



REDUCIBILITY STUDIES ON PELLETS PRODUCED FROM NIGERIAN IRON ORES

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ABSTRACT

The reducibility studies on the produced pellets from Itakpe and Agbaja iron ore blends were carried out. The chemical, morphology and structural analysis of the ores were examined using Thermogravimetry (TG), Differential Thermal Analyzer (DTA), X-Ray Fluorescence (XRF) X-Ray Diffraction (XRD), Optical and Electron Microscopy showing the microstructure of the pellets and Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS). The reducibility studies were performed using a muffle furnace. The produced pellets were taken inside stainless steel containers with diameter 60.75 mm x 59.40 mm inside diameter with mouths tightly closed by an air tight cover having an outlet for exit gas, The SEM and EDS tests were performed to study the morphology of the pellets. The reduced pellets at 800°C for 120mins gave an iron(Fe) value of 4.5 wt%, at 920°C for 120mins, iron content(Fe) value obtained was 84.5wt% and at 1000°C and 120mins the iron (Fe) content value was 6.4wt% while the selected samples of the pellets from Agbaja iron ore at the same temperatures were 800°C for 120mins, the iron(Fe) content was 40.7wt%, at 920°C for 120mins, the iron (Fe) content value was 60.2wt% and at 1000°C for 120 mins the iron (Fe) content was 56.2wt%. The Itakpe pellets exhibited better reducibility than the Agbaja pellets when subjected to the same conditions.

Key words: Iron ores, Morphology, Pellets, Reducibility and Studies

1.0 INTRODUCTION

Nigeria is a country endowed with many natural resources. Some of these mineral resources are useful in steel development and production. Such a resource is the iron ore where the deposit was discovered as far back as 1904[1]. Since this discovery; several iron ore deposits have been found in Nigeria. The deposits are hematite, magnetite, goethite or siderite – goethite grades. The reserve is estimated at over 3 billion metric tonnes and their utilization in iron and steel plants will reduce the cost of importation thereby saving foreign exchange[1].

Reducibility: Reducibility relates to the rate of conversion of iron oxides to metals

by treatment with a reductant. A measure of reducibility is represented by weight loss of an ore sample per time unit caused by transition of oxygen in the oxides into gas. The weight loss is due to the change of the oxygen in the solid oxides to gaseous oxygen.

$$R_1 = \frac{A_0}{\Sigma_0} \times 100 (\%)$$

Where R_1 - degree of (indirect) gas reduction

Σ_0 - Total mass of oxygen bound to iron [g]

A_0 - Difference in mass of oxygen in ore during gas reduction [g]

Influence of reducibility on the blast furnace operation is highly important for the determination of fuel consumption and selection of proper lumpiness. The reducibility changes in particular by hot treatment (sintering). The reducibility tests include several procedures used to evaluate the behaviour of natural and processed iron ores and the agglomeration of such pellets under specific conditions. On the other hand, Iron ore is upgraded to a higher iron ore content through beneficiation. The produced iron ore filter cakes are pelletized for steel making processes. Subsequently, they are used, instead of disposing them from beneficiated or run off mine iron fines. The processing of high-grade iron ores does not require beneficiation as the iron ores are ground to very fine level and mixed with limestone or dolomite as a fluxing agent and bentonite or organic binders as a binding agent. Coke or anthracite coal is added to the mix if the ores are hematite, as these serve as internal fuel for firing the pellets.

2.0 MATERIALS AND EXPERIMENTAL PROCEDURE

2.1 Materials and Equipment

The topography of the region is a plateau rising gently to the north – east of Okene in the eastern part of Kogi State, down to the river Niger. The plateau is bestrewn with scattered hills made of Precambrian gneisses and granites that overlook the surrounding by about 200m to 300m [1]. The Itakpe iron ore deposits are part of these hills. Its estimated reserve is over 300 million tonnes while its proven reserve is 200 million tonnes [1]. The iron ore content of the deposit is 36%. The ores are beneficiated at the rate of 8 million tonnes per year to produce 64% Fe concentrate as sinter materials. The beneficiated ores are for usage at the Ajaokuta Steel Company Limited Blast furnace and 60% Fe concentrate as pellet feed for the Direct Reduction Plant (DRP)

at the Delta Steel Company Limited, Aladja, and Delta State. The iron ores are suitable as feedstock to one of the Direct Reduction Methods of iron making in Nigeria. The ores are typical of those formed by magnetic segregation. This iron ore deposit is the most elaborately investigated ferrous deposit in Nigeria, developed for the utilization in the Blast furnace. The picture below shows the sample of the Itakpe iron ore sourced at the National Iron Ore Mining Company (NIOMCO) Itakpe, Kogi State, Nigeria. The specimen is a compacted, crystalline – like, banded iron ore which has various colours like dark grey, brown and black. The Itakpe iron ore is slightly magnetic in nature.



Figure 1: Itakpe Iron Ore (Source: NIOMCO)

The Agbaja Iron ore is an acidic pisolitic/oolitic ore consisting of goethite, magnetite and major amounts of aluminous and siliceous materials [2]. It cannot be used directly in the Blast furnace processes or other reduction processes without further treatment e.g. pelletization or briquetting. The ore is a lean ore with sedimentary origin [2]. It is necessary to work upon the ores in order to add economic value to our national economy. The ore is also known to be oolitic in nature, limonite that occurs in mammillated or stalactite forms having fibrous structure resembling hematite [2]. It is made of brown compacted fine-grained materials that consist of large particles, which show the tendency to be friable. It is strongly magnetic [3]. The ore particles are generally crushed for specific experimental procedures [4]. The picture below shows the iron ore sample sourced

at the Agbaja Plateau in Kogi State [4].The XRD tests were carried out on both samples; these results are indicated in Figures 3 and 4 and Tables 1 and 2 respectively.



