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Investigation on stabilization of ladle furnace slag with different additives

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Investigation on stabilization of ladle furnace slag with different additives

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Abstract

Ladle furnace slag disintegrates into fine powder during cooling due to phase transformations of di-calcium silicate. This creates an adverse impact on working conditions and the environment by dust generation. In this paper, a short overview on different studies to overcome the disintegration problem is provided. An attempt was also made to study the effects of several different additives and their mixtures on disintegration of slag. Phase equilibria calculations were carried out for some additives using FactSage® to understand the phase changes in the slag. Based on the phase equilibria calculations and literature data, initial laboratory experiments were conducted at 1650°C with different additives such as boric acid, aluminium and fly ash. Slag samples were analysed with XRF and XRD for chemical and phase analysis before and after treatment. The disintegration of slag can be prevented either by addition of 0.5 wt% or more of boric acid or 9 wt% of aluminium or 6 wt% of fly ash or 4-8 wt% fly ash along with 0.125-0.25 wt% of boric acid in slag. Based on the optimised conditions, industrial trials were conducted.

Keywords: Ladle furnace slag, Di-calcium silicate, Disintegration, Modification, Stabilisation, Environmental impact.

Introduction

Ladle furnace (LF) slag plays a pivotal role in steel making process as it purifies molten metal by absorption of non-metallic inclusions and desulfurization. The disintegration of ladle furnace slag is a long-witnessed problem in the steel making process, especially while making silicon killed steels. This disintegration hinders its utilisation and significantly increases the landfilling cost. In the steel making process, ferro-alloys are added in order to get the desired composition as well as to reduce the dissolved oxygen to an optimum level. While making silicon killed steels, de-oxidation is done mainly by Si and Mn and these deoxidizers generate large number of primary inclusions such as SiO_2 and MnO in a short time which eventually float and join the slag. Hence, this slag has high silica content compared to aluminium killed steel. On the other hand, high percentage of lime is also maintained in ladle furnace slag to increase the basicity, which enables removal of impurities and helps in desulfurization. This high lime content in the slag combines with SiO_2 forms di-calcium silicate phase (($2CaO.SiO_2$ or C_2S) in the slag. This will undergo phase transition from β-C_2S (monoclinic) to γ-C_2S (orthorhombic) [1] accompanied by a volume increase of around 12% during cooling [2-4]. This causes disintegration of the slag in to a fine powder. The Phase transformation sequence of C_2S at different temperatures is shown below [5].

$$\text{Type } \alpha \xrightleftharpoons{1425^{\circ}\text{C}} \text{Type } \alpha'_H \xrightleftharpoons{1160^{\circ}\text{C}} \text{Type } \alpha'_L \xrightleftharpoons{690^{\circ}\text{C}} \beta \xrightarrow{<500^{\circ}\text{C}} \gamma$$

In addition to di-calcium silicate disintegration, free lime and free magnesia present in slag may hydrate and lead to disintegration during subsequent cooling of the slag. This disintegration takes few days to weeks in case of CaO and even for months in case of MgO. Compositional limits to avoid the disintegration of slags were defined [6] based on the stability factor of C_2S in the $CaO\text{-}MgO\text{-}SiO_2\text{-}Al_2O_3$ slag system, with an adjustment for the calcium sulphide content.

$$CaO + 0.8\,MgO \leq 1.2\,SiO_2 + 0.39\,Al_2O_3 + 1.75\,S \tag{1}$$

$$CaO \leq 0.93\,SiO_2 + 0.55\,Al_2O_3 + 1.75\,S \tag{2}$$

If the slag follows either one of the above conditions and does not comprise large amounts of C_2S then it will not undergo disintegration [7,8]. Various methods have been proposed by different researchers to address the disintegration of steel slag which contains mainly free lime, free magnesia and di-calcium silicate.

β-phase stabilization of C_2S

In order to avoid the disintegration of di-calcium silicate, chemical stabilization is generally considered to be the best method for retention of the high-temperature β-phase down to room temperature [9,10]. It is obtained by the addition of suitable stabilizers, as they form solid solutions with C_2S. Seki et al. [11] first developed a borate based stabilizer for inhibiting the β to γ transformation of C_2S in the stainless steel decarburization slag. The β-polymorph was reported to be stabilized by the presence of smaller ions such as Si^{4+} by BO_4^{5-}, PO_4^{4-} , VO_4^{3-} and SO_4^{2-} in C_2S. It was proved that the doping of the multivalent ions is more effective than the univalent and divalent ions for the stabilization of β-C_2S. The replacement of SiO_4^{4-} by smaller ions of higher negative charge is successful in stabilizing β-C_2S. It can also be stabilized by the addition of B_2O_3, Na_2O, K_2O, BaO, MnO_2, Cr_2O_3 or their combinations. Smith el al. [12] reported that β to γ transformation involves a change in calcium coordination accompanied by a rotation of the SiO_4 tetrahedron [13]. The β to γ conversion of only 4% slag by weight [14,15] is sufficient to cause the dusting phenomenon.

