Research on steel refining

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Abstract— The paper presents the results of laboratory experiments on steel desulphurization and deoxidation with slag from the system $CaO-SiO_2-TiO_2$. To determine the influence, on the desulphurisation and deoxidation 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. 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— desulphurisation and deoxidation process, fluorine, synthetic slag, steel, refining.

I. INTRODUCTION

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 20-40ºC higher than the normal one. In the practice of deoxidation with synthetic slag, we usually use slag that correspond to the binary systems $CaO-Al_2O_3$, $CaO-TiO_2$ and $CaO-CaF_2$, or to the ternary systems $CaO-SiO_2-Al2O_3$ and $CaO-CaF_2-Al_2O_3$. According to the literature, the best results were obtained with synthetic slag that corresponds to the binary system $CaO-Al_2O_3$, 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/m^2 (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 1600ºC to 1470ºC). 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).

At the temperatures of treating the steel with synthetic slag in the ladle, the minimum viscosity corresponds to the slag with 56% CaO. But, taking into account the fact that frequent deviations (1-2%) may occur from this optimum composition under industrial conditions, we should also consider the danger of reaching unwanted values (higher than 57% CaO). Therefore, in the industrial practice it is recommendable a content of 52-54% CaO in slag, for which the normal composition deviations can't provoke sudden viscosity increases.

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 1500ºC, the viscosity is slightly decreasing when adding TiO_2 in the calcium aluminate slag.

Usually, the chemical composition of the synthetic slag that corresponds to the $CaO – Al_2O_3$ system, frequently used in practice, varies between the following limits: CaO = 48 – 55%; Al_2O_3 = 40 -45%; SiO_2 = maximum 3.0%; MgO = maximum 3% and FeO = maximum 1%, the balance being other oxides. Because the diffusion speed in slag increases with increasing temperature (T) and decreasing viscosity (η), we can highlight the special importance of the synthetic slag viscosity (i.e. its fluidity $φ=1/η$) in the process of treating the steel with synthetic slag.

Similarly, the bigger is the contact surface between the synthetic slag and the metallic bath, the faster is the passage of the significant elements to the slag, the contact surface being, along with the viscosity, another determinant element in treating the steel with synthetic slag.

II. PROBLEM FORMULATION

To determine the influence, on the desulphurisation and deoxidation 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 (furnace Tammann), 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 was poured into two pots of 5 kg capacity each. The extra liquid slag was poured into the ladle at a rate of 3%, respectively 150g/laddle (about 300g/stance) before casting the steel, which ensured a good mix between the two melts. A number of 20 batches was elaborated, and each was poured in two pots. By removing the two samples, two bars were made from each pot.

To determine the sulphur distribution coefficient, we took steel and slag samples before and after the treatment, in order to find the sulphur content and chemical composition of the slag. We also measured the steel and slag temperature before and after the treatment. The chemical composition of slag varied among these limits: CaO = 48-58% Al2O3 ≤ 39%, SiO2 ≤ 20% TiO2 = 2-23% MgO ≤ 1 5%, FeO = 0.25% - 3% MnO = 0.25 - 2%.

III. PROBLEM SOLUTION

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), that the degree of removal of oxygen (η_O) The data were processed in Excel and MATLAB programs, the results being presented hereunder, in graphical and analytical forms.
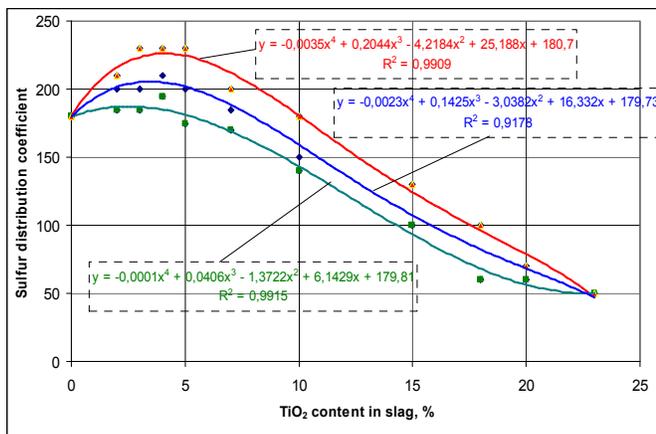

Fig. 1 The variation of the sulphur distribution coefficient versus the TiO_2 content in slag

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^oC. Therefore, we recommend contents of 3-6% TiO_2 in the refining slag.

