Abstract: Slag is a non-metallic by-product obtained in the refining of metals from metallic ores. Slag production at the Delta Steel Company (DSC), Ovwian-Aladja, western Niger Delta, follows the direct iron reduction steelmaking process. Fifteen company slag samples collected were examined by x-ray fluorescence, thin section petrography and electron microprobe analyses to establish the mineralogy and mineral crystallization sequence and thus explain their occurrences. The results show the presence of synthesized silicate minerals of belite, melilite and merwinite; calcium aluminate, wustite, periclase, perovskite and glass in the slag formed at between the temperatures of 1500°C and 500°C. Crystallization sequence is alpha (α) form of belite (1500°C-1420°C), alpha high (α/H) belite (1420°C-1160°C), alpha low (α/L) belite (1160°C-680°C, beta (β-) belite (680°C – 630°C), Melilite (1420°C-680°C), Melilite (1420°C-680°C), aluminate, merwinite, wustite, periclase, perovskite and glass (630°C–500°C) in that order. This study has revealed that in behavior, synthetic minerals also crystallize from high to low temperature forms as is the case with natural minerals formed from silicate magmas. The forming behaviour of these minerals confers on them the important characteristics for industrial use as an industrial mineral compliment to natural materials.

Keywords: Steelmaking Slag, Iron, Reduction, Synthesized Silicate Minerals, Crystallization Sequence, Industry

1. Introduction

Steel slag is produced by the fluxing of mainly limestone with iron ore to produce steel. Generally, it is a byproduct of steelmaking and steel refining process. Delta Steel Company, (DSC) Ovwian-Aladja, Delta State, Nigeria, steelmaking slag is produced through the direct iron reduction steelmaking process. The process involved the use of Lime from Mfamosing Limestone, Calabar, Cross River State, Nigeria, as a flux and direct reduced iron in pellet form from iron ore from Liberia and local scrap as sources of iron. DSC slag formed between 1500°C and 1700°C [5] and remained in liquid form. Solid slag containing crystallized minerals may have started cooling from below 1500°C, ending at 500°C [18] [44].

Pioneering works by [1], [6], [8], [14], [15], [19], [21], [22], [30] and others, using microscopy (SEM), X-ray diffraction (XRD) and electron microprobe analyses (EMPA) methods at different times recorded similarities on the composition and transformation of steelmaking slag and Portland cement clinker minerals. Both are synthesized rocks at about the same temperatures and similar elemental substitutions take place within each. They found a list of slag minerals Alite, Belite of different polymorphs, Tricalcium aluminate, Periclase, Free Lime, Tricalcium ferrite and Wustite that occurred in them. The polymorphs of belite (C₃S), include larnite (β-Ca₃SiO₅), bredigite α-Ca₃SiO₅, melilite (Ca₂MgSi₂O₇) and merwinite (Ca₃MgSi₂O₈). Recent XRD, Scanning Electron Microscopy and Electron Microprobe Analyses (EMPA) studies of steelmaking slags confirm the presence of the crystalline phases of a variety of these minerals. Their presence was due to the chemical composition of steelmaking slag and the slow cooling rate of the slag. Steelmaking slag has been used as material in
construction, cement, ceramic, glass and the blast furnace industries based on their chemical and mineralogical compositions [3], [4], [12], [24], [30], [31], [33], [37], [41], [42].

DSC slag, in physical appearance, looked like magma and the cooling was similar to igneous magma. Petrographic, photographic, x-ray diffraction (XRD), scanning electron microscopy (SEM) and electron microprobe analysis (EMPA) studies of samples of the slag identified the occurrence of the minerals belite, calcium aluminate, periclase, perovskite, periclase, perovskite, melilite, merwinite, wustite as listed on Table 1 in a crystallization sequence [39]. Belites identified were the five well defined polymorphs, high temperature alpha (α), alpha dash high (α /H), alpha dash low (α l), beta (β-C₂S) and gamma (γ-C₂S) of low temperature [11], [16], [17]. The mineral crystallization sequence of steel slag belite has been studied and reported [20]. This sequence has been used to indicate the general mineral crystallization sequence of DSC slag, limited in literature.

