

## MULTISTAGE DILUTE ACID LEACHING OF A MEDIUM GRADE IRON ORE TO SUPER-CONCENTRATE

A.A. Adeleke, J.O. Olawale<sup>#</sup>, K.M. Oluwasegun, M.D. Shittu, A.D. Azeez, O. Falana

Obafemi Awolowo University, Department of Materials Science and Engineering,  
Ile-Ife, Nigeria

(Received: October 18, 2013; Accepted: July 7, 2014)

### Abstract

The phosphorous laden Koton Karfe iron ore is a medium grade iron ore deposit in Nigeria that can be upgraded as a super-concentrate for use at the Aladja Steel Midrex plant. The 75  $\mu\text{m}$  size sample fraction of the ore was pre-concentrated with shaking table and leached in the oven at atmospheric pressure with dilute hydrochloric acid in single and multistage leaching sequences of  $\text{H}_2\text{O-HCl-H}_2\text{O}$  and  $\text{HCl-H}_2\text{O-H}_2\text{O}$ . The as-received, as-tabled and as-leached samples were then subjected to X-ray fluorescence and microscopic analyses. The results obtained showed that the  $\text{H}_2\text{O-HCl-H}_2\text{O}$  route produced a higher grade concentrate that assayed 68.54% Fe indicating about 58% upgrade in iron content; while the phosphorus and sulphur contents were reduced by about 77 and 99.6% respectively. In addition, the silicon, manganese, and titanium contents were drastically reduced, while potassium was completely eliminated. The upgrade of iron content in the ore to 68.54% and the drastic reduction in phosphorous and sulphur contents has thus rendered the Koton Karfe iron ore suitable for use as a super concentrate for the Aladja steel plant direct reduction iron making process.

