# **CHARACTERIZATION OF THE MINERALOGY OF STEELMAKING SLAG BY X-RAY DIFFRACTION FOR INDUSTRIAL APPLICATIONS: CASE STUDY OF DELTA STEEL COMPANY, NIGERIA, STEELMAKING SLAG**

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#### **ABSTRACT**

Fifteen representative samples of Nigerian steelmaking slag were subjected to X-ray Diffraction (XRD) analysis with a Phillips PW 1050 diffractometer using copper radiation attenuation in order to characterize the slag mineralogy for possible industrial applications. Representative oven-dried powdered samples ground 1x30 seconds in a Tema mill, sieved through a Bolton No. 120 sieve and ground in an agate mortar were step-scanned from 5 to  $60^{\circ}$  at 4 x  $10^2$  cps for the qualitative and semi-qualitative analysis. The X-ray diffraction patterns of the slag samples were analyzed by comparing the peaks present in the XRD patterns with those provided in The Joint Committee for Powder Diffraction Standards, Hanawalt System for identification of inorganic compounds (JCPDS). There was serious peaks overlap in the XRD diffraction patterns creating a complex situation of mineral occurrence and identification necessitating the use of least intensities to identify mineral occurrence and for qualitative and semi-quantitative interpretation. The mineral phases present were belite, merwinite, melilite, wustite, periclase, peruvvskite, native iron, and tricalcium aluminate. The semi-quantitative mean mineral composition was silicates(33.49%) wustites(44.81%), calcium aluminate(12.66%), periclase (5.38%) peruvskite(1.8%) native iron(1.18%). Qualitatively, mineral phase/polymorph occurrence was beta dicalcium silicateβ(24.70); tri-calcium aluminate, C3A - C(28); calcium silicate hydrate -S(10.24); peruvskite - P(9.05), alpha low dicalcium silicate -  $\alpha'(7.23)$ ; gehlenite - G(7.23); alpha high dicalcium silicate -  $\alpha(6.63)$ ; akermanite - A(6.02); calcium aluminate hydrate - H(6.02); wustite W(2.41); merwinite - M(1.18), magnesio-wustite - R(1.20); and native iron,  $\alpha$ -Fe - F(0.60) out of a mean general total occurrence of 166. Ca, Si, Mg, Al, Fe and Ti were the elemental concentration in the minerals/phases and polymorhs. The mineral and polymorph occurrences jndicated the slag suitability for use in the construction/aggregates, agriculture, blastfurnace and agriculture industries.

**Keywords:** Slag, minerals/phases, construction, agriculture, blastfurnace feed.

#### **INTRODUCTION**

Steelmaking slag is produced in Nigeria at the Delta Steel Company (DSC) through the direct reduction electric arc process of steelmaking. Delta Steel Company is based at Ovwian-Aladja and used lime from Mfamosing limestone, Calabar, direct reduced iron (DRI) and scrap iron as steelmaking raw feed. The direct reduced iron was obtained from low phosphorus iron ore from Liberia. The direct reduction steelmaking process used in the plant presented a low slag volume production, amenability to small capacity plants and the use of abundant local natural gas as reductant for iron ore. The slag produced since inception had been between 9.1 per cent and about 25 per cent of the total steel produced and heaped at the slag dump (Wessey, 1988, April, 2017; Wessey and Egirani, 2017). This work was carried out to determine and characterize the minerals phases/polymorphs present in the slag for use in the construction/aggregates, agriculture, blastfurnace and agriculture industries.

# **LITERATURE REVIEW**

X-ray diffraction (XRD) analysis has long been used as a rapid and accurate method for the determination of the mineralogical composition of cement clinkers; and iron and steelmaking slags (Midgley, 1957; 1974; Gutt, et al., 1971, 1972; Kristmann, 1977; Emery, 1977; Scott et al., 1986; Wessey, 1988; Dippenaar, 2004; Abbaspour et al., 2005; Yildirim and Prezzi, 2011).