Pontikes et al. [7] developed a stability diagram as a function of B_2O_3 content and C_2S fraction. From this diagram, it was confirmed that a minimum fraction of about 20 wt% C_2S has to be stabilized with borate addition. The amount of borate addition required for stabilization of slag increases with increase in C_2S content. Boron containing minerals like borax, kernite, colemanite and soda colemanite can be added to prevent the crumbling of slag during cooling. Often addition of 0.1 to 0.4 wt% of B_2O_3 in steel slag is sufficient to stabilize the slag depend on its slag chemistry. Considering its usefulness, slags stabilized with borate addition were utilized as an aggregates for construction applications [16].

Borates stabilize high temperature polymorphs of pure C_2S to ambient temperatures by forming solid solution. Due to large difference in ionic radius between Si^{4+} and B^{3+} ions, it is assumed that the SiO_4^{4-} units are to be replaced by BO_3^{3-} units [17]. Hence the Ca^{2+} migrations and SiO_4^{4-} rotations required for β to γ transformation are inhibited [8]. Fletcher et al. anticipated the most possible mechanism for borate solid solution in di-calcium silicate as shown in equation (3), where $\square$ is a cation vacancy. During B_2O_3 addition it forms solid solution with Ca_2SiO_4 that results in the formation of a stable ternary compound $Ca_{11}B_2Si_4O_{22}$.

$$2[(SiO_2)^{4-}] + Ca^{2+} = 2[(BO_3)^{3-}] + \square (3)$$

Although there is a slight difference in chemical composition of basic oxygen furnace (BOF) slag and ladle furnace slag, both contain C_2S; basic oxygen furnace slag (BOF) however, does not disintegrate. This occurrence is mainly due to the presence of 2-5% of P_2O_5 in BOF slag which acts as a stabilizer of for β-C_2S in the BOF.

The other way of minimizing the disintegration of ladle furnace slag is through fast cooling by means of dry granulation and it is considered to be effective in suppressing the β to γ transformation of C_2S [18,19] for basicity CaO/SiO_2 as high as 2.2. The fast cooling is mainly adopted in cement industry in order to prevent the γ polymorph. Laboratory studies also proved that the effect of cooling rate on disintegration and the required slag cooling rate is to be about 5ºC/sec to prevent the crumbling behavior of slag.

Phase modification

In order to stabilize the steel slag, along with borate sources the other modifiers are namely sandstone, slate, volcanic ash, silica sand, waste glass [20] coal ash [21] copper regules, zinc regules, aluminium dross, magnesium slag [22] foundry waste sand, granite etc., can also be added.

An alternative stabilization mechanism to boron is the addition of alumina and red mud obtained from aluminium industry [23] as these additions also avoid the disintegration of slag by formation of the stable C_2AS (di-calcium alumino silicate) compound. Addition of alumina reduces slag basicity by changing the slag chemistry subsequently avoiding the formation of C_2S by moving the system out of the C_2S stable region in the CaO-SiO_2-Al_2O_3 phase diagram. Doping of Al^{3+} [24] into the framework of di-calcium silicate also stabilizes the β-form by replacing the silicate units and generating oxygen vacancies.

Mudersbach et al. suggest additions of bauxite, Al_2O_3 [25] containing residues and aluminium metal to decrease the disintegration of stainless steel EAF slags by the formation of spinel type phases during solidification. The concept of using pure alumina and alumina/borate mixtures to stabilize C_2S in AOD slag was verified at the University of Leuven at lab scale [21]. A 4-8% addition of alumina was found to reduce the borate requirement by 50%. Actual alumina requirement depends on the calcium oxide to silica ratio in the slag.

The presence of free CaO or MgO in the slag leads to a long-term volume instability due to the expansive hydration to $Ca(OH)_2$ and $Mg(OH)_2$ [26]. The addition of SiO_2 containing materials [27] such as quartz sand, fly ash, glass cullet and spent foundry sands forms a stable matrix of calcium silicates and ferrites by reacting with free CaO and MgO. Eriksson et al. [28] proved that it is possible to prevent disintegration of di-calcium silicate in slag from stainless steelmaking by increasing the MgO content of the slag. Reducing the slag basicity below 1.7 by adding 5 to12 wt% of sand can also successfully stabilize the slag as the formation of $2CaO.SiO_2$ phase is avoided. Fly ash, a solid industrial waste product can also be used to stabilize steel slags [29]. Faylite slag contains SiO_2 and FeO as major constituents can also be used to stabilize steel slags of higher basicity [30]. FeO acts as an additional energy source due to its exothermic reaction to Fe_2O_3 and hence a minimum of 25 wt% faylite slag is required to stabilize the slag.

Even though there has been a quite bit of studies reported on preventing disintegration of ladle furnace slag, most of them were limited to laboratory experiments and require systematic investigation. Furthermore, there is no major study available with different additives on a single sample for comparing their effect on slag stabilization. Hence, in the present study, the proportions of different additives were optimized using FactSage® modeling and laboratory trials were carried out. Also, the experiments were conducted at industrial level and the results have been verified with those obtained from laboratory experiments.

Experimental Procedure

Laboratory experiments were carried out using slag samples of 100 g each with required quantity of stabilizers. The raw materials used in this study were boric acid, aluminium, fly ash (a waste product of thermal power plant), and an industrially produced ladle furnace slag. The boric acid additions are varied from 0.25-2 wt%. The aluminium and fly ash were added 4-10 wt% and 6-12 wt% respectively. The samples were put into a graphite crucible and loaded in a Carbolite gero melting furnace. The samples were heated to 1650°C at 5°C/min and were kept at this temperature for 1 hour to uniform soaking followed by slow cooling at 5°C/min to room temperature, under static air. Chemical analysis was done for slag before and after stabilization using Panalytical axiosXRF. The phase analysis was carried out using BrukerD8 Advance XRD. The XRD analysis was performed between 2θ range of 10° to 70°, CuK$_\alpha$ radiation under 45kVand 35mA. Phase equilibria calculations were performed with FactSage 7.0 software using the FactPS and FToxid databases.

