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# Evaluation of Lead Yield Based on Ferric Nitrate Concentration and Reaction Time during Leaching of Galena in the Nitrate Solution

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**Abstract:** ***This paper presents an evaluation of lead yield during processing of galena in ferric nitrate solution based on the input parameters such as ferric nitrate concentration and reaction time. The analysis was carried out using an empirical model derived from experimental results. The validity of the model was rooted on two correspondingly approximately equal quantities. Statistical analysis of the lead yield for each value of the input ferric nitrate concentration as obtained from experiment and derived model-predicted results show standard errors 0.2051 and $1.2167 \times 10^{-8}$ % respectively. Result evaluations indicate that lead yield per unit ferric nitrate concentration as obtained from experiment and derived model-predicted results were 11.25 and 11.0 ppm/M respectively. The maximum deviation of the model-predicted lead yield (from experimental results) was of less than 9%. This implies a derived model confidence level above 91% as well as over 0.91 response coefficients for lead yield dependence on the ferric nitrate concentration and reaction time.***

**Keywords**: Evaluation, Lead yield, Galena, Ferric nitrate concentration, Reaction time.

## 1. Introduction

Galena deposit at Enyimgba in Ebonyi state of Nigeria has shown a lead ore with both sphalerite and galena occurring in massive aggregates [1]. Generation of large amount of sulphur dioxide and sulphur trioxide gaseous pollutants has become a source of concern associating the conventional processing of this ore type. This is basically due to high demand for the process which from all indication is not environment friendly as a result of pollution [1]-[18].

It has been reported [19] that the average grain size of Ishiagu galena concentrate is approximately 100μm, following a sedimentation analysis of the lead ore. Results of the investigation on the mechanism of bioleaching of Ishiagu galena concentrates reveal indirect mechanism. This was sequel to the dominance of $Fe^{3+}$ ions over $H^+$ during the leaching process.

Research [20] has shown the feasibility and viability of extracting lead using microorganisms. Findings from the research show that higher silica contents of the ore reduce acidity, iron mobility and oxidation during bioleaching of Ishiagu lead-zinc ore, using mixed cultures of Acidithiobacillus Ferrooxidans, Acidithiobacillus Thiooxidans and Leptospirillum Ferrooxidans,

Results of studies [21] carried out on the roles of Acidithiobacillus Ferrooxidans (ATF) and Acidithiobacillus Thiooxidans (ATT) during a leaching process indicate that ATF are able to oxidize ferrous ions and the reduced sulphur compounds while (ATT) are able to oxide only reduced sulphur compound. Furthermore, ATF has been discovered [22] to posses the ability to reduce arsenic from complex galena. The research also shows that that arsenopyrite was totally oxidized during the leaching process.

It was therefore concluded that on using ATF for the process, the sum of arsenic remaining in solution and removed by sampling represents from 22 to 33% in weight (yield) of the original content in the mineral. The remnant of the bio-oxidized arsenic from amorphous compounds that precipitate galena (PbS) was totally oxidized too, anglesite ($PbSO_4$) formed is virtually insoluble and remains in the solids. The research [22] further revealed that the maximum rate of arsenic dissolution in the concentrate could be found using the following levels of factors; small surface area of particle exposure; low pulp density, injecting air and adding the leaching medium to the system. During the leaching process, ferric chloride and carbon dioxide were observed to decrease the arsenic dissolution rate. For a continuous culture, bioleaching kinetic data of arsenic solubilization [22] were used to estimate the dilution rate which was relatively small.

Galena concentrate has also been successfully leached in ferric chloride-brine solution [23]. The study shows that usage of ferric chloride-brine as leachants has a lot of advantages which includes having a greater potential for the treatment of complex sulfides, easy regeneration by chlorination of ferrous chloride leaching by-products, and exhibition of substantially faster dissolution rates for most sulphides.

The aim of the present work is to evaluate the lead yield based on ferric nitrate concentration and reaction time during processing of galena in the nitrate solution.

