OPTIMIZATION STUDY OF A NIGERIAN DOLOMITE ORE DISSOLUTION BY HYDROCHLORIC ACID

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ABSTRACT

The optimum condition for leaching dolomite ore in hydrochloric acid solutions was determined in this study. The optimized parameters referred to the temperature, the acid concentration, the time and particle size. It was found that the leaching temperature was 80°C, the acid concentration was 2 mol/L, the leaching time - 60 minutes, while the particle size - 0.01 mm. The dolomite ore leaching efficiency reached 99.3 % under these conditions. The dissolution kinetic data were analysed and found to follow diffusion control mechanism.

Keywords: dolomite ore, leaching, hydrochloric acid, diffusion control mechanism, optimization.

INTRODUCTION

Dolomite ore (CaCO₃·MgCO₃) is best considered as combining one layer of CaCO₃ from calcite and one layer of MgCO₃ from magnesite. The replacement of Mg²⁺ by Fe³⁺ has the effect of increasing the size of the unit cell. Dolomite occurs in metamorphic rocks chiefly in contact or regionally metamorphosed with magnesian or dolomitic limestones where it may recrystallize to form a dolomitic marble. At a higher extent of metamorphism the dolomite may break down in two stages [1], leading to the formation of talc, tremolite, forsterite and periclase [1]. It may be temporarily re-formed according to the reaction:

\[
\text{MgO} + \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 \quad (2)
\]

CaMg(CO₃)₂ \rightarrow CaCO₃ + MgO + CO₂ \quad (1)

In the course of siliceous dolomite-bearing limestones metamorphism, the dolomite takes part in the formation of talc, tremolite, forsterite and periclase [1]. It may be temporarily re-formed according to the reaction:

\[
2 \text{talc} + 3 \text{calcite} \rightarrow 1 \text{tremolite} + 1 \text{dolomite} + \text{CO}_2 + \text{H}_2\text{O} \quad (3)
\]

However, dolomite is different from limestone and may contain minimum 45 % of MgCO₃. Dolomite has either coarse, granular or fine-grained compact mass. The crystal structure of dolomite is hexagonal - rhombo-
Dolomite is naturally white but due to impurities it can be creamy gray, pink, green or black [2]. Dolomite refractories are currently in use in some countries like China, England, France, India, etc., and thus have wide applications in steel industry [3].

Dolomite is also used as a layer within the media bed of a SSF (Slow Sand Filter) to raise the effluent pH and alkalinity to target levels desired by the Oregon Health Division. The use of dolomite instead of calcite limestone is considered because of the slower rate of dissolution. Calcite provides greater changes of effluent water chemistry for the same media, but the required media replacement intervals are correspondingly shorter [4]. Dolomite dissolution optimization is possible through varying acid concentration, particle distribution, temperature, pulverization and leaching duration, among others [5].

Dolomite leaching has rarely been studied in the past [2 - 7], but two major prominent industrial processes for treating dolomite for metal production are: (i) thermal reduction of magnesium oxide, mainly from dolomite with ferrosilicon, known as silicothermic process; and (ii) recovery of magnesium chloride from raw material prior to its conversion to the metal through molten salt electrolysis [6]. The aforementioned methods require high energy usage. This material treatment can become profitable by conventional leaching operation which does not require much energy consumption. Apparently, during leaching, the ions from the leachant (acid) migrate by diffusion from the bulk solution through the film to the reaction zone where they react with the ore. The product diffuses in opposite direction from the reaction zone, through the film, to the bulk solution according to the Fick’s Law [8]. The leachant concentration, the reaction temperature and the dolomite particle size are optimized in this study aiming to meet some array of applications as a basic refractory material in machine building and steel industries. Detail characterization before and after leaching for better understanding of the dissolution mechanism was also discussed.

**EXPERIMENTAL**

**Materials**

Dolomite ore sourced from Oreke village, Ifelodun L.G.A. of Kwara State, Nigeria was used in this study. After grinding and sizing, its elemental analysis was performed using XRF. The elemental composition of the sample is given in Table 1, while its XRD pattern is presented in Fig. 1. SEM and EDS analyses of the ore were also performed prior to and after leaching the sample.

The sample comprised of Mg and Ca oxide. The impurity found is mainly silica (SiO$_2$) in correspondence with Table 1.

It can be seen from Fig. 1 that the dolomite ore sample contains calcium carbonate (1) \{07-0763\}, calcium carbonate in the form of: aragonite (2, 5) \{41-1475, 43-0697\}, calcium magnesium carbonate (dolomite) (3) \{03- 0743\}, magnesium carbide (4) \{41-1475\},

<table>
<thead>
<tr>
<th>Element</th>
<th>CaO</th>
<th>MgO</th>
<th>SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (%)</td>
<td>55.23</td>
<td>40.15</td>
<td>4.62</td>
</tr>
</tbody>
</table>

Table 1. Results of the dolomite ore sample elemental analysis.

