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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

Napoleon A. Wessey
Department of Geology,
Niger Delta University, Wilberforce Island,
Amassoma, Nigeria

Email: napwessey [AT] yahoo.com

ABSTRACT--- ***This work investigated the bulk geochemistry of fifteen (15) samples of Delta Steel Company (DSC) dump slag produced by the direct reduction steelmaking process, using the X–ray fluorescence spectroscopy (XRF) method and glass discs prepared from each of the fifteen test slag samples. The results indicate the presence of major amounts of CaO(36.62%), MgO(9.77%), Fe_2O_3(27.32%), SiO_2(19.86%), Al_2O_3(5.43%), low amounts of MnO(1.46%), TiO_2(0.42%), Cr_2O_3(0.17%), P_2O_5 (0.53), and minor amounts of SO_3(0.04). The geochemical composition of the slag indicates suitable use as iron making blastfurnace feed and as fertilizer. The low amount of MnO in the slag is advantageous as it can reduce the disadvantage of probably causing refractory lining destruction in the presence of a notable amount of K_20. The use of this slag would contribute to the conservation of natural steelmaking resources, improved crop yeild and reduction in CO_2 emission in the company environment.***

Keywords--- Steelmaking slag, x-ray fluorescence spectroscopy, geochemistry, blast furnace feed, fertilizer

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1. INTRODUCTION

Steelmaking slag is the by-product of processing molten iron into a specific type or grade of steel. In iron and steel manufacture, the fusion of a flux material such as limestone, dolomite, or lime, etc with ash from coke, and iron ore/scrap iron produces slag. The steelmaking slag at the Delta Steel Company (DSC) Ovwian-Aladja, was produced using the direct reduction steel making process. The process involved the use of the Mfamosing limestone and company direct reduced iron/scrap. The direct reduced iron was produced from Liberian iron ore.

Results of bulk samples X-ray fluorescence spectroscopic (XRF) studies on steelmaking slags and Portland cement clinkers by many researchers indicated the presence of SiO_2, Al_2O_3, CaO, Fe_2O_3, TiO_2, MnO, MgO, K_2O, Cr_2O_3, P_2O_5, SO_3 and Na_2O. This showed the reported geochemical similarity between steelmaking slags and Portland cement clinkers (Yamaguchi and Tagaki, (1968); Gutt, (1971); Thom and Wood, (1973); Pugh and Fletcher, (1973); Medlan, (1973); Lee, (1974); Atwell, (1974); Joseph and Haddad, 1973, 1975); Barton, (1975); Piret and Lesgardeue, (1975); Emery, (1977); Kristman(1977); Blunk and Geissler, (1980); Scott, et al,(1986); Shi, et al., (2004), Shen, et al., (2009), Barra et al., (2001); Sitien et al., (2009); Branca, T. A. and Colla, V(2012) have recent published data on the chemistry of steelmaking slags and their uses.

Table 1: Chemical composition of some BOF, EAF, and Ladle Slags (Shi, 2004), (Shen et al, 2009)+, (Barra et al, 2001}*, (Setien et al, 2009)** in comparison with DSC slag composition.

Oxide Composition %	Slag type			
	BOF	EAF	Ladle	DSC slag
S_IO_2	8-20	9-20	2-35	18-22.42
T_IO_2	0.4-2	-	-	0.39-0.46
Al_2O_3	1-6	2-9	5-35	4.50-6.00
FeO	10-35	15-30	0-15	-
Fe_2O_3	- (38.6)+	- (32.56)*	- (1.6-3.3)**	17.93-41.00
MnO	2-8	3-8	0-5.0	1.03-2.03
MgO	5-15	5-15	1-10	7.05-13.43
CaO	30-55	35-60	30-60	27.23-44.20
P_20_5	0.2-2	0.0-0.3	0.1-0.4	0.44-0.77
SO_3	0.1-0.2	0.1-0.2	0.1-1	0.00-0.14
Free CaO	-	-	-	

Shi et al (2004) presented the iron present as FeO in the three slag types while Shen et al, (2009); Barra et al, (2001); and (Setien et al, (2009) reported iron found as Fe_2O_3. Shen et al., Barra et al., and Sitien et al., cited in Yildirim and Prezzi, (2011), also reported that BOF, EAF and Ladle slags were composed of 38.6%, 32.56% and 1.6- 3.3 % of Fe_2O_3 respectively. The iron found in DSC slag was reported as Fe_2O_3 and the slag samples were composed of Fe_2O_3 ranging in occurrence between 17.93% and 41.00%.

