Assessment Evaluation of Removed Phosphorus Concentration Based on Its As-Beneficiated Content and Treatment Temperature

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ABSTRACT
An assessment evaluation of removed phosphorus concentration was carried out based on its as beneficiated concentration and treatment temperature. Powdered potassium chlorate (KClO₃) was mixed with iron ore concentrate and the mixture heated for 600 secs. in a laboratory furnace at within temperature range: 400-600°C. A model was derived from the generated experimental results, validated and used as a tool for the analysis. The validity of the two-factorial model expressed as;

ζ = 0.0969 ln θ - 0.531 + 0.01ɤ

was found to be rooted on the expression ζ - 0.01ɤ = 0.0969 ln θ - 0.531 where both sides of the expression are correspondingly approximately equal. Statistical analysis of the experimental and derived model-predicted removed phosphorus concentrations for each value of the treatment temperature considered shows standard errors of 0.0093 and 0.0011% respectively. Furthermore, removed phosphorus concentration per unit rise in the treatment temperature as obtained from experiment and derived model-predicted results were 2.31 x 10⁻⁴ and 2.05 x 10⁻⁴ % / °C respectively. Deviational analysis indicates that the derived model gives best-fit process analysis at deviations 4.63, 4.68 and 5.8% from experimental results and invariably, operational confidence level range: 94.2 - 95.37%. The deviations corresponded to treatment temperature range: 450-550°C.

Keywords: Assessment, Removed phosphorus concentration, KClO₃, Agbaja Iron Ore.

INTRODUCTION
Embrittlement resulting from presence of phosphorus in produced steel materials, above the admissible quantity has caused series of structural failures in the oil industry. This awakens the need for intensive researches geared towards reducing the phosphorus content of pig iron below the admissible level.

Some researches [1-5] have evaluated ways of achieving successful dephosphorization of iron oxide ore and also predicting removed phosphorus concentrations using empirical models. A model was derived for predictive analysis of the concentration of phosphorus removed during leaching of iron oxide ore in sulphuric acid solution [6]. The work indicated that phosphorus removal from the iron oxide ore as obtained from experiment and derived model is dependent on the initial and final pH of the leaching solution. This is because the final pH of the leaching solution is greatly determined by the initial pH which is function of hydrogen ion concentration.

A similar work [7] shows that phosphorus removal is dependent on leaching temperature. The model derived using experimental results indicated that at a leaching temperature range 45-70°C, the maximum deviation of the model-predicted removed phosphorus concentration (from the corresponding experimental values) was less than 29%.

Empirical analysis of phosphorus removal was carried out [8] based on its as-beneficiated concentration and mass-input of KClO₃. A model was derived and used as a tool for the analysis. The model is expressed as: Pr = -
The validity of the two-factorial model was found to be rooted on the expression \(100PR + 1.81 = - 0.05 \alpha^2 + \alpha + 0.24 \gamma^2\) where both sides of the expression are correspondingly approximately equal. Statistical analysis of the derived model-predicted, regression model-predicted and experimental removed phosphorus concentrations for each value of the mass-inputs of KClO\(_3\) considered shows standard errors of 0.0015, 3.45 \times 10^{-5} and 0.0025\% respectively. Furthermore, removed phosphorus concentration per unit mass-input of KClO\(_3\) as obtained from derived model-predicted, regression model-predicted and experimental results were 3.0 \times 10^{-3}, 2.975 \times 10^{-3} and 2.475 \times 10^{-3} \% g\(^{-1}\) respectively. Deviational analysis indicates that the derived model gives best-fit process analysis with a deviation range of just 1.35 – 12.29\%, from experimental results and invariably an operational confidence level range 87.71-98.65\%. The deviation range corresponded to the removed phosphorus concentration range: 0.0213-0.0333 \% and KClO\(_3\) mass-input range: 11-15g. This implies that the derived model can exclusively be significantly useful and viably operational within these process conditions.

The aim of this work is to assess the removed phosphorus concentration based on its as-beneficiated concentration and treatment temperature. The essence of this work is to ascertain the level of dephosphorization achievable at different treatment temperatures where all other input process parameters are kept constant.

**MATERIALS AND METHODS**

Agbaja (Nigeria) iron ore concentrate used for this work was obtained from Nigeria Metallurgical Development Centre (NMDC) Jos. This concentrate was dried in air (under atmospheric condition) and used in the as-received condition with particle size; 150\(\mu\)m. Weighed quantities of the dried iron ore concentrate and powdered KClO\(_3\) (obtained from Fisher Scientific Company Fair Lawn, New Jerry, USA) were mixed on five different iron crucibles. The mixtures were poured into the crucibles and then heated to a temperature of 400\(^{\circ}\)C in a Gallenkamp Hot pot electric furnace at NMDC Laboratory for 600 secs. and thereafter were emptied on white steel pans for observation. The experiment was repeated using varied treatment temperatures i.e 450, 500, 550, 600\(^{\circ}\)C and constant mass-inputs of iron ore and KClO\(_3\). Weighed quantities of the sample mixtures for each experiment set were taken (after heating) for chemical analysis (to determine percentage phosphorus removal) using wet analysis method. The average of the removed phosphorus concentration determined in each experiment set was taken as the precise result.