The development of steel industry has provided solutions for environmental protection issues and the use of the main production waste, slag aimed at mineral resources and energy conservation. Steel slag has been or can be used as a valuable raw material for many industries including construction, iron and steelmaking, and agriculture industries (Juckes, 2003; Shi, 2004; Ali and Shahram, 2007; Wessey, March, April, 2017). Steel slag shows good technical and ecological properties suitable for use as aggregates successfully substituting natural materials (Gieseler, 1996; Motz & Geiseler, 2001). The reuse of blast furnace and steel making slags for road construction and in other industries must comply with essential requirements. For construction purposes, the essential requirement for steel slag to meet is volumetric stability arising from its composition having free calcium and magnesium oxides. This is a condition to be met especially by steel slag, its composition having free calcium and magnesium oxides, the hydration of which increases its volume, possibly causing important damages. Any steel slag found to be composed of free CaO and MgO, needs a so-called "ageing" time of 6 to 12 months for use without creating any problems. Nigeria is in dire need and in search of alternative sources of raw materials for industrial applications and a clean environment for industrial development away from the overdependence on crude oil derivatives and continuing in polluted industriial environments. There was the need to investigate the mineralogical composition of the slag to determine the possible industrial applications as raw material.

The X-ray diffraction analysis carried out gave a clue as to the mineralogical composition of Nigerian steel slag produced at the Delta Steel Company (DSC slag) and its suitability for applications in industry.

# **METHODOLOGY**

The slag samples were collected in the field from the Delta Steel Company, Ovwian-Aladja, Nigeria, slag dump site. The steel slag was produced using the direct reduction steelmaking process (Wessey, 1988; 2016; 2017). Fifteen samples of one Kilograms (1Kg) each were randomly collected, labeled accordingly (N7, N8, N9, N10, N11, N12, N13, N14, N15, N16, N17, N18, N19, N20 and N21, put in sample bags and taken to the laboratory for preparation and analysis.

The samples were reduced to appropriate sizes first using the rock cutter and jaw crusher to obtain sand grade sizes. The sand grade sizes were then ground in a Tema mill (1x30seconds) to obtain powder forms of each sample. Representative portions of representative samples sieved through a Bolton No 120 sieve were used for both qualitative and semi-quantitative XRD analysis. For the quantitative analysis, each of the samples that had passed through the Bolton No. 120 sieve was ground in a mortar until there was no roughness between mortar and pestle. But for the semi-qualitative analysis, 10 grams of each ground slag sample was mixed with half a gram of pure quartz powder, followed by the same grinding of mortar and pestle. The pure quartz was used as an internal standard. After grinding, the powder was finally packed into an aluminium cavity mount for qualitative and semi-quantitative analysis separately. The samples were then irradiated using copper (Cu) tube operating at 40kv and  $30$ mA. Other operating conditions included, a time constant of 4 seconds, scan range of  $5<sup>0</sup>$  to  $60^0$ , count rate of 4 x 10<sup>2</sup>cps, lower level of 275, window of 200 and a chart speed of 10mm/min.

# **RESULTS**

The results of XRD analysis of the slag are presented in Figure 1, Figure 2, Table 1, Table 2, Table 3, Table 4, Table 5 and Table 6.



**Figure 1.** X-ray Diffraction Traces of DSC Slag



**Figure 2**.Iintense Mineral peak overlap in the diffraction traces of DSC slag.



**Table 1**. XRD diffraction peaks used for the identification of mineral phases in the DSC slag with their intensities



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**Table 2**. Typical mineral phases identified present in DSC test slag by XRD using 2 Theta, d(A) and I/Ii.



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**Key:**  $\alpha = \alpha - C_2S$ ;  $\alpha' = \alpha' - C_2S$ ;  $\beta = \beta - C_2S$ ; M = Merwinite; A = Akermanite; G = Gehlenite; C = Calcium Aluminate; H = Calcium Aluminate Hydrate (CAH); S = Calcium Silicate Hydrate (CSH); W = Wustite (FeO); R = Magnessio-Wustite; L = Ferro-Periclase; P = Perovskite; and F =  $\alpha$ -Fe (native iron).

