# Dissolution Kinetic Evaluation of Manganese-rich Iron ore by Sulphuric acid Solution

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## Abstract

This study investigated the optimum conditions for the leaching of manganese-rich iron ore for subsequent beneficiation studies in laboratory scale. The experiments were carried out by varying the concentration of $H_2SO_4$ solution and the leaching temperature. The properties of the iron ore was characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) as well asphoto-micrographic examination. The leaching experiments showed that the ore leaching increases with increasing acid concentration and temperature. About 78.9% of the iron ore was reacted within 120 minutes by 4M $H_2SO_4$ solution at a temperature of 80oC. The activation energy (Ea) and the order of reaction were determined to be 31.14kJ/mol and 0.979, respectively. The leaching data were fitted to the shrinking core model and the experimental results followed a diffusion controlled mechanism. The residual product at optimal leaching was appropriately characterized and was found to contain silicate compound.

***Keywords:*** *Iron ore, Characterization, Leaching, Dissolution mechanism.*

## Introduction

Iron ores often rich in iron-oxides are important minerals from which metallic iron (the abundant element on earth) is economically extracted. They usually occur as magnetite ($Fe_3O_4$, 72.4% Fe), hematite ($Fe_2O_3$, 69.9% Fe), goethite (FeO(OH), 62.9% Fe), limonite (FeO(OH).n($H_2O$)) or siderite ($FeCO_3$, 48%

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Fe) [1,2]. World iron ore resources have been estimated to exceed 800 billion tonnes and world iron ore production is on the high increase since 2006 till date [3,4]. In Nigeria, for example, vibrant locations of iron deposits with percent Fe content and approximate reserve in tons are found in Agbaja (45-54% Fe, 2 billion); Itakpe (36% Fe, 200 million); Ajabanoko (35.61% Fe, 62.5 million); Chokochoko (37.43% Fe, 70 million); Agbade-okudu (37.43% Fe, 70 million) and Nsude Hills (37.43% Fe, 60 million) [5,6]. Despite these abundances, limited efforts have been carried out on the extraction or purification of the ore to obtain pure iron metals or as products of industrial values [7,8].

In the processing of iron ore for diverse industrial applications, many routes have been proposed by several workers. Some of these include the use of different physical, chemical and microbial leaching method for the treatment of iron ore with the aim of removing the associated gangues from the ore [1-8, 12-14]. From these studies, it was observed that the dissolution of iron ore or even the extraction of iron metal from a typical ore have been found to increase with increasing acid concentration, temperature, time and stirring speed. However, most of the working conditions according to literature are carried out at elevated temperature which often resulted to residual acid generation, associated cost and environmental pollution

[15, 16]. Hence, the formulation of a new technique to address the aforementioned problems in commercial hydrometallurgical process to recover high grade metals through acid leaching. Therefore, the aim of this work was to provide useful data on the kinetic parameters on the leaching of the ore for its subsequent beneficiation. In spite of vast deposit of iron ore in the studied area, there has been sparse availability of data relating to this research [7].

**Experimental**

*Materials and characterization*

The manganese-rich iron ore sample was collected from National Iron Ore Mining Project (NIOMP), Itakpe, Kogi State, Nigeria. This ore was pulverized using an acetone rinsed mortar and pestle and sieved into different particle sizes: 0.1 mm, 0.3 mm and 0.6 mm mesh respectively. Unless otherwise stated, all experiments were carried out using the 0.3 mm fraction, owing to its large surface area. The elemental composition of the ore was analyzed by X-ray Fluorescence technique (AMPTEK, Model XR-100CR), while the mineralogical purity was examined by X-ray diffraction using an Empyrean diffractometer. The photo-micrographic examination of the ore was carried out, while the surface morphology of the ore was characterized by scanning electron microscopy using a SEM model Leo1450 with $LaB_6$ Filament. The EDS

detector is an Oxford X-max and uses INCA software to analyze the spectra. Also, selected residual products after optimal leaching were appropriately characterized for better understanding of the dissolution mechanism.