**Key words:** iron ore, pre-concentrate, leaching, multistage leaching, super-concentrate.

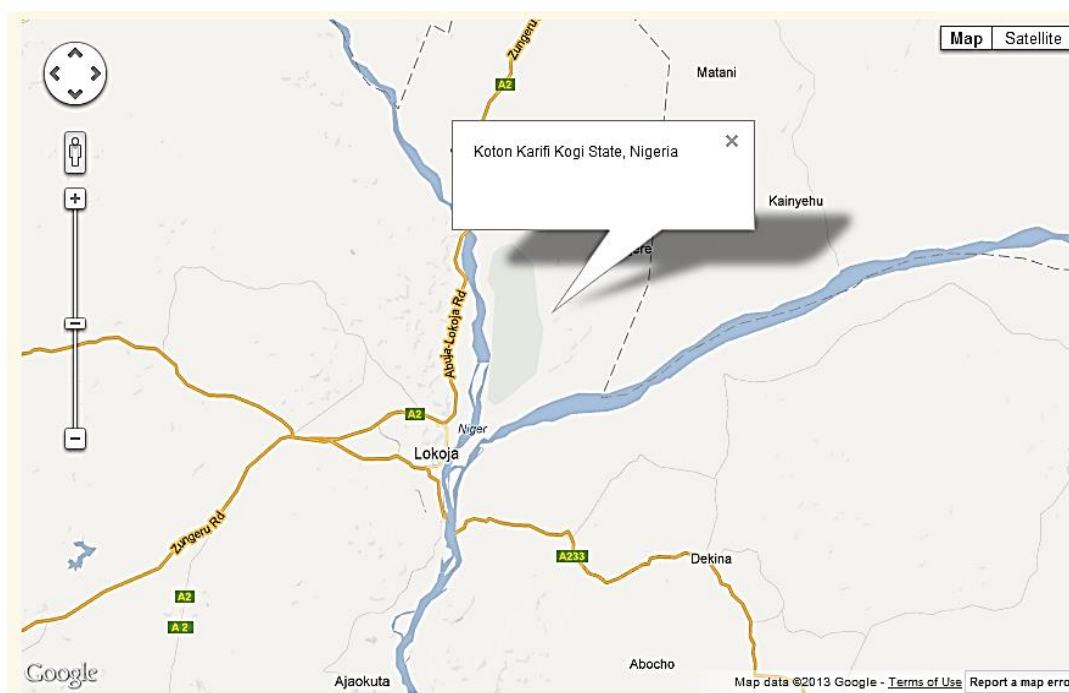
### 1. Introduction

Iron ores are rocks and minerals from which metallic iron can be economically extracted. The ores are usually rich in iron oxides and vary in colour from dark grey, bright yellow, deep purple, to rusty red. The iron itself is usually found in the form of magnetite ( $\text{Fe}_3\text{O}_4$  containing 72% Fe), hematite ( $\text{Fe}_2\text{O}_3$  containing 70% Fe), goethite ( $\text{FeO(OH)}$  containing 62.5% Fe), limonite ( $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) containing variable amount of Fe), Siderite ( $\text{FeCO}_3$  containing 48.3% of Fe), pyrrhotite ( $\text{FeS}$  containing 61.5% of Fe) and pyrite ( $\text{FeS}_2$  containing 46.7% of Fe). Ores carrying very high quantities of hematite or magnetite (greater than 60% iron) are known as natural ore [1].

The estimate of workable iron ore deposits in Nigeria is in excess of 2.5 billion tons most of which belong to hematite, hematite-magnetite, hematite-goethite and siderite-goethite grades [2]. The Nigeria iron deposit and their locations are as presented in Table 1, while the geographical location of the Koton Karfe iron is indicated in Fig. 1.

From this table, it can be seen that Agbaja, Koton Karfe and Bassa Nge deposits have the highest contents of iron. These deposits also account for over 1 billion metric tons reserve of iron ore in Nigeria [2]. However, their high phosphorus, potassium and silicon contents, and fine-grained texture constitute the major problems for their utilization in the blast furnace or direct reduction process [3].

<sup>#</sup>Corresponding author: Amir.khademian@mi.iut.ac.ir



**Figure 1.** Geographic Map of Koton Karfe Area

**Table 1.** Nigerian iron ore deposits and their locations

S/N	Deposit	Location	%Fe
1	Itakpe	Kogi	32-39
2	Oshokoshoko	Kwara	28-38
3	Ajabanoko	Kwara	37-43
4	Muro	Nassarawa	25-38
5	Agbaja	Kogi	43-49
6	Koton Karfe	Kogi	43-49
7	Bassa Nge	Kogi	43-49
8	Akiona	Kwara	41-47
9	Tajimi	Kwara	39-43
10	Rishi	Bauchi	10-19
11	Ayiwawa	Bauchi	6-23
12	Karfa	Borno	34-45
13	Sokoto	Sokoto	27-30

Source: Uwadiale, 1984 [4]

However, the need for constant and stable supply of iron ore super concentrates to the

Aladja Steel Midrex plant necessitates further studies to upgrade these iron ore deposits. Hence, the aim of this research work is to upgrade the Koton Karfe iron ore from these deposits to a super-concentrate through multistage leaching using dilute hydrochloric acid.

## 2. Materials and methods

### 2.1. Material

The sample of Koton Karfe iron ore used for this research was obtained from the National Metallurgical Development Centre, Jos, Nigeria. About 10 kg of the iron ore was selected from the bulk sample sourced at a depth of 4.0 to 5.5 m. The chemical composition of this ore as obtained from X-Ray Fluorescence Spectrometer is presented in Table 2.

**Table 2.** Elemental composition of as-received iron ore

Fe	Si	Mn	Ti	K	Ca	Na	Mg	P	S
43.45	25.85	0.8215	0.261	0.3272	0.6298	0.4092	0.4263	0.0246	0.098

### 2.2. Sample Preparation

The ore was broken into smaller sizes that could be fed into the jaw crusher using a sledge hammer. Crushing was done using the laboratory jaw crusher (BD 1028), roll crusher (168FD39) and cone crusher (HZ24KL) at the National Metallurgical Development Centre, Jos. Representative Sample was obtained through cone and quartering. Thereafter, the sample was air dried for about 48 hours to remove surface moisture in the ore.

### 2.3. Sieve Analysis

The ore was screened in accordance with ASTM E-11 standard procedure. The sieves selected for the test were arranged in a stack, with the coarsest sieve on the top and the finest at the bottom. A tight-fitting pan was placed under the bottom sieve to receive the final undersize and a lid was placed on top of the coarsest sieve to prevent escape of the sample. About 250 g of the sample was weighed and placed in the uppermost coarsest sieve, and the nest was then placed in a sieve shaker which vibrates the material in a vertical plane. After shaking for about 30 minutes, the nest was removed from the shaker and the amount of material retained on each sieve was weighed and recorded as retained size.