In Fig. 2, we see that the increase of the MgO content up to approx. 8% leads to the increasing of the L.S., fact explicable, from a technological point of view, by the favourable influence of this oxide on the viscosity (the viscosity is decreasing). Therefore, from a technological point of view, we recommend the maximum MgO content to be 6%.
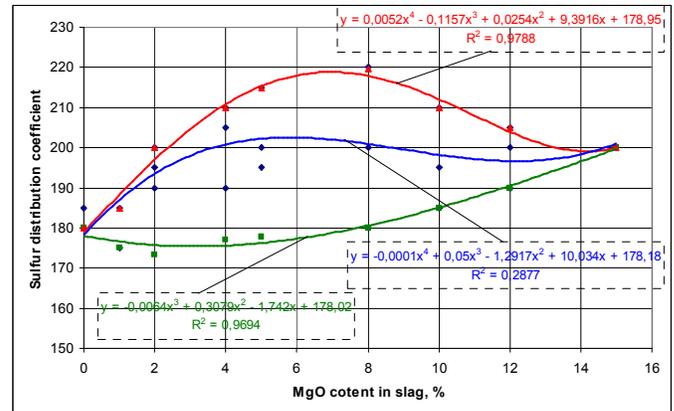

Fig. 2 The variation of the sulphur distribution coefficient versus the MgO content in slag

In Fig. 3, we see that the increasing of the SiO_2 content leads to the decreasing of the L.S., which can be explained, from a technological point of view, on the one hand by the slag viscosity increasing with the SiO_2 content increasing and, on the other hand, by the decreasing of the free CaO content, the main oxide in slag that directly participates to the desulphurisation process. From the graphical representation, we can see that, when the SiO_2 content is increasing, the variation range of the L.S. becomes narrower and narrower, especially for values higher than 5%. Technologically, we recommend the maximum SiO_2 content to be 3%.
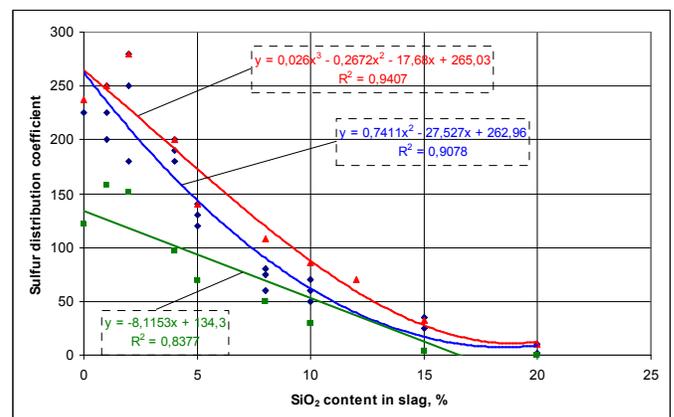

Fig. 3 The variation of the sulphur distribution coefficient versus the SiO_2 content in slag

The graphical representation presented in Fig. 4 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 [5] 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.
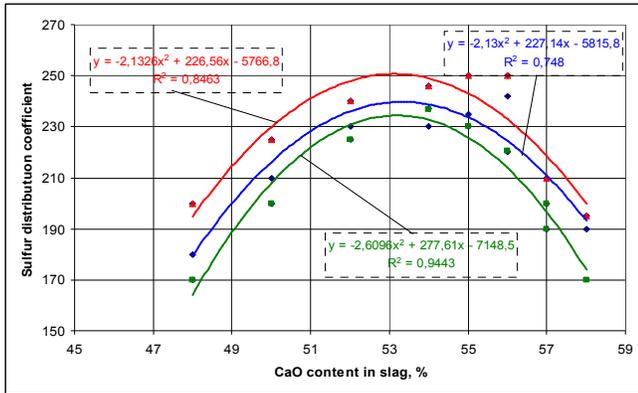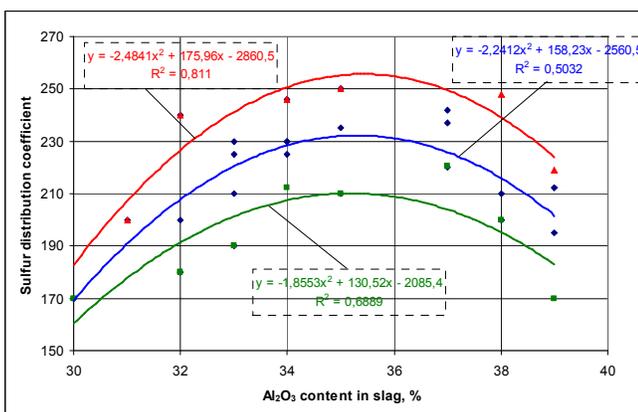

Fig. 4 The variation of the sulphur distribution coefficient versus the CaO content in slag

Analysing the graphical representation presented in Fig. 5, 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. 5 The variation of the sulphur distribution coefficient versus the Al_2O_3 content in slag

From the graphical correlations presented in Fig. 6 and 7, we can see that the increasing of the FeO and MnO contents in slag leads to the decreasing of the L.S., which is consistent with the fact that the steel desulphurisation is encouraged by strong basic slag (which presents high $[O^{2-}]$ values) and low

