

## Conference Paper

# Chemical Stabilization Features of Ladle Furnace Slag in Ferrous Metallurgy

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Nowadays due to the application expansion of secondary steel processing methods, which provide high-degree metal desulfurization, a problem of the ladle furnace slag (or high-calcium refining slag) stabilization arose in the ferrous metallurgy. This slag cannot be stabilized because of its self-disintegrating properties [1].

It is known that this kind of disintegration is driven by the presence of dicalcium silicate (belite, or  $2\text{CaO}\cdot\text{SiO}_2$ , or  $\text{C}_2\text{S}$ ) in the refining slag. Approximately 80% particles of disintegrated slag have grain sizes less than  $30\ \mu\text{m}$ . Such particles are easily aerated and carried by the wind for long distances; they pollute soils, dissolve in ground, sedimentary and sewage waters. However, it is noted in [2–5] that there are four known widespread ways to prevent decomposition of secondary steel processing slags.

1. Thermal stabilization of high-temperature  $\text{C}_2\text{S}$  modifications by fast cooling (quenching). Due to quenching, the high-temperature  $\beta\text{-C}_2\text{S}$  modification acquires the ability to maintain its properties in the temperature range from 25 to  $700^\circ\text{C}$ .
2. Slag stabilization by boron addition based on the partial replacement of  $\text{SiO}_4^{4-}$  units by  $\text{BO}_3^{3-}$  units in the  $\text{C}_2\text{S}$  structure, which interfere the transformation of  $\beta\text{-C}_2\text{S}$  into  $\gamma\text{-C}_2\text{S}$  under polymorphic transformation.
3. Non-boron stabilization based on isomorphous replacement of  $\text{Ca}^{2+}$  units by  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$  units, and  $\text{SiO}_4^{4-}$  units by  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$  as well. To stabilize high temperature modifications of  $\alpha\text{-C}_2\text{S}$  and  $\alpha'\text{-C}_2\text{S}$ , an  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{BaO}$ ,  $\text{K}_2\text{O}$ ,  $\text{P}_2\text{O}_5$  and  $\text{Cr}_2\text{O}_3$  oxides are used. For  $\beta\text{-C}_2\text{S}$  stabilization  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{BaO}$ ,  $\text{MnO}_2$ ,  $\text{Cr}_2\text{O}_3$  oxides or its combination are used.

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Figure 1: The plan of A-B-C experiment conducting in the area of CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> phase diagram.

Material type	Content in the slag, [mass. %]						
	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	MnO	MgO	Cr <sub>2</sub> O <sub>3</sub>
Model refining slag	70,10	15,01	3,64	0,54	0,43	10,05	0,23

TABLE 1: Chemical composition of model slag.

- Alternatively, slag decomposition can be averted by modifying the slag phase composition in order to avoid the presence of C<sub>2</sub>S.

In this work the possibility of belite chemical stabilization by its transformation into more stabilized phases containing Al<sub>2</sub>O<sub>3</sub> is estimated. The secondary alumina production wastes (SAPW) were used as a source of Al<sub>2</sub>O<sub>3</sub> [6].

To determine phase composition change of the slag according to corrective additives in it, an experiment optimization was carried out by simplex-lattice planning. A plan of A-B-C experiment conducting in the area of CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> phase diagram is shown in Figure 1.

Material type	Content in SAPW, [mass. %]				
	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Al <sub>met</sub>	MgO	NaCl + KCl + NaF + KF + Na <sub>2</sub> O + K <sub>2</sub> O
The secondary alumina production wastes	20,0-75,0	1,0-10,0	5,0-20,0	5,0-12,0	5,0-20,0

TABLE 2: The chemical composition of the secondary alumina production wastes.