2. Results

Test results for the bulk mineralogy and mode of appearance of the slag are presented in Table 1 and Figures 1 to 13.

Table 1. A list of DSC slag minerals and their chemical formulae.

<table>
<thead>
<tr>
<th>Mineral Name</th>
<th>Chemical formulae</th>
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<tbody>
<tr>
<td>Belite</td>
<td>2CaO.SiO₂(C₂S)</td>
</tr>
<tr>
<td>Calcium Aluminate</td>
<td>CaO.Al₂O₃(C₃A)</td>
</tr>
<tr>
<td>Periclase</td>
<td>MgO</td>
</tr>
<tr>
<td>Melilite</td>
<td>2CaO.MgO.2SiO₂</td>
</tr>
<tr>
<td>Merwinite</td>
<td>3CaO.MgO.2SiO₂</td>
</tr>
<tr>
<td>Perovskite</td>
<td>CaTiO₃</td>
</tr>
<tr>
<td>Wustite</td>
<td>FeO</td>
</tr>
</tbody>
</table>

From Table 1, Belite, Calcium Aluminate, Periclase, Melilite, Merwinite, Perovskite and Wustite were the minerals that crystallized from the cooling of liquid slag.

Figure 1, Figure 2, Figure 3… Figure 11, show typical back scattered mode Scanning electron microscope (S. E. M) photomicrographs of polished thin sections of DSC slag samples.

Figure 1. (200µ) shows a fractured composite wustite crystal (Wu) with a darker central region resulting from a higher Mg concentration (Wu₅) by EMPA analysis results.

Figure 2. Shows round, rectangular and angular (gray) periclase (MgO) crystals on both a mixed and wustite groundmass but always surrounded by a thin shell of wustite. The wustite had protected the periclase from possible inter-phase or liquid reactions.
Figure 3. (100µ) Shows periclase shape and roundness and occurrence as in Figure 1.

In all Figure 1, Figure 2 and Figure 3, periclase shape was sometimes obscured by edge rounding and grain coalescence with round blebs in some areas. Rounded blebs on wustite (white) indicated a second stage crystallization. Dendritic wustite were also seen on a mixed ground mass as in Figure 3.

Figure 4. (20µ) Shows a clearer highly fractured grayish belite in contact with whitish wustite (Wu).

Figure 5. (40µ). Belite (Bt- brown) of different shapes and sizes in contact with whitish and grayish wustite (WU) of different shapes and sizes. Tiny grains of wustite (white), enclosed in aluminate- (dark gray).
Figure 4 and Figure 5 show highly fractured belite (Bt, grayish colour), the α and α polymorphs unable to transform to the lower temperature forms during faster cooling and in direct contact with wustite- Wu (white).

**Figure 6.** Camera photomicrogram showing light gray and brown belite crystals radiating in different directions from a nucleus or from a larger belite crystal or criss-crossing.

**Figure 7.** Shows dendritic wustite (Wu-white) in contact with lenticular belite (Bt-light to dark gray) and dark aluminate (Al) of no definite shape. Some wustite grains occur on alumimates.

**Figure 8.** (20µ). Shows dendritic whitish wustites (Wu), lenticular belite (light to dark gray (Bt), radiating from a larger crystal or criss-crossing and tiny grains of wustite (white) on dark aluminate.
Figure 7 and Figure 8 show aluminate crystals of no definite shape, dark gray lenticular belite (Bt) crystals radiating from nuclei or from a larger belite crystal or criss-crossing (Figure 8). Figure 8 shows white dendritic wustite crystals (Wu) of no definite shape and direction and belite crystals (light to dark gray).

Figure 9. (20µ). Shows light gray to white fibrous wustite (Wu) in dark aluminate and wustite crystals of random orientation.

Figure 10. (10µ). Shows radiant lenticular belite, wustite laths and round grains (white) in belite (gray) and aluminate (dark).