[O] contents. Technologically, for the slag types we have studied, we recommend the maximum FeO content to be 1.5% and the maximum MnO content to be 1.0%.
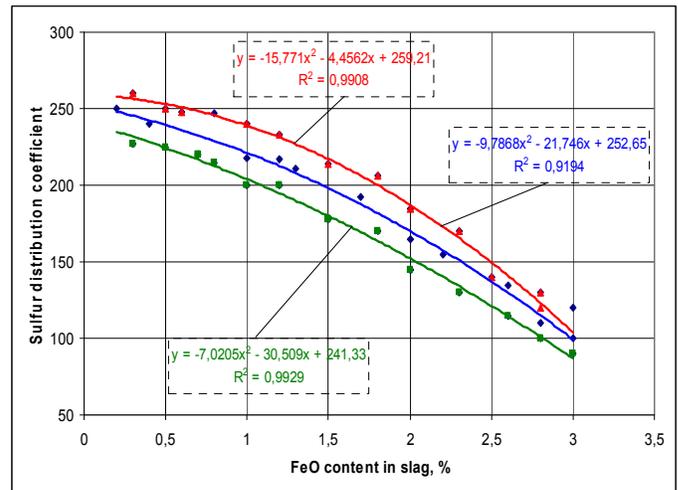

Fig. 6 The variation of the sulphur distribution coefficient versus the FeO content in slag
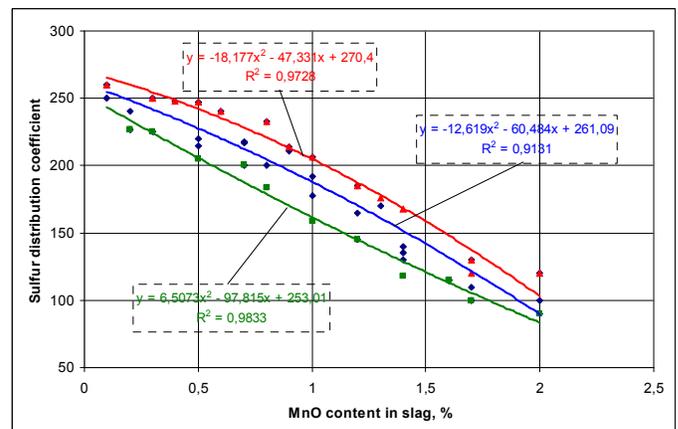

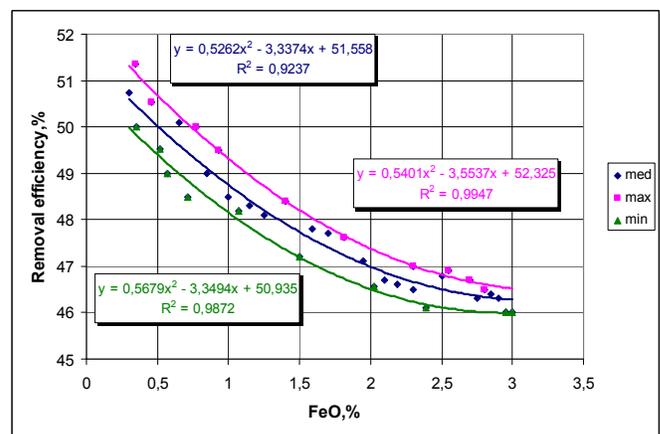Fig. 7 The variation of the sulphur distribution coefficient versus the MnO content in slag

Fig. 8 Oxygen removal efficiency depending on FeO

From Fig. 8 and 9 there is a decrease in oxygen removal effi

ciency with increasing FeO and MnO that caused the decrease of slag reducing character due to the increase in oxygen content.
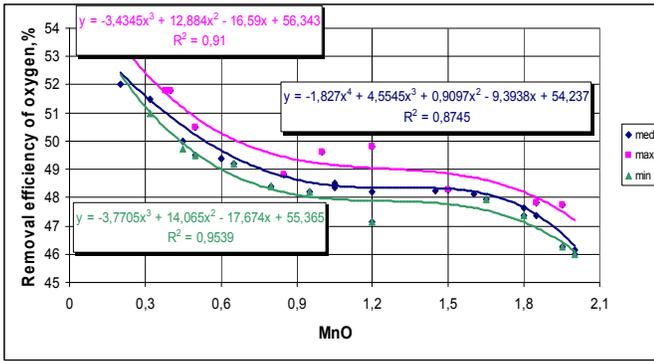