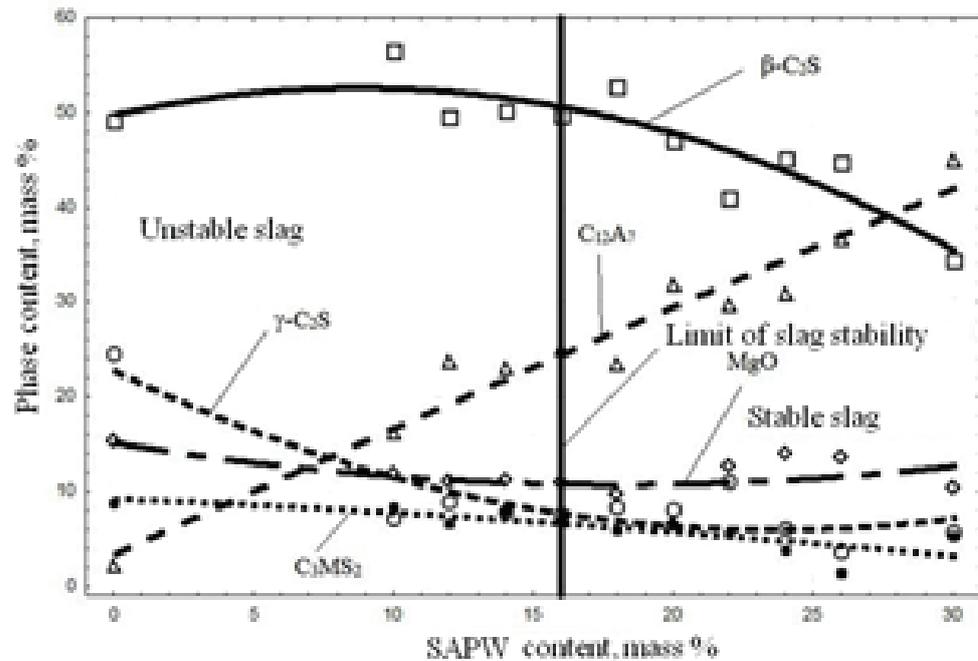
The plan is located in the area, where the CaO content varies from 40 to 80 mass. %, SiO<sub>2</sub> from 10 to 50 mass. % and Al<sub>2</sub>O<sub>3</sub> from 10 to 50 mass. %. It covers the area of CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> where metallurgical slag compositions are located. These slag compositions are used for the steel refining. The content of model slag and quartz sand as well as secondary alumina production wastes content were used as variable factors in the experiment. The chemical composition of model slag is presented in Table 1.

The quartz sand with the SiO<sub>2</sub> content more than 99,0 mass. % meets normative requirements. The chemical composition of the secondary alumina production wastes is presented in Table 2.

The dynamic viscosity (Pa·s) of the slag at 1500°C was adopted as a response function in the experiment.

According to the plan of the experiment, model slag was mixed with SiO<sub>2</sub> and SAPW, and then the mixture was placed into a periclase-graphite crucible which was heated to the measurement temperature. The viscosity of slags was measured by a vibrational viscometer of the S.V. Stengel'meyer. The measurements were taken at 14 points in accordance with the experiment plan which is shown on the Figure 2. After the measurements, the crucibles were taken out of the furnace and placed in a heat-insulating block for slow cooling. The results of the viscosity measuring were described by a polynomial of the third degree. The qualitative X-ray phase analysis (XRD) was used to determine the type of phases contained in the cooled slag. The quantitative XRD was used to determine phase amount in the slag. The results of the viscosity measurement obtained by regression equations were visualized in the ternary graphs.

Figure 2 shows the response function isolines of slag viscosity (Pa·s) at 1500°C in the factor space. It also shows approximate area boundaries of basic slag phases. From the test results it can be seen that SAPW addition reduces the slag viscosity. The area with significant SiO<sub>2</sub> content demonstrates minimal slag viscosity (0,267 Pa·s). However, it should be taken into consideration that diopside CMS<sub>2</sub> and akermanite C<sub>2</sub>MS<sub>2</sub> are formed in that area. These magnesium-silicate phases bind free MgO and hence they have a negative effect on lining life of secondary steel processing units. In accordance with the experiment results shown in Figure 2, the slag becomes stable



