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LABORATORY EXPERIMENTS ON THE DESULPHURATION PROCESS OF STEEL USING SYNTHETIC SLAGS WITH TITANIUM OXIDE ADDITION

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ABSTRACT: To determine the influence, on the desulphurisation process, of the titanium oxide added in calcium aluminate slag, we experimented, in the laboratory phase, the steel treatment with a mechanical mixture consisting of lime, aluminous slag and slag obtained from the titanium making process through the aluminothermic technology. In the practice of deoxidation with synthetic slag, we usually use the slag from the binary systems: $\text{CaO}-\text{Al}_2\text{O}_3$, $\text{CaO}-\text{TiO}_2$ and $\text{CaO}-\text{CaF}_2$, or from the ternary systems: $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3$ and $\text{CaO}-\text{CaF}_2-\text{Al}_2\text{O}_3$. According to the literature, the best results were obtained with synthetic slag from the binary system $\text{CaO}-\text{Al}_2\text{O}_3$ (50-52% CaO and 38-42% Al_2O_3). The paper presents the results of laboratory experiments on steel desulphurisation with slag from the system $\text{CaO}-\text{SiO}_2-\text{TiO}_2$. During the research, we aimed to establish correlation equations between the sulphur distribution coefficient and the slag components (CaO , Al_2O_3 , TiO_2 , FeO , MgO and MnO). The data obtained in the experiments were processed in Excel and MATLAB programs, resulting simple or multiple correlation equations, which allowed the elucidation of some physical-chemical phenomena specific to the desulphurisation processes.

KEYWORDS: steel, deoxidation, desulphurization, synthetic slag

INTRODUCTION

In case of electric steel works, the sulphur reaches in the steel bay from the metallic charge and from adding's. Because the sulphur content of these sources cannot be lowered below certain limits, the elaboration process must be so developed to perform an advanced desulphurisation, both in the oven and in the casting ladle. During the last years, it is more and more manifested the tendency to perform the desulphurisation outside the elaboration aggregates (desulphurization with synthetic cinders under vacuum, with reactive powders injection), obtaining this way important energy saving, deoxidizers and desulphurants, as well as an productivity increase [1,2].

The steel refining with liquid slag or various powder mixtures of synthetic slag is based on the intensification of the unwanted impurities (sulphur, non-metallic suspensions & oxygen) passage from the liquid steel in the slag, mainly by diffusion, or partly through the entrainment of some suspensions by settling the synthetic slag particles found in the treated steel bath. The synthetic slag can be also obtained by adding mechanical mixture directly in the casting ladle; in this case, for compensating the cooling of the steel in the casting ladle due to the addition of materials (melting and superheating), the steel temperature should be at least 20-40°C higher than the normal one. In the practice of deoxidation with synthetic slag, we usually use slag that correspond to the binary systems $\text{CaO}-\text{Al}_2\text{O}_3$, $\text{CaO}-\text{TiO}_2$ and $\text{CaO}-\text{CaF}_2$, or to the ternary systems $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3$ and $\text{CaO}-\text{CaF}_2-\text{Al}_2\text{O}_3$. According to the literature, the best results were obtained with synthetic slag that corresponds to the binary system $\text{CaO}-\text{Al}_2\text{O}_3$, containing 50-52% CaO and 38-42% Al_2O_3 .

The viscosity of the synthetic slag has significant influence on the development of physical and chemical processes during the treatment of the liquid steel, interfering with significant weight on the emulsifying capacity of slag. The increase of the slag viscosity from 0.15 to 0.45 Ns/m² (from 1.5 to 4.5 Poise) determines the decrease with approx. 30% of the steel-slag interaction surface. Such increasing of the calcium aluminate slag viscosity can be seen when its temperature is decreasing (for example, from 1600°C to 1470°C). Therefore, it is very important to ensure, during processing the steel with liquid slag, the optimum thermal regime specific to the chosen slag type and to realise its convenient fluidity (viscosity).

The viscosity of the synthetic slag is also influenced by other components; it increases significantly with the increasing of the SiO_2 content, while MgO contents up to 8% are favourable. At temperatures higher than 1500°C, the viscosity is slightly decreasing when adding TiO_2 in the calcium aluminate slag.

LABORATORY EXPERIMENTS

To determine the influence, on the desulphurisation process, of the addition of titanium oxide in the calcium aluminate slag, we performed laboratory experiments, i.e. we treated the slag with liquid synthetic slag obtained by melting the mixture consisting of limestone, aluminate slag and slag obtained from the titanium making process through the aluminothermic technology.

The steel melting was carried out in an induction furnace of 10 kg capacity and the slag melting was carried out in a crucible furnace, both existent in the "METALLIC MELTS" laboratory of the Engineering Faculty of Hunedoara.