The main chemical constituents of basic-oxygen-furnace (BOF) steelmaking slag are reported as CaO, FeO/Fe_2O_3, and SiO_2 [Wachsmuth, et al, (1981); Schoenberger, (2001); Juckes, (2003); Shi, (2004); Yildirim and Prezzi, (2011); Gautier et al, (2013; Piatak et al, (2015)]. The conversion of molten iron into steel during the steelmaking process is not complete, a percentage of the iron (Fe) in the hot metal could not be recovered into the steel produced (Yildirim and Prezzi, 2011). This oxidized iron was observed in the chemical composition of the BOF slag. The iron oxide (FeO/Fe_2O_3) content of BOF slag was as high as 38% (refer to Table 1) which was determined by the efficiency of the furnace (Gauntier et al, 2013). This was the amount of oxidized iron that could not be recovered during the conversion of molten iron into steel. The silica (SiO_2) content of BOF slag ranged from 7 to 18%, the Al_2O_3 and MgO contents 0.5–4% and 0.4–14%, respectively. The free lime content was as high as 12%. Very high CaO content (CaO >35%) was typical of BOF slag and was as a result of large quantities of lime or dolomotic lime used during the process of conversion from iron to steel. From Table1, there was a similar chemical composition between electric arc furnace (EAF) and BOF slags. The chemical composition of the former, produced essentially from steel scrap recycling process depended significantly on the properties of the recycled steel. Compared to BOF slags, the typical main chemical constituents of EAF slags were FeO, CaO, SiO_2, Al_2O_3, and MgO, occurring in the ranges of 10–40%, 22–60%, 6–34%, 3–14%, and 3–13%, respectively, with a wide variation. MgO, MnO, and SO_3 oxidized impurities were minor components of EAF slags. Free CaO and MgO along with other complex minerals and solid solutions of CaO, FeO, and MgO were also constituents of EAF slags. FeO content of EAF slags generated from stainless steel production processes were as low as 2% (Shen et al (2004). During the steel refining process, different alloys were fed into the ladle to obtain the desired steel grade making the chemical composition of ladle slag to be highly dependent on the grade of steel produced. This accounted for the comparatively high variable chemical composition of ladle slag than BOF slag. The FeO content of ladle slag was much lower (<10%) than that of EAF and BOF slags. The contents of Al_2O_3 and CaO were typically higher for ladle slags and that of Fe_2O_3, was low (1.6-3-3%). These values were much lower than those composing DSC slag, for example, Fe_2O_3(27.32%) (refer to Table 1). Based on such investigation results steelmaking slag has been used in a number of industries particularly as a blast furnace feed; and in the lime and phosphate fertilizer industries.

Nigeria produces large volumes of solid industrial byproducts including steelmaking slag with potentials as industrial raw materials to conserve natural resources. This work therefore, investigated the geochemistry of the Delta Steel Company (DSC) slag using the X-ray fluorescence method to determine its potential use as ironmaking blastfurnace feed and as fertilizer.

2. MATERIAL AND METHODOLOGY

Sampling: Slag sampling was done by random spot hand picking of fifteen (15No) DSC dump slag samples (N7-N21) for laboratory testing. Samples of each spot were put into thick but transparent bags and labeled with indelible ink. The fifteen (15) bulk size samples were finally taken to the laboratory for testing according to BS812 (Part 3, 1975:1988) Standard Specifications.

2. 1 Test sample preparation

Blocks of each sample of slag were cut into suitable rock size specifications for the jaw crusher and the fly press using rock cutting machines. The latter produced gravel sized grades from which powders were produced by grinding 1 x 30 seconds in the Tema mill. The powders were then used to produce quenched glass discs for geochemical analysis by melting the powder with Johnson Matthey spectroflux 105 followed by air quenching. The melting with the flux was to overcome grain size and packing density influence on the emission of x-rays. Glass discs were used because they had a low absorption capacity for X-rays and reduced inter-element effects to such an extent that they did not influence the analysis (Ludwig and Richard, 1978). With the use of glass discs, different types of slag samples were analyzed using the same calibration factors and the achievement of accurate results.

2.2 Laboratory Geochemical analysis of DSC slag

The chemical oxide compositions of DSC slag samples were determined using the X-ray fluorescence (XRF) analysis method. The Phillips PW1212 XRF machine with a Chromium target tube was used for the analyses, set at operating conditions of 60 Kv and 26mA.. The bulk chemistry of fifteen (15) glass disc samples of the slag, were analyzed. The bulk geochemical analyses results of the fifteen samples and the mean respectively, are presented on Table 2 and Table 3.