Fig. 9 Oxygen removal efficiency depending on MnO

On Fig. 10 and 11 is observed that reaches a maximum removal efficiency of oxygen that has a CaO content 52-56% and 34-38% clay content which has good fluidity, basic feature of slags .
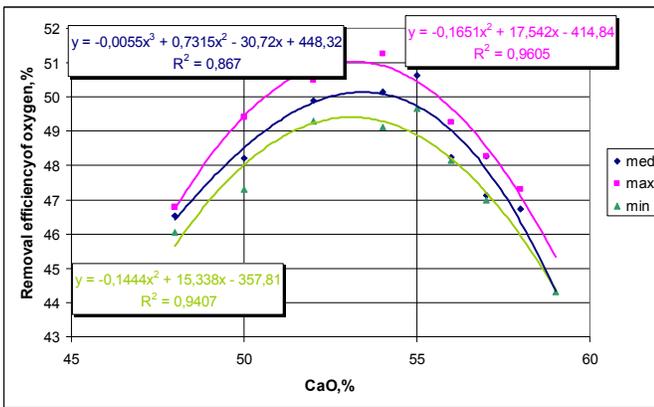

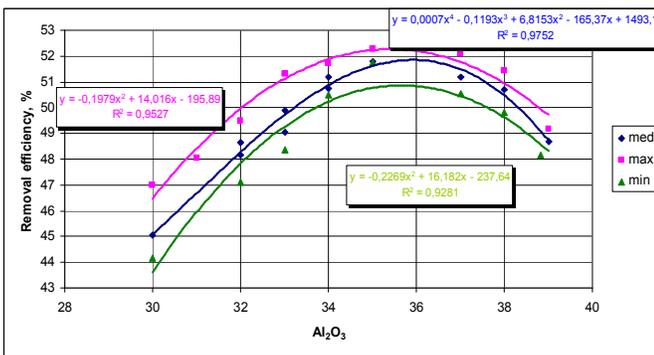Fig. 10 Oxygen removal efficiency depending on CaO

Fig. 11 Oxygen removal efficiency depending on Al_2O_3

In the TiO_2 content (Fig. 12) is getting good results of the oxygen removal efficiency if the slag is 2-9% TiO_2 content, known as the ability to break the oxide anions complex network, so flow positive influence, (as Al_2O_3).

Fig. 12 Oxygen removal efficiency depending on TiO_2

For each correlation, we determined the equation of the regression curve, along with the equations afferent to the curves that bound the variation range (both upper and lower limits). 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.
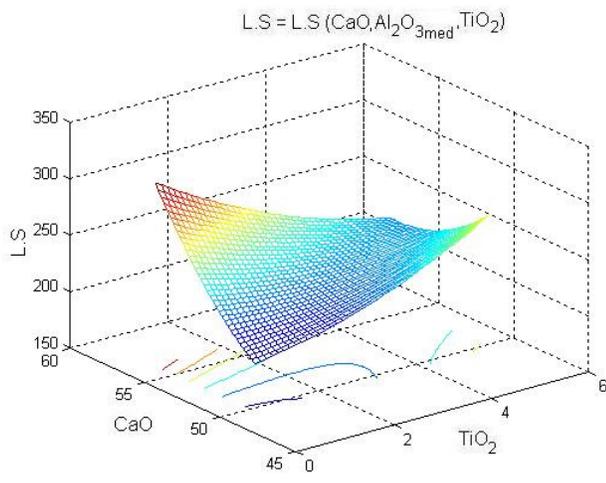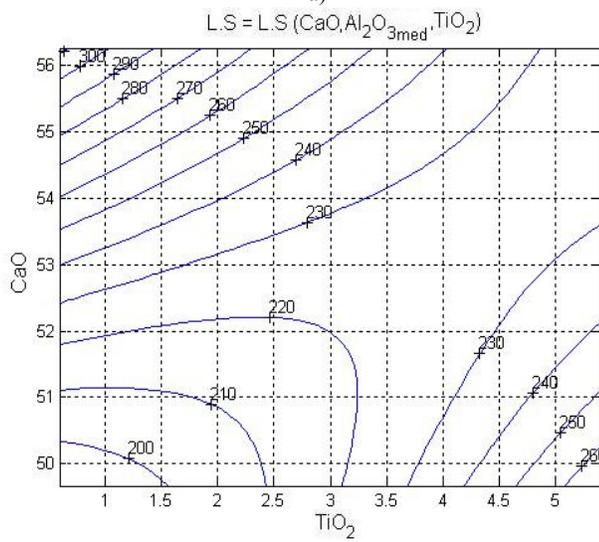

a)

b)

