



Quantitative Leaching of a Nigerian Iron Ore in Hydrochloric Acid

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ABSTRACT: A study on the quantitative leaching of iron ore in hydrochloric acid solution has been undertaken. The elemental composition of the iron ore was also carried out using ICP-MS technique. The major elements in the iron ore include: Fe(66.7%); Al (0.2%); Si (5.2%); Ti (0.02%) and O (28.0%). Some traces of V, Ni, Zn, Ce, Cr, La, Y and Zr were also found. The effects of contact time, acid concentration, temperature, particle size and, the stirring speed on the dissolution of the iron ore have been investigated. The dissolution rate depends on the hydrogen ion concentration and temperature of the reaction system. The mechanism of dissolution appears to follow an exothermic pathway. The activation energy for the dissolution reaction was 13.63 kJmol^{-1} . About 92% of the total iron in the ore was dissolved within 120 min. by 12M HCl solution and 80°C using 0.1mm particle size. The optimum stirring speed was 300rpm. @JASEM

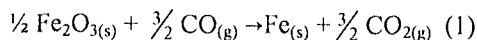
Nigeria is one of the richest countries of the world as far as mineral resources are concerned including iron ores. The estimates of workable iron ore deposits stand in excess of 2.5 billion tones most of which belong to hematite, hematite-magnetite, hematite-geothite and siderite-geothite grades are found in Itakpe. However, Agbaja iron ore deposit (proven reserve – 1 billion metric tonnes) is the largest in Nigeria. However, its high phosphorus (1.4 – 2.0%) and how silicon modulus ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 0.89$) and fine-grained texture constitute a major problem for utilization in the blast furnace or direct reduction process (NMS Proceedings, 1999). Iron is the sixth most abundant element in the universe and the most abundant metal in the earth's crust after aluminum (Encycl. Americana, 1992). On the surface of the earth, iron occurs native (uncombined with other elements) in very small quantities, but with other elements, it is found in a number of ores which include haematite (Fe_2O_3), magnetite (Fe_2O_4), limonite ($2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), goethite (HFeO_2), turgite – $[\text{Fe}_4\text{O}_5(\text{OH})_2]$, siderite (FeCO_3), pyrite (FeS_2), chalcopyrite (CuFeS_2) and iron silicate that may include chloropal ($\text{H}_5\text{Fe}_2\text{Si}_3\text{O}_{12} \cdot 2\text{H}_2\text{O}$) (Encycl. Sc. & Tech., 1997). In Nigeria, extensive high grade iron ore deposits are found in Itakpe and Ajabanoko hills between Okene and Lokoja in Kogi State (Min. & Ind. in Nigeria, 1987). A summary of the important iron ore reserves in Nigeria is given in Table 1.

Table 1: Estimated Iron Ore Reserves in Mt. (NMS Proceedings, 1999)

S/No	Location	Indicated	Inferred
1.	Itakpe	95.0	309.9
2.	Oshokoshoko	10.0	85.2
3.	Ajabanoko	25.0	65.0
4.	Agbaja	962.0	1250
5.	Kotonkarfe	248.0	850
6.	Bassa-Nge	82.5	400

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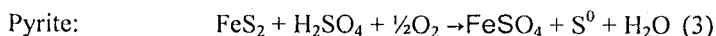
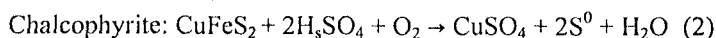
Metallurgy of iron is a process of extracting iron from ores and preparing it for use. These extraction and preparation processes involve the conversion of naturally occurring iron-bearing minerals into metallic iron. The major process for the production of iron is the iron blast furnace. It entails two major procedures: ore preparation and reduction of oxide concentrates, and the overall reaction for the reduction of say hematite to metallic iron with carbon monoxide is:



Iron may be efficiently extracted from its principal ores with hot conc. HCl, but not with conc. H_2SO_4 or HNO_3 . The efficiency of HCl extraction is ascribed to the formation of ferric chloride complexes (Encycl. Sc. & Tech., 1997). Ore also contain Si and SiO_2 and silicates. Iron may be extracted from some kinds of silicates, provided that the sample is finely ground, but the process is slow. SnCl_2 increases the rate of extraction by reducing Fe(III) to Fe(II), and is particularly effective for haematites and magnetites (Blaede and Meloche, 1985).

