Conference Paper

# Reduction of Environmental Pressure by Giving Cementing Material Properties to the Ferrous Slags

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There are two main kinds of slag in modern steelmaking industry: the electric arc furnace slag (the EAF slag) which is produced in the manufacture of crude steel by the electric arc furnace process and the ladle furnace basic slag (the LF slag) which is produced at the final stages of steelmaking, when the steel is desulfurized in the transport ladle, during what is generally known as the secondary metallurgy process. Table 1 demonstrates the chemical composition of these slags.

X-ray diffraction analysis has showed [1] that EAF slag contains wuestite FeO, magnetite $Fe_3O_4$, merwinite $C_3MS_2$ ($3CaO\ MgO\ 2SiO_2$) phases and the high-temperature modification $\beta$-$C_2S$ which is known as bilithlarnite. XRD analysis also shows that LF slag contains three main phases: mayenite $C_{12}A_7$ ($12CaO.7Al_2O_3$), periclase MgO and shannonite $\gamma$-$C_2S$ ($\gamma$-$2CaO.SiO_2$), the latter being the low-temperature modification of belite. In accordance with semiquantitative analysis the slags have different phase compositions (mass. %): 20,4 FeO; 24,1 $Fe_3O_4$; 15,9 $C_3MS_2$; 38,15 $\beta$-$C_2S$; 1,45 of the others for the EAF slag and 37,2 $C_{12}A_7$; 12,5 MgO; 41,4 $\gamma$-$C_2S$; 8,9 of the others for the LF slag.

The EAF slag consists of stable phases and so it is used for processing by simple methods of grinding and classification [2, 3]. Final crushed stone produced that way is only used as aggregate in road construction.

However, the ladle furnace slag is difficult to utilize a due to the significant content of shannonite ($\gamma$-C2S) generated when the slag is cooled to 830°C. Shannonite is generated during the high-temperature phase transformations from one polymorph to

| The slag type | Content, % | | | | | | | $M_o$* | $K_{act}$** |
|---|---|---|---|---|---|---|---|---|---|
| | CaO | $SiO_2$ | $Al_2O_3$ | FeO | MnO | MgO | $Cr_2O_3$ | | |
| EAF slag | 26,2 | 13,8 | 3,72 | 26,0 | 5,51 | 6,7 | 1,69 | 1,88 | 0,27 |
| LF slag | 53,8 | 8,0 | 21,6 | 1,1 | 1,42 | 9,8 | 0,23 | 2,15 | 2,7 |

Table 1: The chemical composition of steelmaking slags. *$M_o$ = CaO + MgO/$SiO_2$ + $Al_2O_3$ **$K_{act}$ = $Al_2O_3/SiO_2$.

| The slag type | The content in the slag, mass. % | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | CaO | $SiO_2$ | $Al_2O_3$ | FeO | MnO | MgO | $Cr_2O_3$ | $\Delta m_{calc}$ |
| EAF slag | 26,20 | 13,80 | 3,72 | 26,00 | 5,51 | 6,70 | 1,69 | 0,23 |
| LF slag | 53,80 | 8,00 | 21,60 | 1,10 | 1,42 | 9,80 | 0,23 | 0,03 |
| Limestone | 54,60 | 0,20 | 0,04 | 0,32 | 0,00 | 0,00 | 0,00 | 44,00 |

Table 2: The chemical composition of burden material.

another ($\alpha$-C2S → $\alpha'$-C2S → $\beta$-C2S) and the process is accompanied by a volume expansion; high internal stresses finally cause the slag disintegration to the dust fraction [4]. The significant amount of dust fraction after the LF slag disintegration prevents its massive processing to crushed stone and also pollutes the environment by dust emissions on the waste slag storage dumps.

