



## Investigation of Chemical and Microbial Leaching of Iron ore in Sulphuric acid

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**ABSTRACT:** Investigations on the chemical and microbial leaching of a Nigerian Iron-ore in sulphuric acid have been carried out. The influence of physico-chemical parameters such as acid concentration, temperature, particle size and stirring speed on the chemical dissolution of the ore was investigated. The dissolution rates are significantly influenced by the temperature and acid concentration while the increase of percentage dissolved with stirring speed and particle size was very moderate. The rate of the reaction based on reaction-controlled process was found to conform with the shrinking core model:  $1-(1-\alpha)^{1/3} = kt$ . With 12M H<sub>2</sub>SO<sub>4</sub> and at a temperature of 80°C with a stirring speed of 360rpm and particle size 0.04-0.05mm, about 76.80% of iron-ore was dissolved within 120min. The activation energy of 38.29kJ/mole was calculated for the process. The reaction is first order with respect to H<sup>+</sup> ion concentration. An attempt to dissolve the ore via microbial action of *thiobacillus ferrooxidans* was not successful. This has been attributed probably to very low sulphur content of the mineral. @JASEM

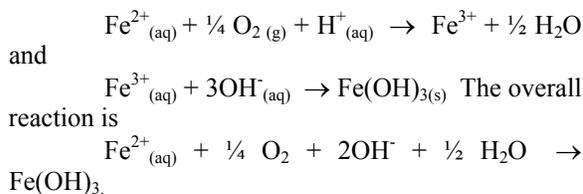
Iron is one of the biggest eight element in the earth's crust, being the fourth most abundant element at about 5% by weight. The main ores are the oxides which include: Magnetite – Fe<sub>3</sub>O<sub>4</sub> (72.4%Fe and 27.7%O); Haematite-Fe<sub>2</sub>O<sub>3</sub>(69.4% Fe, 31.06% O); Limonite – HFeO<sub>2</sub> (goethite or FeO(OH)-lepidocrocite; Siderite – FeCO<sub>3</sub>; pyrite-FeS<sub>2</sub> (46.6% Fe and 53.4% S); Beudannite [PbFe<sub>3</sub>(As<sub>2</sub>O<sub>4</sub>,SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>], and Awaruite, formed by the association of nickel with iron. Other minerals of iron include ilmenite-FeTiO<sub>3</sub>, which is formed by titanium and iron. Iron, along with magnesium, is a constituent of the fibrous silicate minerals, which were collectively given the commercial name asbestos. This mineral includes tremolite, riebeckite and grunerite (Encycl. of Anal. Sci, 1995; McGraw – Hill Encycl. of Sci. & Tech., 1997 and Silver, 1993). The Nigerian mineral appraisal and monetization programme NIMAMOP, 1996, identified about 33 solid mineral commodities including iron at various stages of exploration and exploitation and which occur in about 450 locations nationwide (Rahaman, 2004).

The high grade ferruginous quartzite iron deposit is found in the Itakpe hill. The geological proven reserve is 200 million tonnes. Since this reserve estimate is based on wide grid (100m) pre-exploitation drilling need to be continuously embarked upon, for economic exploitation of the deposit. A deposit of over 6 million tonnes is also found in Ajabanoko which is 4km north-west of Itakpe in Kogi State, Nigeria. The Ajabanoko deposit has similar chemical properties to that of Itakpe hill (Nat. Iron Ore Min. Co., 2001). Iron ore is also widely distributed in all the continents. The most important source of iron ore from United State is the Lake Superior district. In Canada, the ore is found in four principal areas which are newfound land,

Labrador trough in Quebec, the north shore of the great lake and the coast of British Columbia. Iron deposits are also found in South America, Australia and other parts of West Africa, (Encycl. of Chem. Tech., 1996). The intrinsic nature of chloride leach liquors resulting from the hydrometallurgical treatment of sulphide ores is rather complex. These solutions usually contain relatively high concentrations of basic materials, as well as small contents of other rare metals, frequently precious metals (Dutrillac et al, 1993).