The kinetics of dissolution of sulphidic minerals or the related form in chloride media has received considerable attention recently. There are several justifications for this interest. Among them is the ability of materials of construction with improved resistance to chloride attack. More importantly, however, are the substantially faster dissolution rates exhibited by most sulfides in chloride media and the potential application of such electrolytes in the treatment of complex sulphide [Zuo-mei Jin *et al*, 1984]. They reported and proposed results of the overall leaching reaction which are consistent with

the following stoichiometry (Harvey and Yen, 1998), relating to pressure oxidation of the base metal sulphides:



Furthermore, the leaching of the iron-ore in different media has been studied by many investigators (D'Hugues, *et al*, 2002; Baba, *et al*, 2003 and Bolorunduro, *et al*, 2003). To the best of our knowledge, there is no reported works viz a viz the quantitative leaching of a Nigerian iron ore. Therefore, this work will provide data on the quantitative leaching and the kinetics of dissolution behaviour of the iron ore in hydrochloric acid solutions. This work is interesting from the industrial perspective, as it could provide optimum conditions for the commercial production of ferric chloride from the indigenous iron ore. Ferric chloride is an important material for water and industrial liquid effluents treatment (Morris, 1990).

EXPERIMENTAL

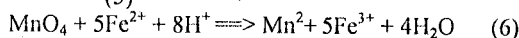
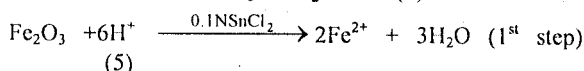
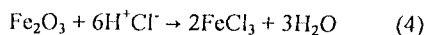
Material Collection and Preparation: The sample of the iron ore concentrate used for this research work was obtained from National Iron Ore and Mining Project, Itakpe, Kogi State, Nigeria. The mineral was finely pulverized and sieved to produce four different particle size fractions: 0.1mm, 0.2mm, 0.3mm and 0.4mm.

Chemical composition: Chemical analysis of the sample was carried out using standard procedures as detailed elsewhere [Baba, 2001]. The elemental analysis of the iron ore was carried out using Inductively Coupled Plasma – Mass Spectrometry Technique (ICP-MS). An atomic absorption spectrophotometer (Buck Model 200) and redox titrimetric method [Kalthoff, *et al*, 1989] were further used to confirm the concentration of the total iron content in the ore. As the three techniques did not differ from each other by more than 5%, redox titrimetric method was therefore used for subsequent determinations of iron in aqueous solutions. Hydrochloric acid solutions used were prepared from the analytical grade chemical by serial dilution with doubly distilled water.

Leaching Procedure: 0.1mm sieved sample of the pulverized iron ore was used for this experiment at different concentrations of HCl and at different contact time and fixed temperature of 55°C. 1.0g of a given particle size sieved sample was weighed, and then transferred into 500ml conical flask containing 100ml of 0.5M HCl. The reaction mixture was agitated with the aid of magnetic stirrer and covered with glass lid. The mixture was agitated with the aid of magnetic stirrer and covered with a glass lid. The mixture was stirred and heated at

55°C for various contact time: 5, 10, 20, 30, 60, and 120 min. respectively. At the end of each period, the solution was cooled and filtered into a 100ml standard flask. The residue was collected, washed to neutrality 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 same procedure described above was repeated for 1.0M, 2.0M, 4.0M, 8.6M and 12M HCl respectively. The results obtained were recorded and kept for further analysis. The kinetics of iron ore dissolution was also investigated as a function of temperature. The following temperatures were examined: 28°C, 40°C, 55°C, 70°C and 80°C. The rate constants obtained at these temperatures were used to compute the energy of activation for the process. The effect of stirring rate on the rate of dissolution of the mineral was also studied.