Figure 2: Agbaja Iron Ore (Source: NMDC)

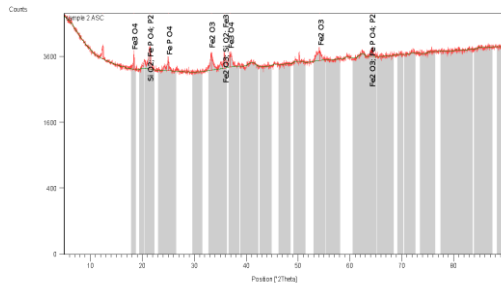


Figure 3: X-ray Diffraction on Itakpe Iron ore

Table 1: Identified Patterns List: Itakpe Iron Ore

Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	85-0599	50	Hematite	0	0.692	Fe ₂ O ₃
*	76-0931	49	Silicon Oxide	0	0.929	SiO ₂
*	74-1910	31	Magnetite	0	0.405	Fe ₃ O ₄
*	31-0647	22	Iron Phosphate	0	0.147	Fe P O ₄
*	23-1301	12	Phosphorus Oxide	0	0.138	P ₂ O ₅

Source from the XRD Analysis

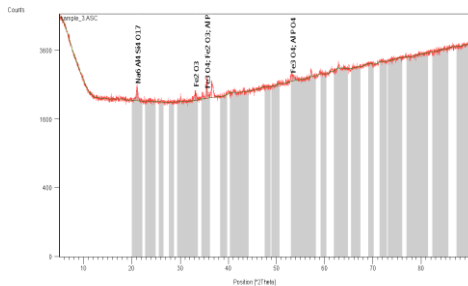


Figure 4: X-ray Diffraction on Agbaja Iron ore

Table 2: Identified Patterns List: Agbaja Iron Ore

Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	03-0863	40	Magnetite	0	0.57	Fe ₃ O ₄
*	76-2385	35	Sodium Aluminum Silicate	0	0.354	Na ₄ Al ₄ Si ₄ O ₁₇
*	86-0550	28	Hematite, syn	0	0.129	Fe ₂ O ₃
*	48-0652	9	Aluminum Phosphate	0	0.099	Al P O ₄

Source from the XRD Analysis

2.1.1 Metallurgical Coking Coal from Ajaokuta Steel Company Limited

The coals used for these experiments were randomly selected from among the imported Metallurgical coking coal at the Ajaokuta Steel Company Limited. The vendor that supplied the coals did analysis of the coal before delivering them to the steel company. The chemical compositions of the coal are shown in the table 3. figure 5 shows the coal originally with very dark colour, while the colour of the coal used for the reducibility tests turns to ash or grey as shown in figure 6. The coals were used as the reductants during the reducibility tests. They were crushed to sizes and used to surround the pellets in stainless cups. Thereafter they were subjected to tests in line with the design of the research work.

Table 3: Chemical Analysis of Metallurgical Coking Coal

S/No	Chemical Composition	Percentage (%)
1	Fixed Carbon	85
2	Volatile Matter	2.95
3	Ash Content	9.5
4	Moisture	2
5	Sulphur	0.5
6	Phosphorus	0.05

Source: Ajaokuta Steel Company Limited, Ajaokuta



Figure 5: The Metallurgical coking Coal before it was used as reducing agent



Figure 6: The Metallurgical Coking Coal after being used as reducing agent

2.2 Methods:

The materials used for the work include Itakpe and Agbaja Iron Ore, and Metallurgical coking coal, from the Ajaokuta Steel Co., Ltd. The equipment includes a Ball milling machine, pelletizing Machine, Electronic Digital Weighing Balance, Muffle furnace, Laboratory Drying Oven, Inverted Microscope, X-ray Diffractometer (XRD), XRF Analyzer, Thermogravimetric Analyzer (TGA), DTA, Optical and Electron Microscopes, Scanning Electron Microscope/ Energy, Dispersive Spectrometer (SEM/EDS).

The chemical compositions of the ores were determined using X-Ray Diffraction (XRD) methods. The produced pellets were used for these experiments, while a metallurgical coking coal obtained from the Ajaokuta Steel Company Limited was used as reductant. The collected iron ores lumps were crushed to 15-20 mm sizes. The Metallurgical coking coal was crushed to -5+ 15 size. The vendor that supplied them to the company determined the chemical compositions of the Metallurgical Coking coal. The pellets were put inside stainless steel containers (size: 60.75mm height \times 59.40mm inside diameter) with mouths tightly closed by an airtight cover having an outlet for exit gas. The pellets were surrounded with coking coal that served as a reducing agent in the experiments at various periods and time [5]. The experimental procedures were strictly followed. The muffle furnace was used to heat up sample pellets to the

required temperatures of 800°C, 840°C, 860°C, 880°C, 920°C, 960°C and 1000°C, at 8°C per minutes rate. The samples were all allowed to soak at various temperatures by varying the soaking period in the range of 20 - 120minutes. The degrees of reduction (%) at the stipulated temperatures were determined. Each of the containers was properly labelled for specific experiments. The samples were brought out from the muffle furnace at designated intervals of 20 minutes. The containers containing the samples that were brought out from the muffle furnace were all allowed to cool to room temperature (in normal air atmosphere) and thereafter the weight losses of the pellets were determined and recorded.