Future sustainable development requires measures to reduce the dependence on non-renewable raw materials and the demand for primary resources. New resources for metals must be developed with the aid of novel technologies. In addition, improvement of already existing mining techniques can result in metal recovery from sources that have not been of economic interest until today. Metal-winning processes based on the activity of micro-organisms offer a possibility to obtain metals from mineral resources not accessible by conventional mining (Sugio et al, 1994; Sukia et al, 1993). Microbes such as bacteria and fungi convert metal compounds into their water soluble forms and are biocatalysts of these leaching processes. Additionally, applying microbiological solubilization processes, it is possible to recover metals values from industrial wastes which can serve as secondary raw materials (Wildman et al, 1993).

In general, the forms in which iron is found in nature depend on the pH and the oxygen concentration. At neutral pH and in the presence of oxygen, ferrous iron (Fe<sup>2+</sup>) is oxidized to ferric iron (Fe<sup>3+</sup>). Under these conditions, ferric iron forms highly insoluble precipitate, Fe(OH)<sub>3</sub>, (Manchee, 1977) according to the reaction.



At low pH and in the presence of oxygen, the chemical oxidation of ferrous iron is very slow. Under these conditions acidophilic chemolithoautotrophic iron-oxidizing bacteria catalyze the oxidation of ferrous ion. The best known representative is *Thiobacillus ferrooxidans*. This bacteria uses ferrous ion ( $\text{Fe}^{2+}$ ) as their sole energy source, by oxidizing ferrous ion to obtain electron for the reduction of  $\text{NADP}^+$  and proton that enters the cytoplasm through ATP syntheses. Thereby, the bacteria can maintain the natural proton motive force that results from the pH difference across the membrane (Stum and Morgan, 1981). The use of *Thiobacillus ferrooxidans* in the isolation/metal extractions including iron in different media have been extensively reported (Bartels et al, 1989; Boon et al, 1998; Drobner et al, 1990; Malik et al, 2006; Volkova – Volchanova and Cham, 1994; Suzuki et al, 1990). However, dissolution kinetics of iron ore has equally been studied in details (Anthonijevic et al, 2004; Baba et al, 2005; Olanipekun, 1999; Paspaliaris and Tsolokis, 1987).

This paper presents a detailed data on both the chemical and microbial leaching of a Nigerian iron ore in sulphuric acid medium. So far, there is no data to this effect viz-a-viz the Nigerian iron ore mineral is concerned. Equally, this work is a continuation of the recent research on a Nigerian iron-ore mineral (Baba et al, 2005).

## EXPERIMENTAL

**Material:** The sample of the iron ore concentration used for this research work was obtained from National Iron Ore and mining projects Itakpe, Kogi State, Nigeria. The mineral was finely pulverized and sieved to produce three different particle fractions: 0.04–0.05, 0.05–0.063 and 0.063–0.080mm in particle size. The experiments were carried out, with the rusting iron sample, the source of thiobacillus ferrooxidans, was made available from vehicle dumping site at Ipata Oloje, Ilorin West Local Government Area of Kwara State, Nigeria. The  $\text{H}_2\text{SO}_4$  used was reagent grade (BDH chemical). Distilled water was used in the preparation of all aqueous solutions. Chemical analysis was carried out using standard procedures as detailed elsewhere (Baba, 2002). The elemental analysis of the iron ore was carried out using inductively coupled plasma-mass spectrometry technique (ICP-MS).

