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# DESULPHURATION OF STEEL WITH SYNTHETIC CINDERS CORRESPONDING TO THE BINARY SYSTEM CAO-AL$_2$O$_3$

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**ABSTRACT**
By processing of fluid steel in the casting ladle with synthetic cinders in installations without/with heat contributions with the desulphuration is transferred from the elaboration aggregates in the casting ladle. The processes that take place during the refining, there are mainly conditioned by the characteristics of synthetic cinder (temperature, inter-phase power between the synthetic steel - cinder, viscosity, chemical composition), by the exhaustion speed, falling height of the steel jet and by the quantity of cinder. The synthetic cinders used in the development process correspond to the binary systems $CaO-Al_2O_3$, $CaO-CaF_2$ and respectively, to the ternary systems $CaO-Al_2O_3-CaF_2$, $CaO-Al_2O_3$, fluorides of Ca, Na, Al, with variable contents of $SiO_2$, MgO, but with very low contents of iron and manganese oxides. Industrially, the desulphuration process with synthetic cinders may be influenced the easiest by the chemical composition of cinder (resulted by the variety of cinder receipt) and by the cinder specific adding.
We present in the work paper the industrial experiences and the obtained results on the steel desulphuration by synthetic cinders, corresponding to the system $CaO-Al_2O_3$. The experiments have been performed for the purpose of establishment of the desulphuration capacity of synthetic cinders, obtained by the cindering of solid mixes in the composition of which lime and bauxite are included, used for the elaborated steels upon the technology with foam cinders. The industrial experiments have been performed on a number of 16 steel rates designed for the pipe production, elaborated at an electric steel works, provided with an electric oven with arch of EBT type, with the capacity of 100 tones and permanently cast.
**Keywords:** steel, synthetic cinders, desulphuration process, industrial practice, experiments

## 1. 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 desulphuration, both in the oven and in the casting ladle. During the last years, it is more and more manifested the tendency to perform the desulphuration outside the elaboration aggregates (desulphuration 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].

By processing of fluid steel in the casting ladle with synthetic cinders in installations without/with heat contributions with the desulphuration is transferred from the elaboration aggregates in the casting ladle. The processes that take place during the refining, there are mainly conditioned by the characteristics of synthetic cinder (temperature, inter-phase power between the synthetic steel - cinder, viscosity, chemical composition), by the exhaustion speed, falling height of the steel jet and by the quantity of cinder.[1,2,3].

The synthetic cinders used in the development process correspond to the binary systems $CaO-Al_2O_3$, $CaO-CaF_2$ and respectively, to the ternary systems $CaO-Al_2O_3-CaF_2$, $CaO-Al_2O_3$, fluorides of Ca, Na, Al, with variable contents of $SiO_2$, MgO [1,2] but with very low contents of iron and manganese oxides [2,3,4].

Also, in the industrial practice, it must be taken into account the temperature, too, both for its direct influence on desulphuration and indirectly, by the cinder viscosity, especially when, for the formation of synthetic cinder, in the ladle there are added solid mixes.

Industrially, the desulphuration process with synthetic cinders may be influenced the easiest by the chemical composition of cinder (resulted by the variety of cinder receipt) and by the cinder specific adding.

## 2. INDUSTRIAL EXPERIMENTS

We present in the work paper the industrial experiences and the obtained results on the steel desulphuration by synthetic cinders, corresponding to the system $CaO$-$Al_2O_3$.

The experiments have been performed for the purpose of establishment of the desulphuration capacity of synthetic cinders, obtained by the cindering of solid mixes in the composition of which lime and bauxite are included, used for the elaborated steels upon the technology with foam cinders.

The industrial experiments have been performed on a number of 16 steel rates designed for the pipe production, elaborated at an electric steel works, provided with an electric oven with arch of EBT type, with the capacity of 100 tones and permanently cast.