Fig. 13 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
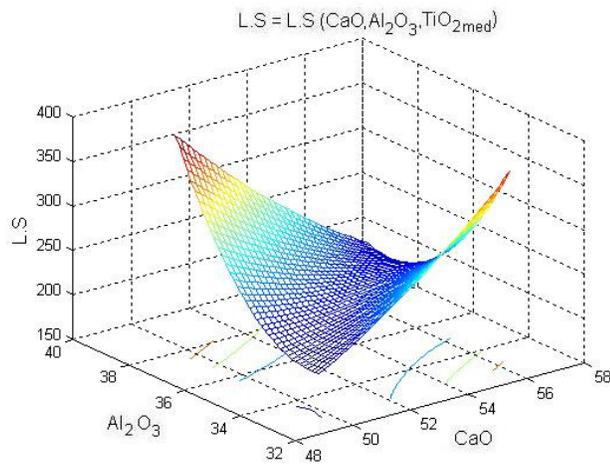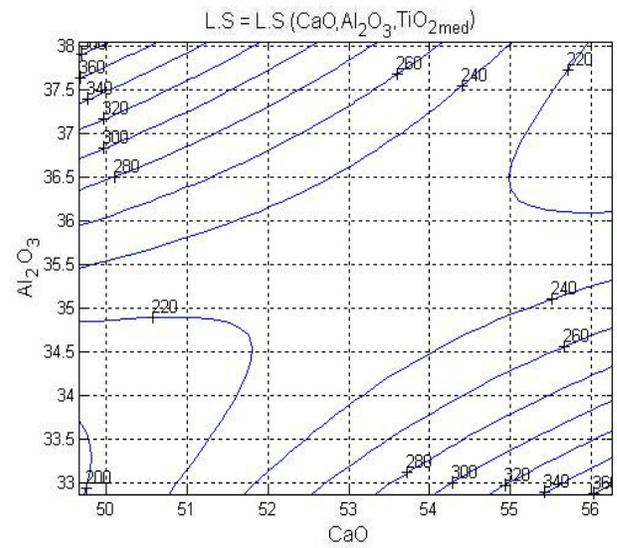
a)

b)

Fig. 14 The variation of the sulphur distribution coefficient (L.S)
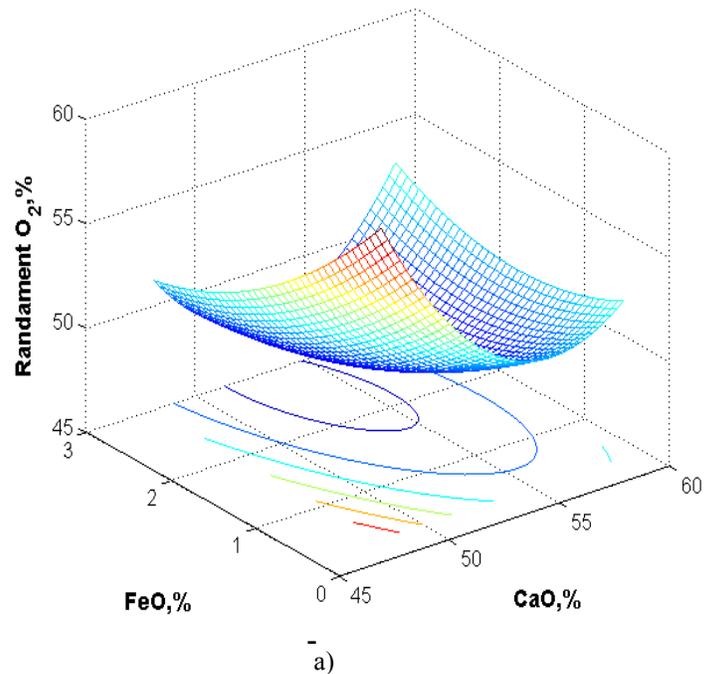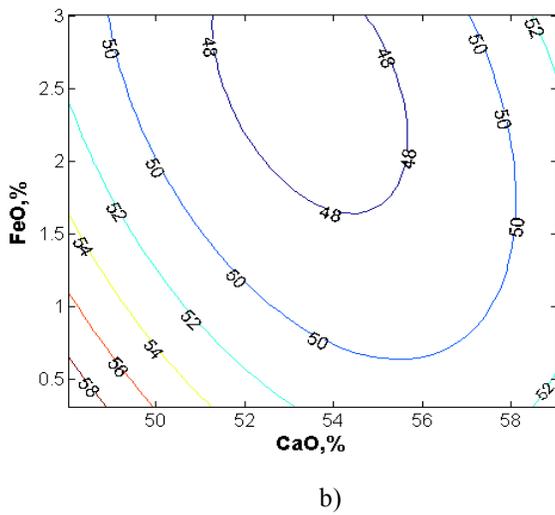versus the TiO$_2$ and CaO content in slag: a) surface; b) contour lines

a)

b)

