Full Paper

# STUDIES ON THE THREE-STAGE DILUTE HYDROCHLORIC ACID OVEN LEACHING OF A LOW GRADE IRON ORE

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## ABSTRACT

Iron ore for use in the blast furnace are required to contain at least 63% Fe. The -63 µm fraction of Itakpe iron ore having 34.70% Fe was leached with dilute hydrochloric acid in single and multiple stages (with intermediate water washing) in the sequences $H_2O$-HCl-$H_2O$ and HCl-$H_2O$-$H_2O$. The ore as-received and as-leached were also subjected to X-ray fluorescence analysis, while the efficiency of the concentration process was evaluated semi-quantitatively and quantitatively by weight loss % and changes in the chemical compositions obtained. The results obtained showed that the three-stage leaching of the iron ore in the sequence $H_2O$-HCl-$H_2O$ at 0.375M dilute hydrochloric acid concentration produced the highest weight loss and yielded iron ore concentrate with 64.5% Fe, indicating a 85.9% upgrading of the Fe content. Similarly, the Si, Al, Ti, Ca, Na, Mg, K and P were reduced by 66.7, 75.8, 40, 96.6, 89.7, 90.1, 89.1 and 94.7 percents, respectively. The Fe content of the concentrate exceeds the 63% specification for the blast furnace use and is only 2.5% below the 67% required for Midrex direct reduction process. The very high reductions in the alkali oxides, phosphorous/sulphur are significant because of their negative roles in iron and steel making.

**Keywords**: *iron ore, leached, dilute acid, stages, concentrate*

## 1. INTRODUCTION

Iron is one of the largest eight elements in the earth's crust and is the fourth most abundant element at about 5% by weight. The main ores of iron include magnetite, hematite, limonite, goethite, siderite, pyrite and ilmenite (Silver, 1993). Nigeria has several deposits of iron ore found in Itakpe, Agbaja, Ajabanoko, Koton Karfe and Toto Muro. The Itakpe iron ore has a proven reserve of about 200 million tons and has been designated to supply sinter grade concentrates of 63% to 64% Fe for the blast furnace ironmaking at Ajaokuta The deposit extends approximately 3,000 m in length and includes about 25 layers of ferruginous quartzite. The deposit with an average iron content of approximately 35% is a banded iron formation containing a mixture of magnetite and hematite with ratio varying throughout the deposit (Adepoju and Olaleye, 2001; Umunakwe, 1985).

Elements such as phosphorous (P) and potassium (K), within the lower quality iron ore have detrimental effect on steelmaking process. The quality of iron ores have been improved by methods such as washing, heavy media separation, jigging, drying, flotation, magnetic and electrostatic concentration (Wills, 1992). Leaching is a widely used extractive metallurgy technique which converts metals into soluble salts in aqueous media. There are a variety of leaching processes, usually classified by the types of reagents used in the operation. The reagents required depend on the ores or pretreated material to be processed. Baba *et al* (2005) and (2007) studied the leaching dissolution of Itakpe iron ore using sulphuric and hydrochloric acids. The ore dissolution rate was found to be significantly influenced by temperature and acid concentration and only moderately by stirring speed and particle size. Model to predict the concentration of phosphorus removed relative to the initial and final pH of the leaching solution during leaching of iron oxide ore in sulphuric acid solution also has been derived (Nwoye *et al*, 2008). Adeleke (2011) developed a multistage leaching method with intermediate water leaching at the normal atmospheric pressure for the economic demineralization of selected coals.

The aim of this study is to determine the response of the low grade Itakpe iron ore to multistage leaching with dilute hydrochloric acid at the normal atmospheric pressure.

## 2. EXPERIMENTAL PROCEDURE

### 2.1. Materials

#### 2.1.1. *Iron ore sample preparation*

About 5 kg of Itakpe iron ore was obtained from the bulk sample at the National Iron Ore and Mining Project, Itakpe, Kogi State, Nigeria. The ore was broken into sizes that could be fed into the jaw crusher using a sledge hammer. The sample was crushed in a laboratory dodge crusher and afterward ground in a laboratory ball mill model number Lf-b-32. Representative sample was then taken and air dried for about 48 hours.