### 2.4. Tabling

About 250 g of the iron ore was mixed with water to form slurry. The slurry was charged into the table via the feeding point together with wash water. As the slurry spreads out across the inclined surface of the table the particles were separated on the basis of particle specific gravity, with denser

particles moving along the top of the flowing film to discharge off at the far end as the concentrate, while lighter particles moved down the inclined slope of the table to discharge at the bottom as tailings. The particle separation was assisted by the backward and forward motion (strokes) of the table, the tilt (both longitudinally and laterally), the wash water applied along the length of the table and the riffles.

### 2.5. Leaching

The single stage leaching was carried out with about 1 g of the pre-concentrated samples (subjected to 5 minutes preliminary agitation in a 250 ml beaker and thereafter covered with aluminium foil) at 0.25 and 0.75M HCl in a 2<sup>3</sup> factorial design with temperatures of 30 and 90°C and leaching contact times of 20 and 80 minutes at atmospheric pressure. Further single stage leaching were also conducted at 0.875 and 1M HCl at a temperature of 90°C and leaching contact time of 80 minutes to determine the optimal hydrochloric acid concentration. The leaching was further carried out with water only in a 2<sup>2</sup> factorial design at 30 and 90°C, and 20 and 80 minutes contact times. The oven leached sample was then filtered into a conical flask using the Whatman filter. The residue was collected, oven dried at about 90°C and re-weighed. The difference in weight was noted for determining the fraction of the iron ore that has been dissolved. The solid residue was the product concentrate while the solution contained the dissolved undesirable gangue. The efficiency of HCl dissolution of Fe oxide is ascribed to the formation of ferric chloride as described by the chemical reaction below:



For the multistage leaching, the procedure described in single stage leaching was repeated in three steps but at a temperature of 90°C and 80 minutes contact time. In the first stage, the sample was leached with water, then with 0.875M hydrochloric acid and the final stage water leaching to clean the iron ore in the H<sub>2</sub>O-HCl-H<sub>2</sub>O leaching sequence. The three stage leaching procedure was repeated but in the sequence HCl-H<sub>2</sub>O-H<sub>2</sub>O. The elemental analysis of final residue of the two three stage routes that gave the highest percentage dissolution of gangue minerals was taken from X-ray fluorescence spectrometer and its photomicrography from electron microscope. The elemental analysis and photomicrograph of as-received and tabled concentrate were also taken.

### 2.5. Elemental Analysis

About 0.5 g of as-received, tabled and leached samples was pressed to obtain cylindrical pellets. The pellets were then mounted on the sample holder of the X-ray fluorescence spectrometer machine (Model HERZOG PW 1606) and were irradiated for 20 minutes at a fixed X-ray tube operating condition of 25 KV and 6 Ma. Afterwards the results of elemental composition of ore concentrate in as-received, tabled and leached conditions were displayed on the desktop computer which was connected to the X-ray fluorescence spectrometer.

### 2.6. Photomicrography

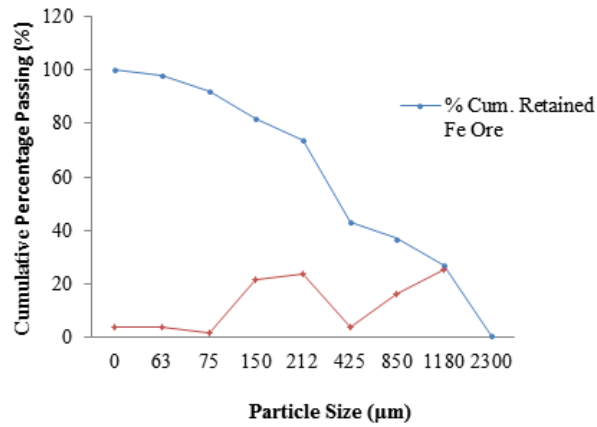
This test was carried-out to determine the liberation size of the iron ore and the concentration of iron content in as-received, tabled and leach sample. The iron ore sample fraction was prepared by mixing araldite (resin) and araldite (hardener) thoroughly

together in equal proportion in a square container. Thereafter, about 0.5 g of the screened iron ore was poured into the mixture that has been prepared and this was mixed together. The whole mixture was then placed on a glass slide having a rectangular shape and then left on a table for about an hour to get hardened. After hardening, a grinding wheel machine Model No. BD112 was used to thin the sample on the glass slide, while the finishing thinning to the appropriate diameter was carried out on a lapping/thinning plate which has been sprayed with silicon carbide. Due to the presence of some percentage of water, the sample was heated on a hotplate for about 5 minutes for drying. After the drying, Canada balsam paste was applied on the sample surface, then, a cover slip was then used to cover the surface for preservation. Thereafter, the slide prepared as described above was viewed with Phillips light transmission microscope Model No. 682.