**Chemical leaching:** The solution was investigated in a 1 litre glass reactor equipped with a glass stirrer. The reactor was filled with 200ml of known concentration of sulphuric solution, which was heated to the desired temperature. When the desired temperature was attained a charge of 0.5g of iron-ore was added to the sulphuric acid solution, stirring was started and the temperature of the reaction mixture was then maintained constant. The fraction of iron-ore dissolved was followed over time; at definite time intervals. The reaction residues after oxidation were washed with distilled water, air dried and oven dried at about 60°C and then reweighed. The difference in weight was noted for determining the fraction of the iron ore that had been dissolved. The kinetics of iron ore dissolution was also investigated as a function of temperature. The rate constants at each temperature were obtained, from which the energy of activation for the process was calculated. The effect of stirring rate on the mineral dissolution was also investigated.

**Microbial leaching:** 10g of iron ore sample and 1.0g of rusting iron sample were weighed and transferred into a sterilized test tube and 9ml of the *thiobacillus* medium (prepared according to (Atkinson and Movituna, 1991)) was measured with the aid of 10ml syringe into the test tube containing the samples, and was covered with aluminium foil. The cultural media were then kept in an incubator at a temperature of 50°C for days. Daily changes were monitored and recorded.

**Characterization of the thiobacillus bacteria:-** The solidified nutrient agar was melted in a boiling water bath to a liquid solution. The cork was then removed and quickly poured into three Petri-dishes (sterilized in an incubator at 160°C). The melted nutrients in the Petri-dishes were allowed to set and 1ml of each of the prepared culture medium was drawn with the aid of a syringe into two of the dishes and the third being a control. They were all kept in the incubator for 24 hours, so that the bacteria present in the cultured medium will grow to form a colony, where they can be characterized by staining, and then view under a high-powered objective lens microscope.

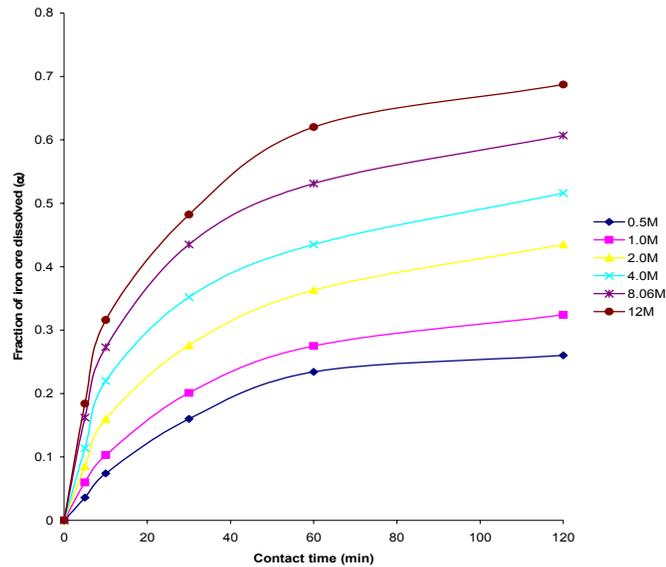
## RESULTS AND DISCUSSION

**Elemental analysis of the iron ore by ICP-MS:** The ICP-MS technique showed that the percentage of the total iron in the ore is 66.7%. The minor elements in the ore are Si(5.20%), Al(0.20%), Ca(0.09%), P(0.06%), K(0.05%), Mn(0.02%), Na(0.02), Ti(0.02%), and Mg(0.01%). Elements such as Cu, Zn, Ni, V, La, Cr, Ce, Zr, Y and As are recorded at trace levels. Oxygen content calculated by difference is 28%. A non-stoichiometry value was obtained for

the atomic ratio Fe:O, which implies that the ore is most likely to be a mixture of hematite and magnetite (Baba et al, 2005).