These experiments have presented a special interest not only under the aspect of use of the reducing cinder, but more for the desulphuration output in the LF installation (Ladle Furnace), taking into account the short period of processing in the EBT oven. We don't present the evolution of parameters on the steel elaboration period in the aggregate, because the experiments had as purpose the steel processing in the casting ladle.

## 3. RESULTS, DISCUSSIONS

In the casting ladle, any adding is introduced, practically the exhaustion is performed in an empty ladle. After the ladle is filled in the rate of about 25%, it is made the necessary adding of SiMn or, if necessary, FeSi and FeMn.

The desulphurated (reductor) adding has been formed by burnt lime (60-70% of the total of mix) and bauxite (40-30% of the total of mix). Of this mix, about 33% has been added during exhaustion, the moment when the ladle was filled in rate of 50%. The rest of mix has been added in 3 regains, in the LF installation, approximately distributed in equal quantities. The total of reducing mix is included between the limits of 3000-3500 Kg /charge.

For the evolution (establishment of output) of sulphur, the steel and cinder products have been sampled.

The first sampling was made before the exhaustion, the second one - after the finalization of filling the ladle, and before the introduction into LF and at the finalization of treatment in LF, respectively. On each sampling, the steel temperature has been also measured. For the procurement of correlations between the desulphuration degree and the specific quantity of cinder (Kg/t steel), the characteristics of cinder in the system ($CaO$-$Al_2O_3$), respectively. The resulted data within the experiments have been processed in the Excel and Matlab computation programs, and the obtained results are both presented under the analytical and graphic form.

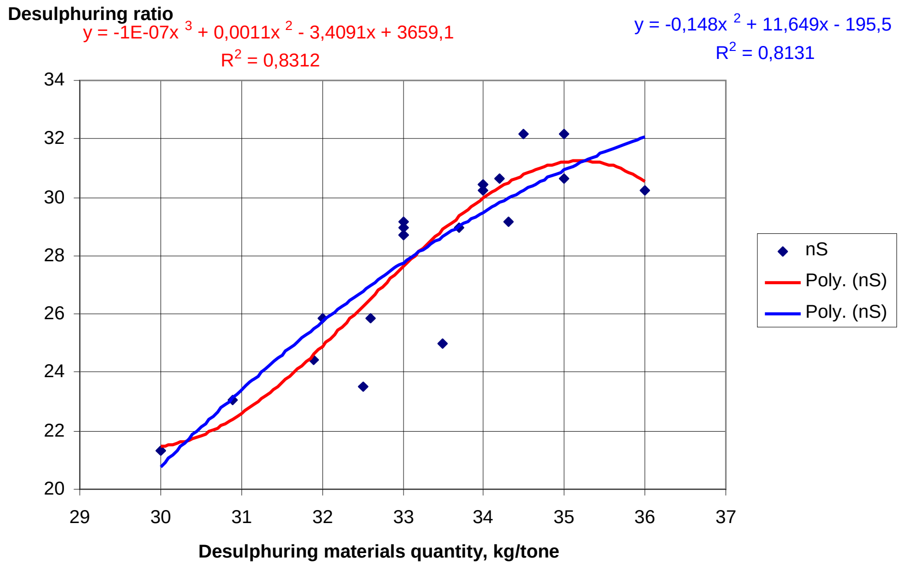



Fig.1. The variation of the desulphuration degree depending on the quantity of desulphurating mix.

Therefore, in fig.1, it is presented the variation of the desulphuration degree depending on the quantity of synthetic cinder, used in the casting ladle. By the presented data, it results that, independently by the composition of the desulphurating mix, the desulphuration degree increases by the increase of the quantity of cinder. In figure 1, there are presented the correlations of degree 2 and 3, respectively between the studied parameters, the obtained results being very close. The correlation of degree 3 presents a maximum coordinates point in the technological domain (35,25; 31,08). We consider, based on the obtained results, that the desulphurating mix adding must be included between the limits of 32-36 kg/tone.

