

Assessment Evaluation of Dissolved Lead Based on Ferric Sulphate Concentration, Reaction Temperature and Time during Leaching of Galena

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Abstract

Assessment evaluation of dissolved lead based on ferric sulphate concentration, reaction temperature and time during leaching of galena in ferric sulphate solution has successfully been carried out. A multi-variant model was derived, following computational analysis of experimental results. The dissolved lead concentrations for various values of the reaction time as obtained from experiment and derived model-predicted results were subjected to statistical analysis. The evaluated standard errors obtained from the analysis were 0.06 and $6.66 \times 10^{-9}\%$ respectively. Further evaluation of generated results indicates that dissolved lead concentration per unit reaction time as obtained from experiment and derived model-predicted results were 0.056 and 0.062 ppm/hr respectively. Deviation analysis of model-predicted dissolved lead concentration (from experimental result) shows a maximum deviation of less than 8%. This implies a derived model confidence level above 92% and well over 0.92 response coefficients for dissolved lead dependence on the ferric sulphate concentration, reaction temperature and time.

Keywords: Assessment evaluation, Dissolved lead, Galena, Ferric sulphate concentration, Reaction temperature and time.

1. Introduction

The usefulness of lead in domestic and industrial scene has aroused the need for specialized research and development aimed at improving ways of extracting lead from their respective sulphides.

Extraction of lead from their ores through acid leaching has gained wide recognition and popularity due to its environmental friendliness.

Researches [1-5] have shown the potentiality of leaching galena in different acids. The possibility of extracting lead from Ishiagu galena using different acid types has been explored [6]. The results of the investigation reveal that the concentration of lead after leaching with dilute nitric acid, sulphuric acid and aqueous solution of both acids are 39.5% w/w, 14.16% w/w and 15.18% w/w respectively. These results indicate that nitric acid gave the best result of recovery (84.2%), with original lead in the ore being 46.9% w/w.

Report [1] on acid leaching of lead sulphide using HCl and H₂SO₄ indicate that prior to mineral addition, the redox potential of the acid solutions was $360 \pm 10\text{mV}$ (SHE). Dissolution of oxidation products formed during grinding of galena produced dissolved Pb(II) and sulphur concentrations significantly higher than in the case of sphalerite leaching. However, concentrations of both species decreased over the first hour of the experiment, probably due to restricted solubility of PbCl₂ and PbSO₄, the latter phase having a particularly low solubility product $K_{sp}(\text{PbSO}_4) = 10^{-7.86}$.

Extracted lead concentration has been evaluated [7] using empirical model derived from experimental result. The model prediction is based on initial and final solution pH during leaching of galena in butanoic acid.

The model expressed as:

$$Pb = \text{Antilog} \left[\exp \left(\frac{\gamma}{\alpha} \right)^{0.7407} \right] \quad (1)$$

indicates that the concentration of dissolved lead during the leaching process is dependent on the values of the initial and final leaching solution pH. The validity of the model was rooted in the core expression $(\log Pb)^N = \exp \left(\frac{\gamma}{\alpha} \right)$

where both sides of the expression were correspondingly approximately almost equal. The maximum deviation of the model-predicted concentrations of dissolved lead from the corresponding experimental values is less than 7% which is quite within the acceptable deviation limit of experimental results.

The aim of the present work is to carry out an assessment evaluation of dissolved lead based on ferric sulphate concentration, reaction temperature and time during leaching of galena in the sulphate solution.

3. Materials and methods

The galena samples used in this study were collected from the deposit, at Enyimgba, Abakaliki, Ebonyi State. The galena which was in association with other minerals (valuable and gangue) was obtained in lumps of about 500 mm. These lumps were crushed and the galena cubes isolated from the gangue by careful hand picking. The isolated galena crystals were further crushed and a set of screen used to size them into fines, 80 x 100, 60 x 80 mesh, 40 x 60, 20 x 40 mesh, 10 x 20 mesh and oversize. This range of particle size was used throughout the experiment. Based on the atomic absorption spectrometric analysis carried out, the samples used contain 86.55% Pb, indicating that the sample was essentially pure.