**Figure 2:** The results of phase definition amount in the samples of model slag with SAPW addition.

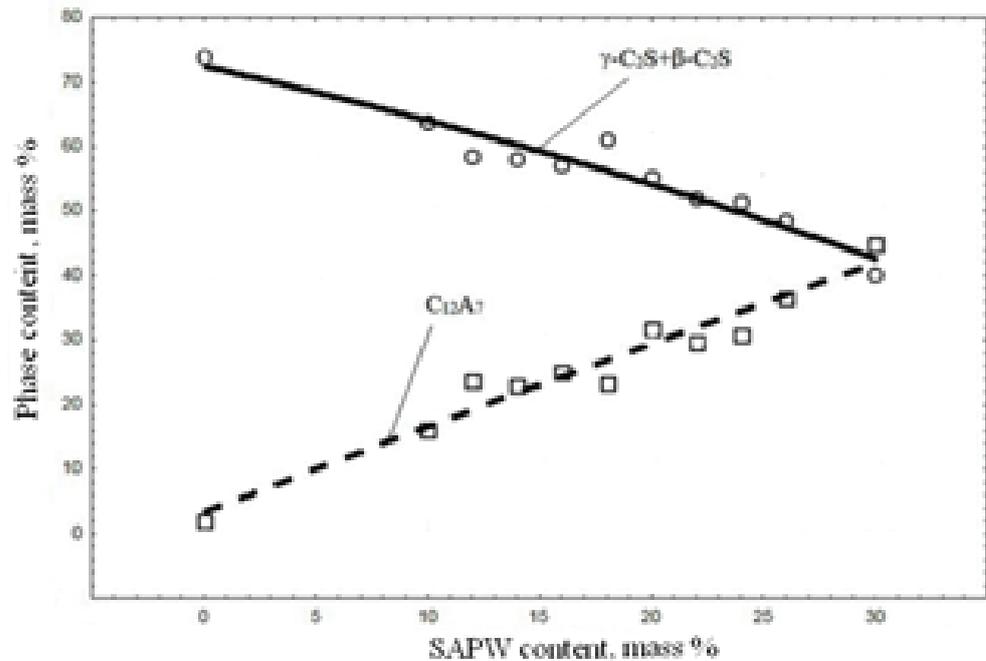
with the SAPW content increasing. The optimal area of stable slag is located in the range of SAPW content from 10 mass. % to 20 mass. %. If the SAPW content is lower than 10 mass. %, the slag is not stable. If its more than 20 mass. %, a fire-resistant spinel AM ( $\text{Al}_2\text{O}_3 \cdot \text{MgO}$ ) is formed which increases slag viscosity.

Since preliminary evaluation tests of the SAPW stabilizing effect were conducted by the experiment planning methods in a large area of the  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  factor diagram with a large variation interval of the SAPW content (13.3 wt%), the boundaries of the optimal SAPW content where the slag is stabilized were determined with a very high margin of error.

To determine the slag stabilization mechanism and its precise boundaries under the SAPW addition, the SAPW additives in the amount from 10,0 to 30,0 mass.% were introduced with the step of 2,0 mass.% into the model slag. Slag with SAPW addition was placed in a crucible and heated to 1350°C, it then was exposed under the temperature for 2 hours and cooled in the furnace.

The results of phase amount determination in the samples of model slag with SAPW addition are demonstrated Figure 3.

From the test results one can conclude that the SAPW content increment increases the mayenite  $\text{C}_{12}\text{A}_7$  ( $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ ) content in the slag while the amount of belite phases is decreased. Figure 2 shows the total amount of belite phases ( $\beta\text{-C}_2\text{S}$ ,  $\gamma\text{-C}_2\text{S}$  and mayenite  $\text{C}_{12}\text{A}_7$ ) depending on the SAPW amount.



**Figure 3:** Belite and mayenite phase content dependence from SAPW content in the slag.

## 1. Conclusions

The belite stabilization in refining slag with the SAPW addition has a chemical mechanism. It is provided by increasing the content of the mayenite  $C_{12}A_7$  phase while general content of belite phases in the slag is simultaneously decreased.

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