Determination of iron in aqueous solution: A redox titrimetric method was used for iron determination (Kalthoff, *et al*, 1989). The details of the procedure are given below: 50ml of filtrate solution of the leaching process was heated in 250ml conical flask to almost boiling. Keeping the solution hot, solution of 0.2M SnCl₂ was added dropwisely until all of the iron(III) ions have just been reduced to iron(II) ions. The disappearance of the yellow colour signals the completion of this reduction. Few drops (2 – 3) of the SnCl₂ solution were added. The solution was cooled completely and without much delay, 30ml of 0.4M HgCl₂ solution was added. A white opalescent precipitate was formed. The solution was allowed to stand for 5min. At the end of which, the solution was diluted to 150ml with cold distilled water. 25ml of Zimmerman-Reinhardt reagent solution was added. The cold solution was titrated at once with standard permanganate solution to a pink colour end-point that persisted for 30sec, while the solution was being titrated. The second half of the filtrate was also treated following the same procedure described above. The chemical reaction can be described thus:



At equivalence,

$$5[\text{Fe}^{3+}] = [\text{MnO}_4^-] \text{ or } [\text{Fe}^{3+}] = \frac{[\text{MnO}_4^-]}{5} \quad (7)$$

RESULTS AND DISCUSSION

Elemental Analysis of the iron ore by ICP – MS: The results of the elemental analysis are presented in Table 2.

Table 2: ^aElemental composition of the iron ore.

Fe	Mn	Ca	Mg	Na	K	Ti	Al	Si	P	O*
66.7	0.02	0.09	0.01	0.02	0.05	0.02	0.20	5.2	0.06	33.0
Cu	Zn	Ni	Sr	V	La	Cr	Zr	Ce	Y	As
1.6	15	9.7	6.0	16	6.0	9.3	7.5	12	3.8	<1

^a concentrations of the first and second row elements are expressed in % and ppm respectively. *: oxygen is obtained by difference

The percentage of total iron in the ore is 66.7%. The minor elements in the ore are Mn, Ca, Mg, Ti, Al, Na, K, Si and P. 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.

Both AAS and redox titrimetric methods gave value of 64.3% for the total iron in the same iron ore material. The three techniques are therefore in agreement with each other, but differs by 1.53% s.d. (s.d. = standard deviation).

Effect of stirring rate: Table 3 summarizes the results obtained on the effect of stirring speed on the dissolution of iron ore in 12M hydrochloric acid.

Table 3: Results of effect of stirring rate on iron ore dissolution.

Stirring rate (rpm)	% of iron ore dissolved
0	79.3
100	85.9
200	88.6
300	91.8
350	89.5
400	86.7

From Table 3 above, it is evident that the amount of iron ore dissolved is dependent on the stirring speed over the range 0 – 300rpm. Above 300rpm, the stirring rate no longer has any observable effect on the solid dissolution. Hence, the dissolution reached a steady rate at 300rpm. Therefore, stirring rate of 300rpm is chosen for further investigation. These results are in accordance with the works earlier reported (Olanipekun, 2000 and Baba *et al.*, 2003).

Effect of Concentration: Results of fraction of iron ore dissolved as a function of contact time at various concentrations of HCl are illustrated in Fig. 1.