### 2.2. Methods

#### 2.2.1. *Sieve analysis*

About 150 g of the ore was placed in the uppermost sieve in a nest of sieves with standard apertures of 425, 300, 212, 150 and 63 µm. The loaded nest of sieves was then allowed to vibrate for about 15 minutes. Afterward, the sieves were taken apart and the amount of material retained on each sieve was weighed (Adepoju and Olaleye, 2001). The -63 µm fraction size that constituted the largest proportion of the Itakpe ore was selected for this study.

#### 2.2.2. *Single and multistage leaching*

Firstly, a 6M dilute solution of hydrochloric acid was prepared by adding 100 ml of distilled water into 100 ml of the 12M BDH

Laboratories Limited concentrated hydrochloric acid solution. Afterwards, dilute solutions of 0.75, 1, 1.25 and 1.5M were prepared by serial dilution. For the single stage leaching, about 1 g sample of -63 µm size fraction was weighed and transferred into a 250 ml beaker containing 30 ml of 0.75M hydrochloric acid. The reaction mixture was stirred for 5 minutes and then covered with an aluminium foil. The mixture was then placed in the Gallenkamp 7B 16590 oven and heated for 1 hour at about 80°C. After heating, the solution was cooled in the oven for another 1 hour and then filtered into a conical flask using a Whatman filter paper. The residue was collected and oven dried at about 80°C and then re-weighed. The difference in weight was noted for determining the fraction of the iron ore that had been dissolved. The same procedure described was repeated for 0.0625, 0.125, 0.25, 0.375, 0.50 and 1M hydrochloric acid. The procedure was again repeated with 0.375M solution but for 45, 75, 90 and 105 minutes contact times. The latter test was further repeated but at 45, 65, 75, 85 and 95° C temperatures for 75 minutes.

For the three-stage step leaching, about 1 g of the -63µm size fraction was leached in 95° C for 75 minutes with 30 ml 0.375 M dilute hydrochloric acid and the residue filtered and dried as described in the single stage leaching. The procedure was repeated on the residue obtained from the first stage but with water. The latter water cleaning procedure was finally repeated as the third stage of the $HCl-H_2O-H_2O$ sequence. The three stage leaching was further repeated but in the sequence $H_2O-HCl-H_2O$. The procedure described for the $H_2O-HCl-H_2O$ and $HCl-H_2O-H_2O$ sequences were further repeated but with 1.2 and 2.4 g of the iron ore to make 40 and 80 g/litre pulps.

The final residue of the two three stages routes that gave the highest percentage dissolution of gangue minerals was taken for X-ray fluorescence analysis and photomicrography under the light transmission microscope.

### 2.2.3. *X-ray fluorescence analysis*

About 0.5 g of the leached sample was pressed to obtain cylindrical pellets by the X-ray fluorescence spectrometer machine model HERZOG PW1606. Then, the pellets was mounted on the sample holder and each sample was irradiated for 20 minutes at a fixed tube operating condition of 25KV and 6MA.afterwards the results were displayed on the desktop computer which was connected to the X-ray fluorescence spectrometer.

## 3. RESULTS AND DISCUSSION

### 3.1. Results

The results of the XRF analyses carried out on the iron ore as-received and as-leached XRF are presented in Table 1, while Fig.1 shows the X-ray diffraction results on the as-received iron ore sample:

*Table 1: Chemical Composition of Itakpe iron ore as-received (ar) and as-leached (al) by X-ray fluorescence analysis*

| Elements | -63 µm Itakpe iron ore (ar) | -63 µm Itakpe iron ore (al) | % Increase/ Decrease |
|---|---|---|---|
| Iron (Fe) | 34.70 | 64.5 | 85.9 |
| Silicon (Si) | 20.10 | 6.70 | -66.7 |
| Aluminium (Al) | 1.65 | 0.40 | -75.8 |
| Titanium (Ti) | 0.10 | 0.06 | -40 |
| Calcium (Ca) | 0.87 | 0.03 | -96.6 |
| Sodium (Na) | 0.39 | 0.04 | -89.7 |
| Magnesium (Mg) | 0.22 | 0.02 | -90.1 |
| Potassium (K) | 0.55 | 0.06 | -89.1 |
| Phosporous (P) | 0.95 | 0.05 | -94.7 |
| Sulphur (S) | 0.03 | Nd | -100 |