15 kg of both materials were charged at different times into a ball-milling machine made by BicoSprecher and Schn (2287) Industrial control, United State of America. One Thousand six hundred balls of varying diameters ranging from 15 mm to 40 mm were charged into the ball mill (15 mm balls – 320 pieces, 20mm balls-320 pieces, 25mm balls-320 pieces, 30 mm balls -320 pieces and 40mm-320 pieces) [5].

The samples were milled for six (6) hours after which they were discharged and sieved using 0.63mm sieve size. The oversize materials were recycled until they all passed through the 0.63mm sieve. At this point, the samples prepared were worked upon. The two ores of 15 kg each were pulverized to – 0.63 mm sieve size, 15kg blended Iron ore was weighed with Itakpe iron ore in the blend- 1425g. (95%) and Agbaja iron ore in the blend-75g.(5%) were weighed using Salter Digital weighing balance with trade mark – Mettler Pm 2000. The weighed samples were charged into a clean and moisture-free Erich 2287 Pelletizing disc machine of 35cm diameter wide pelletizing disc. 4% lime was also added, while the Machine rotated at the speed of 25 rpm.

The samples were properly mixed after which 1000 mls of water by volume was measured and added to the iron ore mix in the rotating pelletizing disc which worked gradually; while the charge was scraped on a continuous basis to avoid sticking to the disc. As the experiment progressed, pellets of varying diameters ranging from 10mm to 20mm were formed. Rotation of the Pelletizing disc continued at a reduced speed of 15rpm after satisfactory formation of pellets, and this further added desired strength to the pellets formed.

3.0 RESULTS AND DISCUSSION

3.1 Structure Analysis

The ore samples collected were crushed, ground and pulverized. The samples were formed into pellets of various sizes. The samples were then air dried before they were subjected to the reducibility processes.

3.1.1 Microscopic Examination

The Inverted Metallurgical Microscope was used to examine the pellets as shown in figure 7. Some important distinct phases may be identified in the Itakpe ore by optical microscopy. These structures and features were observed with the inverted Metallurgical Microscope. The micrographs of the Agbaja iron ore have some characteristic texture, suggesting that it has a pisolitic structure on the surface as indicated in figure 8. The iron ore shows a concentrated material in the pisolite nature while the matrix present consists of major impurities.

3.1.2 SEM/EDS Analysis Results: Scanning Electron Microscope (SEM) of Itakpe Iron Ore

Examination by Scanning Electron Microscopy (SEM) /Energy-Dispersive Spectroscopy (EDS) shows that there are grey phases was quartz, the white phase hematite, and the mottled areas intergrowths of hematite and magnetite.

Figure 9 shows the three-spectrum locations taken in order to determine the concentration of ore. The locations of the spectrum are 57 38 and 39 at 10 μ m. Figure 9c shows the EDS spectrum 39 where the concentration of the elements as distributed with weight (%) concentration ranging from Fe, O Al, Si and C and also with their corresponding density values. Examination by Scanning Electron Microscopy (SEM)/Energy-Dispersive JSpectroscopy (EDS) shows fine and whitish structures.

Figure 10a shows the Scanning Electron Micrograph SEM of the Agbaja Iron ore at 100 μ m

Figure 10b shows the three-spectrum locations that were taken in order to determine the concentration of ore at the electron image of the spectrum location 36 at 10 μ m of the Agbaja Iron Ore:

Figure 10c shows spectrum 39 where the concentration of the elements was distributed with weight (%) concentration ranging from O, Fe, C, Al, Si and P and also with their corresponding intensity values.

Figure 10d is the Energy-Dispersive Spectroscopy analysis (EDS) of Agbaja Iron Ore.

3.2 Thermogravimetric Analysis (T.G.A)

Results

3.2.1 The Thermogravimetric Analysis (TGA) of Itakpe Iron Ore

The line with blue colour runs on 30°C and moves upwards until it got to the peak value of Deriv. weight (%C) of 0.0048. This value dropped and then rose until it achieved a stable value and then finally attained a value of 0.0007at the Dervi weight (%C). On the other hand the line with light green colour indicates weight (%) versus temperature. The weight (%) started from 100 and continued to decline until it got to 1000°C with corresponding value at 99.2. Figure 11(a) shows the trends in the thermal decomposition of the Itakpe iron ore.