## 2. Materials and Methods

The galena samples used in this study were collected from the deposit, at Enyimgba, Abakaliki, Ebonyi State, Nigeria. 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 10 x 20 mesh. Based on the atomic absorption spectrometric analysis carried out, the samples used contain 86.55% Pb, indicating that the sample was essentially pure.

Ferric nitrate 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. Also 0.05M $Fe(NO_3)_3$ was used at the temperature (50$^o$C) in the presence of 1.0M $NaNO_3$. The experiment was repeated with $Fe(NO_3)_3$ concentrations: 0.075, 0.1, 0.15 and 0.25 M. 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 lead yield with ferric nitrate concentration at constant reaction time [24]

| $(\chi)$ | $(\varphi)$ | $(\xi)$ |
|---|---|---|
| 20 | 0.05 | 2.08 |
| 20 | 0.075 | 2.25 |
| 20 | 0.10 | 2.94 |
| 20 | 0.15 | 3.46 |
| 20 | 0.25 | 4.33 |

### 2.1 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;

$$\xi - N\chi \approx K\varphi + S \qquad (1)$$

Introducing the values of N, K and S into equation (1) reduces it to;

$$\xi - 0.0011\chi = 11\ \varphi + 1.60 \qquad (2)$$

$$\xi = 11.0\varphi + 0.0011\ \chi + 1.60 \qquad (3)$$

Where

$(\xi)$ = Conc. of lead yield (ppm)

$(\varphi)$ = Ferric nitrate conc. (M)

$(\chi)$ = Reaction time (mins.)

N = 0.0011, K = 11.0, and S = 1.60. These are empirical constant (determined using C-NIKBRAN [25]

## 3. Boundary and Initial Condition

Galena was placed in cylindrical flask 30cm high containing leaching solution of ferric nitrate. 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 and time used were 50$^0$C and 20 mins. respectively, while the ferric nitrate concentration range used was 0.05 – 0.25 M.

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.

## 4. Model Validation

**Table 2:** Variation of $\xi - 0.0011\chi$ with $11.0\varphi + 1.60$

| $\xi - 0.0011\chi$ | $11.0\ \varphi + 1.60$ |
|---|---|
| 2.058 | 2.150 |
| 2.228 | 2.425 |
| 2.918 | 2.700 |
| 3.438 | 3.250 |
| 4.308 | 4.350 |

Equation (3) is the derived model. The validity of the model is strongly rooted on equation (2) where both sides of the equation are correspondingly approximately equal. Table 2 also agrees with equation (2) following the values of $\xi - 0.0011\chi$ and $11.0\varphi + 1.60$ evaluated from the experimental results in Table 1. Furthermore, the derived model was validated by comparing the lead yield predicted by the model and that obtained from the experiment. This was done using the 4$^{th}$ Degree Model Validity Test Techniques (4$^{th}$ DMVTT); statistical graphical, computational and deviational analysis.

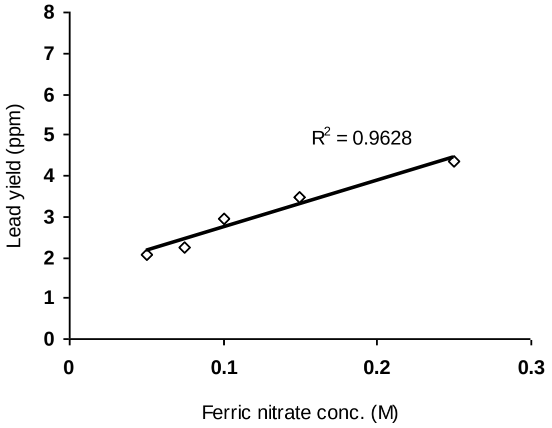

**Figure 1:** Coefficient of determination between lead yield and ferric nitrate concentration as obtained from experiment