### 3.2. Discussion

The results obtained showed that an initial increase in leaching rate of Itakpe iron ore occurred with increasing molar concentrations of hydrochloric acid, the maximum being determined as – at 0.375M. The weight losses obtained might have been due to the dissolution of gangue mineral oxides in the ore. It is known that sodium oxide reacts exothermically with cold water to produce sodium hydroxide solution. As a strong base, sodium oxide also reacts with acids. For example, it reacts with dilute hydrochloric acid to produce sodium chloride solution. Also, magnesium oxide reacts with warm dilute hydrochloric acid to give magnesium chloride solution. Aluminium oxide is amphoteric and thus reacts as both a base and an acid. Aluminium oxide does not dissolve in water. The oxide ions it contains are held too strongly in the solid lattice to react with water (Hughes, 2012).

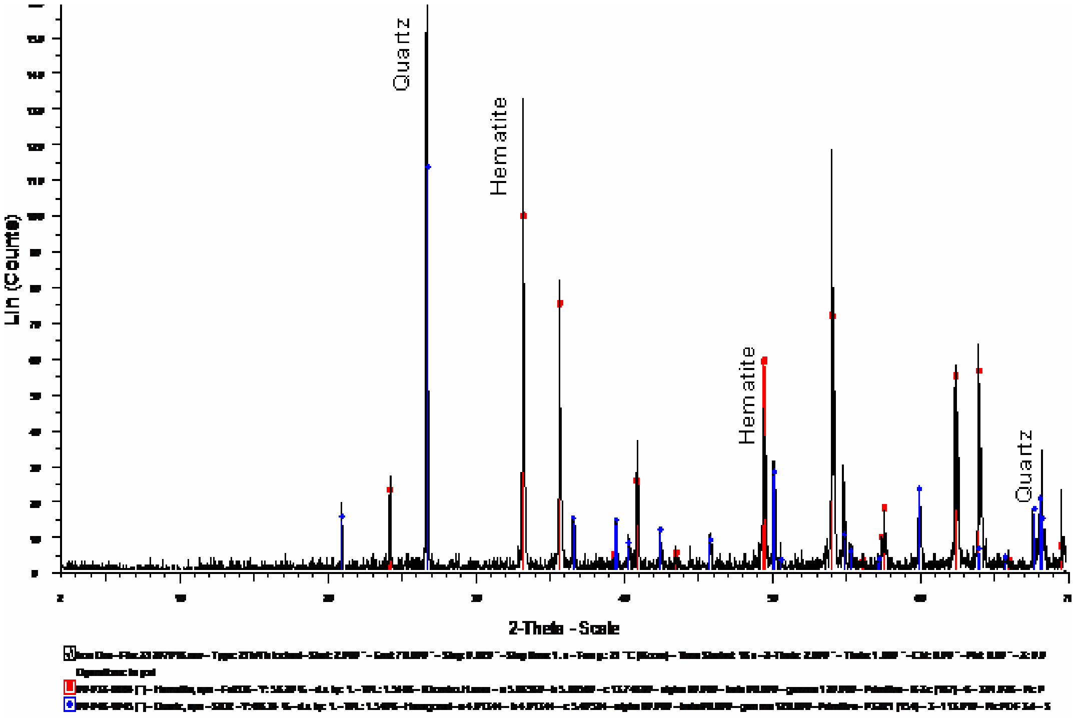

*Fig.1: X-ray diffractogram of the iron ore as-received*

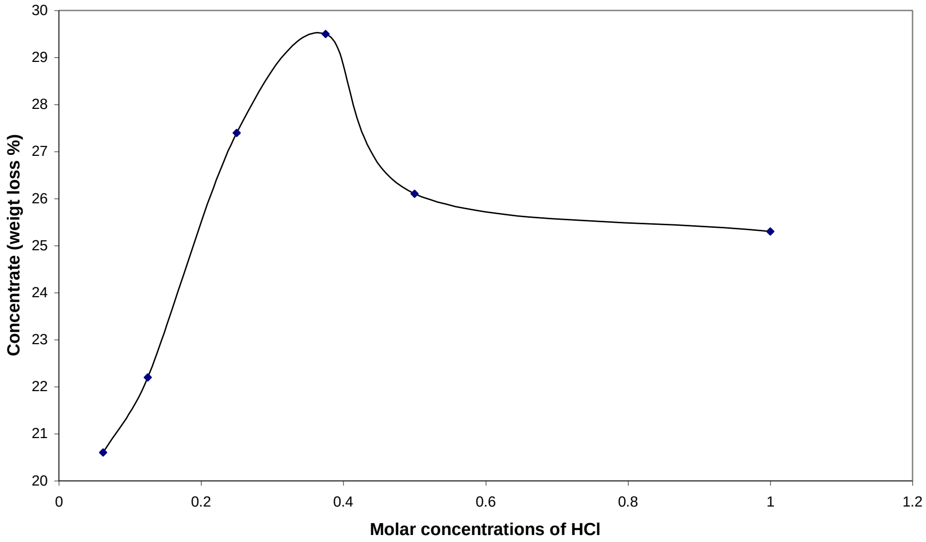

*Fig. 2: Effect of HCI molar concentration on the one stage leaching rate of -63µm Itakpe iron ore sample*

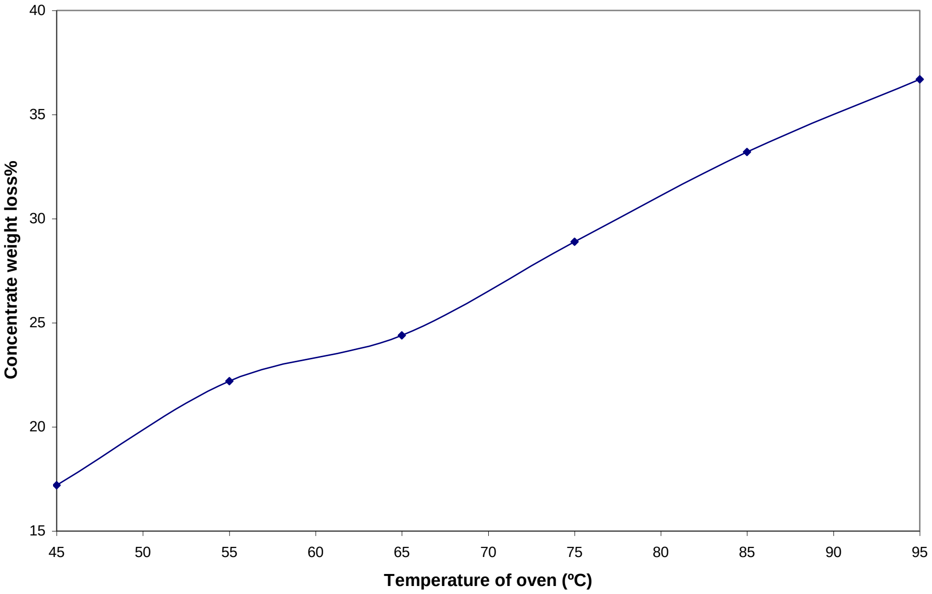

*Fig 3: Effect of temperature on the one stage leaching rate of -63µm Itakpe iron ore sample*