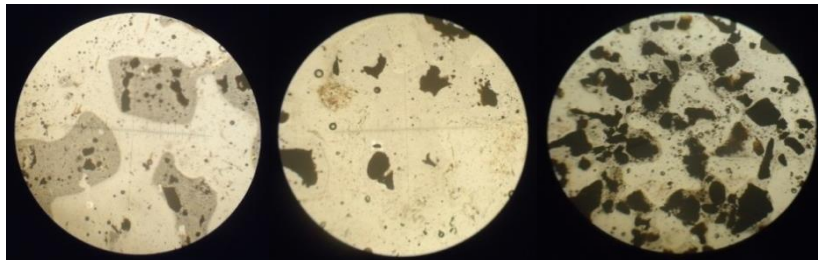
The magnification was set at ×400 for proper viewing and the microscope was adjusted to get the best possible view and afterwards the view was taken using a digital camera.

## 3. Results and discussion

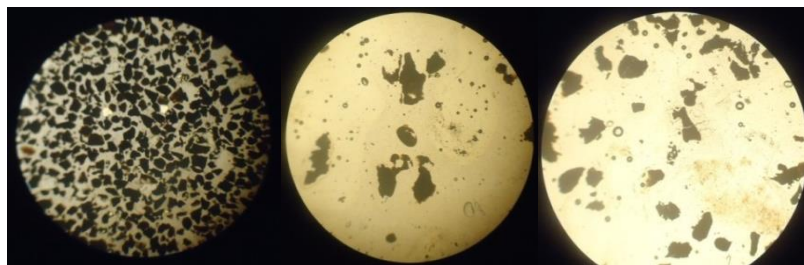
Screen distribution analysis shows that about 99.37% of the ore passed through the largest sieve size (2300 μm sieve) while about 1.96% passed through the entire sieve size (Figure 2). The light transmission micrograph reveals that the iron ore concentration increases as the percentage resultant weight decreases (Figure 3). The concentration of iron ore is the least in 1180 μm sieve size where the percentage resultant weight is the highest (25.53%) and the highest in 75 μm sieve size where it is the least. Hence, the liberation size (the size to which the iron ore can be economically grinded to ensure effective beneficiation) was determined to be 75 μm.



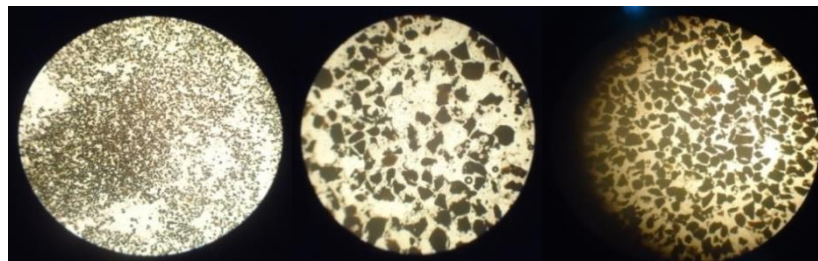
**Figure 2.** Particle size distribution



a) Sample from 2.300 mm sieve size b) Sample from 1.180 mm sieve size c) Sample from 0.850 mm sieve size



d) Sample from 0.425 mm sieve size e) Sample from 0.212 mm sieve size f) Sample from 0.150 mm sieve size



g) Sample from 0.075 mm sieve size h) Sample from 0.063 mm sieve size i) Sample from pan

**Figure 3.** Photomicrograph of iron ore on each sieve size (Mag. ×400)

Table 3 presents the results of single stage leaching which indicated that the weight loss obtained generally increased with increasing molar concentration.