Results and discussion

The disintegrated LF slag, collected from the site, is shown in Figure 1. The results of XRF analysis carried out on the disintegrated slag and the fly ash are presented in Table 1 and Table 2 respectively. It was observed that the disintegrated slag consists of various major constituents such as CaO, SiO_2, Al_2O_3 and MgO. Also, the major constituents identified in the fly ash are SiO_2,Al_2O_3 and Fe_2O_3. The XRD studies conducted on the LF slag revealed certain phases such as γ-C_2S, Periclase and Gehlenite is shown in Figure 2. The γ-C_2S was found to be the major one.

Results from laboratory experiments

Phase equilibria calculations

Phase equilibria calculations were carried out using FactSage® tool to estimate the optimum amount of additives required to suppress the formation of dicalcium silicate or to stabilize the β-phase. However, the calculations were not done for boric acid as the database of FactSage doesn't contain boron doped dicalcium silicate phase. Effect of aluminium on the phase equilibria of the slag is shown in Figure 3. It was observed that the amount of dicalcium silicate decreases with an increase in aluminum. The rate of decline was found to be lower when the amount of aluminum ranges from 5-10 g. Also, the dicalcium silicate was found to be minimum at 10 g of aluminum. This is due the formation of a new phase named melilite.

Figure 4 shows the effect of fly ash on the phase equilibria of slag. As it can be seen, 16 g of fly ash is required to reduce the dicalcium silicate to a minimum. As in the case of aluminum, here also, the rate of decline was found to vary at almost 5 g of fly ash.

Laboratory scale experiments were carried out based on the literature and FactSage calculations.

Effect of Boric acid addition

Laboratory scale experiments were carried out with varying boric acid content ranging from 0.25 to 2.0 wt% (0.25, 0.50, 0.75, 1.0, 1.5 and 2.0 wt%). The crumbling of ladle furnace slag during cooling without any stabilizer is shown in Figure 5. It was observed that 0.25 wt% boric acid added to the ladle furnace slag does not fully stabilize the slag on cooling. As it can be seen from Figure 6a, the slag, after few minutes, started to disintegrate and slowly all the slag crumbled to be small fragments and fine powder. This could be due to the presence of a small amount of γ-C_2S in the slag. The slag was found to be fully stabilized when the boric acid added was ranging from 0.50-1 wt%. However, the slag was found to break down to bigger pieces (Fig. 6b) than those observed when 0.25 wt% of boric acid was added. Furthermore, when 2 wt % of boric acid was added, the slag was appeared to be hard rock like shape with color changing from whitish grey to blackish brown as shown in Figure 6c.

XRD studies were conducted on the slag treated with different boric acid additions and the results are shown in Figure 7. The slag treated with 0.50-1.5wt% boric acid was found to have certain major phases such asMerwenite, Clinokurchatovite and Akernite. The slag treated with 2 wt % boric acid revealed boron silicide(B_4Si), calcium bisborate (B_2CaO_4), Merwenite ($Ca_3Mg(SiO_4)_2$) and Clinokurchatovite ($Ca\ (Mg, Mn^{2+}, Fe^{2+})\ B_2O_5$) to be main phases.

Effect of Aluminium addition

Laboratory trials were also carried out using the ladle furnace slag and 4-10 wt% aluminum. From these experiments, it was observed that a minimum of 9 wt% aluminum is required to stabilize the steel slag. β-C_2S, Gehlenite ($Ca_2Al_2SiO_7$) and Mayenite ($Ca_{12}Al_2O_{33}$) were found to be major phases in the stabilized steel slag as shown in Figure 8. This amount was more than the value obtained from the calculated one this might be due to low recovery of aluminium Aluminium converts β-C_2S phase to gehlenite as per the reaction shown in equation 4. It is well known that aluminium is used to the kill the slag i.e. de-oxidation of reducible oxides like FeO and MnO, during this process it reacts with those oxides and forms alumina. This combines with CaO in the slag and forms calcium aluminates and calcium alumino silicates. The LF slag stabilized with aluminium is shown in Figure 9. The results of XRF analysis is also given in Table 3, which shows the increase in alumina content in the slag.

$$2CaO.SiO_2 + Al_2O_3 \rightarrow 2CaO.Al_2O_3.SiO_2 \qquad (4)$$

Effect of Fly ash addition

Laboratory trials were also carried out using fly ash ranging from 6-12 wt% in order to study the stabilization of slag. It was observed that with increase in percentage of fly ash, glassy phase was found to be formed in the slag and this may could be due to presence of higher percentage of SiO_2. In fact, with addition of fly ash, the overall slag chemistry is changed in such a way that the basicity of slag comes down to less than 1.7 and hence the steel slag is stabilized. XRF analysis of the slag treated with fly ash is shown in Table 4. Comparison of compositional limits was done for slag before and after treatment with fly ash and the same is shown in Table 5. Praker et al. proposed a compositional limits to avoid the disintegrating slags, our slag treated with fly ash falls within those limits and may not comprise large amounts of C_2S this could be the reason it not undergone disintegration during cooling.