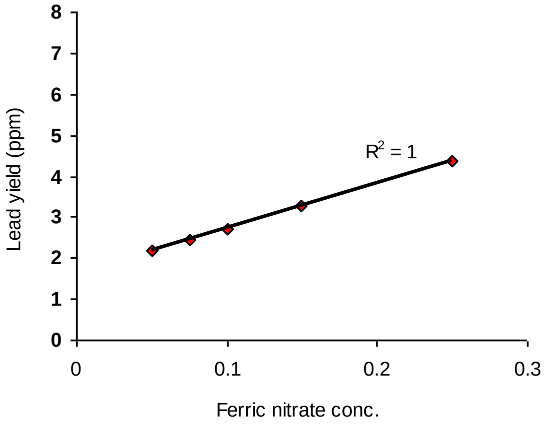

**Figure 2:** Coefficient of determination between lead yield and ferric nitrate concentration as obtained from derived model

### Statistical Analysis

Standard Error (STEYX)

The standard errors incurred in predicting lead yield for each value of the leaching time considered as obtained from experiment and derived model were 0.2051 and 1.2167 x 10$^{-8}$

% respectively. The standard error was evaluated using Microsoft Excel version 2003.

Correlation (CORREL)
The correlation coefficient between lead yield and ferric nitrate concentration were evaluated from the results of the derived model and experiment, considering the coefficient of determination R2 from Figures 2 and 3. The evaluation was done using Microsoft Excel version 2003.

$$R = \sqrt{R^2} \quad (4)$$

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 ferric nitrate concentration

| Analysis | Based on ferric nitrate conc. | |
|---|---|---|
| | ExD | D-Model |
| CORREL | 0.9812 | 1.0000 |

### Graphical Analysis

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

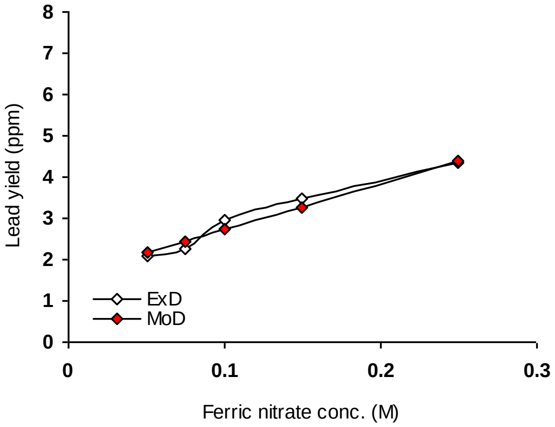

**Figure 3:** Comparison of lead yields (relative to ferric nitrate concentration) as obtained from experiment and derived model

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

### Computational Analysis

Computational analysis of the experimental and model-predicted lead yield was carried out to ascertain the degree of validity of the derived model. This was done by comparing lead yield per unit ferric nitrate concentration using experimental and model-predicted results.

### Lead yield per unit ferric nitrate concentrate

The lead yield per unit ferric nitrate concentration $\xi_C$ was calculated from the expression;

$$\xi_C = \frac{\Delta\xi}{\Delta\varphi} \quad (5)$$

Equation (5) is detailed as

$$\xi_C = \frac{\xi_2 - \xi_1}{\varphi_2 - \varphi_1} \quad (6)$$

Where
$\Delta\xi$ = Change in lead yield at two different ferric nitrate concentrations $\varphi_2$, $\varphi_1$.

Considering the points (0.05, 2.08) & (0.25, 4.33), and (0.05, 2.172) & (0.25, 4.372) as shown in Figures 1 and 2, and designating them as ($\xi_1$, $\varphi_1$) & ($\xi_2$, $\varphi_2$) for experimental and derived model predicted results respectively, and then substituting them into equation (6), gives the slopes: 11.25 and 11.0 ppm/M as lead yield per unit ferric nitrate concentration respectively.

### Deviational Analysis

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

$$Dv = \left[\frac{\xi_{MoD} - \xi_{ExD}}{\xi_{ExD}}\right] \times 100 \quad (7)$$

Where
$\xi_{ExD}$ and $\xi_{MoD}$ are lead yields from experiment and derived model respectively.

Critical analysis of the lead yield 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.