*Effect of  $H_2SO_4$  concentration:* The experiments were carried out by varying the initial  $H_2SO_4$  concentration

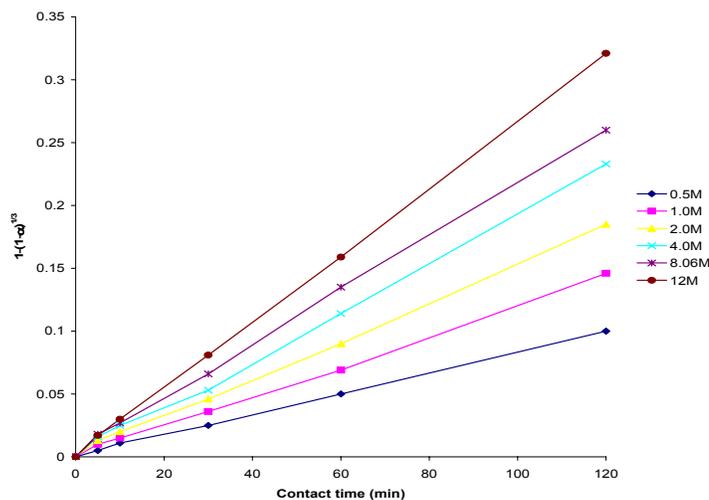
from 0.5M–12.0M at 55°C. Increasing the  $H_2SO_4$  concentration accelerated considerably, the fraction of the iron-ore dissolved at various time of contact (Fig. 1).



**Fig. 1:** Fraction of iron ore dissolved vs contact time at different concentrations of  $H_2SO_4$ .

From Fig. 1, it is evident that the rate of iron ore dissolution is directly proportional to the concentration of hydrogen ion  $[H^+]$ . These are in accordance with the reports recently published (Anthonijevi et al, 2004; Baba et al, 2005 and Baba, 2002) on separate studies involving the leaching of sulphidic minerals including iron-ore. The plot of the

fraction of iron ore dissolved at different concentrations of  $H_2SO_4$  at various contact time in Fig. 1, was linearized using the shrinking core model  $1-(1-\alpha)^{1/3} = k_1t$ ,  $k_1$ , being the rate constant. To this end, the plot of  $1-(1-\alpha)^{1/3}$  as a function of time at different  $H_2SO_4$  concentrations is presented in Fig. 2.



**Fig. 2:** Plot of  $1-(1-\alpha)^{1/3}$  vs time at different  $[H_2SO_4]$ .

From Fig. 2, the rate constants,  $k_1$ , were calculated. By constructing the plots of  $\ln k_1$  versus  $\ln[H_2SO_4]$ ,

the order of reaction was determined from a straight

time graph of Fig. 3, which gives a slope of  $0.654 \approx 1$ . This suggests that the order of reaction with

respect to  $\text{H}_2\text{SO}_4$  concentration is approximately first order.

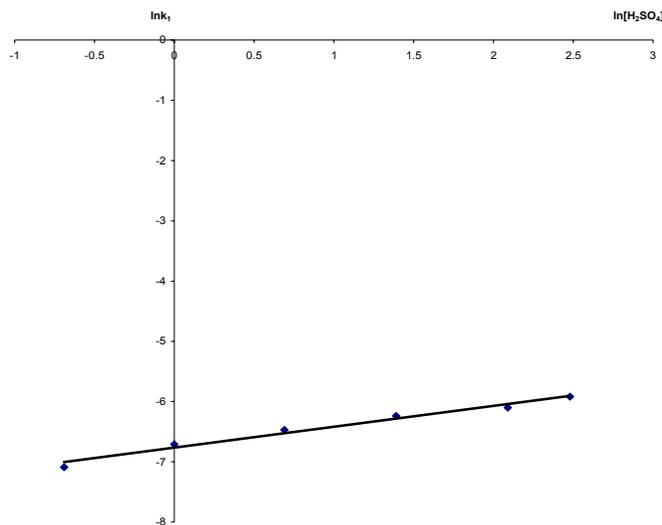


Fig. 3:  $\ln k_1$  versus  $\ln [\text{H}_2\text{SO}_4]$ .

Similar work on a first order with respect to hydrogen peroxide concentration was found also for pyrite oxidation by this oxidant in sulphuric acid solutions (Anthonijevij et al, 1997).