Chemical composition of slag before and after treatment with fly ash was plotted in ternary system $CaO-Al_2O_3-SiO_2$ and it is shown in Figure 10. From the ternary diagram it is evident that before the treatment slag contains more C_2S and it was shifted to merwenite region after fly ash addition. The results of XRD studies performed on the slag treated with fly ash were presented in the Figure 11. As it can be clearly seen, the major phases were found to be Larnite ($Ca_2O_4Si_1$), Mayenite ($Al_{14}Ca_{12}O_{33}$) and Gehlenite ($Ca_2Al_2SiO_7$). These phases are considered to be harmless as they do not cause volume expansion during the cooling of slag. This shows that the addition of fly ash is beneficial in preventing the formation of γ-dicalcium silicate and eventually in avoiding disintegration of slag during its cooling. The stabilized slag after being treated with 6 wt%, 8 wt% and 12 wt% fly ash is presented in Figure 12. As it can be clearly observed that the slag treated with 12 wt% fly ash was found to be more stable.

Effect of Fly ash and borate addition together

An attempt was also made to study the combined effect of both boric acid and fly ash additions in LF slag. In this way, the reduced amount of fly ash addition can cause operational ease. These additions were found to minimize the crumbling of slag by reducing basicity and elimination of γ-C_2S formation in the slag. Furthermore, the slag treated with fly ash and boric acid was found to have certain additional phases such asHowlite ($Ca_2B_5SiO_9(OH)_5$), Danburite ($CaB_2Si_2O_8$) along with Merwenite ($Ca_3Mg(SiO_4)_2$) is shown in Figure 13.

Industrial trials

From the laboratory experiments, it was observed that 0.5 wt% boric acid, fly ash of 6-12 wt% and minimum Al of 9 wt% in slag individually is sufficient to stabilize the β-C_2S phase in LF slag. Industrial trials were planned in 150 t steel ladle based on the results obtained from laboratory experiments.

Though during laboratory experiments addition of 0.5 wt% boric acid gave desired results, the same quantity of boric acid might not be sufficient at industrial scale trials. Hence, trials were conducted with various quantities of boric acid varying from 0.5 to 1 wt%. The main advantage of boric acid is that, addition of very less quantity is required to prevent disintegration. Boric acid additions are done at ladle furnace area before dispatch of heat for casting. After addition of boric acid, mild rinsing is done for homogenization of slag composition. It was found that at 0.75 to 1.0 wt% the slag gets stabilized as can be seen in Figure 14.

Even though 9 wt% Al addition adds cost to the steel making, it gives additional advantage of slag killing. The steel slag contains reducible oxides like MnO and FeO in certain percentages and causes re-oxidation of steel. Addition of small amounts of Al in slag is useful for slag de-oxidation, also makes the slag fluid that helps in better de-sulphurisation and inclusion absorption. Hence, this practice of Al addition in slag has twin advantages of minimizing steel slag crumbling along with other metallurgical reasons.

In fly ash trails the quantity was varied from 6 to 12 wt%. As additional heat was required for melting of this silicious material for proper participation in reaction with slag. This was provided by regular arcing in ladle furnace. The arcing provides sufficient heat required for the reactions in slag with fly ash. It was observed that about 8 to 12 wt% of fly ash given desired results as shown in Figure 14. Few trails were also conducted in combination with 0.25 wt% boric acid along with 4 wt% fly ash. It was observed that results were encouraging. This combination was tried in order to reduce fly ash handling problems as quantity requirement of fly ash is huge.

Conclusions:

1. The effects of boric acid, fly ash and aluminum additions on stabilization of LF slag were investigated.
2. Phase changes in the LF slag, upon treating with various additions, were understood using FactSage tool.
3. Laboratory experiments revealed that the LF slag gets stabilized when a minimum of 0.5 wt% boric acid, 9 wt% aluminum and 6 wt% fly ash are added to the slag. Furthermore, the addition of 4-8 wt% fly ash along with 0.125-0.25 wt% boric acid was also found to minimize disintegration of LF slag.
4. From the trials performed in industrial scale, it was observed that adding of 0.75-1.0 wt% boric acid and 8-12 wt% fly ash can avoid disintegration of the slag.

On behalf of all authors there is no conflict of interest.

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Table 1. XRF analysis of as received LF slag

CaO	SiO_2	Al_2O_3	MgO	TiO_2	FeO	MnO	P_2O_5	S	Basicity
53.5	23.6	9.9	9.58	0.73	1.43	0.40	0.05	0.27	2.3

Table 2 Typical composition of Fly ash at RINL-VSP

SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	TiO_2	K_2O	Na_2O	LOI
59	33.85	4.85	0.55	0.57	1.2	0.175	0.13	0.9

Table 3. XRF analysis of slag treated with Aluminum

Sl.No	wt% Al addition	CaO %	SiO_2 %	Al_2O_3 %	MgO %	FeO %	Basicity CaO/SiO_{27}
1	0	53.5	23.6	9.9	9.58	1.43	2.3
2	9.6	43	21.7	21.3	12.34	0.7	2