The charge to be melted consisted of steel samples (samples of steel for tubes, taken from the casting ladle before the LF treatment, i.e. before introducing the steel in the LF).

To form the liquid synthetic slag, we melted in the crucible furnace a mechanical mixture consisting of limestone, calcium aluminate slag (from melting the aluminium scrap) and slag obtained from the titanium making process through the aluminothermic technology. The steel quantity obtained was 10 kg/heat, and the addition of liquid slag was 3% (300 g/heat). The synthetic slag was added directly in the casting ladle; so, the slag reached the ladle before the steel, ensuring a good mix between the two melts. To determine the sulphur distribution coefficient, we took steel and slag samples before and after the treatment, to find the sulphur content and the chemical composition. We also measured the steel and slag temperature before and after the treatment.

RESULTS OBTAINED FROM PROCESSING THE EXPERIMENTAL DATA

By processing the data obtained in the laboratory phase, we obtained equations of correlation between the chemical composition of the synthetic slag and the sulphur distribution coefficient (L.S.). The data were processed in Excel and MATLAB programs, the results being presented hereunder, in graphical and analytical forms.

In Fig. 1, we can see that a TiO_2 content increase up to 5-6% leads to the increasing of the L.S., fact explicable, from a technological point of view, through to the positive influence of the titanium oxide on the slag fluidity, especially at temperatures above $1500^{\circ}C$. Therefore, we recommend contents of 3-6% TiO_2 in the refining slag.

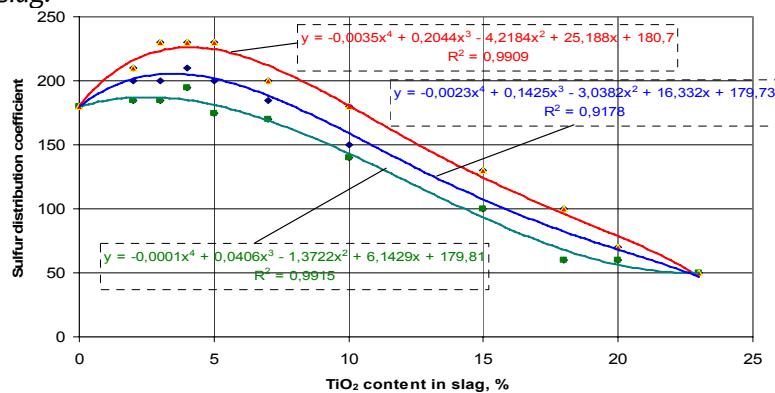


Fig.1 The variation of the sulphur distribution coefficient versus the TiO_2 content in slag

The graphical representation presented in Fig. 1 shows that the higher values for the L.S. (230-250) were obtained for a CaO content of 52 -54%. According to the data presented in the literature [2] the minimum viscosity of the slag that corresponds to the $CaO - Al_2O_3$ system is obtained for contents of approx. 56% CaO , which confirms the results obtained for the slag used in our experiments. The CaO contents higher than 55%, determine the decreasing of the L.S. values, because the slag viscosity is increasing. Having in view that, in industrial conditions, there are frequent deviations from the above mentioned range of chemical composition, we recommend contents of 52-56% CaO .

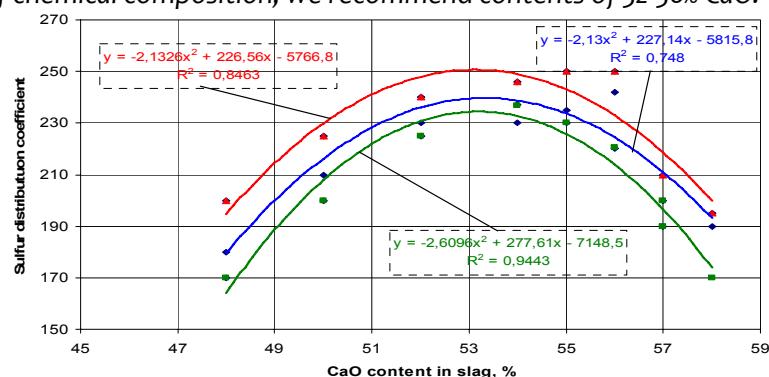


Fig.2 The variation of the sulphur distribution coefficient versus the CaO content in slag

Analysing the graphical representation presented in Fig.3, we can see a variation in the L.S. depending on the Al_2O_3 content, similar to the variation depending on the CaO content in slag. The maximum L.S. value was obtained at 34-37% Al_2O_3 . The increasing of the aluminium oxide content up to values that vary between the above mentioned limits is due to the decreasing of the slag viscosity and, in consequence, the intensification of the sulphur diffusion in the slag bath. The increasing of the Al_2O_3

content beyond the above mentioned limits determines the decreasing of the L.S. values, as a consequence of the slag viscosity increasing. We recommend contents of 33-37% Al_2O_3 in slag.

