

Steel desulphurization with synthetic slag*

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Abstract

Generally speaking, sulphur is considered a harmful element for steel quality, reason why all the technological steps are being taken in order to eliminate it from the metal bath. This paper deals with the influence of the chemical composition, on the slag quantity and of the bath stirring condition upon the desulphurization process in the casting ladle by treatment with synthetic slag. The experiments were made at an open-hearth plant with the steel tapping in two ladles (the desulphurization was made with synthetic slag at one ladle while the other one was considered standard) and at the electric steel plant and for the synthetic slag formation a mix was used, made, according to several receipts, of: lime (50-75%), fluorine (0-17%), bauxite (0-32%) and aluminous slag (8-22%). The data were processed in the calculation programs EXCEL and MATLAB, which resulted in a series of correlations between the desulphurization degree and the chemical composition of the slag, respectively the slag quantity both for the charges bubbled with Argon and the unbubbled ones.

Keywords

Steel. Desulphurization. Synthetic slag. Treatment. Ladle.

Desulfuración del acero con escorias sintéticas

Resumen

En general, el azufre es considerado un elemento nocivo para la calidad del acero y, por eso, en la práctica, se toman todas las medidas de orden tecnológico para su eliminación del baño metálico. En este trabajo se analiza la influencia de la composición química, de la cantidad de escoria y del estado de agitación del baño sobre el proceso de desulfuración en la cuchara para fundir por tratamiento con escoria sintética. Los experimentos se han realizado en una acería evacuando el acero en dos ollas (en una cuchara se efectuó la desulfuración con escoria sintética y a la otra se consideró como patrón) y en un acería eléctrica y para la formación de la escoria sintética se utilizó una mezcla producida según muchas recetas, formada por: cal (50-75%), fluorina (0-17%), bauxita (0-32%) y escoria aluminosa (8-22%). Los datos han sido procesados en los programas de cálculo EXCEL y MATLAB, resultando una serie de correlaciones entre el grado de desulfuración y la composición química de la escoria, la cantidad de escoria respectivamente, tanto para las cargas burbujeadas con argón como no burbujeadas.

Palabras clave

Acero. Desulfuración. Escoria sintética. Tratamiento. Cuchara.

1. GENERAL CONSIDERATIONS

Sulphur reaches the steel bath through the metallic charge, fuels and added elements. Because the sulphur contents in these sources cannot be reduced below certain limits, the elaboration process has to be

carried out in such a way that an advanced desulphurization be achieved both in the furnace and in the casting ladle. There has been an ever growing tendency lately towards desulphurization outside the elaboration aggregate (desulphurization with synthetic slag), which leads to significant saving of energy, de-

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oxidizing and desulphurization agents, as well as to an important increase in productivity

By treating liquid steel with synthetic slag, desulphurization is being transferred from the elaboration aggregate to the casting ladle. The processes taking place during refining are mainly conditioned by the characteristics of the synthetic slag (the inter-phase strain between the steel and the synthetic slag, viscosity and chemical composition), by the process rate, the height of steel jet descent and the quantity of slag.

The synthetic slag used in the desulphurization process corresponds to the binary systems CaO-Al₂O₃, CaO-CaF₂ and, respectively, to the ternary systems CaO-Al₂O₃-CaF₂, CaO-Al₂O₃-Ca, Na, Al, fluorides with variable contents of SiO₂, MgO^[1 y 2] but with very low contents of iron and manganese oxides^[3-5].

Also, in industrial practice, one has to take into account steel temperature, both for its direct influence upon the desulphurization process and indirectly, by means of slag viscosity, particularly when, in order to obtain the synthetic slag, solid mixtures are being added into the ladle.

At industrial level, the desulphurization process using synthetic slag can be most easily influenced by means of the chemical composition of the slag (resulting from the variation of slag recipe) and by a specific adding of slag.

2. INDUSTRIAL EXPERIMENTS

Experiments have been done in view of determining the desulphurization capacity of certain synthetic slag types obtained by slagging solid mixtures including aluminum slag (rich in Na and Al fluorides), resulting from aluminum electrolyze.

Industrial experiments have been carried out in a steel plant endowed with 400t steel elaboration aggregates (Siemens-Martin furnaces), respectively 100 t aggregates (electric arc furnaces). During the experimentation, an increase of the sulphur content in steel has been noticed, its main cause being the inappropriate desulphurization of the coke plant gas. We do not give the evolution of parameters inside the aggregate, as the experiments aimed at processing the steel inside the casting ladle.

These experiments have been particularly interesting not only in terms of using aluminum slag as component of the synthetic slag, but also as we could compare a standard ladle (with no desulphurization additives) to a ladle in which were added desulphurization elements, whose smelting resulted in obtaining some synthetic slag (for the high capacity aggregates steel tapping being done into two casting ladles).