Figure 11. (40µ). Shows intergrowth texture exhibited by DSC slag minerals (belites and wustites, prominently).
Figure 9 shows fibrous wustite (light to dark gray) in dark aluminates and lenticular belite radiating from larger belite crystals or inter-crossing. Figure 10 shows the radiant belites, wustite laths and round grains (white) in belite (gray). Figure 11 shows the intergrowth texture exhibited by the DSC slag minerals, prominently by the belites and the wustites.

3. Discussion

DSC slag cooling process started from high temperatures and mineral crystallization starting at below 1500°C continuing to lower temperatures of about 500°C in the ladle and in the slag dump[20][44]). During the cooling, silicates of belite of different polymorphs, mellilite, merwinite; and wustite, calcium aluminate, periclase, peruvskite and glass crystallize occurring in different forms as listed in Table 1. Figure 1, Figure 2, Figure 3…. Figure 11, showed the back scattered mode scanning electron microscope (SEM) and the Zeiss Ultraphot photomicrographs of polished thin sections. These depict the mineral phases that crystallized as the slag cooled and their occurrence was used to explain the possible sequence of crystallization.

3.1. Mineral Material Occurrence

Belite (brown or dark gray colour) in the beta form was present as large discrete crystals and as small crystal inclusions in wustite (white), (see Figure 1, Figure 4 and Figure 5). Some melilite (gehlenite (2CaO.MgO.2SiO₂) co-existed with wustite (FeO) and calcium aluminate (CaO.Al₂O₃ - C₃A) as interstitial material (Figure 11). The melilite, merwinite, wustite and calcium aluminate also occurred enclosed in the belite and formed the glass (Figure 4 and Figure 5). Periclase grains occurred as euhedral or spherical shaped crystals with the cryptocrystalline wustite groundmass in certain areas and surrounded by thin shells of wustite in other areas (Figure 2 and Figure 3). Peruvskite occurred in association with belite and wustite but sometimes as rectangular and irregular light gray shades on wustite (Figure 11). Minor amounts of iron occurred as whitish rounded droplets. These may have formed from the immiscibility of the metal phase formed in the slag. The minor differences in slag sample chemical composition was reflected in the general similarity of the crystalline phases occurring in the slag samples.

3.2. Tertiary diagrams

The Geochemical data of DSC slag have been plotted along with the relevant phase boundaries onto the various triangular systems of these oxides. Figure 12 shows the mineral equilibrium relations and crystallization sequence of the slag minerals. Accurate interpretation of the data from the comparison with these systems has not been possible. This is because the planes of the phase diagrams were fixed but the slag component minerals and glass did not lie exactly within any of these planes. The minor elements present in the slag (alkali, S, P) may also have had some effect on the phase chemistry.

3.3. Mineral Crystallization Sequence

From the phase diagrams (Figure 1, Figure 2, Figure 3…… Figure 13), it was possible to suggest that, at above 1500°C the slag was in liquid form in the furnace. Crystallization may have started below 1500°C as the slag started cooling in the slag ladle and in the dump. As cooling continued, it is likely that the α-belites formed and remained stable at a temperature of above 1420°C. A temperature drop below 1420°C it changed to the α-belites (alpha high) form which existed till 680°C when the beta-belite formed, began to crystallize. However, the presence of fractured belite crystals (Figure 1) suggest that some of the α- and α'-forms may have been stabilized between 1420°C and 680°C with faster cooling when water was sprayed on the slag to assist in cooling. The fracturing may have resulted from the inability of these higher temperature polymorphs to change to the lower temperature β-C₃S and γ-C₃S forms (γ-C₃S stable form was not detected). The occurrence of belite as large discrete crystals and as small crystal inclusions in wustite suggested that it was the first major solid phase to form in the slag. The crystallization must have started with the α- and α'-forms between below 1500°C and 680°C. This was a strong pointer that belite crystallization took place throughout the cooling process of the slag. The β-C₃S form may have started forming at 680°C and remained stable till 630°C below which, it could have started transforming into the gamma-belite (γ-C₃S) form. The γ-form should exist at temperatures below 500°C (Figure 13).
With an increase in temperature to 690°C from 630°C, the \( \beta - C_2 S \) could transform to the \( \alpha - C_2 S \) form which might seem to be the plausible reason for the non detection of the \( \gamma - C_2 S \). But the history of the slag has been that of a continuous cooling process and an increase in temperature may not have occurred and cannot account for the non detection of the \( \gamma \)-form. The presence of unstabilized \( \beta - C_2 S \) (un-crosshatched) form suggested that some of the \( \beta \)-form of belite could have converted to the \( \gamma \)-form with a temperature fall. But the non detection of \( \gamma \)-form in the slag suggested that the \(<500^\circ C\) form forming temperature may not have been attained during the process of slag solidification. Most of the belite existed in the meta-stable beta form possibly between 680°C and about 630°C.