*Leaching Protocol*

The leaching experiments were carried out in a 500mL glass reactor equipped with a mechanical agitator, a reaction control unit and a condenser to avoid loss of solution through evaporation. The experimental procedure was initiated by adding 10mL of sulphuric acid solution of known concentration into the glass reactor and bringing it to the desired reaction temperature. A given amount of the solid sample was then added to the solution. The dissolution process was carried out for various reaction times up to 120 minutes. At the end of each leaching experiment, the fraction of the ore dissolved was determined. The conversion fraction of iron ore dissolved was calculated as follows:

$$\alpha = \frac{\text{mass of iron passing to the solution}}{\text{Initial mass of the ore}} \quad (1)$$

The leaching rate of iron ore was determined as a function of time by changing the sulphuric acid concentration, particle size and reaction temperature. While the effect of one parameter was investigated during experiments, the values of other parameters (e.g. acid concentration) were kept constant. The leaching data obtained were plotted as a function of conversion fraction, x, against leaching time. In all cases, appropriate kinetic curves were made from the dissolution data to estimate the activation energy for predicting the dissolution mechanism for dissolution process [9-13].

**Results**

*Characterization Studies*

The elemental composition of the iron-ore by XRF revealed Fe (87.1401%) as the principal constituent, while other constituents include Mn (0.9486%), Cr (0.3312), Pb (0.1338%), Ti (0.1173%), V (0.0544%) and Sn (0.0032%). The mineralogical purity of the iron ore by XRD technique showing the identified compounds detected with their respective Joint Committee on Powder Diffraction Standard (JCPDS) file number is summarized in Table I.

**Table 1.** XRD analysis of iron ore.

| Compound | $Fe_2O_3$ | $Mn_5O_8$ | $Al_2O_3$ | $MgSiO_3$ | $MnSiO_3$ | $SiO_2$ |
|---|---|---|---|---|---|---|
| **JCPDS file no.** | 16-0653 | 39-1218 | 46-1131 | 35-0610 | 13-0138 | 44-1394 |

As seen in Figure I, the material under study is a finely polished manganese-rich iron ore, which shows the presence of three distinct micro-regions with different texture and morphology. The micro-regions with brownish golden contrast marked as "A" comprised anhedral grains (granular mineral with no definite morphology) and are manganese-rich (confirmed by SEM/EDS). The shinning yellow portion labelled "B" informs of the mixture of iron and manganese which may also be rich in manganese as reported previously by Miaha et al. [13], while the dark region "C" represents other compounds present in the ore.
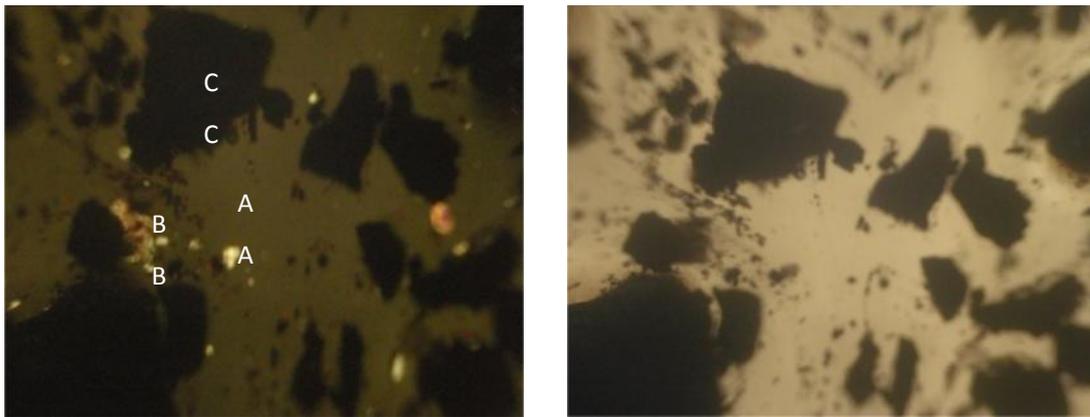