Table 4. XRF analysis of slag treated with fly ash

Sl.No	wt% fly ash addition	CaO %	SiO_2 %	Al_2O_3 %	MgO %	TiO_2 %	FeO %	Basicity CaO/SiO_2
1	0	53.5	23.6	9.9	9.58	0.73	1.43	2.3
2	6	41.7	30.7	15	9.5	0.86	1.2	1.3
3	8	40.5	31.1	15.5	9.57	0.88	1.4	1.3
4	12	41.5	34.6	10.8	10.61	0.98	0.6	1.2

Table 5. Comparison of compositional limits for slag treated with fly ash

Sl.No	wt% Fly Ash	CaO (a)	0.93 SiO_2 + 0.55 Al_2O_3 + 1.75 S (b)	a≤b	CaO + 0.8 MgO (c)	1.20 SiO_2 + 0.39 Al_2O_3 + 1.75 S (d)	c≤d
1.	0	53.5	27.8	Yes	61.16	32.66	Yes
2.	6	41.7	37.2	Yes	49.3	43.1	Yes
3.	8	40.5	37.9	Yes	48.1	43.8	Yes
4.	12	41.5	38.3	Yes	49.9	45.9	Yes

Figure 1. Disintegrated steel slag after cooling

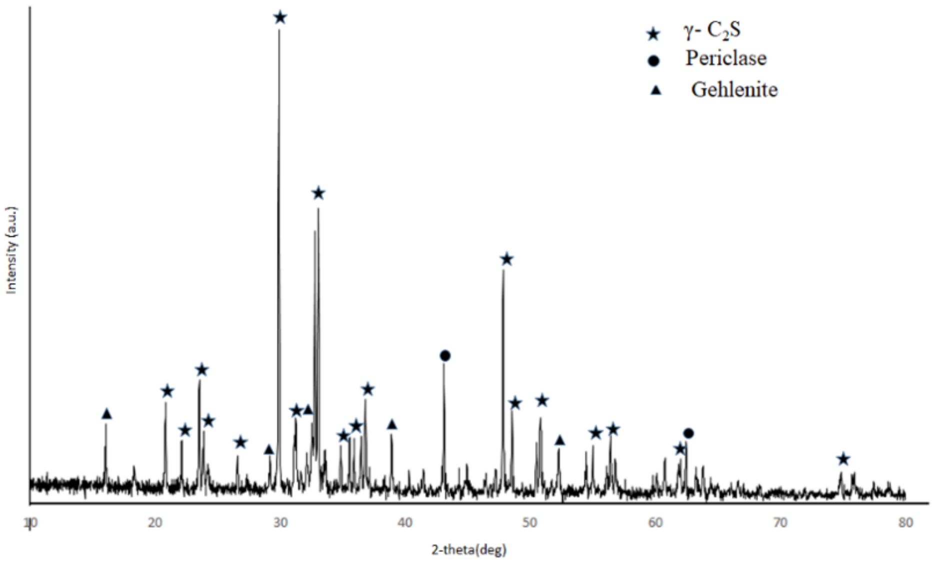

Figure 2. XRD of as received Ladle furnace slag

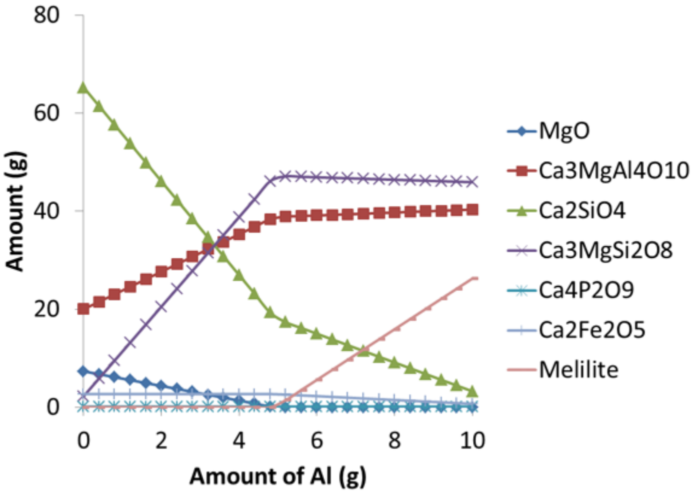

Figure 3. Effect of Al on phase equilibria of slag at 550°C

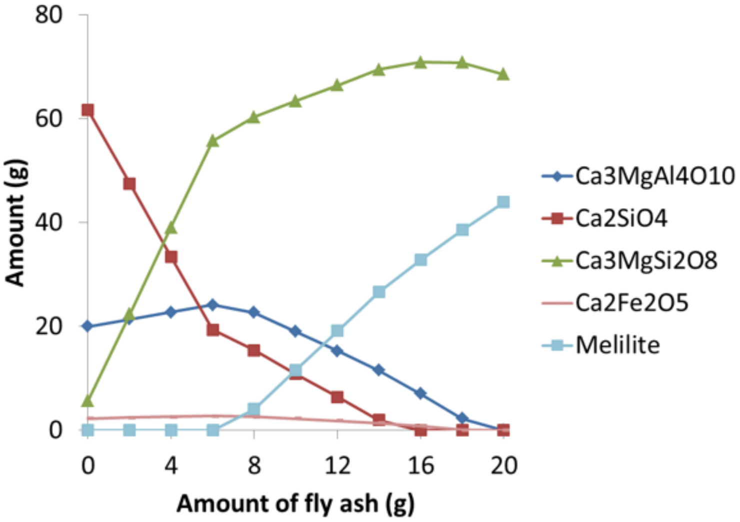

Figure 4. Effect of fly ash on phase equilibria of slag at 550°C

Figure 5. Crumbling of ladle furnace slag during cooling without any stabilizer

(a) Slag stabilized with 0.25 wt % boric acid (b) Slag stabilized with 0.5 wt % boric acid (c) Slag stabilized with 2 wt % boric acid