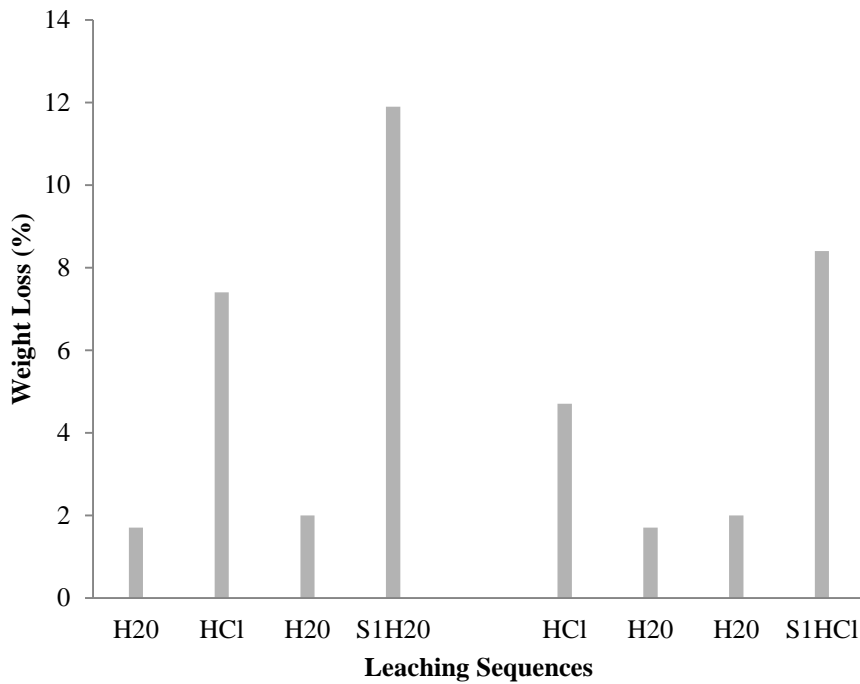
**Table 3.** Result of single stage atmospheric oven leaching

Concentration (M)	Temperature (°C)	Time (min)	Weight loss (%)
0.25	30	20	0.8
0.25	30	80	1.8
0.25	90	20	1.8
0.25	90	80	2.2
0.75	30	20	1.0
0.75	30	80	2.5
0.75	90	20	1.2
0.75	90	80	3.5
0.875	90	80	4.7
1.00	90	80	2.8
H <sub>2</sub> O	30	20	0.6
H <sub>2</sub> O	30	80	1.1
H <sub>2</sub> O	90	20	0.8
H <sub>2</sub> O	90	80	1.8

The results obtained for the 2<sup>3</sup> factorial designed single stage leaching showed that the lowest and highest losses (of 0.8 and 3.5%) occurred at hydrochloric acid molar concentration, leaching temperature, contact time of 0.25M, 90°C, 20 minutes and 0.75M, 90°C, 80 minutes; respectively. Further leaching to determine the optimal molar concentration showed that leaching at 0.875M, 90°C, 80 minutes and 1M, 90°C, 80 minutes produced 4.7 and 2.8% weight losses, respectively. The results obtained for the multistage leaching thus indicate that the weight loss of the iron ore generally increased with increasing molar concentration, temperature and leaching contact time. However, further leaching at higher molar

concentrations showed that the optimal concentration occurred at 0.875M beyond which a decrease in weight loss set in. The decrease in weight loss may be due to the precipitation of some insoluble reaction products. The leaching with water only as a control step at the same temperature and contact time of 90°C and 80 minutes gave a weight loss of only 1.8% indicating that the higher weight loss of 4.7% obtained with 0.75M dilute hydrochloric acid was due to the potency of hydrochloric acid as a leaching reagent.

Figure 4 shows the results of multistage leaching with H<sub>2</sub>O-HCl-H<sub>2</sub>O and HCl-H<sub>2</sub>O-H<sub>2</sub>O sequences. The results obtained showed that the H<sub>2</sub>O-HCl-H<sub>2</sub>O leaching sequence gave the higher weight loss of 11.9% as against the 8.4% for the HCl-H<sub>2</sub>O-H<sub>2</sub>O sequence. This observation agrees with the conclusion of Adeleke et al. (2011; 2013) that the H<sub>2</sub>O-Na<sub>2</sub>CO<sub>3</sub>-H<sub>2</sub>O leaching sequence gave higher ash and sulphur reductions in Lafia-Obi coal than the Na<sub>2</sub>CO<sub>3</sub>-H<sub>2</sub>O-H<sub>2</sub>O leaching sequence [5, 6]. The reason for the higher leaching potency of the H<sub>2</sub>O-HCl-H<sub>2</sub>O sequence may be because in the route the preliminary water washing might have prepared the ore matrix for the subsequent acid leaching, making it more efficient and the last water washing might have helped in dissolving some of the soluble product of the acid leaching. Dilute acid leaching has been shown to be efficient leaching reagents. Alafara et al. (2005) have quantitatively evaluated leaching dissolution of Itakpe iron ore in hydrochloric acid [7]. Adeleke et al. (2012) developed a multistage dilute sulphuric acid leaching process route for upgrading low grade Itakpe iron ore for Ajaokuta Steel Plant [8]. Also, Alafara et al. (2007) applied microbial leaching in sulphuric acid to upgrade Itakpe iron ore for steel making [9].