**Table 3** DSC steelmaking slag mineral phase diagnostic diffraction peaks with intensities (I/Ii) used for mineral phases/polymorphs identification as represented by selected test samples.



**Table 4** DSC slag mineral phase/polymorph qualitative occurrence by XRD analysis



**Key:**  $\alpha = \alpha - C_2S$ ;  $\alpha' = \alpha' - C_2S$ ;  $\beta = \beta - C_2S$ ; M = Merwinite; A = Akermanite; G = Gehlenite; C = Calcium Aluminate;  $H =$  Calcium Aluminate Hydrate (CAH);  $S =$  Calcium Silicate Hydrate (CSH);  $W =$  Wustite (FeO); R = Magnessio-Wustite; L = Ferro-Periclase; P = Perovskite; and F =  $\alpha$ -Fe (native iron).  $\alpha$ -C<sub>2</sub>S is alpha dicalcium silicate;  $\alpha'$ -C<sub>2</sub>S is alpha high dicalcium s, all polymorphs of dicalcium silicate. and  $\beta$ -C<sub>2</sub>S is beta dicalcium silicate, belite.

**Table 5.** Identified mineral phase/polymorph names in DSC slag by XRD and formulae.



**Table 6**. Typical semi-quantitative (partial mode) presence of mineral phases and native iron as shown in some selected DSC slag samples by XRD analysis.



Figure 1 shows XRD diffraction traces of selected slag samples (N7, N8 and N9, typical mineral phase/polymorph identification) and Figure 2 shows a simple plot of identified mineral phases and polymorphs in the slag occurring at  $d(\hat{A})$  CuK $\alpha$ . Table 1 shows mineral phases/polymorphs identifying XRD diffraction peaks in selected samples of DSC slag using 2 Theta( $2\theta$ [<sup>0</sup>] and d(Å), Table 2 shows mineral phases and polymorphs identified present in the slag using 2θ, d(Å) and diffraction intensities (I/Ii), Table 3 shows mineral isolation XRD diffraction peaks for each phase/polymorph, Table 4 shows the qualitative occurrence of DSC slag minerals using selected samples and the slag mineral mean occurrence, Table 5 presents the names of minerals/polymorphs occurring in the slag with formulae and Table 6 presents semi-quantitative occurrence of industrial applications determining mineral phases- the silicates (belite polymorphs, akermanite-ahermanite (solid solution series) merwinite and melilite); wustite, calcium aluminate, periclase, peruvsskite.and then native iron.

### **DISCUSSION**

Table 1, Table 2, Table 3 and Figure 1, show that belite, merwinite, melilite, gehlinite and akermanite were the silicate minerals identified as occurring in the slag. The belite was occurring in the polymorphic forms of the high temperature bredigite and the lower temperature lanite. Calcium aluminate hydrate, calcium silicate hydrate, wustite and magnesium-rich wustite, iron-rich periclase, peruvskite and native iron were other mineral phases and polymorphic forms identified as occurring in DSC slag.