Figure 6. Images of steel slag stabilized with (a) 0.25 wt%, (b) 0.5 wt% ((c) 2 wt% of boric acid

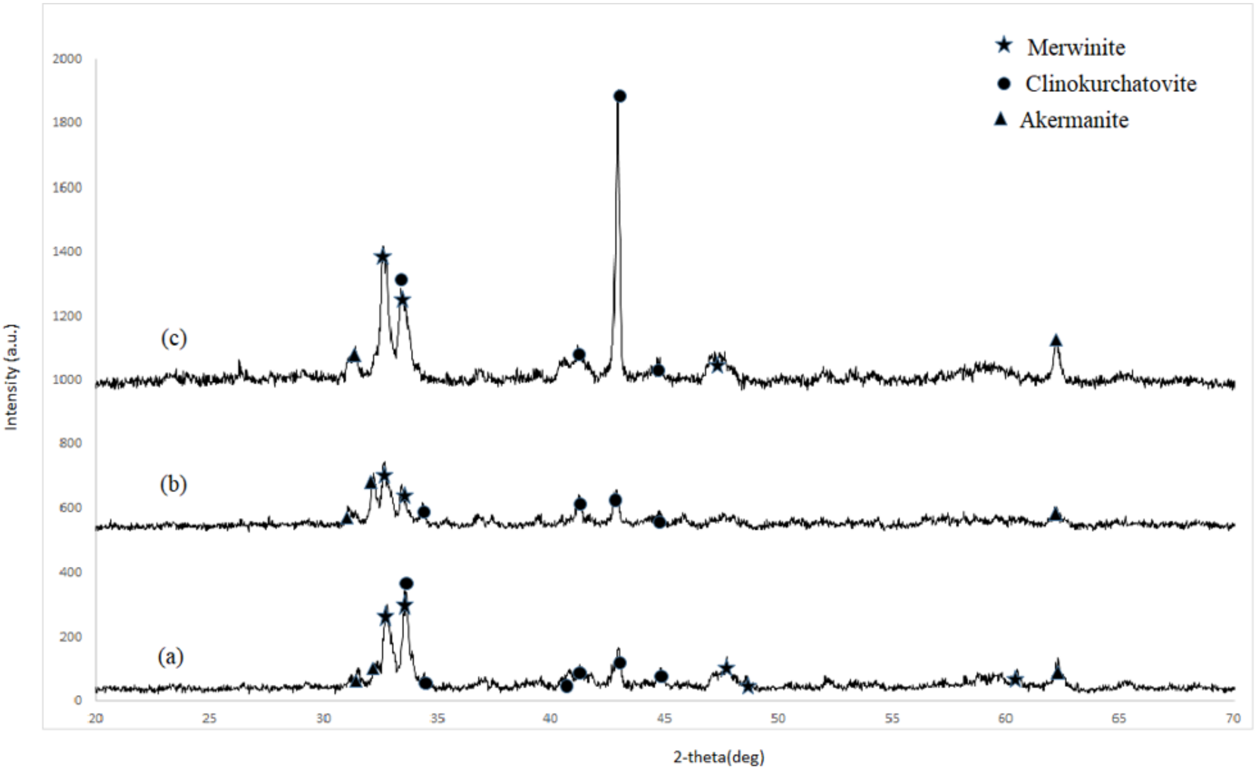

Figure 7. XRD of slag stabilized with a) 0.5wt% boric acid b) 1.0 wt% boric acid c) 2 wt% boric acid