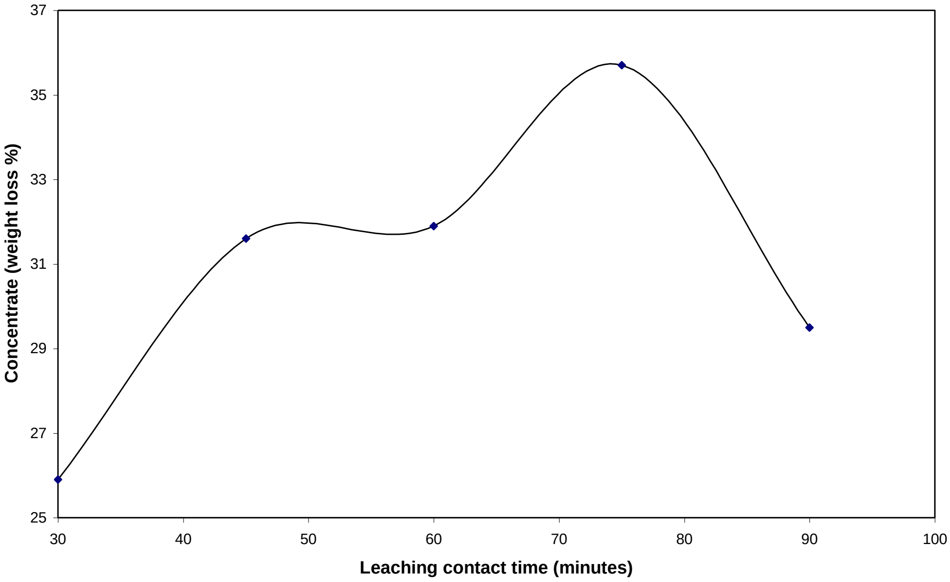

*Fig 4: Effects of contact time on the one stage leaching rate of -63µm Itakpe iron ore sample*

Since alumina contains oxide ions, it reacts with acids in the same way as sodium or magnesium oxide. For example, aluminium oxide reacts with hot dilute hydrochloric acid to produce aluminium chloride solution (Hughes, 2012). Phosphorus (V) oxide reacts violently with water to give a solution containing a mixture of acids. On the other hand, silicon dioxide has no basic properties and so it does not react with acids. Instead, it is very weakly acidic, reacting with strong bases. In addition, silicon dioxide does not react with water, because of the difficulty of breaking up the giant covalent structure. The decrease in leaching rate beyond the 0.375M hydrochloric acid concentration might be due to the precipitation of dissolved oxides at high concentrations of the acid leachant. An average ash oxides increase of +29.38% has been reported in the autoclave alkali leaching of a -75μm Illinois no. 5 coal sample under air/oxygen pressure at 150ºC with 0.2 M sodium carbonate in 1 hour. This result shows that very high concentrations of a leaching reagent may cause an increase in ash gangue content. (Chuang *et al*. 1983). Formation of potassium aluminosilicates has been shown to cause increased ash gangue content of Indian Makun coal on leaching it at 150ºC with potassium hydroxide (Mukherjee and Borthakur, 2003).

The results obtained further showed that the leaching rate of the Itakpe iron ore increased almost linearly with increasing oven temperature (Fig. 3). These results thus indicate that increasing temperature favours the dissolution reactions of the gangue oxides in the ore. The general increase in weight loss % with increasing temperature is due to the fact that at higher temperatures, rates of reactions are faster. Chemical equilibrium is therefore more likely to be closely attained in the entire macro-system than at lower temperatures (Ghosh and Ray, 1982). Also, when the temperature of the leaching reaction was increased, more heat was supplied to the heterogeneous system consisting of particles of the iron ore and the reagents. Since heat is a form of energy, part of the energy supplied caused an increase in the kinetic energy of the reagent molecules and this will increase their collision rates with the iron ore particles. Temperature has been described as being analogous to concentration when applying the Le Chatelier's principle to heat effect on a chemical reaction.

The results obtained also showed that leaching dissolution rate of the gangue oxides in the ore increase linearly with contact time at first and later non-linearly to reach a maximum at 75 minutes. The decrease in leaching rate beyond 75 minutes indicates that precipitations of dissolved gangue oxides might have occurred on prolonged heating of the leached solution. The leaching of calcium hydroxide was reported to be affected by leach contact time (Wang *et al*, 1996).