In view of obtaining the synthetic slag, at the bottom of the ladle we introduced 30 min before the ste-

el was tapped: lime (50-56% with the grain size under 40 mm), bauxite (27-32% and grain size under 30 mm) and aluminum slag (18-20% with the grain size under 25 mm). In contact with the liquid steel, these materials turned into slag and the result was highly emulsified with the liquid steel. Thus, as a result of an increase of the inter-phase surface, the process of sulphur transfer from the bath into the slag intensified. At the same time with the desulphurization process, a process of deoxidizing by precipitation took place in both ladles.

During the experiments we collected in order to determine the chemical compositions: steel samples taken from the jet on pouring into the ladle, steel samples 15 min after the ladle was filled (both from the standard ladle and the one with desulphurization mixtures) and slag samples taken right after the completion of the ladle filling.

It is to be mentioned that 6 recipes of desulphurization mixture were used and the quantity of desulphurization slag was modified within the limits 4-15 kg/t. Also, the tapping temperature was kept 15-35 °C above the normal one, in order to compensate the cooling of steel caused by the melting of the additional elements.

The experiments were carried out on the same steel grade meant for pipe production: 24 charges (4 charges/recipe) of argon, non-bubbled steel and 12 charges (2 charges/recipe), bubbled with argon (for which the tapping temperature was 20-40°C above the normal one).

The experiments at the electric steel plant were carried out on 16 steel charges (4 charges/recipe), elaborated in a 100t-UHP electric arc furnace, steel meant for the production of pipes. In this case, considering the fact that steel tapping is done into a single ladle, the comparison was drawn with other charges of steel having the same grade and being elaborated under similar conditions.

In order to obtain the desulphurization slag we introduced at the bottom of the ladle, 30min. before steel tapping, a mixture of 4-14,5 kg/t of steel, made of: lime (68-75% of the mixture weight and a grain size below 40mm), calcium fluoride (14-17% of the mixture weight and a grain size below 35 mm) and aluminum slag (11-15% of the mixture weight and a grain size below 25 mm). In this case too, in order to compensate the heat loss resulting from the melting of the mixture, the tapping temperature was 20-40°C higher than the normal one.

For all the experimental variants we collected steel samples from the tapping jet and from the casting ladle 15 min after its filling up, as well as slag samples right after the filling of the casting ladle. Using the samples under analysis we determined the che-

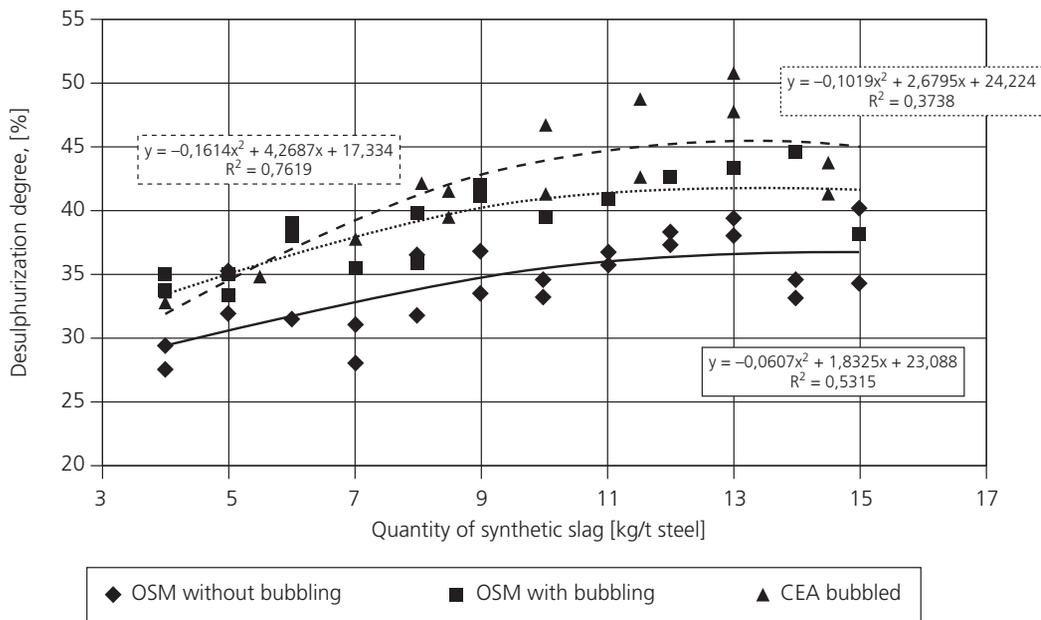


Figure 1. The variation of the desulphurization degree according to the quantity of synthetic slag.

Figura 1. Variación del grado de desulfuración dependiendo de la cantidad de escoria sintética.

mical composition of the steel and slag and, implicitly, we calculated the degree of desulphurization.

3. RESULTS, DISCUSSIONS

The data we obtained were processed under Excel and Matlab calculation programs in order to obtain the correlations between the degree of desulphurization and the specific slag quantity (kg/t of steel), respectively the chemical composition of the slag (CaO, Al₂O₃, fluorides: Me_xF), the results being given both under analytical and graphical form.

Thus, figure 1 shows the variation of desulphurization degree according to the quantity of synthetic slag used in the casting ladle. The given data prove that, irrespective of the experimental variant, the degree of desulphurization increases with the quantity of slag, up to about 11kg/t, after which it tends to stay constant.