**Figure 1.** The photomicrographic examination of the iron-ore sample.

The Scanning Electron Microscopy (SEM) discusses the morphology of the ore sample which is shown in Figure 2. The micrographs of the raw iron ore sample at 10 000 and 50 000 magnifications before leaching reveals the cluster of various compounds present in the iron ore and at the same time shows the material to be non-granular with surface roughness. The abundant iron and its mixture with manganese are seen as the numerous whitish particles spread all over, while other compounds formed the dark portions observed.
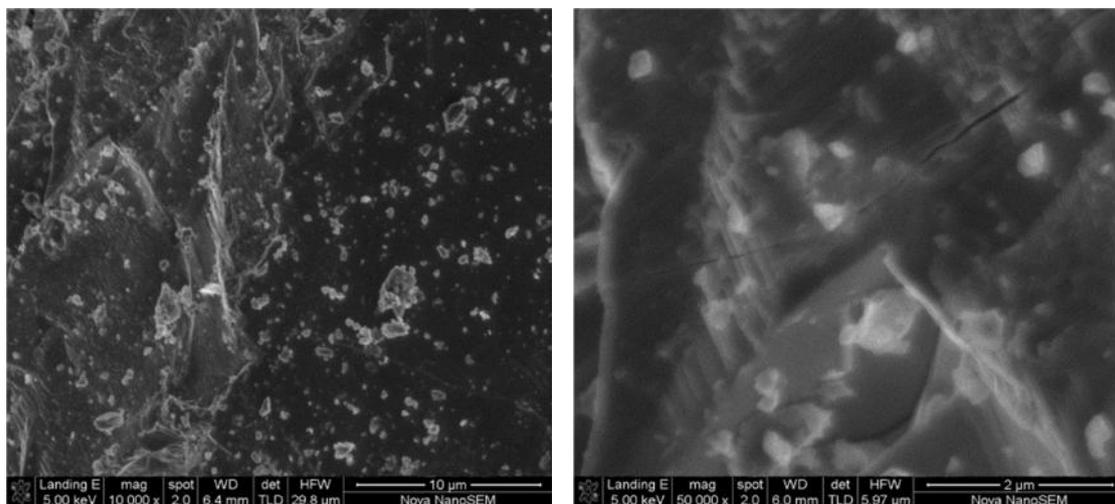


**Figure 2.** SEM micrographs of the iron-ore.

*Leaching Studies*

*Effect of H$_2$SO$_4$ Concentration*

The influence of the concentration of the lixiviant on the iron ore mineral is presented in Figure 3. It is clear from this figure that an increase in the concentration of sulphuric acid results to an increase in the amount of iron ore leached. It also shows that the rate of leaching increases with the leaching time as42.1% of the ore was reacted by 4 M H$_2$SO$_4$ within 120 minutes. However, acid concentration beyond 4 M was not considered due to excessive loss of solution through evaporation.
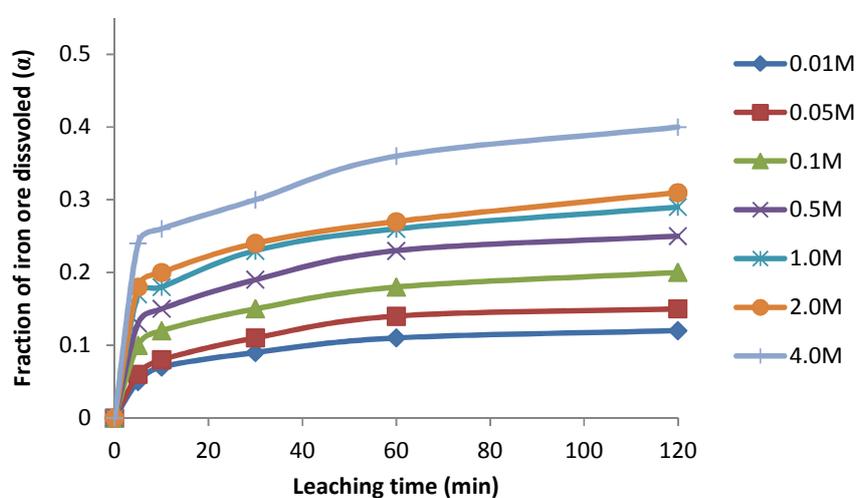


**Figure 3.** Plot of fraction of iron ore dissolved (α) versus contact time (min) at different H$_2$SO$_4$concentration. *Experimental conditions: Temperature: 55°C, mass of the iron = 10g/L, stirring speed: moderate.*