For the three-stage leaching, weight loss percents of 13.6, 14, 5.2 and 20.1, 4, 2.2 were obtained for the $H_2O$-HCl-$H_2O$ and HCl-$H_2O$-$H_2O$ leaching sequences for the three consecutive stages, giving total weight loss percents of 32.8 and 26.3, respectively;. The results obtained showed that though the first stage acid leaching at 33.3 g/litre produced a higher leaching rate than the first stage water leaching; the subsequent leaching of the product of the latter yielded much higher leaching rates than the product of the former. Leaching at higher pulp densities of 40 and 80 g/litre gave lower weight loss percents of 25.2, 21.3 and 24.6, 17.5 for the $H_2O$-HCl-$H_2O$ and HCl-$H_2O$-$H_2O$ leaching sequences, respectively. The results obtained further confirmed the leaching sequence $H_2O$-HCl-$H_2O$ as better and also showed that the increase in pulp density from 33.3 to 80 g/litre only decreased the weight loss percent by 8.2 in the $H_2O$-HCl-$H_2O$ leaching sequence. The results obtained thus strongly suggest that dilute hydrochloric acid leaching is an economic mean of upgrading the Itakpe iron ore for ironmaking. The analysis conducted on the $H_2O$-HCl-$H_2O$ leaching sequence product at the 33.3% pulp density showed that the iron (Fe) content was increased to 64.5% implying an 85.9% upgrade, while the contents of Si, Al, Ti, Ca, Na, Mg, K and P were reduced by 66.7, 75.8, 40, 96.6, 89.7, 90.1, 89.1 and 94.7, respectively. The content of sulphur in the concentrate could also not be detected, implying an almost 100% sulphur removal from the ore. The increase of the Fe content to 64.5% makes the Itakpe iron ore suitable for the blast furnace ironmaking process (Raw Materials Specification, 1994), while the great reductions in the alumina and alkali oxide contents will improve the efficiency and productivity of the ironmaking process (Loison *et al*, 1989, Malzbender, 2003, Han and Meng, 1987).

## 4. CONCLUSIONS

The -63 μm fraction of Itakpe iron ore that constitutes the highest percentage of the ore has been successfully leached in three stages at atmospheric pressure, 0.375M sulphuric acid concentration and in $H_2O$-HCl-$H_2O$ three-stage leaching sequence to obtain a concentrate assaying 64.5% Fe at 33.3 g/litre pulp density. The quantity of the deleterious alkali oxides and alumina were also greatly reduced making the concentrate obtained suitable for efficient ironmaking by the blast furnace route