![XRD pattern of the raw dolomite ore.](image-url)
and calcium oxide (6)\{37-1497\}. (The corresponding Joint Committee on Powder Diffraction Standard File numbers for the peak attributions to compounds 1-6 are added in brackets). It is also seen that the ore under study contain dolomite primarily, and magnesium carbide at low to trace level (< 2 %). Hence, the XRD results support the chemical analysis by XRF. Figs. 2(a) and (b) show SEM and EDS images of the raw dolomite ore. The ore has a regular pattern morpholohgy (a) with lusture surface appearance (b) prior to leaching. The quantitative examination of the ore by EDS gives carbon (18.87 %), oxygen (25.88 %), calcium (49.16 %) and magnesium (6.09 %). This shows that calcium is the predominant element present.

Methods

The leaching experiments were performed in a 250 ml open-top reactor using 1 g of the ore of 0.03 mm particle diameter. The leaching solution of 100 ml of a concentration ranging from 0.1 mol/L to 4.0 mol/L HCl was introduced. The mixture was heated at a fixed temperature of 55°C. A magnetic stirrer was used for a time interval of 5, 10, 30, 60 and 120 min. The shaking speed was maintained at 200 rpm. After the leaching process, the mixture was withdrawn from the reactor and allowed to cool. The product was filtered using Whatman filter paper Cat No: 1001110. The residue in the filter paper was air- and later oven-dried at 60°C for 1 hour. It was taken out of the oven and then weighed again. The percentage of dolomite ore leached was calculated on the ground of the leach liquor analysis. The material balance for dolomite leached was checked based on the dissolved dolomite referred to the initial mass of the ore. The analysis of the leachate at optimal condition was determined by atomic absorption spectrophotometer (model 210 VGP). The optimum HCl concentration was used in the optimization of other leaching parameters including reaction temperature and particle size for better understanding of the leaching mechanism [7, 9-11]. Appropriate kinetic plots were derived. The
leached residues were examined by the scanning electron micrography (SEM) and energy dispersive spectroscopy (EDS), respectively.

RESULTS AND DISCUSSION

The leaching reaction of dolomite ore in hydrochloric acid solutions may be consistent with the following stoichiometry:

\[ \text{CaCO}_3 \cdot \text{MgCO}_3(\text{s}) + 4\text{HCl}^{(\text{aq})} \rightarrow \text{CaCl}_2^{(\text{aq})} + \text{MgCl}_2^{(\text{aq})} + 2\text{H}_2\text{O}^{(\text{l})} + 2\text{CO}_2^{(\text{g})} \]  

\[ (4) \]

The effect of HCl concentration on dolomite sample dissolution was followed in the concentration range from 0.1 mol/L to 4.0 mol/L. The results obtained are shown in Fig. 4. It is seen that the HCl concentration increase is accompanied with increase of the rate of dolomite ore dissolution. Apparently, the rate of dolomite dissolution is affected directly by hydrogen ion \([\text{H}^+]\) concentration. This is in accord with results on acid dissolution of solid mineral ores [7, 8 - 12]. It should be noted that when HCl concentration reaches 4 mol/L, the leaching rate starts to decrease. Thus, at 55 °C, the percentage of the dolomite ore reacted in presence of 2 mol/L and 4 mol/L HCl solution within 120 minutes is 75.9 % and 72.1 %, respectively. This may be due to the presence of impurities or because the viscosity of HCl is apparently large, and may hence increase the resistance of the leaching solution diffusing to the surface of ore particles [13].

The residual product obtained under the optimum conditions which were determined in the course of this study (2.0 mol/L HCl at 55 °C for 120 minutes) is analysed by SEM and EDS. The data are presented in Figs. 5 and 6, respectively.
Calcium, oxygen and carbon are found in the residual product with calcium being the predominant element.

The leaching process is carried out by 2.0 mol/L hydrochloric acid solution in the temperature range from 27 to 80°C. The stirring speed is of 200 rpm while the contact time varied. The effect of the reaction temperature is depicted in Fig. 7.

It is seen that the dissolution rate of dolomite ore increases with temperature increase. Thus the leaching efficiency grows from 58.5 % to 99.3 % with temperature increase from 27°C to 80°C. However, temperatures above 80°C are not considered because of economic factors as well as possible acid loss [10, 14]. The analysis of the residual obtained at 80 °C in 2.0 mol/L HCl is illustrated in Figs. 8, 9.

Fig. 7. Temperature effect on dolomite dissolution (2 mol/l HCl, 1 g mass of dolomite; stirring speed of 200 rpm, particle size of 0.01 mm).

Fig. 8. SEM analysis of dolomite ore leached for 120 min in 2 mol/L HCl at 80°C.

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Fig. 8 shows that the dolomite ore leached for 60 minutes in 2.0 mol/L HCl at 80 °C contains plate-like erosion structures most probably due to the high temperature value. The EDS spectra (Fig. 9) verifies this suggestion. Carbon, oxygen, magnesium and silicon are found to be present in traces, while calcium is not detected. This may be due to the increased leaching temperature which results apparently in calcium dissolution.

The dolomite ore was sieved into three different particle size fractions and experiment were carried out using 2.0 mol/L HCl solution at 80°C. The particle size effect is illustrated on Fig. 10.