In our previous work [5] the alumina flux addition to the LF slag composition formed the stable phases $\alpha$-$C_2S$, $\beta$-$C_2S$, $C_{12}A_7$ providing a good hydraulic activity. The mayneite $C_{12}A_7$ mixed with gypsum and dihydrate hardens according to the following Equation 1 [5]:

$$12CaO\cdot 7Al_2O_3 + 12CaSO_4\cdot 2H_2O + 113H_2O = 4(3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32H_2O) + 6Al(OH)_3 \quad (1)$$

Therefore, we developed and patented the method for the composite waterproof gypsum binder production. Now this binder is commonly used for different construction materials production.

To evaluate the possibility of hydraulically active phase alite ($C_3S$ or $3CaO\cdot SiO_2$) formation on the basis of investigated slags, a multifactorial experiment is conducted by the method of simplex-lattice planning. In the experiment the contents of burden material (Table 2) are used as variable factors demonstrated in Table 3.

The alite $C_3S$ content in the melting products was taken as the response function. Since EAF slags contain significant amount of ferric oxides, the slag heating and melting were performed under reductive conditions which provide possible ferric oxides transition into pig iron. To make reductive conditions and iron carbonization, a coke fine in the amount of 5,0 mass. % over 100 mass % was added into the raw mixtures.

| The factor type | Variability interval | | | |
|---|---|---|---|---|
| | Lower | | Upper | |
| | Code*, ea | Nat.**, mass.% | Code, ea | Nat., mass.% |
| LF slag content | 0,17 | 17,00 | 0,67 | 67,00 |
| EAF slag content | 0,17 | 17,00 | 0,67 | 67,00 |
| $CaCO_3$ content | 0,17 | 17,00 | 0,67 | 67,00 |

Table 3: Factors variability interval. *- coded value, **- natural value.

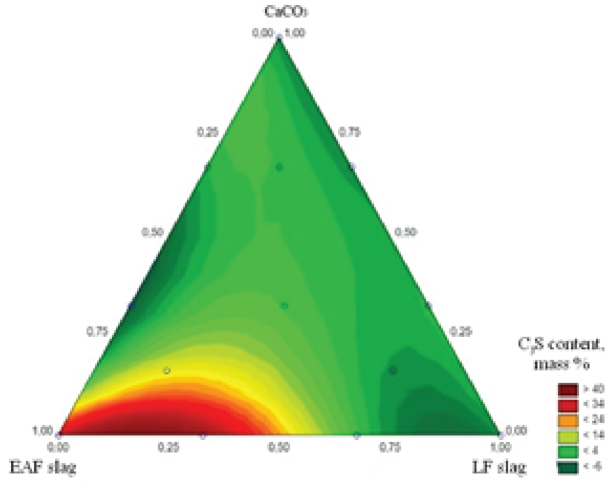


**Figure** 1: Alite $C_3S$ distribution formed in the experiment.

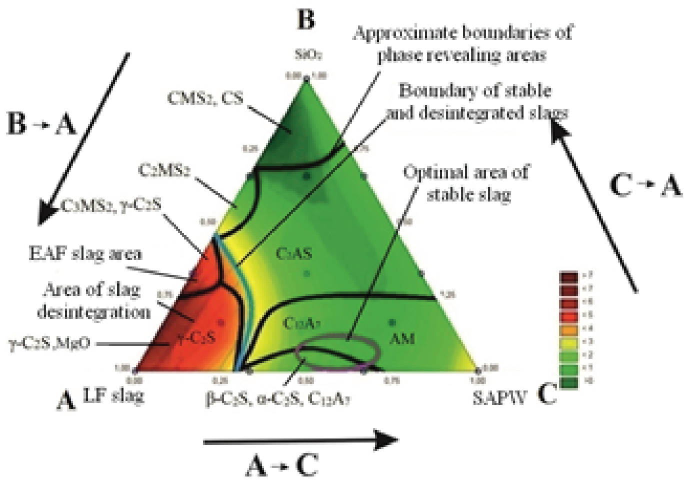


**Figure** 2: The melting products viscosity under 1500°C in the main slag phases.

The samples made from EAF slag, limestone and LF slag were mixed, heated and melted under reductive conditions and then slowly cooled according to the experiment plan. After the slag was cooled, pig iron and slag were separated from each other. X-ray diffraction analysis was used to determine the final slag phase composition. Figure ?? shows the alite distribution formed in the experiment.