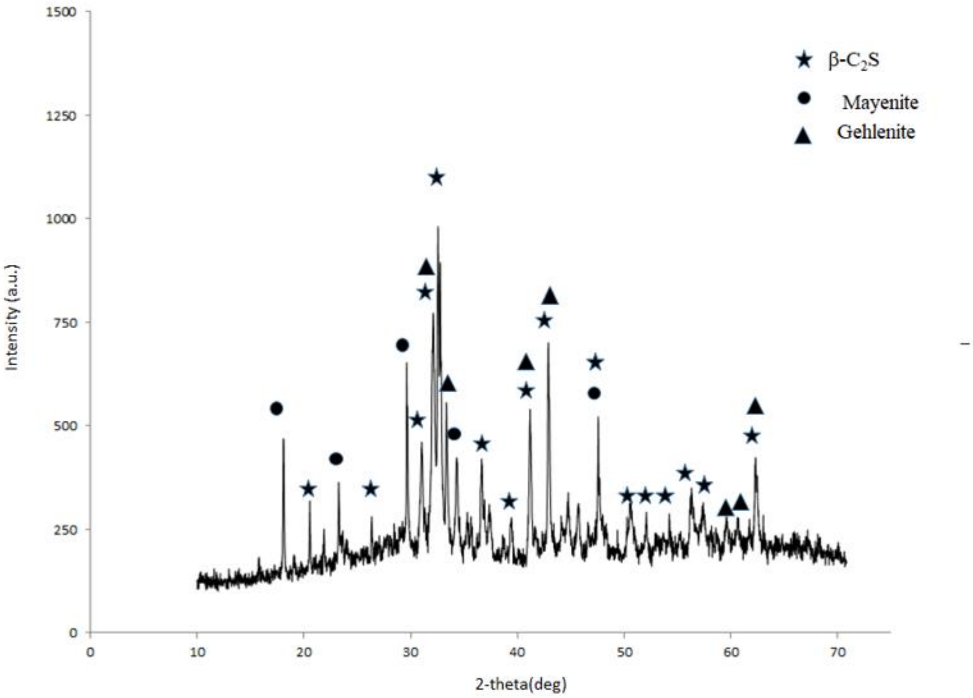

Figure 8. XRD of Steel slag stabilized with 9.6 wt% Al

Figure 9. Steel slag stabilized with 9.6 wt. % Al

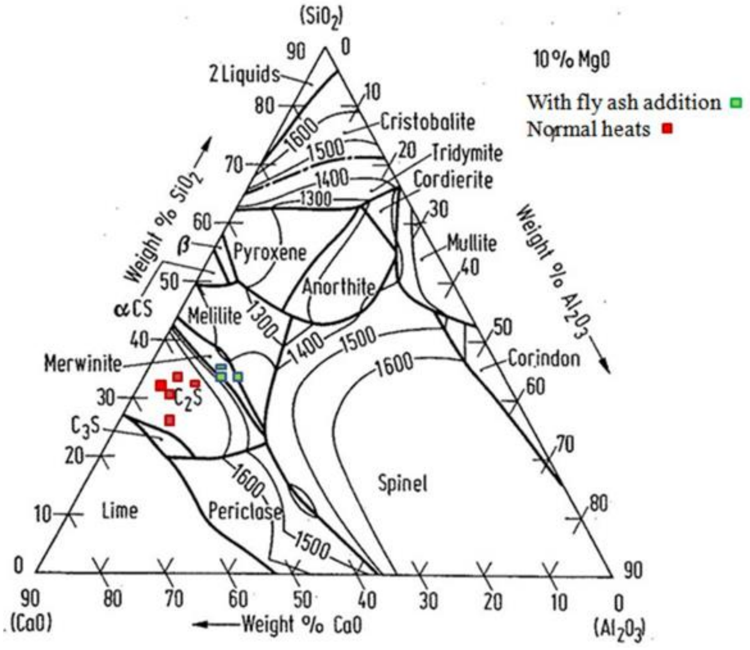

Figure 10. Chemical composition of slag before and after treatment with Fly Ash plotted in ternary system $CaO-Al_2O_3-SiO_2$