Ferric sulphate solution and the galena were kept in separate cylindrical flask and placed in the water bath to attain the desired temperature. Once the temperature was reached the leaching solution was transferred into the vessel containing the galena sample and stirring commenced. In all the experiments, 0.5 gram

each of galena was leached in 500 mls solution which is equivalent to 1 gram of galena in 1 litre of solution. A 5 mls sample each of solution was withdrawn at predetermined time intervals and filtered. Furthermore, 2 mls of this stock solution was further diluted to 100 mls and sampled for analysis.

Table 1: Variation of dissolved lead with ferric sulphate concentration, reaction temperature and time [8]

(γ)	(υ)	(ϕ)	ζ
0.25	4	50	0.92
0.25	6	50	1.10
0.25	10	50	1.35
0.25	14	50	1.62
0.25	16	50	1.71
0.25	20	50	1.91
0.25	24	50	2.04

3.1 Model Formulation

Results generated from the experiment were used for the model formulation. Computational analysis of the results shown in Table 1, gave rise to Table 2 which indicate that;

$$\zeta - N\gamma + \Psi\phi \approx K\upsilon + 0.65 \quad (2)$$

Introducing the values of N, Ψ , K and S into equation (2) reduces it to;

$$\zeta - 0.0011\gamma + 0.0001\phi = 0.062\upsilon + 0.65 \quad (3)$$

$$\zeta - 0.0011\gamma + 0.0001\phi = 0.062\upsilon + 0.65 \quad (4)$$

Where

(ζ) = Conc. of dissolved lead (ppm)

(υ) = Reaction time (hr)

(ϕ) = Reaction temperature ($^{\circ}$ C)

(γ) = Ferric chloride concentration (M)

N = 0.0011, Ψ = 0.0001 K = 0.062, and S = 0.65. These are empirical constant (determined using C-NIKBRAN [9])

4. Boundary and Initial Condition

Galena was placed in cylindrical flask 30cm high containing leaching solution of ferric sulphate. 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, weight of lead used was 0.5g. The reaction temperature used was 50°C. The reaction time range used 4 - 24 hrs. Ferric sulphate concentration used was 0.25M.

The leaching process boundary conditions include: atmospheric level 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.

5. Model Validation

Table 2: Variation of $\zeta - 0.0011\gamma + 0.0001\phi$ with $0.062\nu + 0.65$

$\zeta - 0.0011\gamma + 0.0001\phi$	$0.062\nu + 0.65$
0.9247	0.898
1.1047	1.022
1.3547	1.270
1.6247	1.518
1.7147	1.642
1.9147	1.890
2.0447	2.138

Equation (4) is the derived model. The validity of the model is strongly rooted on equation (3) where both sides of the equation are correspondingly approximately equal. Table 2 also agrees with equation (3) following the values of $\zeta - 0.0011\gamma + 0.0001\phi$ and $0.062\nu + 0.65$ evaluated from the experimental results in Table 1

Furthermore, the derived model was validated by comparing the concentration of dissolved lead

predicted by the model and that obtained from the experiment. This was done using the 4th Degree Model Validity Test Techniques (4th DMVTT); statistical, graphical, computational and deviational analysis.

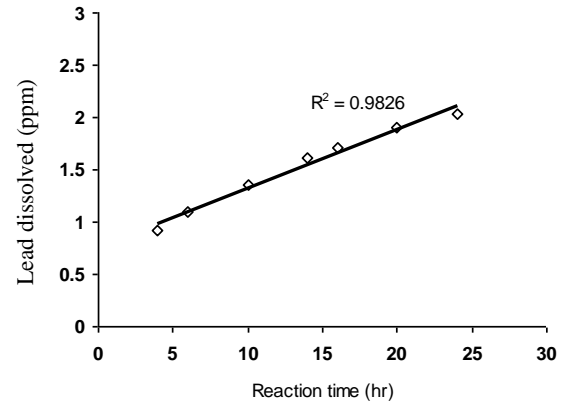


Fig.1: Coefficient of determination between dissolved lead concentration and reaction time as obtained from experiment