**Model Formulation**

Experimental data [9] obtained from the highlighted research work were used for the model derivation. Computational analysis of these data shown in Table 1, gave rise to Table 3 which indicate that;

\[\zeta - K\gamma \approx S \ln \theta - N\] (2)

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

\[\zeta = 0.0969 \ln \theta - 0.531 + 0.01\gamma\] (4)

Where \(\zeta = \text{Conc. of removed phosphorus (\%)}
\]

\(\gamma = \text{As-beneficiated phosphorus content of the ore (\%)}
\]

\(\theta = \text{Treatment temperature (\(^{\circ}\)C)\)}

\(K = 0.01, S = 0.0969\) and \(N = 0.531\); Equalizing constant (determined using C-NIKBRAN [10]).
Table 1: variation of removed phosphorus concentration with treatment temperature [9]

<table>
<thead>
<tr>
<th>(γ)</th>
<th>(θ)</th>
<th>(ζ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>400</td>
<td>0.0507</td>
</tr>
<tr>
<td>0.9</td>
<td>450</td>
<td>0.0734</td>
</tr>
<tr>
<td>0.9</td>
<td>500</td>
<td>0.0758</td>
</tr>
<tr>
<td>0.9</td>
<td>550</td>
<td>0.0854</td>
</tr>
<tr>
<td>0.9</td>
<td>600</td>
<td>0.0769</td>
</tr>
</tbody>
</table>

Boundary and Initial Condition
Consider iron ore (in a furnace) mixed with potassium chlorate (oxidant). The furnace atmosphere is not contaminated i.e. (free of unwanted gases and dusts). Initially, atmospheric levels of oxygen are assumed just before the decomposition of KClO₃ (due to air in the furnace). Mass of iron oxide ore: 50g, treatment time: 600 secs., treatment temperature range: 400-600°C, ore grain size: 150µm and mass of KClO₃ used: 15g.

The boundary conditions are: furnace oxygen atmosphere due to decomposition of KClO₃ (since the furnace was air-tight closed) at the top and bottom of the ore particles interacting with the gas phase. At the bottom of the particles, a zero gradient for the gas scalar are assumed and also for the gas phase at the top of the particles. The reduced iron is stationary. The sides of the particles are taken to be symmetries.

RESULTS AND DISCUSSIONS
The result of the chemical analysis carried out on the beneficiated iron ore concentrate is presented in Table 1. The table shows that the percentage of phosphorus present in the as-beneficiated ore is 0.9%.

Table 2: Result of chemical analysis of iron ore used [9]

<table>
<thead>
<tr>
<th>Element/Compound</th>
<th>Fe</th>
<th>P</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit (%)</td>
<td>78.6</td>
<td>0.90</td>
<td>5.30</td>
<td>11.0</td>
</tr>
</tbody>
</table>

Model Validation
The validity of the model is strongly rooted in equation (3) (core model equation) where both sides of the equation are correspondingly approximately equal. Table 3 also agrees with equation (3) following the values of ζ \(\cdot\) 0.01γ and 0.0969 ln θ \(-\) 0.531 evaluated from the experimental results in Table 1.

Table 3: Variation of ζ \(\cdot\) 0.01γ with 0.0969 ln θ \(-\) 0.531

<table>
<thead>
<tr>
<th>ζ (\cdot) 0.01γ</th>
<th>0.0969 ln θ (-) 0.531</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0417</td>
<td>0.0496</td>
</tr>
<tr>
<td>0.0644</td>
<td>0.0610</td>
</tr>
<tr>
<td>0.0668</td>
<td>0.0712</td>
</tr>
<tr>
<td>0.0764</td>
<td>0.0804</td>
</tr>
<tr>
<td>0.0679</td>
<td>0.0889</td>
</tr>
</tbody>
</table>

Furthermore, the derived model was validated by comparing the removed phosphorus 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 the experimental and model-predicted removed phosphorus concentration was carried out to ascertain the degree of validity of the derived model. This was done by comparing phosphorus removal per unit mass-input of KClO₃ evaluated from
model-predicted results with those from actual experimental results

\[ \zeta^T = \frac{\zeta}{T} \quad (5) \]

Therefore, a plot of the concentration of phosphorus removed against treatment temperature as in Fig. 1 using experimental results in Table 2, gives a slope, \( S \) at points (400, 0.0507) and (550, 0.0854) following their substitution into the mathematical expression;

\[ \zeta^T = \frac{\Delta \zeta}{\Delta T} \quad (6) \]

Equation (6) is detailed a

\[ \zeta^T = \frac{\zeta_2 - \zeta_1}{T_2 - T_1} \quad (7) \]

Similarly, a plot of the concentration of removed phosphorus against mass-input of treatment temperature (as in Fig. 2) using derived model-predicted results gives a slope: 2.05 \( \times 10^{-4} \) %/ \(^\circ\)C on substituting the points (400, 0.0586) and (550, 0.0984) for \((T_1, \zeta_1)\) and \((T_2, \zeta_2)\) respectively into equation (7). This is the model-predicted removed phosphorus concentration per unit rise in treatment temperature.