Fig. 15 The variation of the sulphur distribution coefficient (L.S)
versus the CaO and Al$_2$O$_3$ content in slag: a) surface; b) contour lines

$$v = 0.3260x^2 + 0.1468y^2 + 0.8670z^2 - 0.4988xy -$$
$$- 0.2473xz + 0.3080yz + 4.7016 + 0.7139y -$$
$$- 12.3049z - 37.7535$$
$$Al_2O_{3\,med} = 34.6854$$
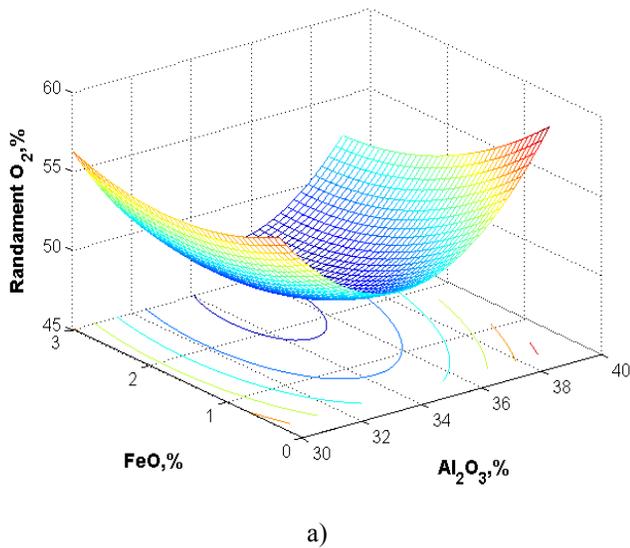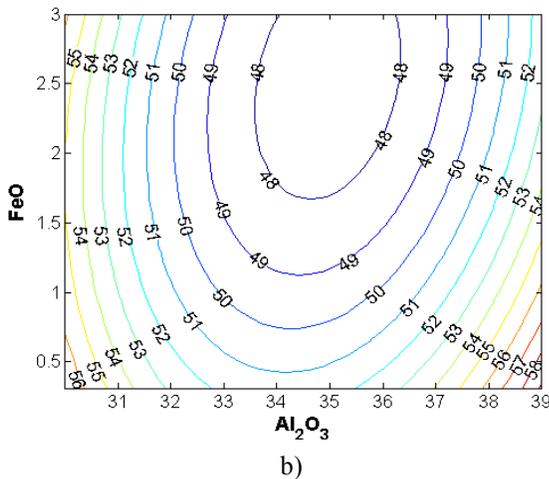$$z = 0.1478x^2 + 0.8670y^2 + 0.3080xy - 16.5878x -$$
$$- 20.8813y + 517.4657$$

a)

b)

Fig. 16 The variation of removal efficiency of oxygen versus the CaO and FeO content in slag: a) surface; b) contour lines

$CaO_{med} = 53.8625$
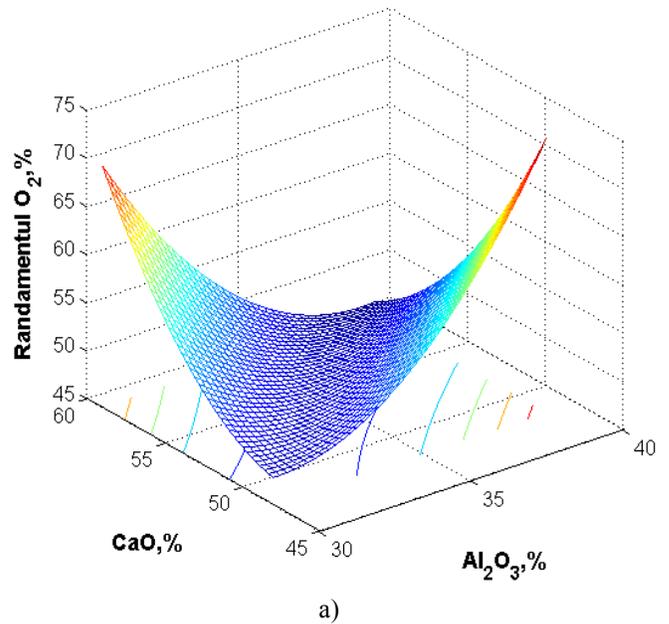
$z = 0.3260x^2 + 0.8670y^2 - 0.2473xy - 22.1060x + 4.2833y + 8.6598$

a)

a)

b)

b)

Fig. 18 The variation of removal efficiency of oxygen versus the CaO and Al_2O_3 content in slag: a) surface; b) contour lines