*Effect of stirring rate:* Table 1 summarizes the results on the effect of stirring rate on iron-ore dissolution in 12M  $\text{H}_2\text{SO}_4$  with the 0.040–0.050mm particle size at  $80^\circ\text{C}$ , using stirring speeds of 90–450rpm.

**Table 1:** Results of stirring rate on iron-ore dissolution

Stirring speed rpm	Fraction of iron-ore dissolved ( $\alpha$ )
90	0.596
180	0.613
270	0.639
360	0.664
450	0.652

Table 1, it is evident that the fraction of iron-ore dissolved increase with stirring rate. This appears to be true up to 360rpm after which the fraction dissolved tends practically to a constant value.

*Effect of particle size:* The experiments were carried out with particle size: 0.040–0.05, 0.050–0.063 and 0.063–0.083mm at  $80^\circ\text{C}$  in 12M  $\text{H}_2\text{SO}_4$ . The smaller the particle size, the greater was the amount of iron-ore dissolution, as can be seen in Table 2. The result in table 2 also shows that the dissolution rates are inversely proportional to the average diameter of the particles.

**Table 2:** Results of the effect of particle size

Particle size (mm)	Amount of iron-ore dissolved (%)
0.040 – 0.050	76.83
0.050 – 0.063	69.37
0.063 – 0.080	64.05

*Effect of Temperature:* The experiments were carried out in the 298 – 353K temperature range in solutions containing 12M  $\text{H}_2\text{SO}_4$ , using particle size 0.04–0.05mm and at a stirring rate of 360rpm. The results are illustrated in Fig. 4 showing the fractions of the iron-ore dissolved against contact time at different temperatures.

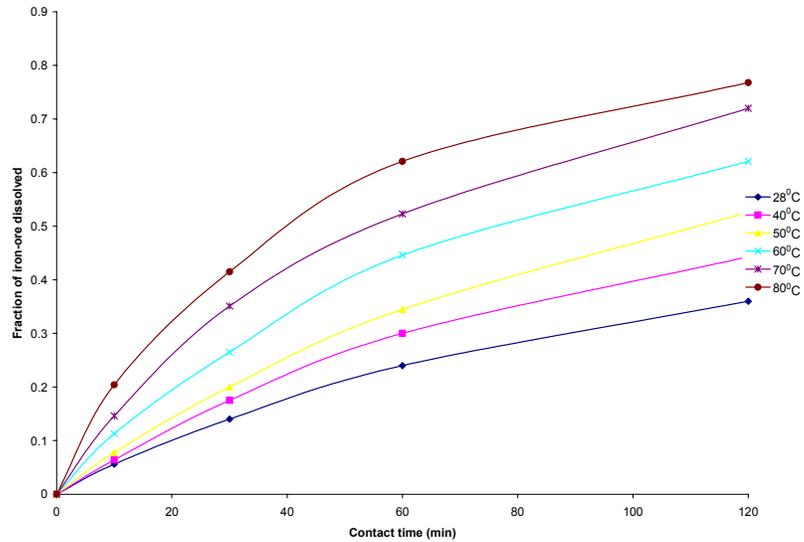


Fig. 4: Fraction of iron-ore dissolved vs contact time at different temperatures.

From Fig. 4, it is seen that increasing temperature greatly accelerates the reaction rate. The apparent rate constant,  $k_2$ , obtained from the slopes of the lines in

Fig. 5, were used to determine an activation energy of 38.29kJ/mole as shown by the Arrhenius plot in Fig. 6