A comparison of this set of values for removed phosphorus concentration (per unit rise in treatment temperature) also shows proximate agreement and a high degree of validity of the derived model.
Statistical Analysis
The standard errors (STEYX) in predicting the removed phosphorus concentration (using results from experiment [9] and derived model) for each value of the treatment temperature were 0.0093 and 0.0011 % respectively. The standard error was evaluated using Microsoft Excel version 2003.

Also the correlations between removed phosphorus concentration and treatment temperature as obtained from experiment and derived model was calculated considering the coefficient of determination $R^2$ from Figs. 1-3. The calculation was done using the equation

$$ R = \sqrt{R^2} $$  \hspace{1cm} (8)

The calculated correlations were 0.9696 and 1.0000 respectively. These evaluated results indicate that the derived model predictions are significantly reliable and hence valid considering its proximate agreement with results from actual experiment.

Graphical Analysis
Comparative graphical analysis of Fig. 3 shows very close alignment of the curves from model-predicted removed phosphorus 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 phosphorus removed concentration.

Fig. 2: Coefficient of determination between concentration of removed phosphorus and treatment temperature as obtained from derived model

Fig. 3: Comparison of the concentrations of removed phosphorus (relative to treatment temperature) as obtained from experiment [9] and derived model
Deviational Analysis

Analysis of removed phosphorus concentrations from the experiment and derived model revealed 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 the iron ore and the physiochemical interactions between the ore and the oxidant (KClO₃) which were found to have played vital roles during the process were not considered during the model formulation. This necessitated the introduction of correction factor, to bring the model-predicted removed phosphorus concentration to those of the corresponding experimental values.

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

$$Dn = \left( \frac{Pv - Ev}{Ev} \right) \times 100$$  \hspace{1cm} (9)

Where

- \(Pv\) = Removed phosphorus concentration as predicted by derived model
- \(Ev\) = Removed phosphorus concentration as obtained from experiment [9]

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

$$Cr = -Dn$$  \hspace{1cm} (10)

Therefore

$$Cr = \left( \frac{Pv - Ev}{Ev} \right) \times 100$$  \hspace{1cm} (11)

Introduction of the corresponding values of Cr from equation (11) into the derived model gives exactly the removed phosphorus concentration as obtained from experiment.

Fig. 4 shows that the maximum deviation of the model-predicted removed phosphorus concentration from the corresponding experimental values is less than 28%. The figure shows that the least and highest magnitudes of deviation of the model-predicted removed phosphorus concentration (from the corresponding experimental values) are - 4.63 and + 27.31 % which corresponds to removed phosphorus concentrations: 0.07 and 0.0979 %, as well as treatment temperature: 450 and 600°C respectively. Deviational analysis also indicates that the derived model gives best-fit process analysis at deviations 4.63, 4.68 and 5.8% from experimental results and invariably, operational confidence level range: 94.2 - 95.37%. These deviations corresponded to treatment temperature range: 450-550°C.
Comparative analysis of Figs. 4 and 5 indicates that the orientation of the curve in Fig. 5 is opposite that of the deviation of model-predicted removed phosphorus concentration (Fig. 4). This is because correction factor is the negative of the deviation as shown in equations (10) and (11).

It is believed that the correction factor takes care of the effects of surface properties of the iron ore and the physiochemical interactions between the ore and the oxidant (KClO₃) which have played vital roles during the process, but were not considered during the model formulation. Fig. 5 indicates that the least and highest magnitudes of correction factor to the model-predicted removed phosphorus concentration are +4.63 and -27.31 % which corresponds to removed phosphorus concentrations: 0.07 and 0.0979 %, as well as treatment temperature: 450 and 600°C respectively.

It is important 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).

CONCLUSIONS
An assessment evaluation of removed phosphorus concentration was carried out based on its as-beneficiated concentration and treatment temperature. A model was derived from the generated experimental results, validated and used as a tool for the analysis. The validity of the two-factorial model was found to be rooted on the expression $\zeta - 0.01\gamma = 0.0969 \ln \theta - 0.531$ where both sides of the expression are correspondingly approximately equal. Statistical analysis of the experimental and derived model-predicted removed phosphorus concentrations for each value of the treatment temperature considered shows standard errors of 0.0093 and 0.0011% respectively. Furthermore, removed phosphorus concentration per unit rise in the treatment temperature as obtained from experiment and derived model-predicted results were $2.31 \times 10^{-4}$ and $2.05 \times 10^{-4} \% / ^\circ C$ respectively. Deviational analysis indicates that the derived model gives best-fit process analysis at deviations 4.63, 4.68 and 5.8% from experimental results and invariably, operational confidence level range: 94.2 - 95.37%. The deviations corresponded to treatment temperature range: 450-550°C.
REFERENCES