*Effect of Temperature*

Figure 4 presents the graphical representation of the result obtained by varying the reaction temperature with respect to the duration of leaching. This result reveals that changes in temperature plays a significant role in the leaching of the iron ore sample as it was observed that an increase in temperature brings about an increase in the fraction of ore reacted with an increase in the rate of leaching over the time range considered. At 80°C, the amount of the ore reacted was 78.9% within 120 minutes.
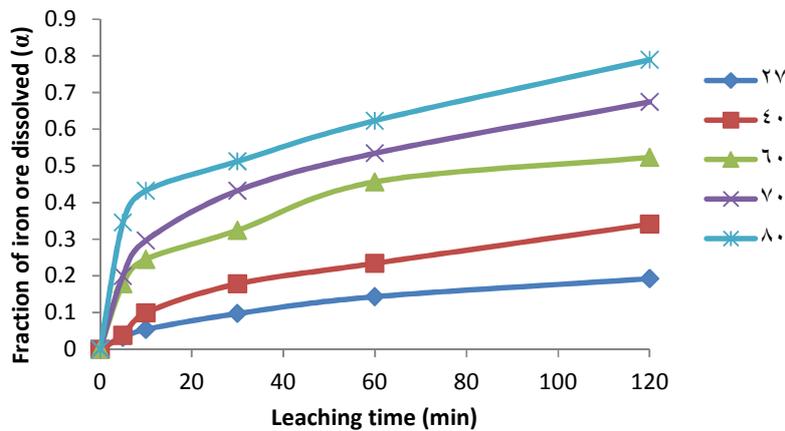
**Figure 4.** Plot of fraction of iron ore dissolved (α) versus contact time (min) at different temperature. *Experimental conditions*: Concentration: 4M, mass of the iron = 10g/L, moderate stirring.

## Discussion

Characterization of the residual product

The residual product at optimal leaching temperature was subjected to SEM analysis at different $H_2SO_4$ concentrations. Figure 5a show the micrographs of the iron ore after leaching with 0.01M H2SO4 at 55ºC, while Figure 5b summarize the micrographs of the iron ore after leaching with 4M $H_2SO_4$ at a temperature of 80ºC for a period of 120 minutes.
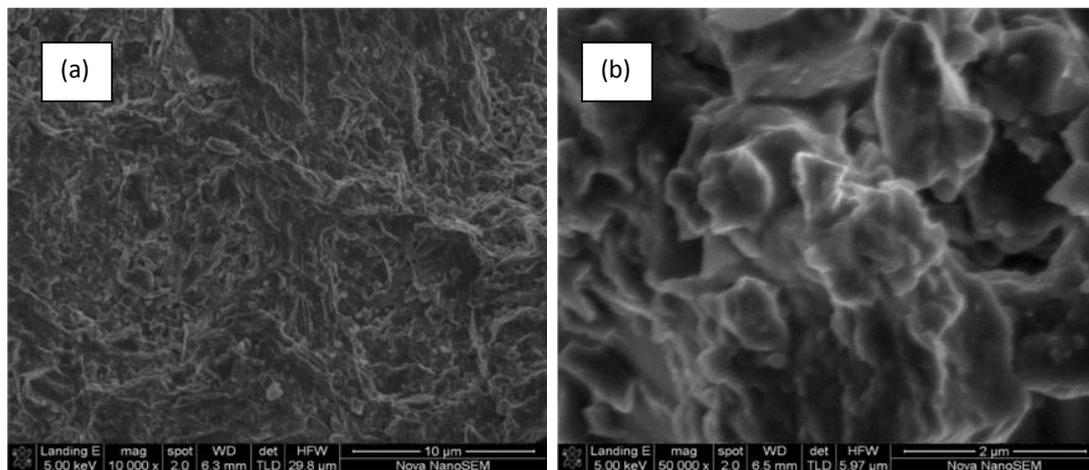


**Figure 5.** SEM micrographs of iron ore after leaching with (a) 0.01M $H_2SO_4$, 55$^0$C, 120 min.;(b) 4M $H_2SO_4$;

It is evident from Figure 5 that the abundant iron and manganese mixture seen after leaching with 0.01M $H_2SO_4$ (Figure 5a) was greatly reduced after leaching with 4M $H_2SO_4$ (Figure 5b). This is a confirmation of the positive influence of acid on the leaching of the iron ore as temperature increases.