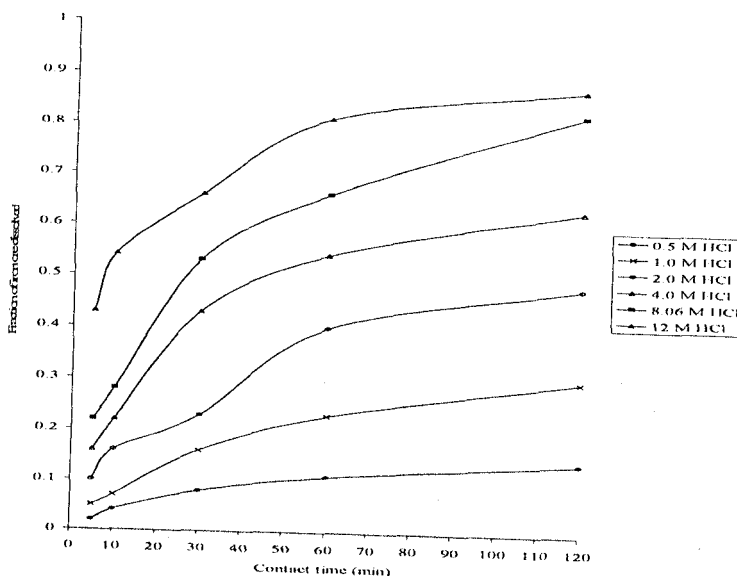


Fig. 1: Plot of iron ore extracted versus contact time at various concentrations of HCl. Experimental condition: Temperature = 55°C; mass of iron ore used = 1.0g; Stirring rate = 300rpm; Particle size = 0.1mm

From Fig. 1 above, it is evident that increase in the concentration of HCl brings about appreciable increase in the amount of iron ore dissolved within 120min. Also with 12M HCl, 90% of the ore passed into solution. In effect, the higher the concentration of HCl, the higher is the percentage of the mineral that is dissolved. Therefore, these results showed that the rate of iron ore dissolution is affected directly by the hydrogen ion $[H^+]$ concentration.

These are in accordance with the report made by (Dutrillac and MacDonald, 1983; Zuo-mei Jin, *et al*, 1984 and Baba, *et al*, 2003) on separate studies involving the leaching of sphalerite minerals.

Effect of Temperature: The rate of iron ore dissolution was studied over the temperature range 28°C to 80°C. The results are shown in figs. 2 and 3

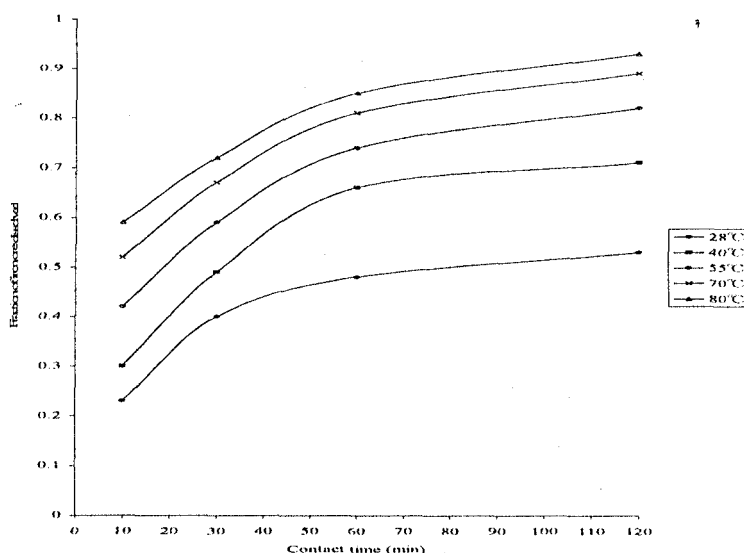


Fig.2: Plot of fraction of iron ore dissolved versus contact time at different temperatures. *Experimental condition:* Temperature = 28°C – 80°C; Mass of iron ore used = 1.0g; Stirring rate = 300rpm; Particle size = 0.1mm

As expected, increasing temperature greatly accelerates the reaction rate (Fig. 2). The apparent rate constants, k , obtained from the slopes of the linear plots in Fig.3 were used to determine the activation energy as shown in Fig. 4. The plot of Fig.4 clearly shows that the kinetic data fitted relatively well into the surface reaction model proposed by (Zuo-Mei Jin *et al* 1983). $1 - \frac{2}{3}\alpha - (1-\alpha)^{\frac{2}{3}} = kt$, where k is the rate of

constant; α is the fraction of mineral dissolved; t is the elapsed time. The activation energy determined using this surface reaction kinetic model was 13.63 kJmol^{-1} . This value falls within the range expected for a rate limiting surface reaction and is consistent with those reported by previous investigators on other types of mineral (Dutrillac and MacDonald, 1983; Jones and Peters, 1986; Rath, *et al*, 1992).