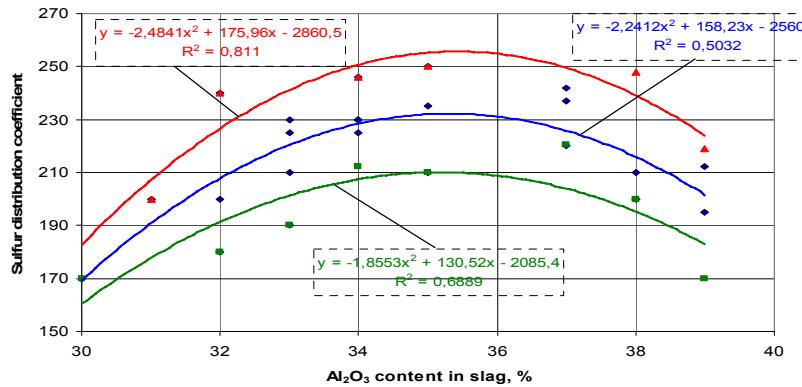


Fig.3 The variation of the sulphur distribution coefficient versus the Al_2O_3 content in slag

By processing the data in the MATLAB program, we obtained multiple correlation equations and, by graphically represented them, we obtained the correlation surfaces. To establish the optimum chemical composition range, we analysed the regression surfaces for finding the value of the L.S., desirable above the average value obtained from the data afferent to the analysed heats.

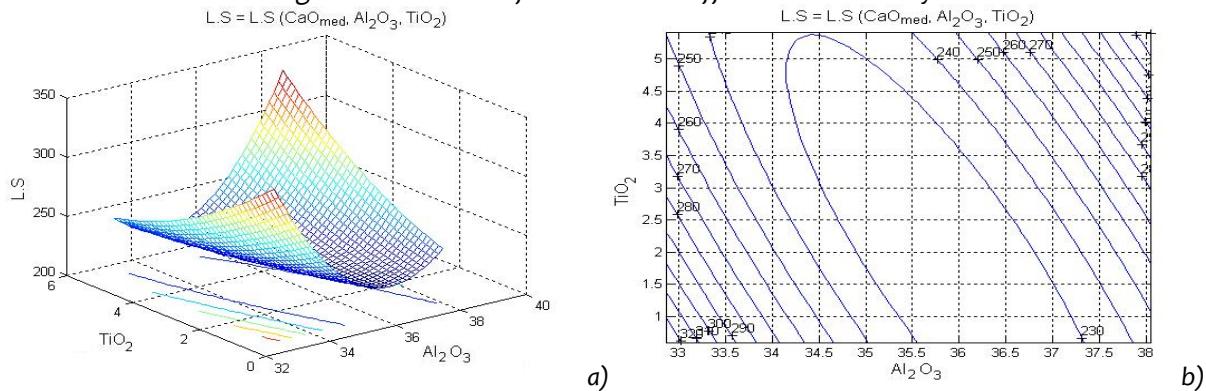


Fig.4 The variation of the sulphur distribution coefficient (L.S.) versus the TiO_2 and Al_2O_3 content in slag: a) surface; b) contour lines

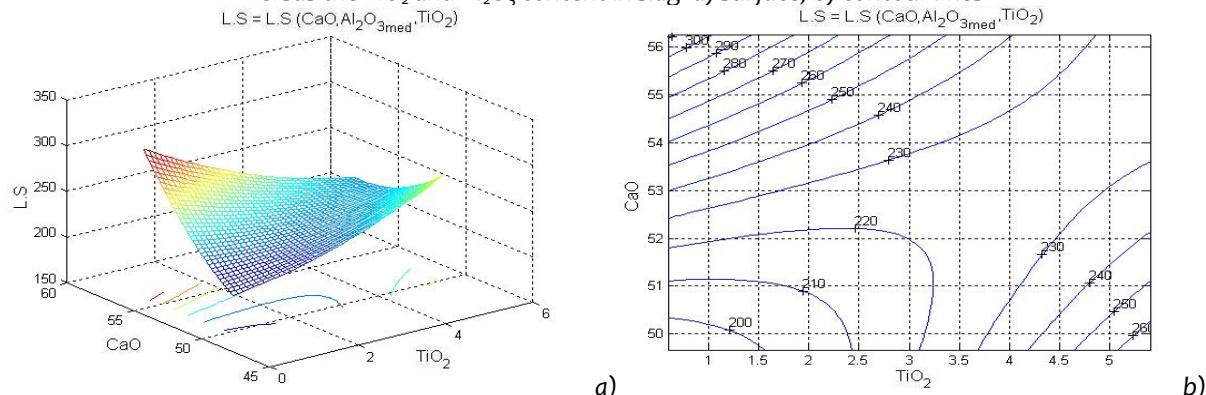


Fig.5 The variation of the sulphur distribution coefficient (L.S.) versus the TiO_2 and CaO content in slag: a) surface; b) contour lines