From the results obtained, the belites of the slag can be classified into:-

Type 1. Belite crystals without twinning features which were dominantly \( \alpha - C_2 S \). Twinning traces were observed in the \( \alpha - C_2 S \) most probably transformed from the \( \alpha - C_2 S \) indicating resulting from a less slow cooling.

Type 2. Belite crystals with wide distinctive lamellae with two or three orientations. These belite crystals were \( \alpha - C_2 S \) and stabilized \( \beta - C_2 S \) from \( \alpha - C_2 S \) inversion; and,

Type 3. Belite crystals with many fine indistinct lamellae and multiple orientation most dominantly \( \beta - C_2 S \), which is similar to clinkers from production kilns \[16,29\].

The general trend observed (see Figure 1) was:

i. The coexistence of melilithe with alpha belite
ii. The inclusion of melilithe in beta belites
iii. The inclusion of wustite (more) in belite,
iv. The inclusion of belites in wustite,
v. The inclusion of aluminate, periclase and peruvskite in belites and wustites,
vi. The inclusion of some round grains and fibrous wustite in aluminates, and;

Merwinithe co-existing with aluminates and some glass.

This mode of mineral occurrence suggested that, these phases probably crystallized with the late stage beta belite phase at low temperatures before 630°C and down to about 500°C, when there may have been complete mineral formation. The non detection of \( \gamma - C_2 S \) form, confirmed this suggestion. It is a pointer that belite crystallization (excluding \( \gamma - C_2 S \)) continued throughout the cooling process of the slag.

The occurrence of euhedral melilithe crystals, sometimes enclosed in the larger beta-belite (\( \beta - C_2 S \)) crystals suggested that their crystallization started before beta belite crystallization. Their occurrence with the alpha belites, also suggested that their crystallization started probably simultaneously with alpha-belite between 1420°C and 680°C. Their associated occurrence with beta belite indicates their possible simultaneous crystallization with \( \beta - C_2 S \) at 680°C.

The coexistence of some melilithe (gehlenite (2CaO·MgO·2SiO\(_2\)) with wustite (FeO) and calcium aluminante (CaO·Al\(_2\)O\(_3\)·C\(_3\)A) as interstitial material indicated a late stage crystallization confirming that melilithe crystallization continued till slag final solidification. This late stage crystallization likely between 630°C and 500°C was confirmed by SEM and EMPA identified occurrence of melilithe, merwinithe, wustite, aluminante and glass as interstitial material.

Periclase occurred with cryptocrystalline wustite groundmass in certain regions and surrounded by thin shells of wustite in other areas. This later situation indicated that they may have crystallized before wustite, but the euhedral or spherical shapes of the periclase grains suggest that periclude, resulted from a higher surface free energy for periclase during its crystallization together with wustite.

Peruvskite occurred in association with belite and wustite. It sometimes occurred enclosed in the wustite and sometimes as rectangular and irregular light grey shades on wustite. The enclosed occurrence indicated that the perovskite crystallized before the wustite, the associated occurrence indicated the crystallization together with late stage belite but, after the wustite. The occurrence as light grey shades indicated that the peruvskite crystallized after the wustite possibly, squeezed out of the belite.