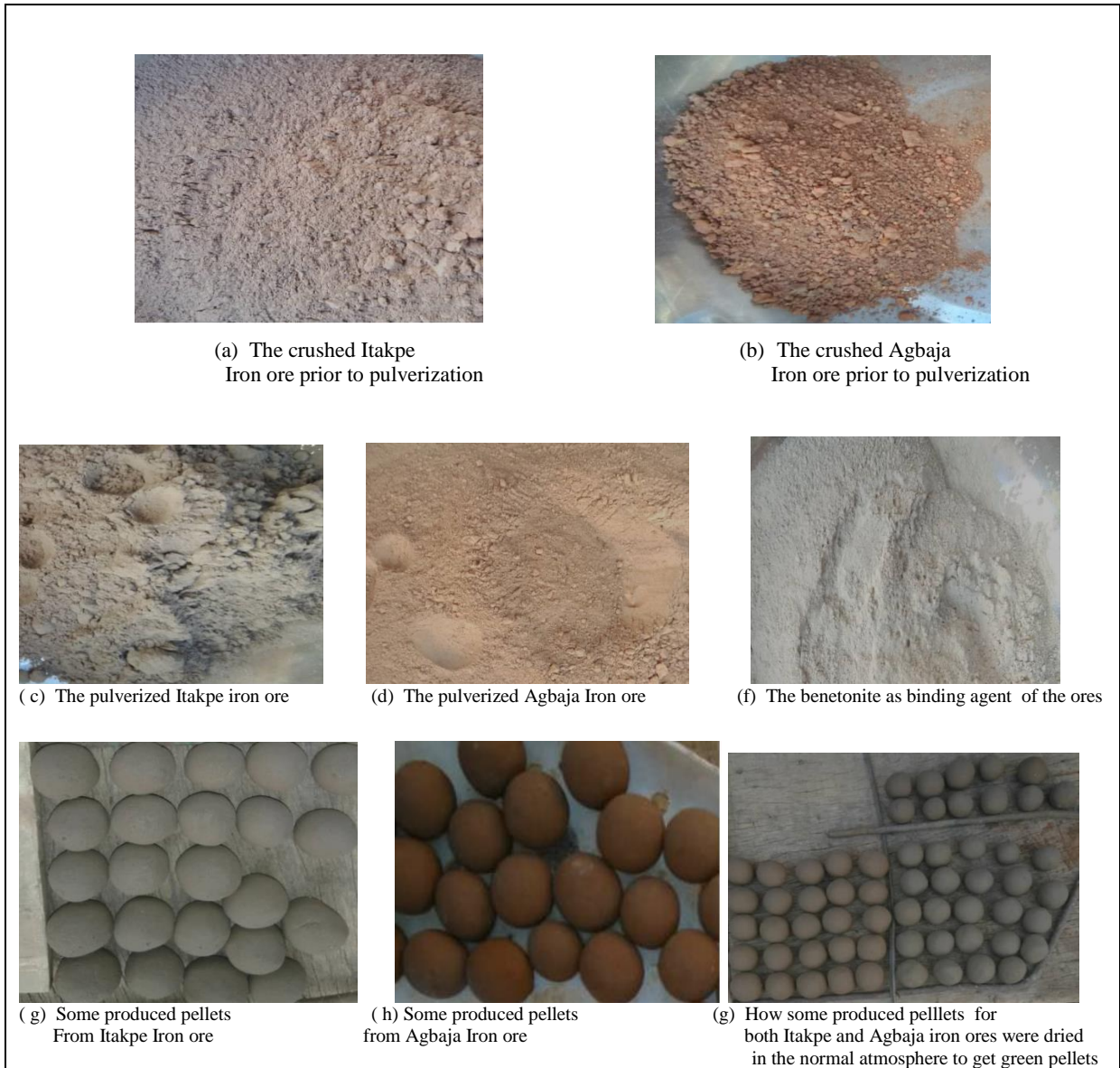


Figure 7: (a-g) The crushed ore samples, pulverized and produced pellets that were dried at the normal atmospheric temperature before the reducibility tests were performed.

3.2.2 Thermogravimetric Analysis (TGA) of Agbaja Iron Ore

The line blue colour ran on 30°C, got to 200°C and moved upwards until it got to the peak value of Deriv.weight (%C) at 0.13 with corresponding temperature value at 300°C. This value declined and continued to decline, and then dovetailed at 0.00 Derive weight (%C). The light green line started from 100 weight (%) and continued to decline and dovetailed at 88.2 (weight%) with corresponding value at 1000°C. Figure 11(b) shows the trend of

the thermal decomposition of the Agbaja iron ore.

3.3.1 Results from Reducibility Studies

In this study, reducibility behaviour of pellets produced were made into various sizes and were fired in muffle furnaces. The reducibility experiments were performed using the metallurgical coking coal obtained from the Ajaokuta Steel Company Limited, Ajaokuta, in Kogi State as reductant. The pellets were subjected to a heating rate of 8°C min⁻¹ for all the experiments.