*Dissolution mechanism*

In order to determine the kinetic parameters and rate-controlling step for the leaching of manganese-rich iron-ore in sulphuric acid solution, the experimental data presented in Fig. 3 and 4 were analyzed on the basis of the shrinking-core model. The shrinking core model (SCM) considers that the rate of controlling step of dissolution process is either the diffusion through solution boundary, the diffusion through a solid product layer, or the surface chemical reaction. Assuming that the manganese-rich iron-ore particles have a spherical geometry and the process is controlled by diffusion through product layer, the integrated equation of the shrinking core model can be expressed as [14, 17-19]:

$$1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}=k_{d}t \quad (2)$$

When the leaching process is controlled by chemical reaction, the kinetics equation may be expressed as:

$$1-(1-\alpha)^{1/3}=k_{r}t \quad (3)$$

where $\alpha$ = the fractional conversion of iron ore, $k$ = reaction rate constant, is the apparent rate constant for diffusion through the product layer, is the apparent rate constant for the surface chemical reaction, and $t$ = reaction time in seconds. For the dissolution kinetics analysis in the present work, the shrinking core models with diffusion through product layer and surface chemical reaction, (Eq. (2) and Eq. (3)) were evaluated. The left sides of these expressions were plotted with respect to the leaching time, and then thecorrelation of the kinetics data with these models was assessed by using correlation coefficient ($R^2$) values. The linear relationship between $1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}$ and leaching time is significant. It was found that the leaching process is controlled by diffusion through the product/ash layer in the temperature range of $27-80\ ^{\circ}C$, and was used to obtain the following relations as shown in figures 6 and 7:
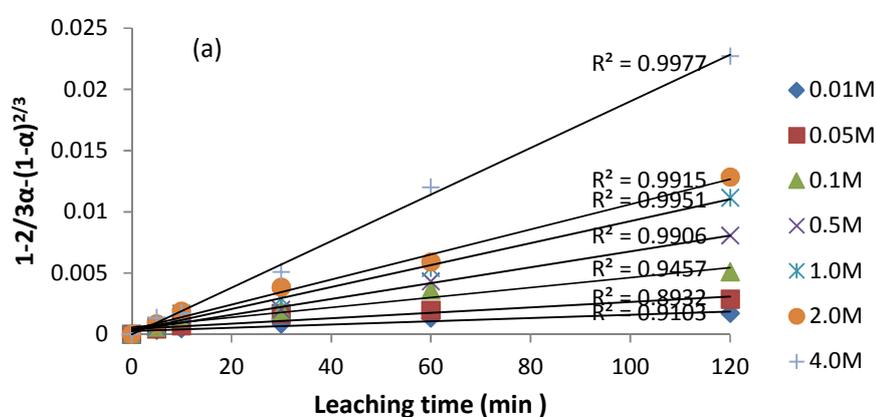


**Figure 6.** Plot of diffusion relation against leaching time (min) at different $H_2SO_4$ concentration, (Extracted data from Figure 3).
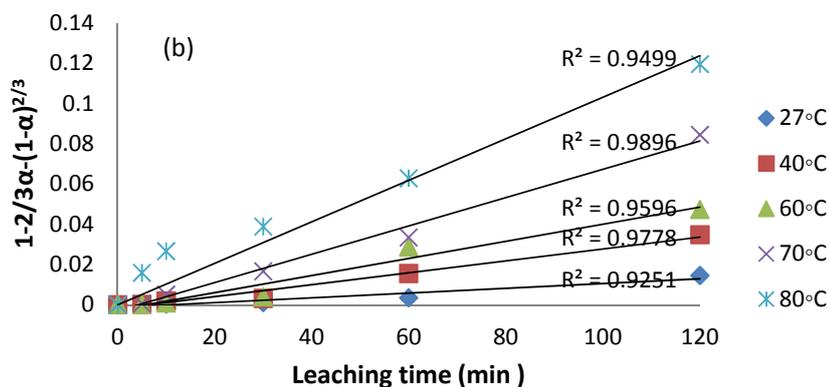
**Figure 7.** Plot of diffusion relation against leaching time (min) at different temperatures (Extracted data from Figure 4).