**Figure 4.** Multistage leaching of KK iron ore in sequences H<sub>2</sub>O-HCl-H<sub>2</sub>O and HCl-H<sub>2</sub>O-H<sub>2</sub>O

**KEY:**

S<sub>1</sub>H<sub>2</sub>O = First stage H<sub>2</sub>O leaching in the H<sub>2</sub>O-HCl-H<sub>2</sub>O sequence

S<sub>1</sub>HCl = First stage dilute HCl leaching in the HCl-H<sub>2</sub>O-H<sub>2</sub>O sequence

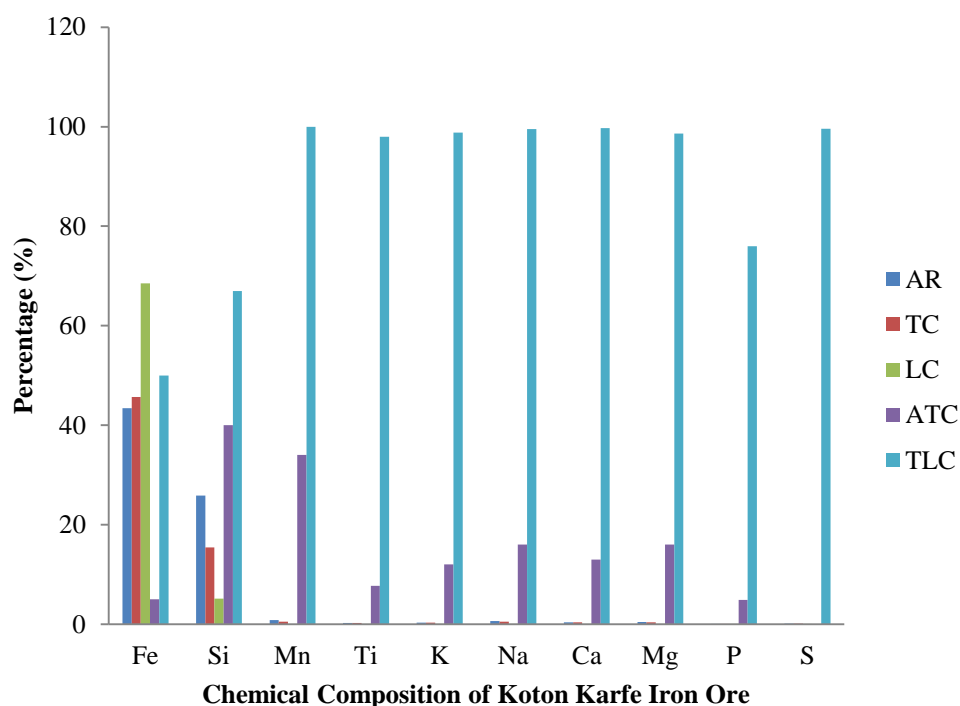
Figure 4 further shows that the first stage dilute HCl leaching in the HCl-H<sub>2</sub>O-H<sub>2</sub>O leaching sequence yielded a higher weight loss than the first stage water leaching in the H<sub>2</sub>O-HCl-H<sub>2</sub>O route that however gave higher weight losses for its last two stages. The results thus showed that the preliminary water treatment with an intermediate acid leaching and a final water washing was more efficient than the first stage acid leaching followed by two stage water cleanings. The results agreed with the observation of Adeleke *et al.* (2012) on the dilute sulphuric acid leaching of Itakpe iron ore [8]. The higher leaching potency of the H<sub>2</sub>O-HCl-H<sub>2</sub>O leaching route may be because the initial water treatment cleaning makes the iron particles more responsive to the leaching reaction.