The XRD diffraction traces shown in Figure 1 and represented in Table 2 and shown in the plot, Figure 2, present a complex situation with the XRD method used for mineral identification though it was a rapid and accurate method. The principal problem encountered was that, there was a general component phase reflections partial or full overlap sometimes broad at high angles which created some problems for component phase identification in the slag (Figure 1, Figure 2 and Table 2). This was a serious overlapping situation. For example, at 2θ, 18.00 and  $d(A)$  4.93, the mineral phases/forms β, A, G, H were detected with overlapping reflections (I/Ii) of 4.6. This reflections overlapping behavior represented as follows: [2θ, d(Å), I/Ii, minerals detected]: [2 19, 4.65, 7.7, α, β], [26.30,3.39, 6.2, α, β, G, H]; [26.57,3.35, 2.0,β, H]; [27.50, 3.24, 9.2,β, C]; [28.15,3.17,6.2,α, C]; [29.00,3.08,6.2 A, G, C]; [31.02,2.88,32.2,  $\alpha$ ,  $\alpha'$ ]; [32.55, 2.75,100,  $\alpha$ ,  $\alpha'$ ,  $\beta$ , M]; [32.80,2.73,30.8,  $\alpha$ ,  $\beta$ , H]; [33.20,2.70,9.2] and [35.20,2.55,26.2, β, G, H, P]; [36.20,2.48, 15.4, A, W, C]; [37.30,2.41, 2.3,β, G, P, C]; [39.10,2.30, 7.7,β, M, G, H, P]; [41.20,2.19, 7.7β, G, R]; [41.70,2.17, 12.3,β, S, W]; [42.30,2.15,75.4,M,W]; [42.20,2.09,6.9,β, S, L, C]; [44.40,2.04,10.8, β, M, A, G, P, C];  $[44.60, 2.03, 8.0, \alpha', M, H]$ ;  $[44.75, 2.03, 10.8, \alpha', F, C]$ ;  $[47.90, 1.90, 110.8, \alpha', \beta, G, S, C]$ ;  $[49.40, 1.84, 3.08, β, H, S, P, C]$ ;  $[51.60, 1.77, 3.08 α', G, S, P, C]$ ;  $[51.05, 1.79, 3.1, A, P]$ ; and [58.55,1.58, 6.2,α, S, P]. The problem of mineral identification arising from the serious overlap of reflections was partially solved by using the lowest intensity diagnostic peaks and not the strongest peaks that were obtained by ratioing I/Ii for some of the minerals (Table 3).

For example, akermanite overlapped by β-C<sub>2</sub>S and  $\alpha'$ -C<sub>2</sub>S at 2.88Å with the highest intensity of 32.2 has diagnostic peaks at 2.11Å and 1.77Å with intensities of 12.0 and 4.6 respectively; gehlenite with a diagnostic peak of 4.6 intensity at 3.74Å was overlapped by β-C<sub>2</sub>S at 2.73Å with 30.8 intensity; Mg-wustite at 2.47Å, (6.2 intensity) and 2.46Å (30.8 intensity), is overlapped by gehlenite and calcium aluminate at 2.19Å with an intensity of 40,  $\alpha'$ -C<sub>2</sub>S at 2.67Å (6.2 intensity) is overlapped at 2.73Å by  $\beta$ -C<sub>2</sub>S (6.2 intensity) and 2.46Å (30.8 intensity) is overlapped by gehlenite and calcium aluminate at 2.19Å with an intensity of 40; α'-C<sub>2</sub>S at 2.67Å (6.2 intensity) is overlapped at 2.73Å by  $\beta$ -C<sub>2</sub>S with an intensity of 30.8; and  $β$ -C<sub>2</sub>S at 4.94Å, 4.24Å, 3.83Å, and 3.80Å with 2.0, 4.2, 6.2 and 3.8 intensities respectively, was overlapped at the highest estimated intensity of 100 at 2.75Å by calcium aluminate and  $\alpha'$ -C<sub>2</sub>S. Using both the overlapped and diagnostic peaks, it was possible to identify belite, wustite, calcium aluminate, merwinite, akermanite, gehlenite and periclase mineral phases and distinguish between the dicalcium silicate polymorphs and mineral hydrates. Some of the overlapping mineral phases could not be determined with certainty. These were identified as probable occurrences.

Only low angle isolated reflections at 2θ were observable for β-C<sub>2</sub>S (2 at 20.95 and 23.20); akermanite(2 at 42.80 and 50.90); gehlenite (1 at 23.80);  $C_3A$  (1 at 29.80) and magnesiowustite (1 at 36.60). These were used for the semi-quantitative estimation of the silicates(33.49%), wustites(44.81%), calcium aluminate(12.66%), periclase(5.38%), peruvskite(1.68%) and native iron(1.18%) contained in the slag though not very reliable (Table 6). This serious overlap of XRD reflections is attributable to the solid solution series in the slag, mineral impurity and metastability.