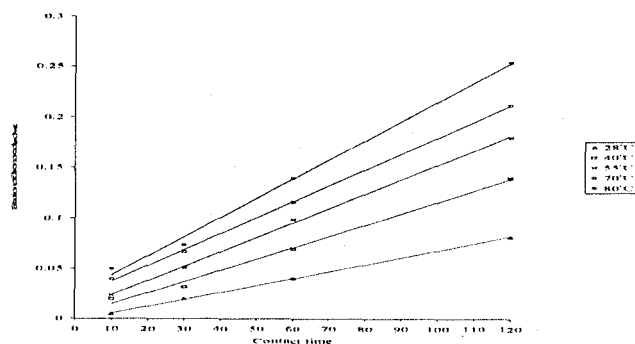


Fig 3: The plot of $1 - \frac{2}{3}\alpha - (1-\alpha)^{\frac{2}{3}}$ versus contact time at various temperatures. Alafara, A. Baba; Adekola, F A; Folashade, A O

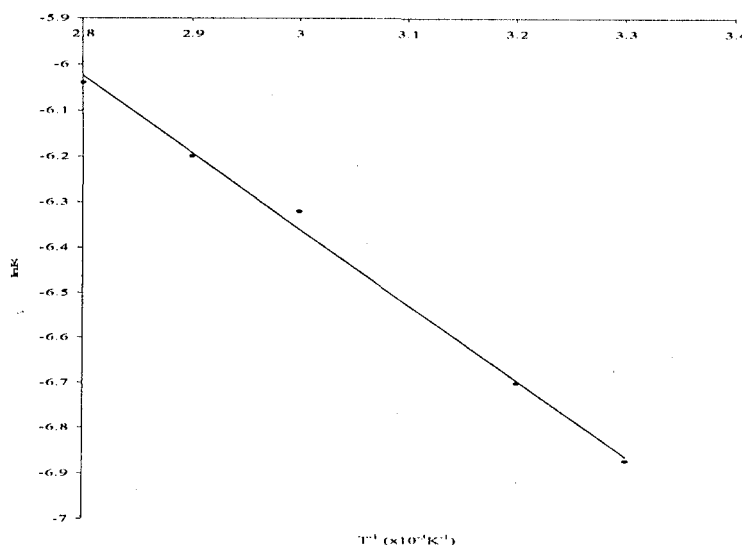


Fig. 4. The plot of $\ln k$ versus $1/T(K^{-1})$

Effect of Particle Size: The effect of particle diameter on the rate of iron-ore dissolution was examined by measuring the kinetics of reaction for four different particle sizes. As expected and due to the large surface area, particles with the smallest size (0.1mm) gave the highest dissolution rate. The data are presented in Table 4.

Table 4: Results of the effect of particle size on iron ore dissolution

Particle size (mm)	Amount of iron ore dissolved (%)
0.1	91.8
0.2	84.3
0.3	79.9
0.4	73.4

Experimental conditions: HCl = 12M;
Temperature = 80°C; Stirring rate = 300rpm;
Contact time = 120min.

Conclusion: The dissolution rate of iron ore at various concentration of HCl depends on $[H^+]$ hydrogen ion concentration and temperature of the reaction system. The study also revealed that the mechanism of the system follows an exothermic pathway, where the activation energy of $13.63 \text{ kJ mol}^{-1}$ was obtained. Therefore, with 12M HCl solution, about 92% of iron ore would pass into solution within 120min, using a pulverized iron ore sample of about 0.1mm particle size and a stirring rate of 300rpm. The percentage of iron in the ore was found to be 64.3%.

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