Figure 5 shows the effects of tabling and leaching on the chemical composition of the Koton Karfe iron ore. The results obtained showed that the tabling separation only increased the Fe content by about 5% but significantly reduced the contents of Si, Mn, Ti, K, Na, Ca, Mg and P by 40, 34, 7.7, 12, 16, 13, 16 and 4.9% respectively (See series ATC of Figure 5). However, shaking tabling has no effect on the S content. On the other hand, dilute hydrochloric acid leaching was found to drastically increase the Fe content of the tabling concentrate by about 50% while it reduces its Si, Mn, Ti, K, Na, Ca, P and S by about 67, 100, 98, 98.8, 99.7, 98.6, 76 and 99.6% respectively (See series TLC of Figure 5). The results obtained thus showed that chemical leaching was far more efficient in



leaching the iron ore than gravity concentration. It was further observed that gravity effect had low effectiveness for the concentration of Fe and S contents. The reduction in sulphur and phosphorous contents is significant as high sulphur and phosphorous contents in iron

and steel causes brittleness. The alkali oxides are also un-desirable in the blast furnace iron making as they causes major blast furnace incidence like frozen hearth that adversely affect iron production [10].



**Figure 5.** Effects of tabling and leaching concentrations on Koton Karfe iron ore

**KEY:**

- AR = Percentage chemical composition of as-received ore
- TC = Percentage chemical composition of tabled concentrate
- LC = Percentage chemical composition of leached concentrate
- ATC = Percentage increase/decrease between AR and TC
- TLC = Percentage increase/decrease between TC and LC

Phosphorous content in steel is required to be low because it decreases ductility and notch impact toughness of steel, particularly in quenched and tempered higher-carbon steels. Phosphorous levels are normally controlled to low levels. It is a deleterious contaminant because it makes steel brittle, even at concentrations as low as 0.6% and it

cannot be easily removed by fluxing or smelting, and so iron ores must generally be low in phosphorus before use. Sulphur also decreases ductility and notch impact toughness especially in the transverse direction. In addition, weldability decreases with increasing sulfur content [11]. Since the phosphorous and sulphur contents are low,



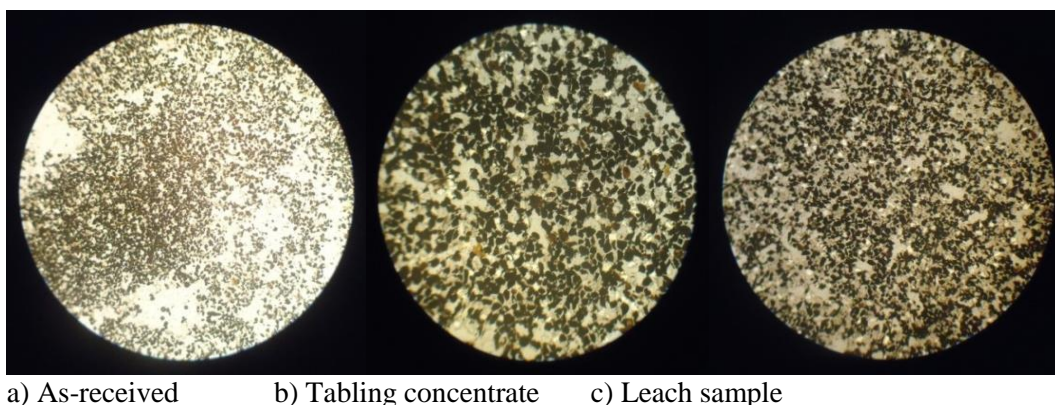
and the pelletizing method to agglomerate ultrafine iron ores has been developed [12] the super concentrate of Koton Karfe iron ore can be used as input in the Midrex iron making.

The elemental analyses of as-received, tabled and leached concentrate are presented in Table 4. The results indicated that Koton Karfe iron ore can be upgraded to super concentrate of 68.5% Fe from 43.5% Fe by combination of shaking tabling and oven dilute hydrochloric atmospheric leaching which gives about 57% recovery of Fe. Figure

6 shows the light transmission micrographs of Koton Karfe iron ore as received, as concentrated after shaking tabling and leaching. The micrographs showed that the iron content of the concentrate was increased after the tabling pre-concentration and acid leaching. The results thus indicate that both tabling and leaching beneficiation successfully upgraded the medium grade iron ore by reducing the associated gangue minerals.