Qualitative estimation of the slag mineral phases and polymorphs using percentage occurrence (Table 3), showed that the abundance was in the decreasing order of beta dicalcium silicate-  $\beta$ (24.70); tri-calcium aluminate, C<sub>3</sub>A - C(28); calcium silicate hydrate -S(10.24); peruvskite - P(9.05), alpha low dicalcium silicate -  $\alpha'(7.23)$ ; gehlenite - G(7.23); alpha high dicalcium silicate -  $\alpha(6.63)$ ; akermanite - A(6.02); calcium aluminate hydrate -H(6.02); wustite W(2.41); merwinite - M(1.18), magnesio-wustite - R(1.20); and native iron, α-Fe - F(0.60) out of a mean general total occurrence of 166.

### **DSC slag industrial mineral applications potentials**

From the qualitative analyses results (Table 3), the silicates had 63.86 per cent and by semiquantitative analysis (Table 6), 39.49 per cent occurrence in the slag accounting mainly for the Ca, Si and Mg present in the slag as shown in the mineral formulae in Table 5. These are important elements for material applications particularly, in the aggregates, blastfurnace and agriculture (Ali and Shahram, 2007) industries. Dicalcium silicate was more abundant in the beta-form (β(24.70%), which has a hydrating cementitious property (Shi,2004). This form of belite could be separated from the slag using standard methods and used in the cement industry as slag cement on activation when made into a non or low metallic iron glassy slag. The calcium silicate hydrates and calcium aluminate hydrates indicating strength development in the slag, can provide cementitious property and used in combination with the beta-dicalcium silicate in industry as construction aggregate which can save natural resources (Wessey, 1988, Motz, and Geiseler, 2001, Wessey and Egirani, 2017). The slag use in industry can also help to improve the environmrnent (Hiltunen and Hiltunen (2004, Wessey, 2017).

Wustites (3.61% by qualitative occurrence and 44.81 by semi-quantitative presence), contain the major Fe and some Mg in the slag. The wustites can be separated and used as a blastfurnace feed material alone or combined with native iron. The Fe and Mg contents are essential for use also in agriculture (Abbaspour et al,. 2005; Torkashvand, A. M., 2011; Wessey, April, 2017).

The other minor mineral phases periclase, peruvskite and native iron contain minor contents of Ca, Mg, Ti and Fe, essential blastfurnace feed and agriculture materials. These can be mixed with the silicates and the wustites for industrial applications.

# **CONCLUSION**

X-ray diffraction (XRD) analysis was used as a rapid and accurate method for the characterization of the mineralogy slag of the Delta Steel Company steelmaking slag. The minerals identified included the silicates and polymorphs, wustites, calcium aluminate as major components; and periclase, peruvskite and native iron as minor components. The geochemistry of these minerals deduced from their formulae was mainly Ca, Si, Mg, Fe and Ti, which are essential elements for applications in the construction/aggregate, blastfurnace and agriculture industries. The slag minerals have potentials for application in these industries complimenting as other sources of industrial raw materials sought for in Nigeria. Slag use can conserve natural natural industrial raw materials. This can increase revenue generation and improve the Delta Steel Company slag production environments.