3.4. Summary of Mechanism of Mineral Formation

The mechanism of mineral formation in the slag cannot be fully explained here, but the indication is that formation may have taken place between above 1420°C and 500°C. From the foregoing, the most probable mineral crystallization sequence in the Slag can be summarized as thus:-

- \( C_2 S \)
- \( C_2 S + Melilithe \)
- \( C_2 S + Melilithe + Merwinithe \)
- \( C_2 S + Melilithe + Merwinithe + Wustite + C_3 A \)
- \( C_2 S + Melilithe + Wustite + Merwinithe + Wustite + Periclase + Peruvskite \)

This order of crystallization sequence suggested, can be seen from the occurrence of discrete crystals of the various phases and the interface relations- inclusions and interfingering co-existence. The crystallization can be explained using Figures 1, Figure 2, Figure 3........ Figure 13).

Figure 13 shows the form of mineral crystallization. It depicts that \( C_2 S \) was the first phase to start crystallizing as cooling started till point G when merwinithe may have started crystallization. Both phases continued crystallizing till the triple point J, where they co-existed with melilithe which may have started crystallizing at an earlier stage. As cooling continued to point K, \( C_2 S \), melilithe, wustite and possibly \( C_3 A \) co-existed having crystallized from a liquid depleted of
merwinite, which may have completed crystallization. This seems to confirm the conclusion that wustite and periclase were the last phases to crystallize whilst C₃S crystallization continued throughout the slag cooling process.

4. Mineral Phase Potential Material Use in Industry

Recent chemical and mineralogical investigation of steelmaking slags has resulted in their applications as industrial materials in construction and building, ceramics, cement, glass and agriculture [9]. Electron microprobe analysis results of DSC slag indicate the richness of the mineral phases in major steelmaking elements from belite, mellite and merwinite silicates, wustites, periclase and perovskite in terms of Si, Ca, Fe, Mg, and Ti [41]. These elements in the slag are required for the blast furnace iron and steel making process [12], [24], [26], [37], slag ceramics [25], slag cement [26], [27], [31], [32], [33], [35] and agriculture [3]. CaO can be a fluxing and mineral forming agent in reaction with unwanted elements from the iron making ingots.

The silicates can be major sources, of Si, Ca and Fe necessary for use in iron and steelmaking blast furnace as feed and in the agricultural industry as fertilizer [3]. Belite in the slag had hydration properties as shown by the presence of beta-belte and therefore suitable for slag cement manufacture [1], [2], [41]. The silicates and perovskite can provide agriculture important phosphorus (P), possibly for direct application or used to produce phosphate fertilizer.

Perovskite contained a good proportion of Ca and can be combined with the silicates for use as fertilizer. Wustite, as a major source of Fe can be used as blast furnace feed, and as fertilizer, combined with perovskite. It can also provide some MnO/Mn, suitable for use in the iron and steelmaking blast furnace. Periclase and wustite can be the major sources of MgO/Mg suitable for use as fertilizer in the agriculture and slag ceramics industry. These mineral phases in DSC slag can be separated using standard mineral separation methods for use in different industries.

5. Conclusion

Mineral crystallization in the slag started at high temperatures of about 1420°C continued till low temperatures of about 500°C when the slag completely solidified. Melilites and the alpha belites formed between 1420°C and 680°C. At a late stage crystallization between 680°C and 500°C there was continuous crystallization of all minerals except the alpha belites till the final solidification of the slag. This crystallization of slag minerals from the cooling of the slag clinker at high temperatures to low temperatures was similar to that of cement clinkers and that of natural minerals from igneous magma. From the temperatures of existence the different mineral phases can be separated for different material uses. For example the meta-stable beta belte (β-C₂S) the phase that provides hydraulic property can be separated between 680°C and 630°C for use as a cement, slag cement, slag ceramics, agriculture and civil engineering material.

References