From the test results one can see that $C_3S$ maximum is formed in the area with maximum EAF slag content. The analysis of steel slags phase composition varying with the $SiO_2$ addition supplemented with secondary alumina production wastes (SAPW) is showed on Fig. 2 which allows the explanation of the test results.

The diopside $CMS_2$ ($CaO{\cdot}MgO{\cdot}2SiO_2$) is formed in the plan factorial area with significant $SiO_2$ content. With the basicity increment in the B → A ($SiO_2 \rightarrow CaO$) direction the diopside initially transforms into the akermanite $C_2MS_2$ ($2CaO{\cdot}MgO{\cdot}2SiO_2$) and then transforms into the merwinite $C_3MS_2$ ($3CaO{\cdot}MgO{\cdot}2SiO_2$). EAF slag contains a high content of merwinite. The diagram shows the area corresponding to the EAF slag composition with the 38% larnite $\beta$-$C_2S$ content and 16% merwinite $C_3MS_2$ content. With further basicity increment the merwinite disintegrates with the belite $\gamma$-$C_2S$ ($2CaO{\cdot}SiO_2$) and periclase MgO formation. Due to this disintegration slag will be mainly formed from the belite phase after ferric oxides reduction.

Lime formed after the limestone disintegration saturates belit $C_2S$ to alite $C_3S$ through dissolving in liquid phase, and as a result maximum amount of alite is formed in the final melt under the maximum content of EAF slag in the raw mixture.

With the basicity increasing the following sequence chain of phase transitions is found (Equation 2):

$$\begin{aligned} CaO \cdot MgO \cdot 2SiO_2 + CaO &\rightarrow 2CaO \cdot MgO \cdot 2SiO_2 + CaO \rightarrow 3CaO \cdot MgO \cdot 2SiO_2 \\ &+ CaO \rightarrow 2(2CaO \cdot SiO_2) + MgO + 2CaO \rightarrow 2(3CaO \cdot SiO_2) + MgO \end{aligned} \tag{2}$$

To prove the possibility of standard Portland clinker synthesis on the basis of EAF slag, LF slag and some corrective additives, the raw mixture calculation was made for the formation in the slag of clinker with following module characteristics: SC - 0,92, s - 2,3 and p - 1,7. Pig iron was formed in the metallic phase and Portland clinker was formed in the slag phase during the raw mixture melting in ore-thermal furnace (OTF).

The quantitative measurements of phase content in the slag by XRD analysis showed the final slag containing 51,3% $C_3S$, 30,1% $C_2S$, 10,7% $C_3A$ ($3CaO{\cdot}Al_2O_3$) and 3,8% MgO. The total silicate phase content in the slag is more than 80%, the $CaO/SiO_2$ relation is 3,05, and the MgO content is lower than 5,0%. The experimental results of final product meet the normative requirements.

The average pig iron output and slag yield depend on the ferric oxides content in EAF slag. The experimental results have shown that slag (clinker) yield is 82,0 mass.% and pig iron output is 18,0 mass. %. The chemical composition of produced pig iron is demonstrated in Table 4. It also meets the normative standards for pig iron.

| The product type | Content, mass. % | | | | |
|---|---|---|---|---|---|
| | C | Mn | Si | P | S |
| Pig iron | 3,13 | 1,26 | 0,109 | 0,036 | 0,021 |

Table 4: The chemical composition of pig iron.

## 1. Conclusions

1. It is established that the composite waterproof gypsum binder can be produced on the basis of ladle furnace slag.
2. The Portland clinker and pig iron can be simultaneously produced on the basis of electric arc furnace slag, ladle furnace slag and limestone.

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