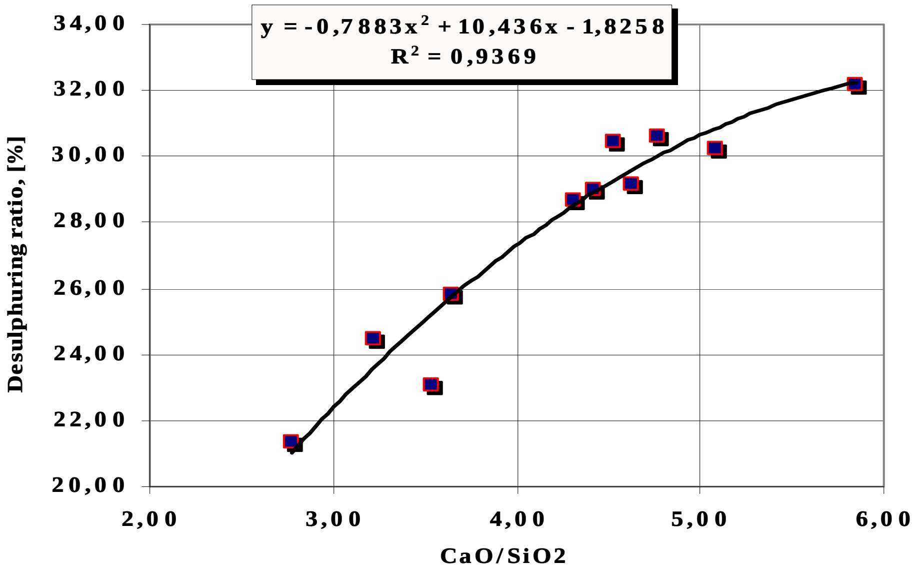



Fig.2. The variation of the desulphuration degree depending on the value $CaO/SiO_2$.

By the figure 2, it notices that together with the increase of basics index, it significantly increases the desulphuration output. By the graphic representation, it results that an index ($CaO/SiO_2$), within the limits of 4-6 insures a good desulphuration output of 28-32%. Within these limits, there is enough CaO for the connection of sulphur and the cinder viscosity is maintained within acceptable limits. Taking into account the value of the correlation coefficient of over 0.95%, we consider that the analytical expression files very well the dependence between the desulphuration output and the report $CaO/SiO_2$. The maximum is reached over the upper limit of the analyzed interval ($CaO/SiO_2$ = 6.619). An increase over this value of the report would lead to an exagerated increase of cinder viscosity, this way to the diffusion decrease of the metallic bay into cinder, and the desulphuration would be under-privileged. Together with the increase of basics, the temperature must increase to maintain the cinder fluidity within acceptable limits.