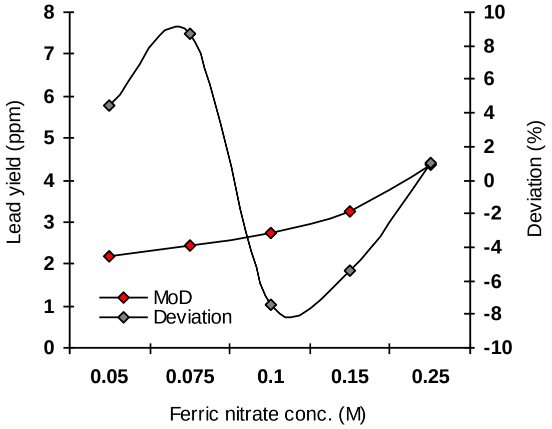

**Figure 4:** Variation of deviation with lead yield (relative to the ferric nitrate concentration)

Deviational analysis from Figure 4 indicates that the maximum deviation of model-predicted lead yield from the experimental results is less than 9%. This translates into over 91% operational confidence and response level for the derived model as well as over 0.91 response coefficient of lead yield to the combined operational contributions of the ferric nitrate concentration and reaction time.

Consideration of equation (7) and critical analysis of Figure 4 show that the least and highest magnitudes of deviation of the model-predicted lead yield (from the corresponding experimental values) are + 0.97 and + 8.76. Figures 1-4 indicate that these deviations correspond to lead yields: 4.372 and 2.447 ppm as well as ferric nitrate concentrations: 0.25 and 0.075 M respectively.

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

$$Cf = -\left[\frac{\xi_{MoD} - \xi_{ExD}}{\xi_{ExD}}\right] \times 100 \qquad (8)$$

Critical analysis of Figures 1-5 indicates that the evaluated correction factors are negative of the deviation as shown in equations (7) and (8).

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 (8) into the model gives exactly the corresponding experimental values of lead yield.

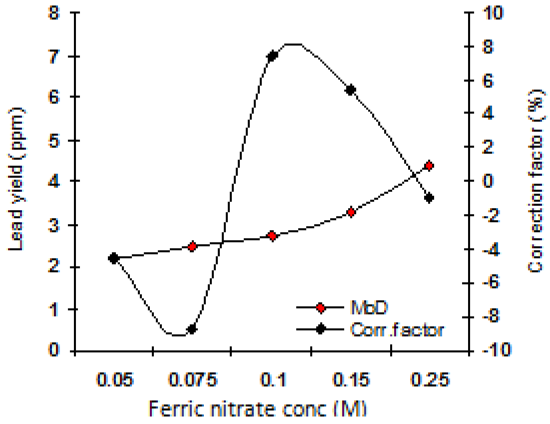

**Figure 5:** Variation of correction factor with lead yield (relative to the ferric nitrate concentration)

Figure 5 shows that the least and highest correction factor (to the model-predicted lead yield) are -0.94 and – 8.76%. Since correction factor is the negative of deviation as shown in equations (7) and (8), Figures 1-5 indicate that these highlighted correction factors correspond to lead yields: correspond to lead yields: 4.372 and 2.447 ppm as well as ferric nitrate concentrations: 0.25 and 0.075 M 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).

## 5. Conclusion

Evaluation of lead yield during processing of galena in ferric nitrate solution was carried out based on input parameters such as ferric nitrate concentration and reaction time. The validity of an empirical model derived, validated and used for the evaluation was rooted on the expression $\xi = 11.0\varphi + 0.0011\chi + 1.60$ where both sides of the expression are correspondingly approximately equal. Statistical analysis of the lead yield for each value of the input ferric nitrate concentration as obtained from experiment and derived model-predicted results show standard errors 0.2051 and $1.2167 \times 10^{-8}$ % respectively. Result evaluations indicate that lead yield per unit ferric nitrate concentration as obtained from experiment and derived model-predicted results were 11.25 and 11.0 ppm/ M respectively. The maximum deviation of the model-predicted lead yield (from experimental results) was of less than 9%. This implies a derived model confidence level above 91% as well as over 0.91 response coefficients for lead yield dependence on the ferric nitrate concentration and reaction time.

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