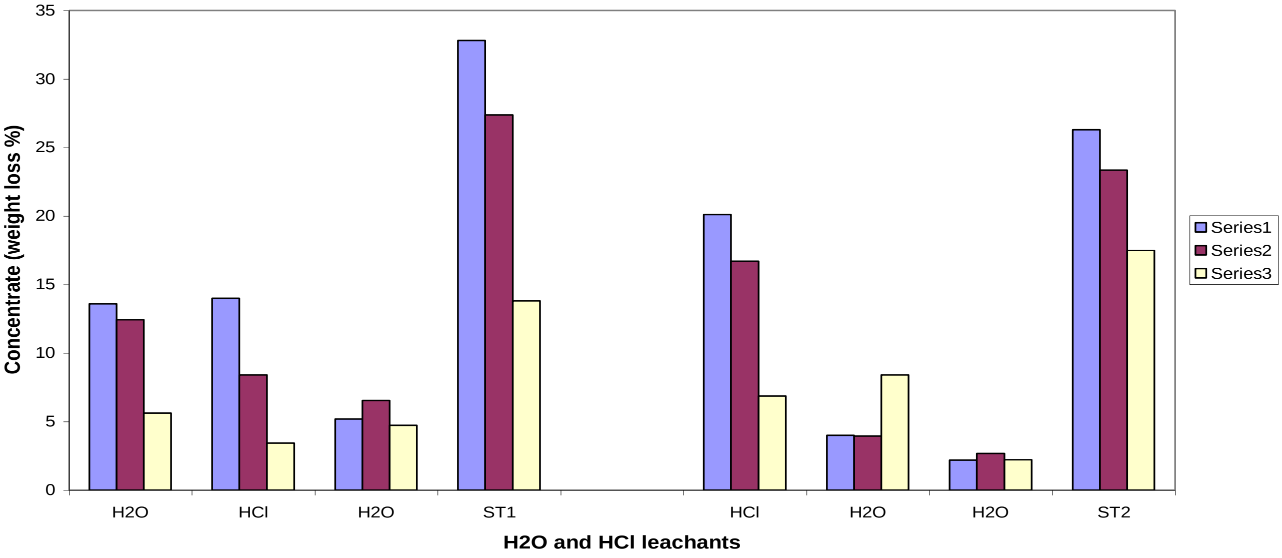

*Fig. 5: Effects of leaching sequences H2O-HCl-H2O and HCl-H2O-H2O and solid-liquid ratios 33.3, 40 and 80 g/l on the three-stage leaching and total weight losses % (ST1 and ST2) for -63 μm Itakpe iron ore*

## REFERENCES

Adeleke, A.A., Development of a process route to upgrade selected coals for iron and steelmaking, Ph,D. Thesis, Department of Materials Science and Engineering, Obafemi Awolowo University, Ile-Ife, Nigeria, 2011.

Adepoju, S.O. and Olaleye, B.M., Gravity concentration of silica sand from Itakpe iron-ore tailings by tabling operation. *Nigerian Journal of Engineering Management* 2(2):51-55, 2001.

Baba, A., Adekola, F.A., and Lawal, A.J., Investigation of Chemical and Microbial Leaching of Iron ore in sulphuric acid. *Journal of Applied Science and Environmental Management*, 11(1):39 – 44, 2007.

Baba, A., Adekola, F.A., Folashade, A.O., Quantitative leaching of a Nigerian iron ore in hydrochloric acid. *Journal of Applied Science and Environmental Management* 9(3):15 – 20, 2005.

Chuang, K.C., Markuszewski, R. and Wheelock, T.D., Desulphurization of coal by oxidation in alkaline solutions. *Fuel Processing Technology*, 7:43-57, 1983.

Ghosh, A. and Ray, H.S., Principles of Extractive Metallurgy. John Wiley & Sons, New York, 1991.

Han, O. and Meng, O., Leaching of pyrite ore in hydrogen peroxide and sulphuric acid. *Hydrometallurgy*, 46:71–83, 1997.

Hughes, P., Oxides and hydroxides. http://www.rod.beavon.clara.net/oxides.htm, 29th February, 2012.

Loison, R., Foch, P, and Boyer, A., Coke quality and Production. Butterworths, 2nd Edition, London, 1989.

Malzbender, J., Comment on hardness definitions. Journal of the European Ceramics Society 23: 1355, 2003.

Mukherjee, S. and Borthakur, P.C., Demineralization of sub-bituminous high sulphur coal using mineral acids. *Fuel Processing Technology* 85(2):157-164, 2004.

Nwoye, C.I., Amara, G.N., and Onyemaobi, O.O. Model for Evaluating Dissolved Iron during Leaching of Iron Oxide Ore in Sulphuric Acid Solution. *International Journal of Natur* [illegible] *Sciences* 4(2):209-211, 2008.

Raw Materials and products specifications. For Federal Government Steel Companies, Nigeria, p. 6, 1994.

Silver, J., Chemistry of iron. Blackie Academic and Professional Inc., New York, 1993.

Umunakwe P.U., Developing a new mine: The Itakpe case, Proceedings of the Annual Conference of Nigeria Mining and Geosciences Society, Jos, Nigeria, 1985.

Wang, J., Zhan-Guo, Z., Kobayashi, Y. and Tomita, A. Chemistry of $Ca(OH)_2$ leaching on mineral matter removal from coal, 1996. (http://pubs.acs.org/doi/abs/10.1021/ef9501307, 22nd September 2010).

Wills, B.A. Mineral Processing Technology. 5th Edition, Pergamon Press, New York, 1992.