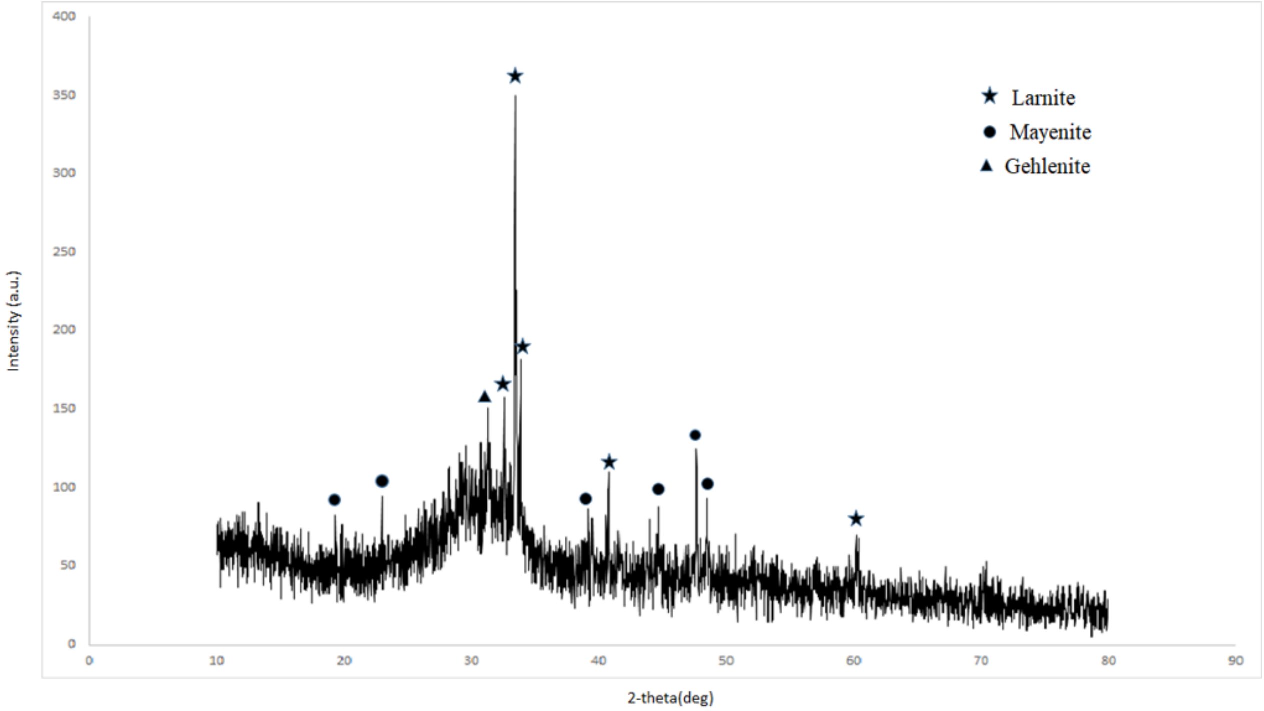

Figure 11. XRD of slag stabilized with 12 wt% Fly ash

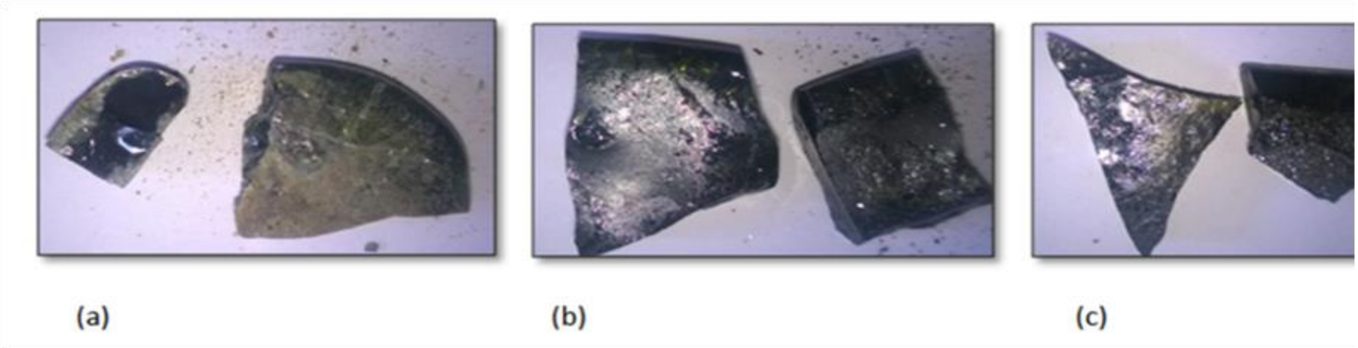

Figure 12. LF slag treated with (a) 6 wt% (b) 8 wt%, (c) 12 wt% of fly ash

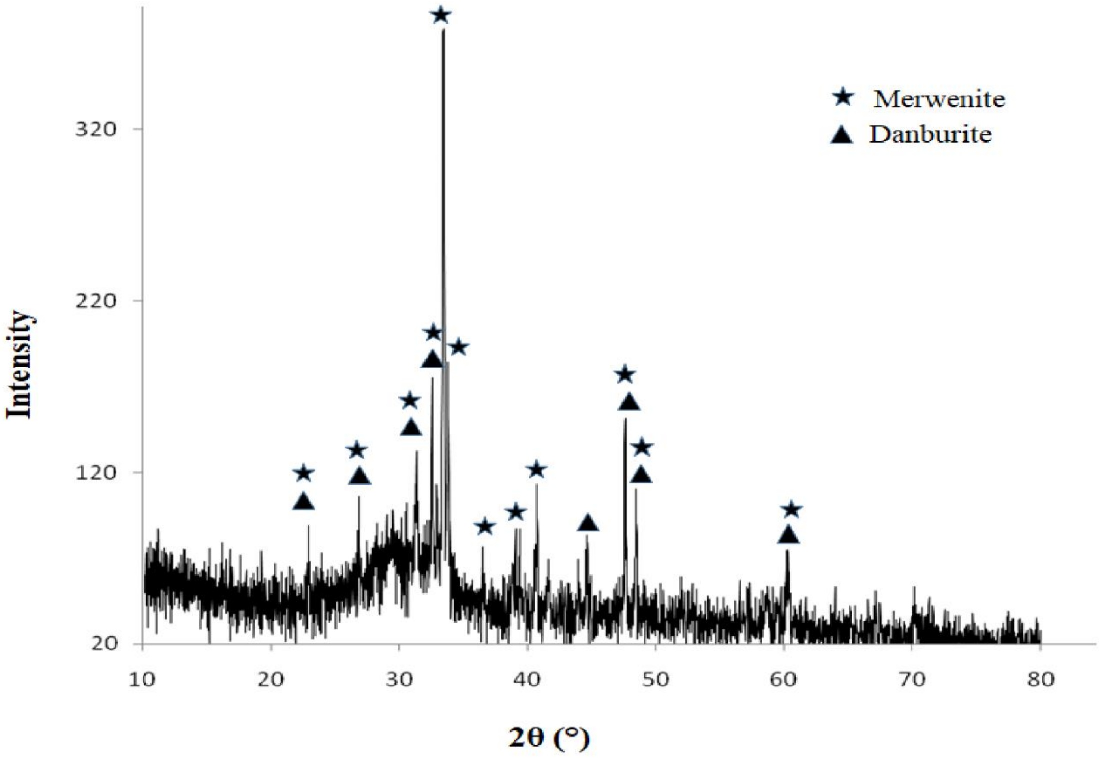

Figure 13. XRD analysis of slag treated with 4 wt% Fly Ash and 0.25 wt% B_2O_3

Figure 14. Ladle furnace slag stabilized with boric acid during industrial trials

Figure 15. Ladle furnace slag stabilized with fly ash during industrial trials