$FeO_{med} = 1.4758$

$z = 0.3260x^2 + 0.1478y^2 - 0.4988xy + 4.3367x + 1.168y - 54.6439$
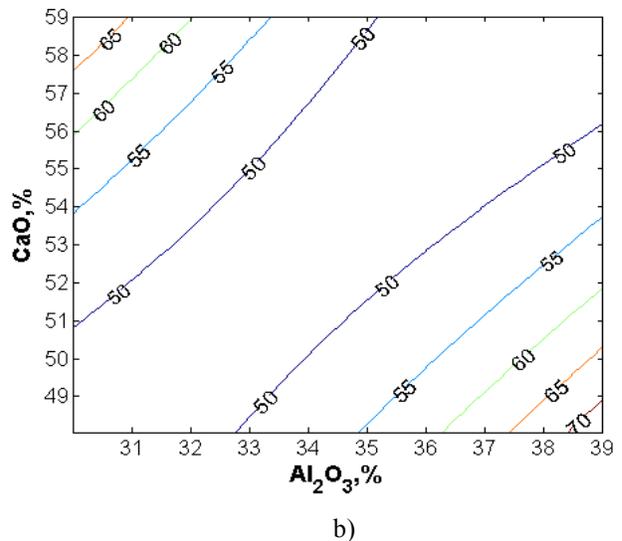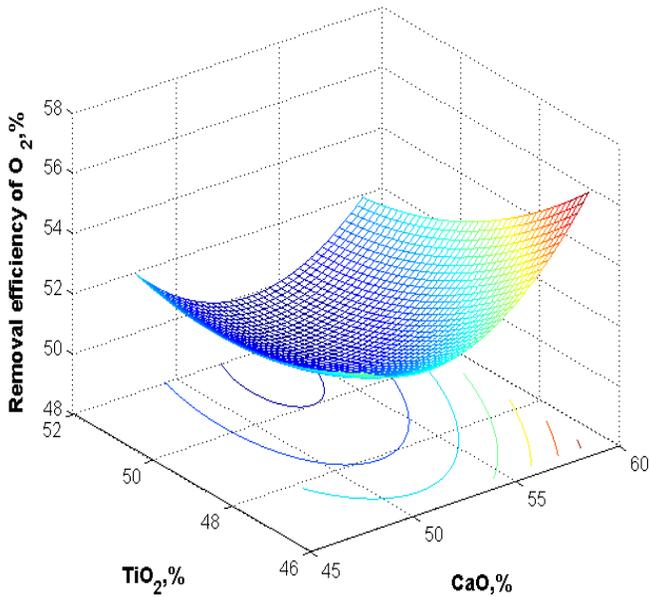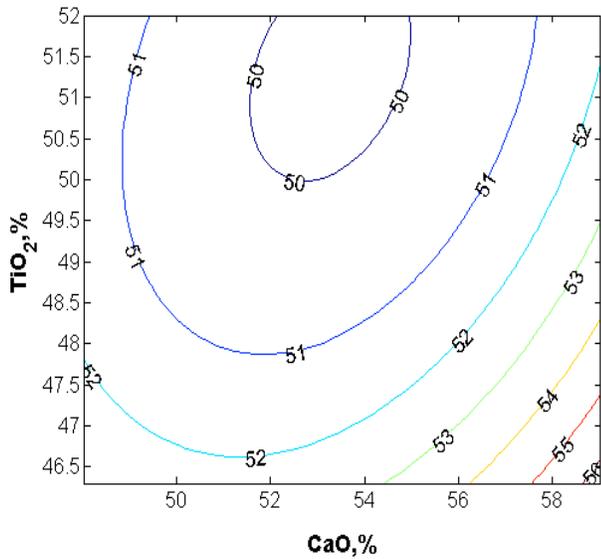
Fig. 17 The variation of removal efficiency of oxygen versus the FeO and Al_2O_3 content in slag: a) surface; b) contour lines

$$v = 0.3247x^2 + 0.0617y^2 + 0.1097z^2 - 0.5732xy +$$
$$+ 0.0825xz - 0.0550yz + 3.6874x + 15.5529y - 11.1903z -$$
$$- 11.903$$