As shown in Fig.10, the dolomite dissolution increases with particle size decrease. The reason for the higher dissolution for 60 min of the finer size fraction is due to the higher specific surface area of the ground sample. The higher the specific surface area of the ore, the higher extent dissolution rate is [14]. It is worth noting that ca 99.3 % of the ore dissolved. Under the conditions pointed above the leachate analysis by AAS gives 5.47 g/L Ca, 3.96 g/L Mg and 0.0012 g/L Fe.

According to the shrinking core model (SCM) the solid reactant is considered to be non-porous, initially
surrounded by a fluid film through which the mass transfer between the solid particle and the bulk of the solid occurs. As the reaction proceeds, an ash/inert layer forms around the core unreacted. It is assumed that the rate limiting step refers either to the chemical reaction (5) at the surface of the core unreacted, or to the diffusion (6) through the ash/inert solid layer [15, 16]. The validity of eqs. (5) and (6) is tested in this study.

\[1 - (1 - \alpha)^{1/3} = k_1 t \]  
\[1 - 2/3\alpha - (1 - \alpha)^{2/3} = k_2 t \]  

In each of the equations pointed above, \(\alpha\) is the fraction of the dolomite ore reacted, \(t\) is time and \(k_1\) and \(k_2\) are the reaction rate constants. It is important to note that eq.(6) gives a correlation of approximately 0.976, compared to 0.723 exhibited in case of application of eq. (5). Hence, eq. (6) is applied to the experimental results in Fig. 4 and the correlation coefficients for each curve at different HCl concentrations are shown in Fig. 11. The reaction rate constants, \(k\), are calculated from the slope of the straight lines in Fig. 11. The values obtained are used to find the reaction order in respect to the acid used (Fig. 12) and for the construction of the Arrhenius plot (Fig. 13). It is seen that the reaction is half-order with respect to \([H^+]\), in the acid concentration range 0.1 - 2.0 mol/L. The Arrhenius relation in Fig. 13 shows that the activation energy of the dissolution process is equal to 20.77 kJ/mol. The latter implies that the dolomite ore dissolution in HCl media is diffusion-controlled. It can also be attributed to the physical but not chemical absorption proceeding [7].

In this study, the contact time and the fraction dissolved are the independent and dependent variables, respectively.

Fig. 10. Particle size effect on dolomite dissolution. (temperature of 80°C, 2 mol/L HCl, 1g of dolomite ore mass, stirring speed of 200 rpm).

Fig. 11. Illustration of eq (6) applicability in case of different HCl concentrations.

Fig. 12. Plot of In\(k_1\) vs. In[HCl].

Fig. 13. Arrhenius plot for activation energy determination.
The SLRM model (eq.7) is applied and the illustration is presented in Fig. 14. It is evident that the fraction of the dolomite ore dissolved increases with the contact time, which supports the empirical accuracy of the dissolution data as summarized in Table 2.

Regression equation model:

\[ y_i = \alpha + \beta x_i + e_i \]  \hspace{1cm} (7)

where \( Y = \) fraction dissolved, \( X = \) time, \( \hat{\alpha} = 0.619 \) and \( \hat{\beta} = 0.002147 \) are regression coefficients.

**CONCLUSIONS**

The optimum conditions for leaching dolomite ore in hydrochloric acid solutions are determined in this study. With 0.01 mm particle, 2 mol/L HCl concentration, 80°C leaching temperature, and 120 min leaching time, dolomite ore dissolution reaches 99.3 % under these process conditions. It is also found that the process is diffusion controlled. The simple regression analysis support the data reported.

**Table 2. Model summary.**

<table>
<thead>
<tr>
<th>Model</th>
<th>R</th>
<th>R Square</th>
<th>Adjusted R Square</th>
<th>Std. Error of the Estimate</th>
<th>Change Statistic</th>
</tr>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>.575(^a)</td>
<td>.331</td>
<td>.307</td>
<td>.13344</td>
<td>.331 13.829 1 28 .001</td>
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Predictors: (Constant), TIME

**ANOVA\(^b\)**

<table>
<thead>
<tr>
<th>Model</th>
<th>Sum of Squares</th>
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<th>Mean Square</th>
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<th>Sig.</th>
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<tr>
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<td>.246</td>
<td>13.829</td>
<td>.001(^a)</td>
</tr>
<tr>
<td>Residual</td>
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<td>28</td>
<td>1.781E-02</td>
<td></td>
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<tr>
<td>Total</td>
<td>.745</td>
<td>29</td>
<td></td>
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<td></td>
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</tbody>
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\(a\). Predictors: TIME  
\(b\). Dependent Variable: Fraction Dissolved

**Coefficients\(^a\)**

<table>
<thead>
<tr>
<th>Model</th>
<th>Unstandardized Coefficients</th>
<th>Standardized Coefficients</th>
<th>T</th>
<th>Sig.</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>B</td>
<td>Std. Error</td>
<td>Beta</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>(constant) TIME</td>
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<td>.036</td>
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<td></td>
<td>2.147E-03</td>
<td>.001</td>
<td>.575</td>
<td>3.719</td>
</tr>
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</table>

\(a\). Dependent Variable: Fraction Dissolved
REFERENCES