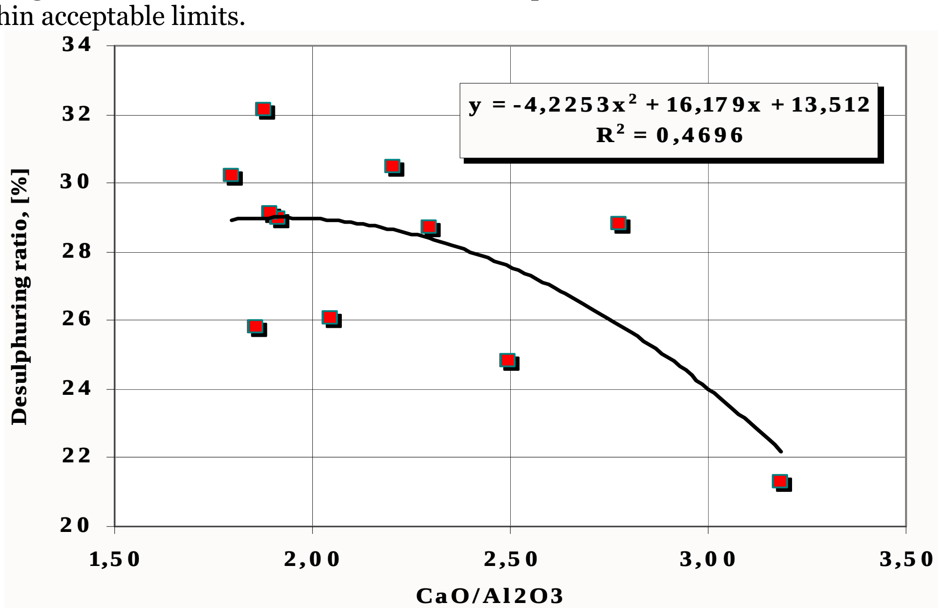



Fig.3. The variation of the desulphuration degree depending on the value $CaO/Al_2O_3$.

By the figure 3, it results that for the variation of report $CaO/Al_2O_3$ within the limits 1.50 – 3.50 the desulphuration output decreases together with its increase. An increase of this report on account of the aluminum oxide negatively influences the cinder fluidity, so it has a negative (indirect) influence on the transfer capacity of sulphur from the metallic bay into cinder.

The maximum value of the desulphuration output is obtained from a value of report $CaO/Al_2O_3$ = 1.8145. Upon the presented data, it results that technologically, it is desired that this report to be included between the limits 1.7-2.3.

In the figure 4, it is presented the influence of report $(CaO+MgO)/(SiO_2+Al_2O_3)$ on the desulphuration output. Taking into account the diagram of figure 2, we may consider that the used cinders within the experiments have a strong basic character, reason for which, we have also studied the report $(CaO+MgO)/(SiO_2 +Al_2O_3)$ taking into account the basic character of oxide MgO and amphoteric character of $Al_2O_3$. By the presentation of correlation in the figure 4, it results for $(CaO+MgO)/SiO_2+Al_2O_3$ =1,85, it is obtained the maximum value for $\eta_s$. We consider that on such a report, we have enough CaO for the connection of sulphur under the form of CaS and also an appropriate (good) fluidity of cinder. We consider as appropriate the limits 1,8 - 2,3.

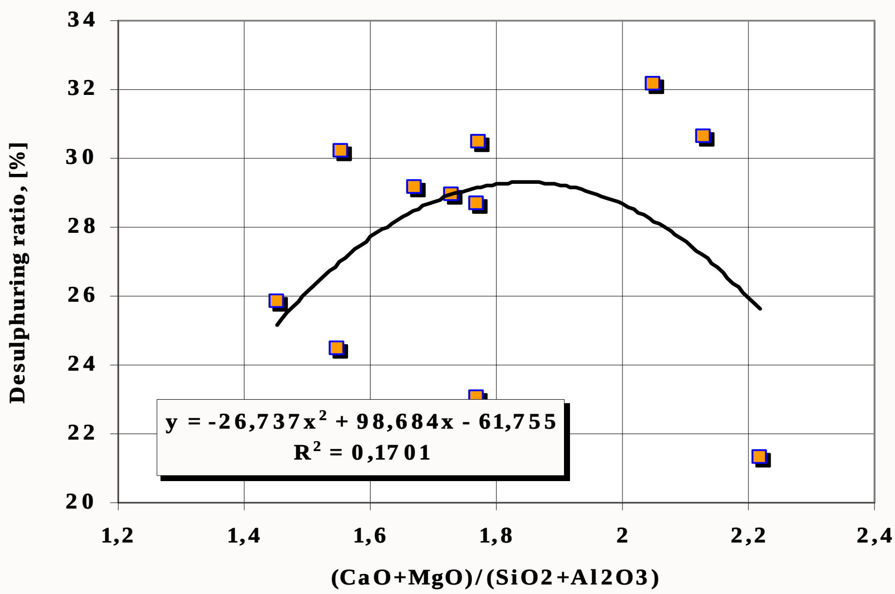



Fig. 4. The variation of the desulphuration degree depending on the value $(CaO+MgO)/(SiO_2+Al_2O_3$

We may also consider that the results of the figure 2 and figure 3 are also found in figure 4 the ascendent part of the curve, the descendant part, respectively.