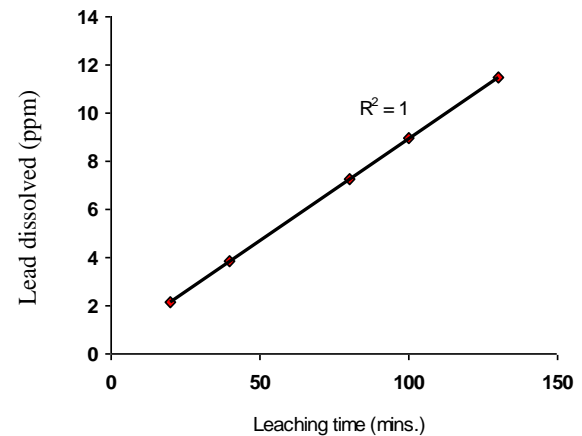


Fig.2: Coefficient of determination between dissolved lead concentration and reaction time as obtained from derived model

Statistical Analysis

Standard Error (STEYX)

The standard errors incurred in predicting the concentration of dissolved lead for each value of the reaction time considered as obtained from experiment and derived model were 0.06 and 6.66×10^{-9} % respectively. The standard error was evaluated using Microsoft Excel version 2003.

Correlation (CORREL)

The correlation coefficients between dissolved lead and reaction time were evaluated from the results of the derived model and experiment, considering the coefficient of determination R^2 from Figs. 2 and 3. The evaluation was done using Microsoft Excel version 2003.

$$R = \sqrt{R^2} \quad (5)$$

The evaluated correlations are shown in Table 3. These evaluated results indicate that the derived model predictions are significantly reliable and hence valid considering its proximate agreement with results from actual experiment.

Table 3: Comparison of the correlations evaluated from derived model predicted and ExD results based on reaction time

Analysis	Based on reaction time	
	ExD	D-Model
CORREL	0.9913	1.0000

Graphical Analysis

Comparative graphical analysis of Fig. 3 show very close alignment of the curves from the experimental (ExD) and model-predicted (MoD) dissolved lead.

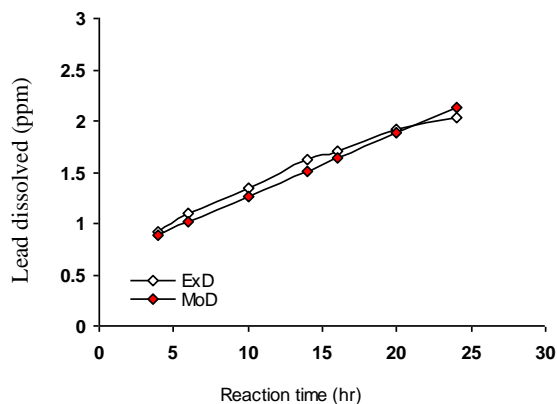


Fig.3: Comparison of dissolved lead concentrations (relative to reaction time) as obtained from experiment and derived model

Furthermore, the degree of alignment of these curves is indicative of the proximate agreement between both experimental and model-predicted dissolved lead concentration.

Computational Analysis

Computational analysis of the experimental and model-predicted dissolved lead was carried out to ascertain the degree of validity of the derived model. This was done by comparing dissolved lead per unit reaction time using experimental and model-predicted results.

Rate of Lead Dissolution

The rate of dissolution of lead ζ_R was calculated from the expression;

$$\zeta_R = \frac{\Delta\zeta}{\Delta\nu} \quad (6)$$

Equation (6) is detailed as

$$\zeta_R = \frac{\zeta_2 - \zeta_1}{\nu_2 - \nu_1} \quad (7)$$

Where

$\Delta\zeta$ = Change in concentration of dissolved lead at two different reaction times ν_2, ν_1 .