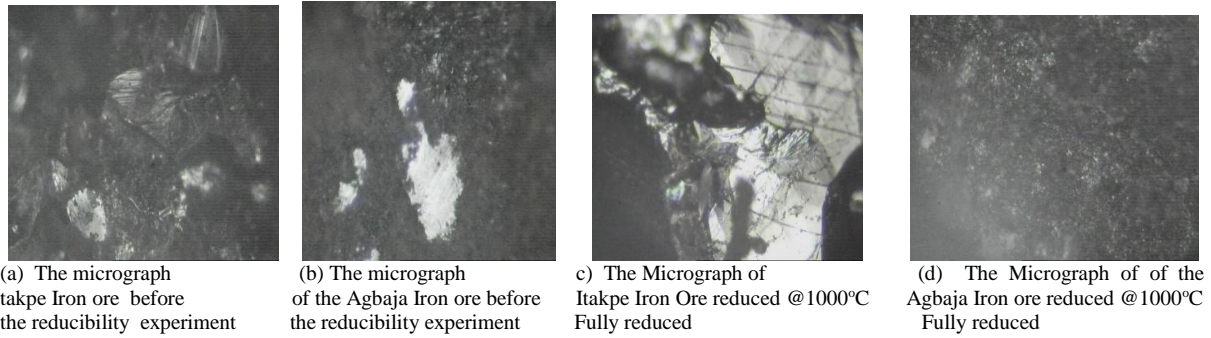


Figure 8 (a, b, c, d): Micrographs of the Ores

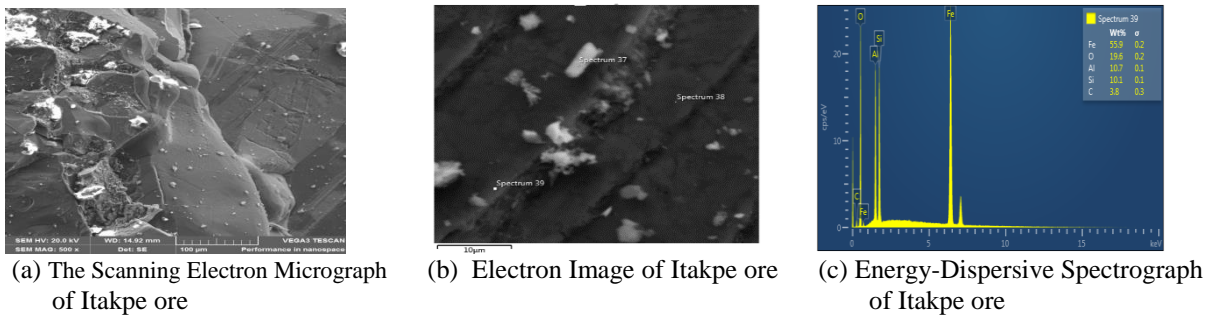


Figure 9 (a, b, c) SEM and EDS of Itakpe Iron Ore (Particles size 100 μm)

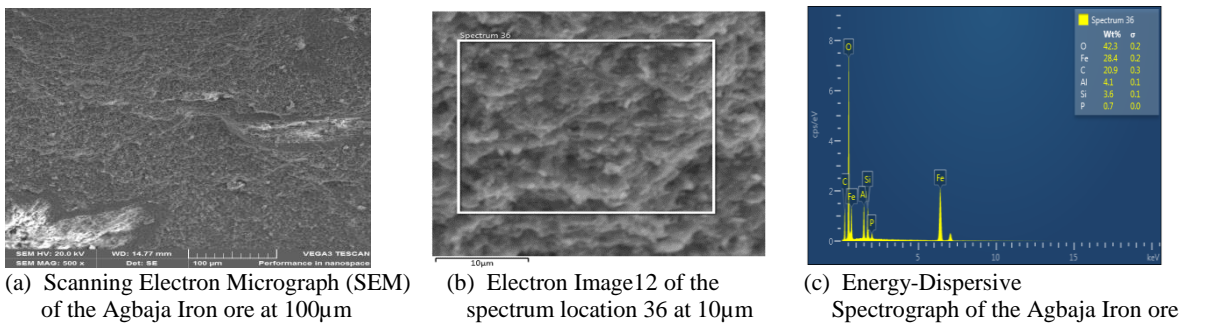


Figure 10 (a,b,c) SEM and EDS of Agbaja Iron Ore

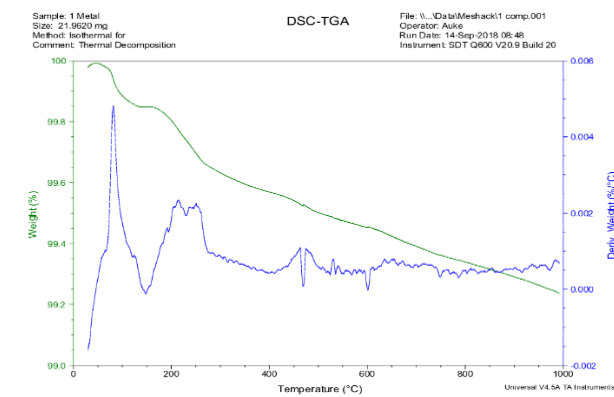


Figure 11(a): Thermogravimetry Analysis (TGA) on Itakpe Iron ore

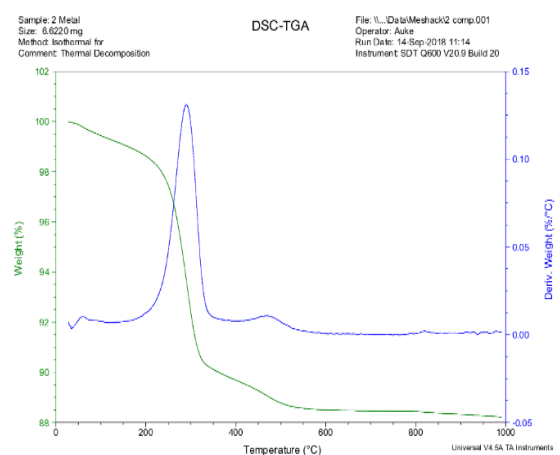


Figure.11(b) Thermogravimetry Analysis (TGA) on Agbaja Iron ore



Figure 12 (a – k): Images showing the reducibility of both pellets at temperature from 800°C -1000°C for 120mins

The samples were heated up to various temperatures, ranging from 800°C - 1000°C, and were allowed to soak for periods, ranging from 20min to 120mins. The corresponding values of % reduction were collected and recorded. The obtained values were used to plot graphs of furnace holding time against the degree of reduction (%) at various temperatures between 800°C – 1000°C.

3.3.2 Effect of Time on Degree of Reduction

The results obtained in this work show that the heating rate has a significant effect on the reduction behaviour of the pellets. All the fired iron ore pellets showed high degrees of reduction (%). It was also

observed that all the fired pellets were almost completely reduced (more than 90% reduction) in about 120 minutes. This indicates that the utilization of these pellets in sponge iron making is likely to allow usage in the Blast Furnace and for Direct Reduced Iron.

The values of reducibility obtained in this work suggests that there will be energy savings and extended lifespan of the furnaces. The high degree of reduction in the first 40 minutes is mainly associated with the release of volatiles from the metallurgical coking coal used due to their reformation into H₂, CO, etc. These reducing gases participate in the reduction of iron oxide (i.e. an appreciable presence of H₂ and CO in the reduction chamber gives a boost to the reduction rate).