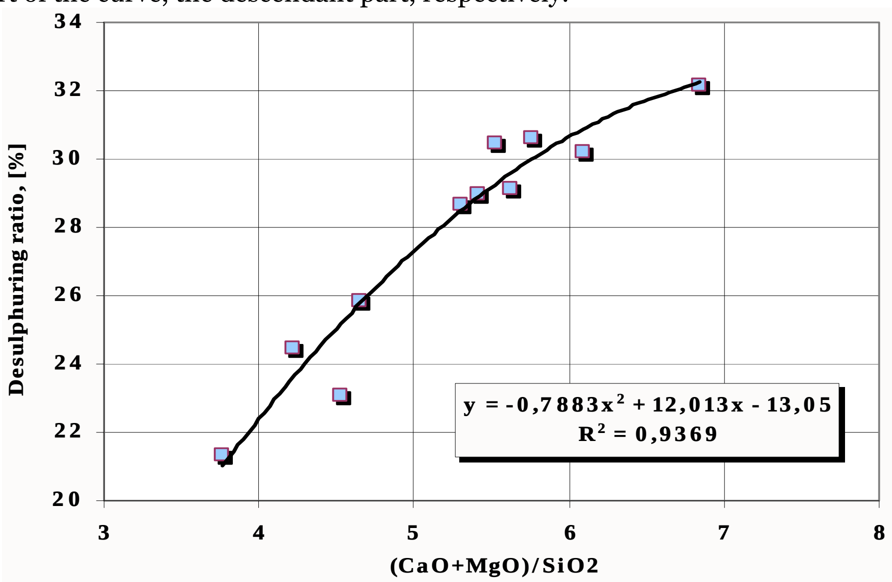


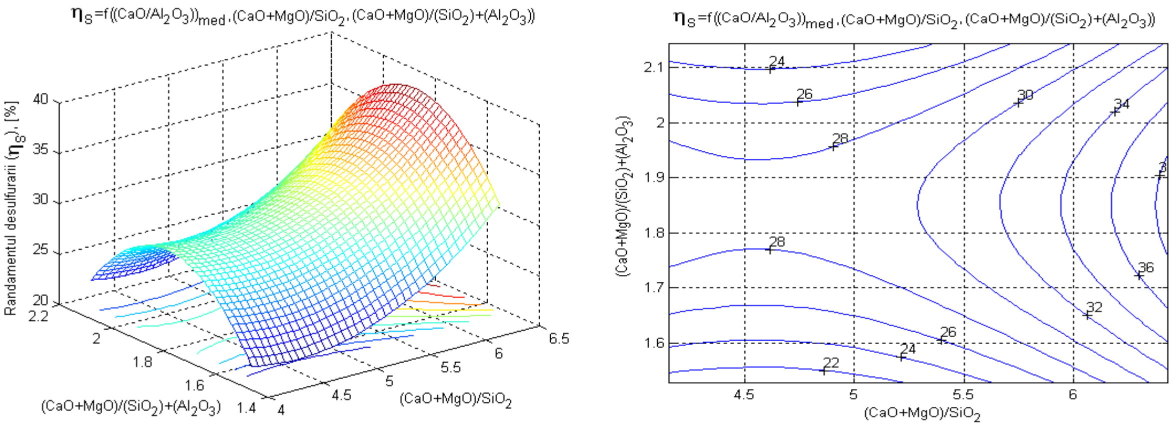

Fig. 5. The variation of the desulphuration degree depending on the value $(CaO+MgO)/SiO_2$

In figure 5 it is presented the result of correlation $(CaO+MgO)/(SiO_2)$ on the desulphuration degree. This case, we considered that the magnesium oxide could have a similar influence with the one of the calcium oxide, taking into account the computation relations for basics, expressed by several researchers. By the graphic representation, it notices that the representation of the curve is similar to that of figure 2, the maximum is slightly outside the domain.