Considering the points (4, 0.92) & (24, 2.04), and (4, 0.8933) & (24, 2.1333) as shown in Figs 1 and 2, and designating them as (ζ_1, ν_1) & (ζ_2, ν_2) for experimental and derived model predicted results respectively, and then substituting them into equation (7), gives the slopes: 0.056 and 0.062 ppm/ hr as rate of dissolution of lead respectively.

Deviational Analysis

The deviation D_v , of model-predicted dissolved lead from the corresponding experimental result was given by

$$D_v = \left[\frac{\zeta_{MoD} - \zeta_{ExD}}{\zeta_{ExD}} \right] \times 100 \quad (8)$$

Where

ζ_{ExD} and ζ_{MoD} are extracted lead concentration from experiment and derived model respectively.

Critical analysis of the concentration of dissolved lead obtained from experiment and derived model shows low deviations on the part of the model-predicted values relative to values obtained from the experiment. This is attributed

to the fact that the surface properties of galena and the physico-chemical interactions between the galena and the leaching solution which played vital roles during the leaching process were not considered during the model formulation. This necessitated the introduction of correction factor, to bring the model-predicted extracted lead concentration to those of the corresponding experimental values.

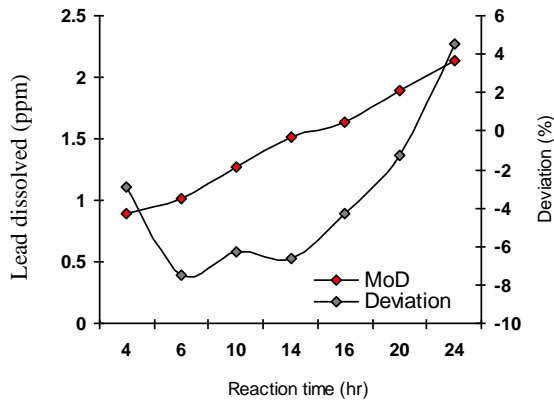


Fig.4: Variation of deviation with dissolved lead (relative to the reaction time)

Deviational analysis from Fig. 4 indicates that the maximum deviation of model-predicted dissolved lead from the experimental results is less than 8%. This translates into over 92% operational confidence and response level for the derived model as well as over 0.92 response coefficient of dissolved lead to the combined operational contributions of the ferric sulphate concentration, reaction temperature and time.

Consideration of equation (8) and critical analysis of Fig. 4 shows that the least and highest magnitudes of deviation of the model-predicted dissolved lead (from the corresponding experimental values) are - 1.29 and - 7.52. Figs. 1- 4 indicate that these deviations correspond to 1.8853 and 1.0373 ppm of dissolved lead as well as reaction times of 20 and 6 hrs respectively.

Correction factor, Cf to the model-predicted results is given by

$$Cf = - \left[\frac{\zeta_{MoD} - \zeta_{ExD}}{\zeta_{ExD}} \right] \times 100 \quad (9)$$

Critical analysis of Figs. 1-5 indicates that the evaluated correction factors are negative of the deviation as shown in equations (8) and (9).

The correction factor took care of the negligence of operational contributions of the surface properties of the galena and the physico-chemical interactions between the galena and the leaching solution which actually played vital role during the leaching process. The model predicted results deviated from those of the experiment because these contributions were not considered during the model formulation. Introduction of the corresponding values of Cf from equation (9) into the model gives exactly the corresponding experimental values of dissolved lead.