The decrease in reduction rate with increasing time above 60 minutes is undoubtedly due to the combined effects of an increase in metallic product layer thickness and diminished evolution of volatile matter from the coal. An increase in the thickness of the product iron layer offers great resistance to the diffusion of carbon and reducing gas to the surface of unreduced iron oxide.

3.3.3 Effect of Heating Mode on Degree of Reduction (% Reduction).

In this research work the effect of heating mode on the samples was studied with a view to determining its effects on the degree of reduction (%) in the pellets. The fired pellets were reduced using metallurgical coking coal with temperature range between 800°C - 1000°C (the soaking times varied from 20mins - 120mins at an interval of 20mins). These experiments were performed under rapid and slow heating conditions using a muffle furnace.

The results show that in comparison to rapid heating, the slow heating to reduction temperature gives appreciably higher degree of reduction. It is likely that rapid heating from 920°C to 1000°C causes a higher rate of volatile matter escaping from the metallurgical coking coal, thereby providing less time for H₂ and CO (reducing gases) to make contact with the pellets.

The results of this work indicate that there was lower degree of reduction during rapid heating of the iron ore lumps than during lower heating operation when the volatile matters were released from coal at a slower rate. The more deposition of highly reactive pyrolytic carbon, and increased time of contact of carbon and reducing gases (H₂ and CO) with the pellets appear to be the obvious reasons for the higher degree of reduction (%). Heating of hematite pellets from room temperature to the required reduction temperature (1000°C) in a reducing atmosphere, to some extent, was also responsible for the higher degree of reduction (%) under slow heating condition.

3.3.4 Electron Image and Energy Dispersive Spectrographs (EDS) after Reducibility Tests

Figure 13 (a, c, e, g, i, k, m, o, q, s, u, w) show the SEM while Figure 13 (b, d, f, h, j, n, p, s, t, v, x) show the EDS of the samples for both Itakpe and Agbaja iron ore and produced pellets respectively. The figures show various concentration distributions in wt.%. The samples were subjected to temperatures of 800°C, 920°C and 1000°C and time duration of 120 mins was maintained.

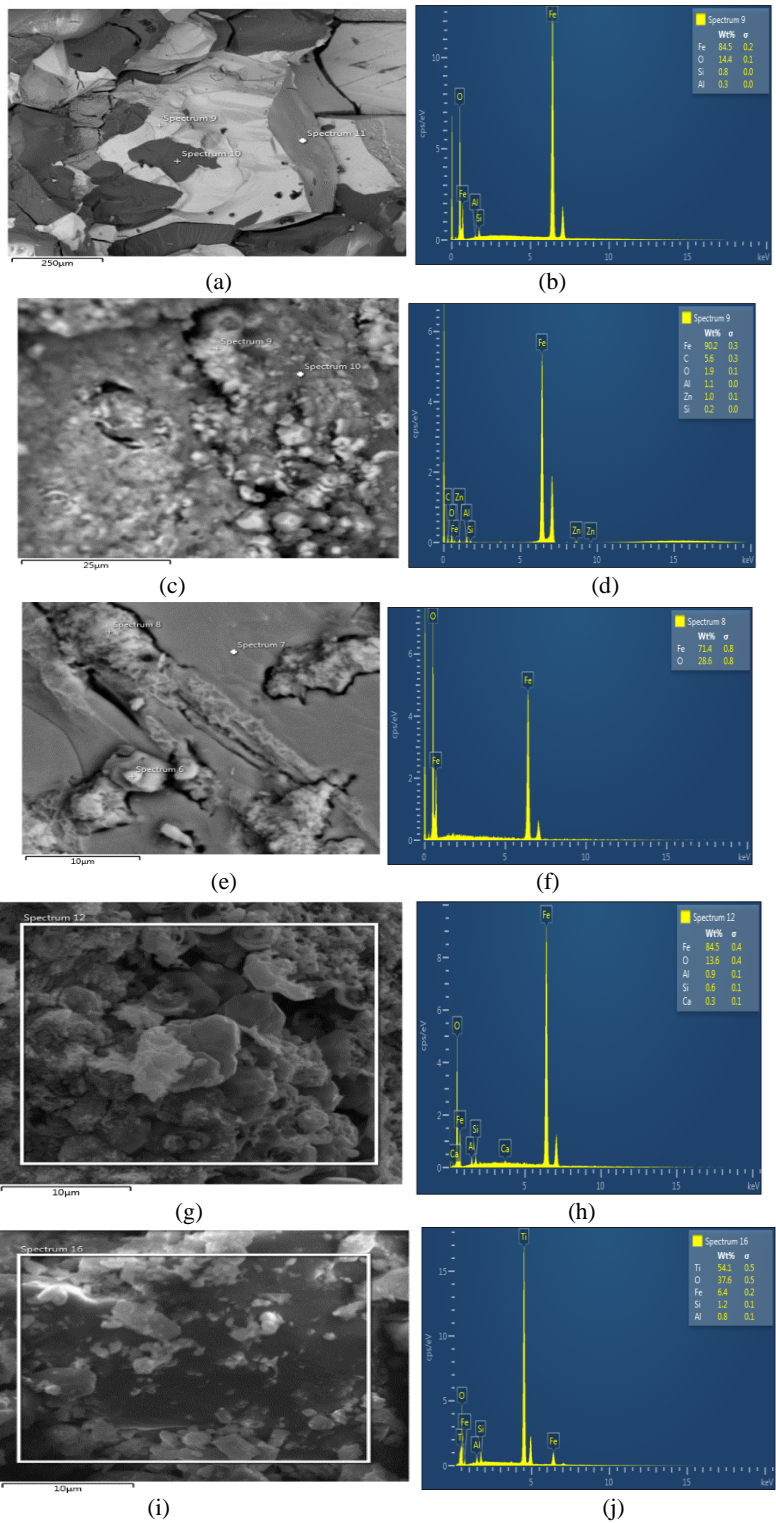
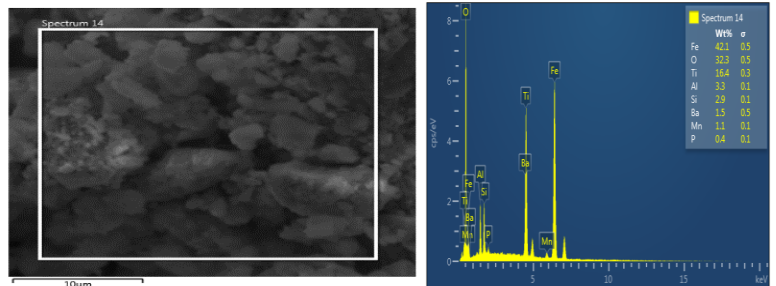
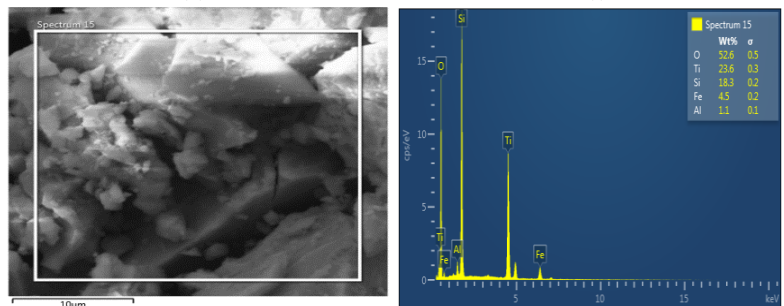