*(i) Order of reaction:*

The experimental rate constants were evaluated from the slopes of Figure 6 and a plot of lnk versus ln [$H_2SO_4$] was generated as shown in Figure 8. The slope of this plot which indicates the order of reaction was evaluated to be 0.979 with respect to hydrogen ion concentration [$H^+$].
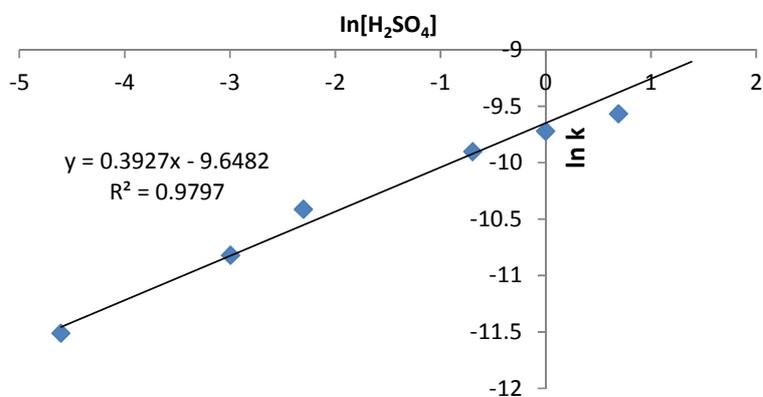


**Figure 8.** Plot of lnk vs ln [$H_2SO_4$].

*(ii) Process activation energy*

The Arrhenius plot for the leaching of iron ore in sulphuric acid solutions was obtained by plotting the values of slopes of the straight lines (apparent rate constant, k) versus (1/$T$) as shown in Figure 9. The Ea which was estimated to be 31.14 kJ/mol falls within the range expected for a rate limiting surface reaction for the diffusion controlled process.
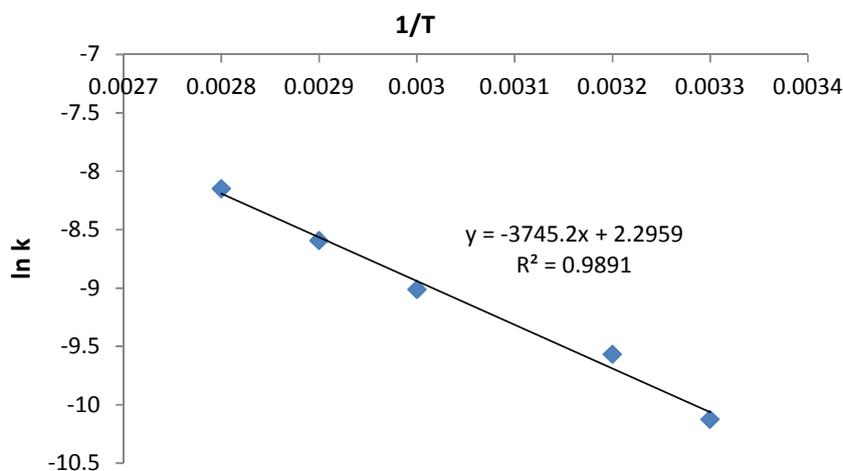
**Figure 9**. Plot of lnk versus 1/T.

## Conclusion

The dissolution kinetics assessment of manganese-rich iron ore in sulphuric acid medium has been studied. Parameters such as effects of acid concentration, temperature and particle size were analyzed during the leaching process. This study clearly established that an increase in the concentration of the lixiviant and leaching temperature did not only result in an increase in the amount of iron ore dissolved, but also displayed an increase in the leaching rate over the time range studied. From the results, the experimental data were accordingly fitted to follow the diffusion control model with the order of reaction and activation energy deduced to be 0.979 and 31.14 kJ/mol respectively, apparently supporting the proposed diffusion. Finally, work is on-going in our laboratory to beneficiate the leachate obtained in this study as pure Ferrous sulphate (FeSO$_4$) crystal (an important compound with many diverse industrial applications).

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