We consider that the MgO influence on desulphuration is well represented in figure 5.

By the processing of data in the MATLAB program, we have obtained multiple correlation equations of form u = f(x,y,z) where: x,y,z are the independent parameters (our case $(CaO)/(Al_2O_3)$...) and one dependent parameter (our case the desulphuration output).

Because we cannot represent graphically (in the three dimensions space) such correlations for each equation with three independent parameters, by permutation, we assign a parameter the average value and therefore we obtained the equation with two independent parameters, equation that may be represented graphically. Certainly, we may obtain directly by processing of the equation with two independent parameters, but we wanted to have analytically an equation with three independent parameters, we considered the most representative ones.




a. b.

Figure 6. The correlation surface (saddle type) in the technological domain

In figure 6, it notices that the correlation surface (saddle type) presents a stationary point in the technological domain. The correlation equation is:

$$\eta_S = -24{,}4402 \cdot \left(\frac{CaO}{Al_2O_3}\right)^2 + 2{,}9031 \cdot \left(\frac{CaO+MgO}{SiO_2}\right)^2 - 74{,}3075 \cdot \left(\frac{CaO+MgO}{SiO_2+Al_2O_3}\right)^2 +$$
$$+0{,}452 \cdot \frac{CaO}{Al_2O_3} \cdot \frac{CaO+MgO}{SiO_2} - 0{,}10471 \cdot \frac{CaO+MgO}{SiO_2} \cdot \frac{CaO+MgO}{SiO_2+Al_2O_3} +$$
$$61{,}9322 \cdot \frac{CaO+MgO}{SiO_2+Al_2O_3} \cdot \frac{CaO}{Al_2O_3} - 3{,}872 \cdot \frac{CaO}{Al_2O_3} - 27{,}324 \cdot \frac{CaO+MgO}{SiO_2} +$$
$$+134{,}692 \cdot \frac{CaO+MgO}{SiO_2+Al_2O_3} - 31{,}2691$$

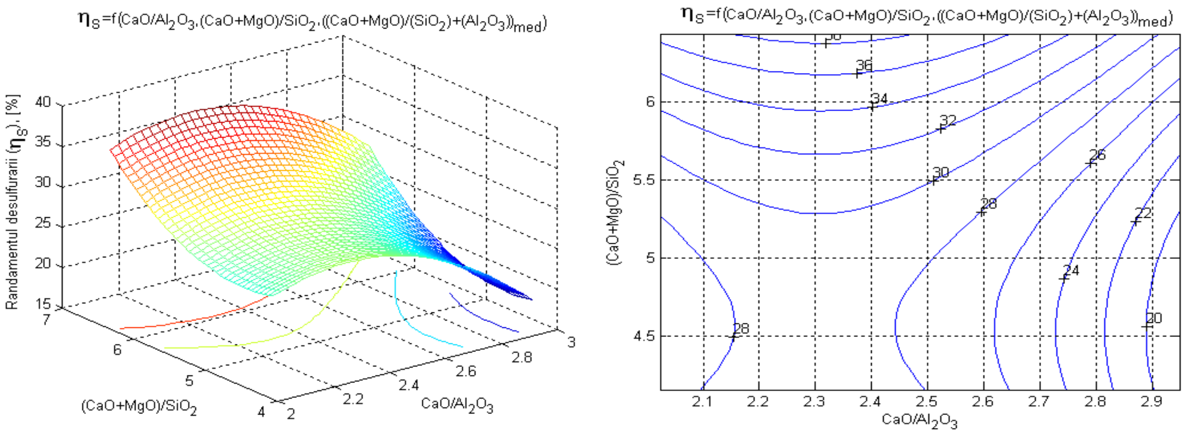
Coefficient of correlation = 0.9103. Saddle point coordinates are:

$$\frac{CaO}{Al_2O_3} = 2{,}3458\,; \quad \frac{CaO+MgO}{SiO_2} = 4{,}5601\,; \quad \frac{CaO+MgO}{SiO_2+Al_2O_3} = 1{,}8807\,; \quad \eta_S = 28{,}5434$$

The graphic representation allows us to select values for the two parameters, so that to be situated in the domain with values for the desulphuration output $(\eta_S) > 25$ %, it would be better to be over the stationary point.