3. RESULTS AND DISCUSSION

3.1 Results

Oxide %	DSC Slag Samples								
	N7	N8	N9	N10	N12	N13	N14	N17	N19	N21
S_IO_2	2.42	21.64	19.74	19.52	19.20	19.27	19.72	20.19	18.18	18.25
T_IO_2	0.42	0.46	0.42	0.39	0.40	0.41	0.45	0.44	0.42	0.41
Al_2O_3	5.16	5.92	5.95	5.25	4.59	5.42	5.00	5.50	5.63	5.55
Fe_2O_3	7.93	21.70	26.33	28.20	27.69	25.50	25.22	26.71	25.97	25.73
Cr_2O_3	0.05	0.10	0.00	0.00	0.06	0.04	0.06	0.01	0.40	0.40
MnO	1.67	1.33	2.03	1.03	1.82	1.53	1.46	1.18	1.23	1.26
MgO	7.94	9.65	10.95	9.00	7.41	9.68	8.02	7.52	12.37	12.54
CaO	44.20	39.57	35.50	37.96	38.96	37.92	38.25	39.88	36.40	35.82
Na_20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K_2O	0.03	0.06	0.05	0.08	0.04	0.08	0.04	0.03	0.02	0.03
P_20_5	0.62	0.51	0.53	0.60	0.77	0.57	0.56	0.46	0.39	0.60
SO_3	0.06	0.14	0.10	0.08	0.03	0.00	0.04	0.02	0.00	0.00

The XRF analyses results (Oxide%) are presented in Table 2 and Table 3, followed by discussions.

Table 2 Geochemistry of DSC Slag selected samples (Oxide %)

Table 3. DSC slag mean, minimum and maximum Geochemistry (Oxide %)

Field	Mean	Std. dev	Min	Max
SiO_2	19.861	1.331	18.180	22.420
Al_2O_3	5.426	0.374	4.590	6.000
Fe_20_3	27.323	5.402	17.930	41.000
Cr_20_3	0.168	0.184	0.000	0.450
MnO	1,456	0.296	1.030	2.030
MgO	9.766	2.171	7.050	13.430
CaO	36.623	4.227	27.230	44.200
Na_2O	0.00	0.00	0.00	0.00
K_2O	0.05	0.02	0.02	0.08
P_20_5	0.565	0.078	0.440	0.770
$S0_3$	0.039	0.043	0.000	0.140
TiO_2	0.423	0.022	0.390	0.460

3.2 Discussion

DSC slag had high element (oxide%) content and wide samples compositional variations (refer to Table 2. Table 3 presents the mean per centage element oxide composition of the slag. Concentrations of the major components were CaO(36.62%), Fe_20_3(27.32%] and SiO_2(19.86%), ranging between (35.82% and 44.20%), (17.935 and 28.20%), and (19.25% and 22.42%) respectively. Constituents of lower concentrations were, MgO(9.77%), Al_2O_3(5.43%) and MnO(1.46%) ranging between (7.525 and 12.54%), (5.165 and 5.95%) respectively, all the constituents contents occurring in that descending order in each sample. This showed great concentration variations in the slag samples. The coefficient of variation was greatest with Cr_20_3 (94.74%) and MnO(20.55%). This elemental coefficient of variation of DSC slag investigated, disagreed with those observed in literature by Thom and Wood, (1973), (Joseph and Haddad, 1975) with results of greatest values (Cr_2O_3(28.1%) and (P_2O_5(22.6%). This indicated that, there was thus a general higher co-efficient of oxide variation in DSC slag except, SiO_2 and Al_2O_3. The slag had some significant amount of K_2O(0.05%). The greater oxide composition variation in DSC slag was attributable to the particular direct reduction (DRI) process of steel/slag production.

3.3 Comparison of dsc slag xrf analyses and literature results.

The comparative XRF analyses results for other steelmaking slags and that of DSC slag are presented in Table 1. High Fe_2O_3 content of DSC slag may be due to the presence of Fe in the elemental state. The literature observed major constituent of slags that have been used as blastfurnace feed and as fertilizer were CaO(30-60%) [Lee, 1974; Pugh and Fletcher; Emery, 1977; Yildirim and Perez, 2011). Iron oxide and silica were the other major components. With a CaO content range of 27.23% and 44.20% (refer to Tables 3), DSC slag falls just a little outside this range of values of 30 – 60 per cent. However, the mean value of CaO content (36.62%) in the slag brought it closer to mixed Electric Arc/BOP steel slag values of CaO(35.60%) [Eggleston (1985)]. The proportions of the other two major constituents Fe_2O_3(27.32%) and $SiO_2$19.86% also vary widely from literature values of Fe_2O_3 (1.6% – 38.6% and SiO_2 (2% – 35%), refer to Table 1. This indicated that DSC direct reduction steel making slag, had great industrial potentials within the family of steelmaking slags, particularly for use as blastfurnace feed and fertilizer (Das et al. 2007); Dippenaar (2007); Branco and Colla (2012).