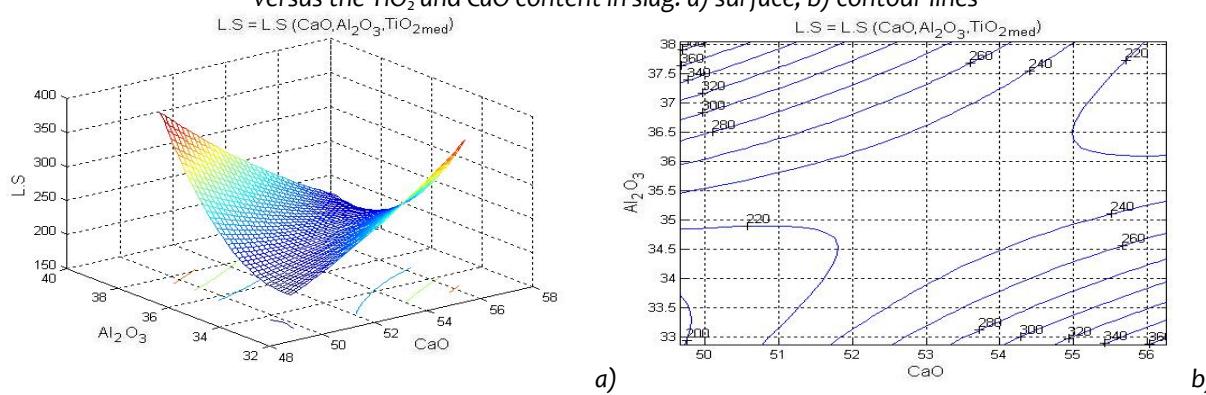


Fig.6 The variation of the sulphur distribution coefficient (L.S.) versus the CaO and Al_2O_3 content in slag: a) surface; b) contour lines

CONCLUSIONS

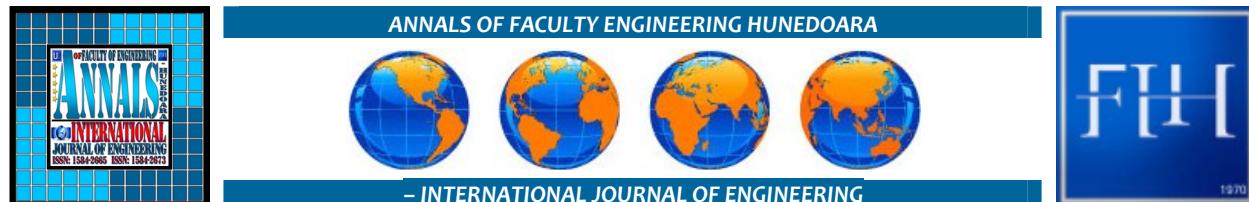
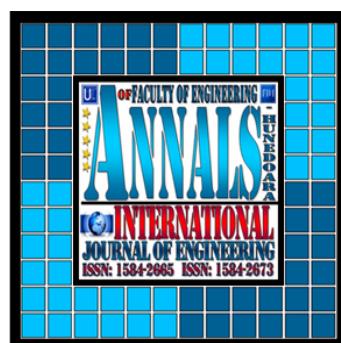
Based on the experiments, on the results obtained from data processing and on the technical analysis of these data, we concluded the followings:

- From a technological point of view, the slag types used in our experiments met our needs, mainly due to their adequate fluidity;
- The chemical composition of the slag has a significant influence on the L.S., either indirectly, due to the viscosity, or directly, due to the affinity of the oxide cations to the sulphur anions;
- We consider that it is possible to obtain very good results in the desulphurisation process by using synthetic slag having the following chemical composition: $\text{CaO} = 48 - 55\%$; $\text{Al}_2\text{O}_3 = 40 - 45\%$; $\text{SiO}_2 = \text{maximum } 3.0\%$; $\text{MgO} = \text{maximum } 3\%$ and $\text{FeO} = \text{maximum } 1\%$

Based on the results obtained during the laboratory phase, we believe that good results can be achieved under industrial conditions, too. So, we propose to perform such experiments in a future stage.

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