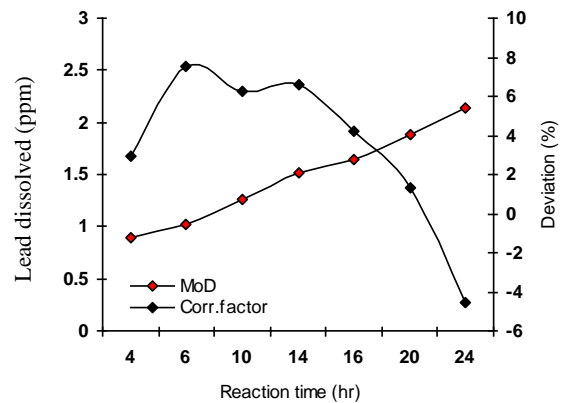


Fig.5: Variation of correction factor with dissolved lead concentration (relative to the reaction time)

Fig. 5 shows that the least and highest correction factor (to the model-predicted dissolved lead) are + 1.29 and + 7.52 %. Since correction factor is the negative of deviation as shown in equations (8) and (9), Figs. 1-5 indicate that these highlighted correction factors correspond to 1.8853 and 1.0373 ppm of dissolved lead as well as reaction times of 20 and 6 hrs respectively.

It is very pertinent to state that the deviation of model predicted results from that of the experiment is just the magnitude of the value. The associated sign preceding the value signifies that the deviation is a deficit (negative sign) or surplus (positive sign).

6. Conclusion

Assessment evaluation of dissolved lead was carried out based on ferric sulphate concentration, reaction temperature and time during leaching of galena in ferric sulphate solution. The validity of the derived model used for the assessment was rooted on the expression $\zeta - 0.0011\gamma + 0.000k\rho = 0.062b + 0.65$ where both sides of the expression are correspondingly approximately equal. Standard errors of 0.06 and $6.66 \times 10^{-9}\%$ were evaluated following statistical analysis of the dissolved lead concentration for each value of the reaction time as obtained from experiment and derived model-predicted results respectively. Evaluation of generated results indicates that dissolved lead concentration per unit reaction time as obtained from experiment and derived model-predicted results were 0.056 and 0.062 ppm/hr respectively. Deviation analysis of model-predicted dissolved lead concentration (from experimental result) shows a maximum deviation of was less 8%. This implies a derived model confidence level above 92% and well over 0.92 response coefficients for dissolved lead dependence on the ferric sulphate concentration, reaction temperature and time.

References

- [1]. Prosper, I. (2005) Acid leaching of lead sulphide, UDFP Report 1204, pp 3-16.
- [2]. Rawlings, D.E. (2005) Characteristics and Adaptability of Iron and Sulphur Oxidizing Microorganisms Used for the Recovery of Metals from Minerals and Their Concentrates, Bio Med Central, 4:13 doi 10:1186/1475-2859-4-13
- [3]. Dutrizac, J.E. (1986) The Dissolution of Galena in Ferric Chloride Media, Metallurgical Transactions B, 17B: 77.
- [4]. Seon-Hyo, K. K., Henein, H., Warren, G.W (1986) An Investigation of the Thermodynamics and Kinetics of the Ferric Chloride Brine Leaching of Galena Concentrate. Metallurgical Transaction B, 17B:26.
- [5]. Dix, R.B., Hendrix, J. L. (1986) Kinetics of Cl_2 - O_2 Leaching of Lead-Zinc Flotation Concentrates. University of Nevada Reno, 89557
- [6]. Okoro, C. C. (2004). Hydrometallurgical Extraction of Lead from Ishiagu Galena, B. Eng. Project Materials and Metallurgical Engineering Dept., Federal University of Technology Owerri.
- [7]. Nwoye, C. I. and Mbuka, I. E. (2010). Model for Predictive Analysis of the Concentration of Dissolved Lead in relation to the Initial and Final Solution pH during Leaching of Galena in Butanoic Acid. Journal of Academia Arena, 2(6), 54-61.
- [8]. C. N. Mbah. Leaching Characteristics of Enyimgba Galena in Aqueous Ferric Salt Lixivants. Ph.D Thesis, Enugu State University of Science & Technology, Enugu, Enugu State. 2012.
- [9]. Nwoye, C. I. Data Analytical Memory; C-NIKBRAN . 2008.