Figure 13(a-j) : shows the SEM and EDS of both Itakpe and Agbaja pellets



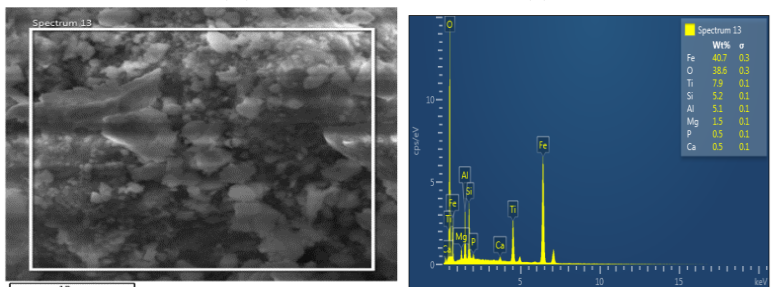
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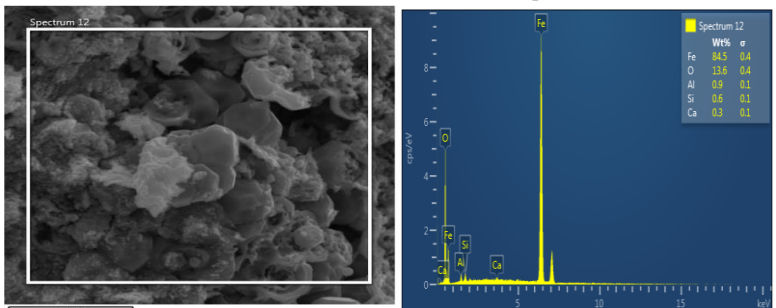
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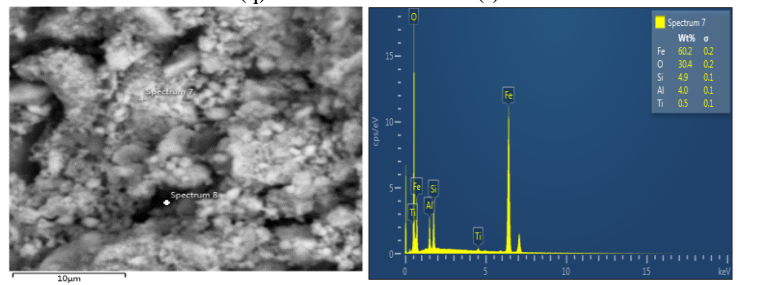
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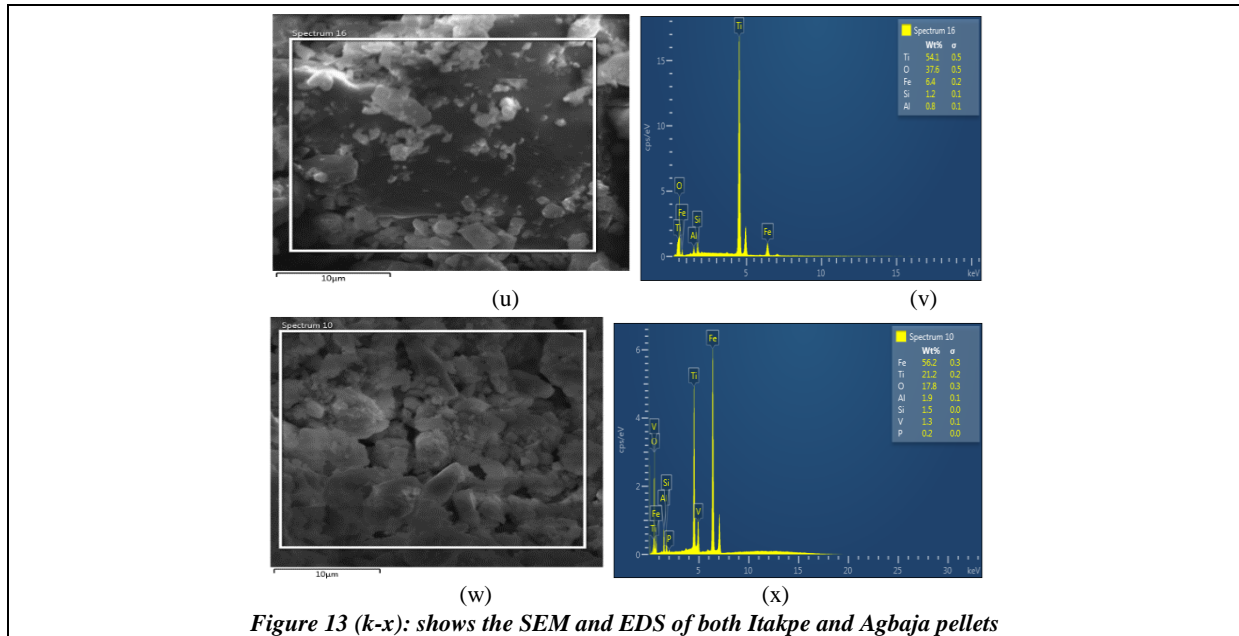