# **R E F E R E N C E S**

- Abbaspour, A., Kalbasi, M., and Shariamadari, H. (2005) Effect of Steel Converter Sludge as Iron Fertilizer and Soil Amendment in Some Calcareous Soils. Journal of Plant Nutition, Vol. 27, No2, pp377-394.
- Ali, M.T. and Shahram, S.H. (2007) Converter slag as a liming agent in the amelioration of acidic soils.InternationalJournal of Agriculture and Biology, Vol. 9, No. 5, pp715- 720.
- Branca, T. A. and Cola, S. S. A. (2012) Possible Uses of Steelmaking Slag in Agriculture: An Overview. PERCO, TeCIP Institute Italy.
- Das, B., Prakash, S., Reddy, P.S.R. and Misra, V.N. (2007) An overview of utilization of slag and sludge from steel industries. Resources, conservation and Recycling, Vol.50, No. 1, pp40-57.
- Dippenaar, R. (2004). Industrial uses of slag The use and reuse of iron and steelmaking slags, Proceedings of VII Intenational Conference on Molten Slags, Fluxes and Salts. The South African Institute of Mining and Metallurgy.
- Emery, J. J. (1977) Steel slag utilization in highway construction, Silicate industries.
- Emery, J. J. (1977) Slags as Industrial Minerals, 3rd Industrial Minerals International congress, pp127-142.
- Geiseler, J. (1996) Use of steelworks slag in Europe.Waste management, Vol. 16, No. 1- 3, pp59-63.
- Gutt, et al. (1971) Manufacture of cement from industrial byproducts. Current paper, 19/71, Building RESEARCH establishment, Watford, U,K
- Gutt, W. (1972). Aggregates from waste materials, Chemistry and Industry, pp 437-439.
- Hiltunen, R. and Hiltunen, A. (2004) Environmental aspects of the utilization of steel industry slags, Proceedings of VII International Conference on Molten Slags, Fluxes and Salts. The South African Institute of Mining and Metallurgy.
- Juckes, L. M. (2003) The volume stability of modern steelmaking slags. Mineral Processing and Extractive Metallurgy, Vol. 112, pp177-197.
- Kristmann, M. (1977) Portland cement clinker mineralogical and chemical investigation. (part I and II, Cement and Concrete Research, 7, pp419-427.
- Midgley, H. G. (1957) A compilation of X-ray data of cement minerals. Magazine of Concrete Research, March, pp17-24.
- Midgley, H. G. (1974) The polymorphism of calcium orthosilicate. Proceedings of Vth International Symposium on Chemistry of cement, (Mosco) Part 1.
- Motz, H. and Geiseler, J. (2001) Products of steel slags an opportunity to save natural resources. Waste Management.Vol. 21, No. 3, pp285-293.
- Scott, P. W., Critchley, S. R., and Wilkinson, F. C. F. (1986) The chemistry and mineralogy of some granulated and peletized blastfurnace slags. Mineralogical Magazine, Vol. 50, pp141-7.
- Shi, C. (2004) Steel slag- its production, processing, characteristics, and cementitious properties, Journal of Materials in Civil Engineering, Vol. 16, No. 3, pp230-236.
- Torkashvand, A. M. (2011) Effect of steel converter slag as iron fertilizer in some calcareous soils.ActaAgriculturaeScandinavica Section B – Soil and Plant Science, Vol. 61, No. 1, pp14-22.
- Wang, X. and Cai, Q. S. (2006) Steel Slag as an Iron Fertilizer for Corn Growth and Soil Improvement in a Pot Experiment.Pedosphere, Vol. 16, No. 4, pp519-524.
- Wessey, N. (1988) The Evaluation of the Industrial Potentials of Nigerian Direct Reduction Steelmaking Slag.University of Hull, Ph. D. Thesis, 316pp.
- Wessey N. and Egirani, D. (2017) Evaluation of the Delta Steel Company (DSC), Ovwian-Aladja, Western Niger Delta, Nigeria, Direct Reduction Steelmaking Slag for Use in the Aggregates Industry, International Journal of Multidisciplinary Academic Research Vol. 5, No. 1, pp1-13.
- Wessey, N., (April, 2017.) Use potentials of Delta Steel Company (DSC), Ovwian-Aladja, western Niger Delta, Steelmaking Slag in Agriculture. Agricultural Science Research Journal Vol. 7(4): pp129 – 134.
- Wessey, Napoleon A. (April, 2017) X-ray Fluorescence (XRF) Geochemical Investigation of Delta Steel Company (DSC), Ovwian–Aladja, western Niger Delta, Nigeria, Steelmaking Slag for use as Iron making Blastfurnace Feed and Fertilizer. Asian Journal of Applied Sciences, Volume 5, Issue 2, pp315-319
- Wessey, Napoleon A. (March, 2017) **E**valuation of Nigeria Direct Reduction (DR) Steelmaking Slag Mineral Phase Chemistry byEelectron Microprobe Analysis (EMPA) for Industrial Applications, International Journal of Development Research, Vol. 07, Issue, 03, pp12132-12136,
- Yildirim, I, Z. and Prezzi. M, 2011. Chemical, Mineralogical and Morphological Properties of Steel Slag, Advances in Civil Engineering, 13p.