002
1	0.097	0.0094
1	0.117	0.0137
1	0.207	0.0428
1	0.327	0.1069
1	0.347	0.1204
$\sum n = 10$		$\sum (x - x_a)^2 = 0.6606$

Substituting the values of $\sum n$ and $\sum(\mathbf{x} - \mathbf{x_a})^2$ into equations (10) and (12), where xa = 4.513 (as calculated from equation (13)) gives variance and standard deviation as 0.0661 and 0.2571 respectively.

Table 4: Variance data for model-predicted values of final solution pH

n	$x - x_a$	$(x - x_a)^2$
1	-0.6559	0.4302
1	-0.3710	0.1376
1	-0.2045	0.0418
1	-0.0830	0.0069
1	0.0183	0.0003
1	0.1099	0.0121
1	0.1633	0.0267
1	0.2394	0.0573
1	0.3814	0.1455
1	0.4017	0.1614
$\sum n = 10$		$\sum(x - x_a)2 = 1.0198$

Also substituting the values of $\sum n$ and $\sum(x - x_a)2$ into equations (10) and (12), where $x_a = 4.4988$ (as calculated from equation (13)) gives variance and standard deviation as 0.1020 and 0.3194 respectively.

Table 5: Standard Deviation (SD) and Variance (V) of Final Solution pH

Experimental		Modell	
SD	V	SD	V
0.2571	0.0661	0.03194	0.1020
0.02571	0.0661	0.03194	0.1020
0.02571	0.0661	0.03194	0.1020

The proximity of values of the standard deviation and variance (Table 5) as obtained from experiment (Nwoye, 2008) and derived model indicates agreement and validity for the model.

6 CONCLUSION

The model evaluates and predicts the final solution pH relative to the initial solution pH and dissolved concentrations of lead and zinc during butanoic acid leaching of Ishiagu (Nigeria) galena. The validity of the model is was rooted on the expression $(\gamma/\alpha) = (Pb/Zn)^n$ where both sides of the expression are approximately equal to 1. The maximum deviation of the model-predicted final solution pH from that of the corresponding experimental value is less than 4% which is quite within the acceptable deviation limit of experimental results. The standard deviation and variance evaluated from model-predicted and experimental values of the final solution pH are 0.3194 & 0.1020 and 0.2571 & 0.0661 respectively indicating proximate agreement and validity for the model.

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