**Table 4.** Percentage elemental composition of iron ore

Ore Concentrate	Fe	Si	Mn	Ti	K	Ca	Na	Mg	P	S
As-Received	43.45	25.85	0.8215	0.261	0.3272	0.6298	0.4092	0.4263	0.0246	0.0980
As-Tabled	45.66	15.43	0.5438	0.242	0.2875	0.5290	0.3542	0.3562	0.0234	0.0980
As-Leached	68.54	5.14	0.0000	0.004	0.0035	0.0024	0.0011	0.0050	0.0056	0.0004



**Figure 6.** Photomicrograph of 75 $\mu$ m sieve size (Mag.  $\times$ 400)

#### 4. Conclusion

The Koton Karfe iron ore has been successfully upgraded to a super-concentrate from an initial iron concentration of about 43.5 to 45.7 and 68.5% by shaking tabling and oven dilute hydrochloric atmospheric leaching indicating 5.1 and 49.9% upgrades, respectively. Furthermore, the contents of alkali elements sodium and potassium and phosphorus/sulphur that are deleterious in iron

making were drastically reduced rendering the iron ore more suitable for both blast furnace and Midrex direct iron making processes. In addition, silica, the highest mineral gangue present was reduced from 25.8% to about 5.5% translating to about 80% reduction. The availability of a pelletizing method for agglomerating ultrafine iron ores makes the product of this work a possible input in the Midrex iron making.

## 5. References

- [1] Lee Tan Yaa Chi-Lung, (1970) Abundance of the chemical elements in the earth's crust. *Int. Geology Rev.*, 12, 778.
- [2] Journal of National iron ore Mining Company Limited, (2001) Itakpe, Nigeria, 3-9.
- [3] Yusfin, Y.S., Chernousov, P.I., Garten, V., Karpov, Y.A., Petelin, A.L. (1999) The role of alkali's and conserving resources in blast-furnace smelting. *Metallurgist*, 43, 54-58.
- [4] Uwadiale, O.O. Beneficiation studies of Agbaja iron ore, (1984), PhD Thesis, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, Scotland.
- [5] Adeleke, A.A., Ibitoye, S.A., Afonja, A.A. (2013) Multistage caustic leaching de-sulphurization of a high sulphur coal. *Petroleum and Coal*, 55 (2), 113-118.
- [6] Adeleke, A.A., Ibitoye, S.A., Afonja, A.A., Chagga, M.M. (2011) Multistage caustic leaching de-ashing of Nigerian Lafia-Obi coal. *Petroleum and Coal*, 53 (4), 259-265.
- [7] Alafara, A.B., Adekola, F.A., Folashade, A.O. (2005) Quantitative leaching of a Nigerian iron ore in hydrochloric acid. *Journal of Applied Science and Environmental Management*, 9 (3) 15-20.
- [8] Lee Tan Yaa Chi-Lung, (1970) Abundance of the chemical elements in the earth's crust. *Int. Geology Rev.*, 12, 778.
- [9] Adeleke, A.A., Ibitoye, S.A., Enajero, M.O., Popoola, A.P.I. (2012) Multi-stage dilute acid leaching of a low grade iron ore. *Journal of Engineering Research*, 17 (4), 15-21.
- [10] Alafara, A.B., Adekola, F.A., Lawal, A.J. (2007) Investigation of chemical leaching of iron ore in sulphuric acid. *Journal of Applied Science and Environmental Management*, 11 (1), 39-44.
- [11] Poos, A. (1992) Future requirements for blast furnace coke quality. *Cokemaking International*, 4, 29-30.
- [12] Mitra, S.K. (2013), Iron ore testing and analysis ([www.mitras.com/ironore-testing-analysis.html](http://www.mitras.com/ironore-testing-analysis.html)). Accessed: 16<sup>th</sup> September, 2013)
- [13] Kumar, S., Srinivasan, T.M. (2013), Sintering and pelletisation of Indian iron ores ([www.iim-delhi.com/.../04 Sintering Pelletising Indian Iron Ore\\_FerroGreen....](http://www.iim-delhi.com/.../04 Sintering Pelletising Indian Iron Ore_FerroGreen....)). Accessed: 16<sup>th</sup> September, 2013)