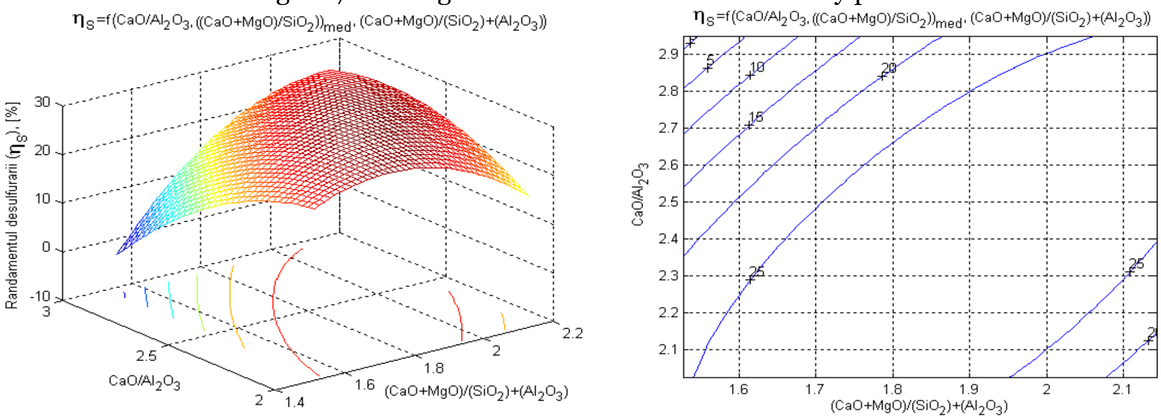
The regression surface presented in figure 7 a) is also of saddle form and presents a stationary point to the coordinates in the technological domain. As we also presented in the case of simple correlations, we wish to obtain for $\eta_s$ values over 28%. To obtain such values, the reports $(CaO+MgO)SiO_2$ and $(CaO+MgO)/(SiO_2+Al_2O_3)$ must vary so that $\eta_s$ to situate in the hachured domain.

As in the case of the previous surface, the correlation surface is of saddle type as stationary point in the technological domain. To obtain values $\eta_s > 28$ % the values of parameters $(CaO+MgO)SiO_2$ and $CaO/Al_2O_3$ must vary so that $\eta_s$ to have in the hachured domain.




a. b.

Figure 7. The regression surface and the stationary point




a. b.

Figure 8. The regression surface and the maximal point

The regression surface presented in figure 8 presents a maximal point in the technological domain. To obtain over 25 % for the desulphuring ratio both independent parameters must vary so that $\eta_s$ to have in the hachured domain.

## 4. CONCLUSIONS

The desulphuration with synthetic cinders in the LF installation is developed in good conditions and in the case of elaborated steel in the EBT oven. By the issued experiments and the analysis of the data of the obtained correlations, it results the following conclusions applicable in the industrial practice:

- ❖ for the desulphuration with synthetic cinder, represented by the system $CaO$-$Al_2O_3$ it may be obtained values for the desulphuration output ($\eta_s$) >28 %;
- ❖ for the desulphuration practice in the LF installation, we indicate the work with specific consumption of reducer cinders in the limits of 32-36 Kg/tone steel;
- ❖ the report $CaO/Al_2O_3$ is desired to be within the limits 1.7-2.3;
- ❖ the report $(CaO+MgO)SiO_2$ is desired to be within the limits 5.25-6.25;
- ❖ the report $CaO+MgO)/(SiO_2+Al_2O_3)$ is desired to be within the limits 1.8-2.3.

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