CaO, Fe_2O_3, SiO_2, MgO, $A1_20_3$, TiO_2, P_20_5, and SO_3, detected in the slag may have come from iron ore, burnt lime and hydrated lime used directly or indirectly in the direct reduction process of steel/slag production whilst the scrap iron may be the sole source of TiO_2, MnO and Cr_20_3, which may have leaked into the slag. All the above elements detected in all the fifteen slag samples though in varying amounts indicated that there was some difference between direct reduction (DR) steelmaking slag and cement clinkers in terms of chemistry.

3.4 DSC slag use as a blastfurnace feed

DSC slag had high contents of lime [CaO(36.62%),] iron [Fe_20_3(27.32%)] and silica [SiO_2(19.86%)] magnesia [MgO-9.77%] and alumina [(Al_2O_3(5.43%);] and minor contents of manganese [MnO-1.46%], in DSC slag as shown in Tables 1, 2 and 3 respectively. The high contents of CaO, Fe_2O_3 and SiO_2 are the major constituents required of a blastfurnace iron making feed. DSC slag as a flux can reduce the iron production temperature in the blastfurnace, Fe_2O_3 of the slag can be reduced to Fe increasing the presence of Fe, CaO can react with SiO_2 not needed in the Iron to produce silicates during the ironmaking process in the blastfurnace (Rayner-Canham and Overton (2006), Science Aid (2007).

The presence of MnO could have been a disadvantage because this could probably create the problem of causing refractory lining destruction if used as a blast furnace feed resulting in possible production of off-quality hot metal. But the content of MnO (1.46%) is acceptably low minimizing the possible negative effect and of no disadvantage for use as a blast furnace feed. Also, a possible disadvantage of MnO presence is overcome by the possible reduction in manganese addition cost during ladle alloying of steel when the slag is used as feed material. The slag therefore qualifies for use as a blastfurnace feed.

3.5 DSC slag use as fertilizer

The presence of MgO, MnO, Cr_2O_3 (Cr), P_20_5 and SO_3 can be considered very useful to the slag because they can contribute to the stabilization of beta-belite(β-C_2S), the most important dicalcium silicate mineral phase polymorph which has high content of CaO and SiO_2 (Ca and Si) suitable for plants in soil (Thilo and Funk, 1953; Savant et al., 1999; Motz and Geiseler, 2001). The high lime (CaO) content present qualifies the slag as a lime fertilizer apart from the lime combined phosphorus in the slag, useful as a phosphate fertilizer material. DSC slag can be efficient in soil neutralization and thus used as a soil neutralizer. The slag being basic, can incresae K, Ca and Mg in soils (Rodriguez et al. (1994); Kühn et al., (2006); Negim et al., 2010) The siliceous liming materials can improve soil structure and reduce fungal infections. This can lead to a better yeild of the crops, soil protection and reduction of natural resources consumption around the company area (Hiltunen and Hiltunen, 2004). DSC slag is SiO_2 rich which can be used to develop potassium silicate fertilizer and used as silica fertilizer to increase the resistance of rice to various diseases and vermin (Tatsuhito and Kazuya, 2006). The presence of K_2O can make it suitable as a ready source of potassium to crops as a fertilizer. The high basicity of DSC slag makes it suitable as fertilizer to condition acid soils by increasing the pH.

4. CONCLUSION

This investigation has shown the rich bulk chemistry of the slag in CaO(36.62%), Fe_2O_3(27.32%), SiO_2(19.8%6), MgO(9.77%), Al_2O_3(5.43%), MnO(1.46%), TiO_2(0.42%), Cr_2O_3(0.17%), P_2O_5(0.53%), and SO_3(0.04%). These are essential for use in the blastfurnace and as fertilizer. DSC slag is therefore valuable as an iron making blastfurnace feed and for use as lime, silicate and phosphate fertilizers. The results from this research should encourage the continuous production, recycling and use of the slag and other solid industrial by-products as industrial minerals. It would contribute to conserving natural resources and improve environment aesthetics.

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