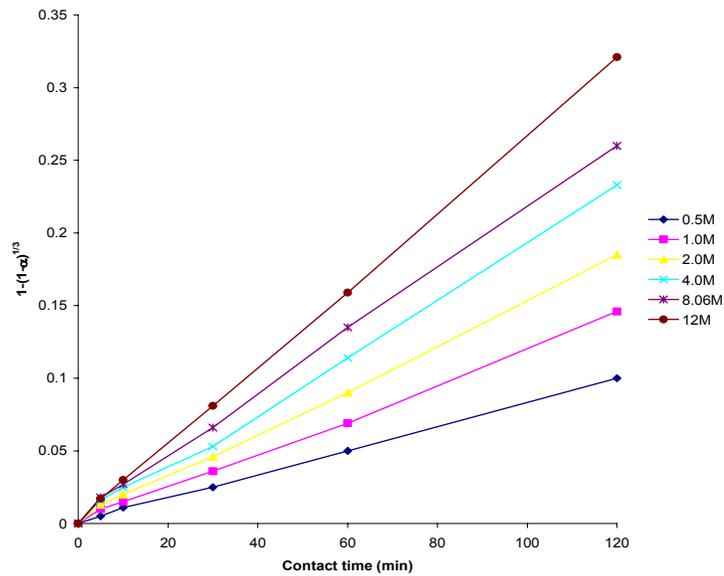


Fig. 5: Plot of  $1-(1-\alpha)^{1/3}$  vs time at various temperatures

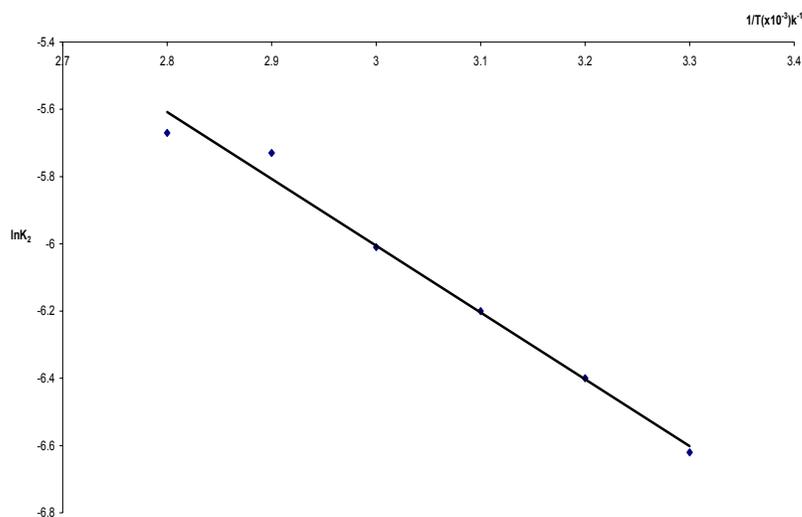


Fig. 6:  $\ln k_2$  vs  $1/T$  ( $K^{-1}$ )

The magnitude of the activation energy of 38.29kJ/mol supports the proposed surface reaction shrinking core model:  $1-(1-\alpha)^{1/3} = kt$ , as earlier suggested (John and Wadsworth, 1979).

From the microbial investigations, it was found that there is no meaningful growth of *thiobacillus ferroxidans* on the iron ore sample. This might be due to the fact that the concentrate of the iron used being non-sulphidic is not favourable to bacterial attack, where the thiobacillus bacteria can oxidize the metal sulphide, and obtained electron directly from the reduced minerals, necessary for its metabolic activities.

**Conclusion:** On the basis of the results of this investigation, the following conclusions can be drawn: (i) Increasing the concentration of  $H_2SO_4$  leads to increase in the amount of iron-ore dissolved at a particular time. Hence, the rate is proportional to the  $H^+$  ion concentration, with a reaction order almost 1. (ii) The dissolution rates are inversely proportional to the average diameter of the particles. (iii) The dissolution kinetics follows a shrinking core model with the surface chemical reaction as the rate controlling step and activation energy of 38.29kJ/mole is obtained for the process.

The ore used is non-sulphidic. Consequently, the microbial studies showed that there is no growth of *thiobacillus ferroxidans* on the iron sample. Therefore, the concentrate may be a mixture of haematite ( $Fe_2O_3$ ) or magnetite ( $Fe_3O_4$ ).

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