$$x = Al_2O_3 \quad y = CaO \quad z = TiO_2$$

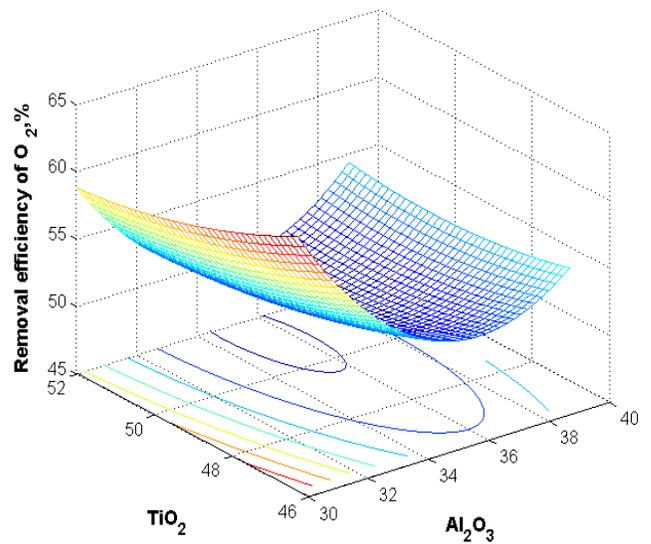$$x_{med} = 34.6854 \quad y_{med} = 53.8625 \quad z_{med} = 49.9613$$
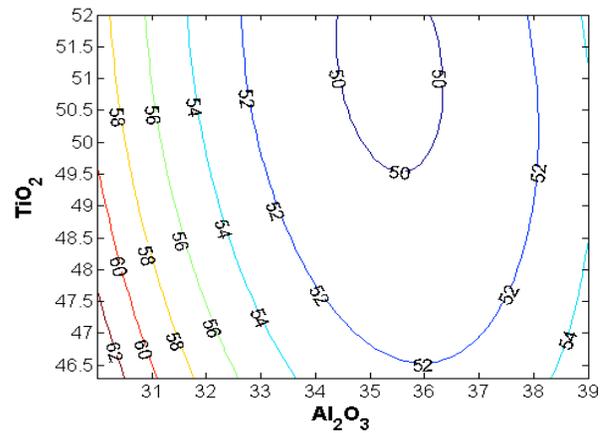

a)

b)

Fig. 19 The variation of removal efficiency of oxygen versus the TiO$_2$ and CaO content in slag: a) surface; b) contour lines
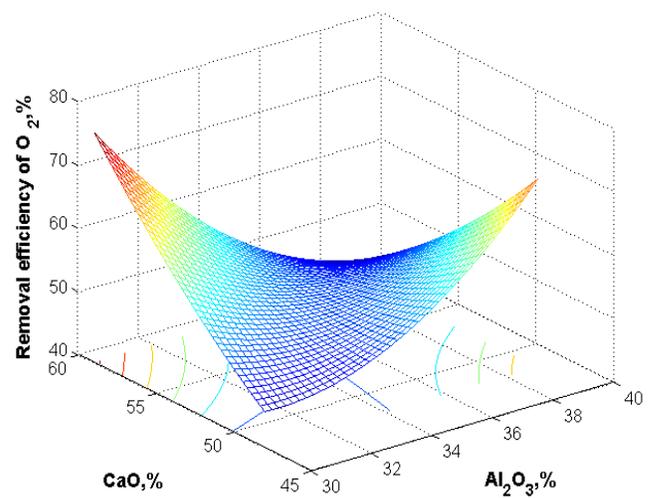

a)

b)

Fig. 20 The variation of removal efficiency of oxygen versus the TiO$_2$ and Al$_2$O$_3$ content in slag: a) surface; b) contour lines
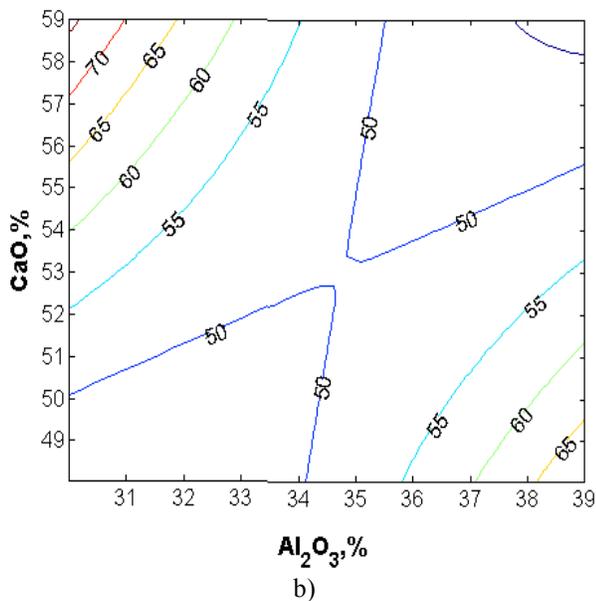

a)

Fig. 21 The variation of removal efficiency of oxygen versus the CaO and Al_2O_3 content in slag: a) surface; b) contour lines

IV. CONCLUSION

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 cautions to the sulphur anions and oxygen;

➢ We consider that it is possible to obtain very good results in the desulphurisation and deoxidation process by using synthetic slag having the following chemical composition: CaO = 50 - 56%; Al_2O_3 = 34 - 38%; $SiO_2 \leq 5\%$; $TiO_2 = 2 - 7\%$; MgO = 5 -10 %; FeO = 0,25% - 3%; MnO = 0,25 – 2%;

➢ Knowledge of graphics in MATLAB PROGRAM allows limits of variation for the chemical composition of slag in order to obtain the value set for sulfur distribution ratio, that the degree of removal of oxygen.

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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