Figure 13 (k-x): shows the SEM and EDS of both Itakpe and Agbaja pellets

3.4 Summary of Results

Table: 4 Analysis of results of samples after performing the reducibility tests on Itakpe and Agbaja pellets (SEM and EDS).

S/N	Sample Name	Temperature in degree	Fe(Wt %)
1	Itakpe Pellets	800°C	4.5
2	Itakpe Pellets	920°C	84.5
3	Itakpe Pellets	1000°C	6.4
1	Agbaja Pellets	800°C	40.7
2	Agbaja Pellets	920°C	60.2
3	Agbaja Pellet	1000°C	56.2

A summary of the results from the tests on Itakpe and Agbaja pellets is presented in table 4. The Itakpe pellets at 800°C for 120mins had Fe Content of 4.5 wt%, while the Agbaja pellets had Fe Content of 40.7% under similar conditions. The pellets for both samples were subjected to 920°C for 120mins, and the values of the Fe contents were 84.5 wt% and 40.7wt%. Similarly, the pellets were further subjected to a temperature of 1000°C for 120mins and the values obtained were 6.4wt% and 56.2wt% respectively. The trend shows that the wt% of both pellets increased at 920°C, and so the pellets were further subjected to a higher temperature at 1000°C upon which the wt% of both samples dropped significantly. The sharp drop of the Itakpe pellets wt% was from 84.5 to 6.4. This suggests that reducibility of the Itakpe pellet is completely achieved at this temperature. The Agbaja pellet may achieve complete reducibility by subjecting it to a higher temperature above 1000°C. These results are presented in figures 14 – 16.

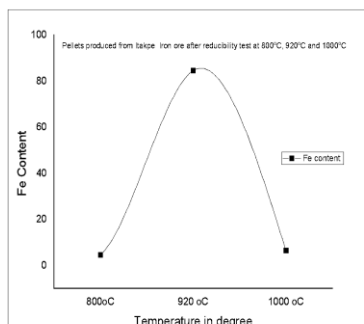


Figure 14: the Fe content of Produced Pellets from Itakpe Iron Ore after the reducibility test @ 800°C, 920°C and 1000°C using SEM and EDS

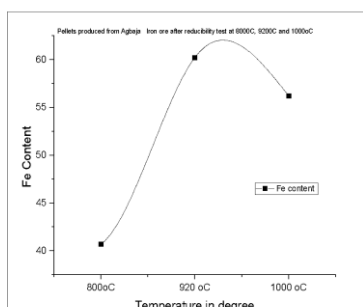


Figure 15: the Fe content of Pellets produced from Agbaja Iron Ore after the reducibility test @ 800°C, 920°C and 1000°C using SEM and EDS

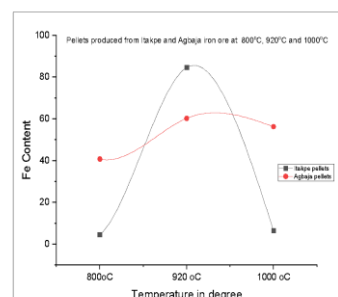


Figure 16: the Fe content from Produced Pellets of Itakpe Iron Ore VS Agbaja Iron Ore after the reducibility tests @ 800°C, 920°C and 1000°C using SEM and EDS

4.0 CONCLUSION

The study on the reducibility of pellets from the Itakpe and Agbaja iron ore blends was intensively carried out. The studies revealed the effect of time of reduction and temperature on the pellets, which indicated that both had effects on the degree of reduction (%). It was observed that the degree of reduction (%) increased with increase in reduction temperature from 800°C -1000°C. The duration of test for the degree of reduction (%) was within the time range of 20 -120mins. The use of the Metallurgical coking coal as reductant had good effects on the pellets, as it significantly affected the degree of reduction (%) of the tested samples. The results and data obtained could be used for further study, and it is suggested that other iron ore deposits in the country be subjected to similar experimental investigations and processes.

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