The quantity of slag influences the desulphurization process as its increase reduces sulphur concentration, therefore reducing a_(MeS) and in this way it helps desulphurization by means of CaO unsaturated slag. An increase in the quantity of additive of more than 11kg/t may lead to an increase of slag viscosity because of the insufficient temperature resulting from the melting of the desulphurization additive.

Further on, we give the results of data processing under Matlab program and the multiple correlation equations obtained in general form:

$$\begin{aligned} \eta S = & c_1 \cdot CaO^2 + c_2 \cdot Al_2O_3^2 + c_3 \cdot Me_xF^2 \\ & + c_4 \cdot CaO \cdot Al_2O_3 + c_5 \cdot Al_2O_3 \cdot Me_xF \\ & + c_6 \cdot CaO \cdot Me_xF + c_7 \cdot CaO + c_8 \cdot Al_2O_3 + c_9 \cdot Me_xF + c_{10} \end{aligned} \quad (1)$$

where, ηS – the degree of desulphurization, (%);
c₁..c₁₀ – coefficients.

In this way, we obtained the dependencies for the desulphurization degree related to the steel elaborated in the Siemens-Martin furnace without bubbling (ηS₁), the steel elaborated in the Siemens-Martin furnace with bubbling (ηS₂) and, respectively for the steel elaborated in the electric arc furnace and bubbled (ηS₃).

$$\begin{aligned} \eta S_1 = & -0.44015 \cdot CaO^2 + 0.9087 \cdot Al_2O_3^2 - \\ & 0.35423 \cdot Me_xF^2 - 0.33658 \cdot CaO \cdot Al_2O_3 - \\ & 0.58185 \cdot Al_2O_3 \cdot Me_xF - 0.2952 \cdot Me_xF \\ & CaO + 56.351 \cdot CaO - 15.9804 \cdot Al_2O_3 + \\ & 41.3073 \cdot Me_xF - 1530.2843 \end{aligned} \quad (2)$$

The correlation coefficient is: R₁²=0.7130 and the coordinates of the saddle point are:

$$\begin{aligned} CaO = & 48.7313 \% ; Al_2O_3 = 23.7414 \% ; \\ Me_xF = & 18.5017 \% ; \eta S_1 = 35.1744 \% . \\ \eta S_2 = & -0.12669 \cdot CaO^2 + 0.46838 \cdot Al_2O_3^2 + \\ & 0.22471 \cdot Me_xF^2 - 0.0010206 \cdot CaO \cdot Al_2O_3 - \\ & 0.19129 \cdot Al_2O_3 \cdot Me_xF + 0.13077 \cdot Me_xF \cdot CaO + \\ & 10.2916 \cdot CaO - 18.8057 \cdot Al_2O_3 - 10.4041 \cdot Me_xF \\ & + 103.608 \end{aligned} \quad (3)$$

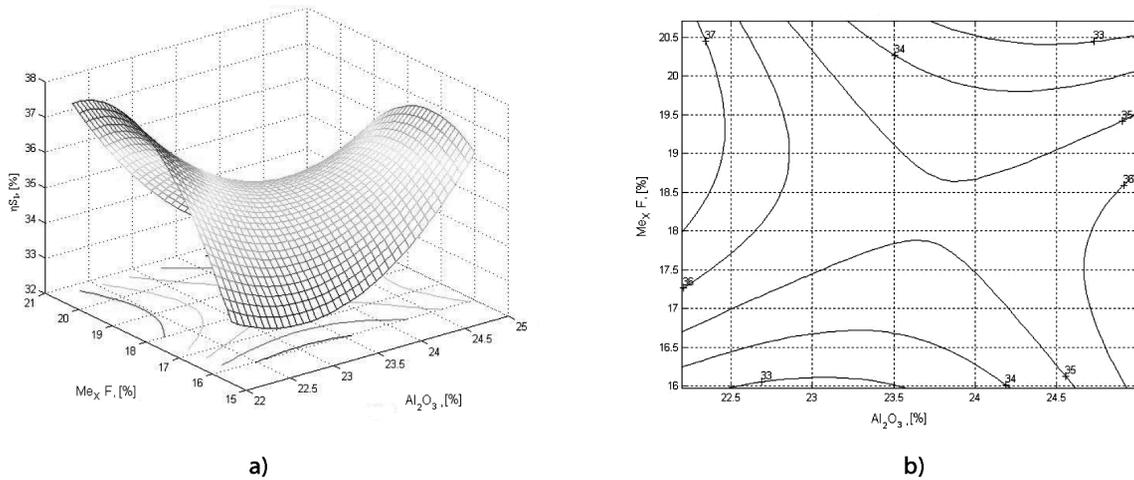


Figure 2. The regression surface (a) and the contour lines (b) for the dependency $\eta S_{1(CaO\ med)} = fc(Al_2O_3, Me_xF)$.

Figura 2. Superficie de regresión (a) y las curvas de nivel (b) para la dependencia $\eta S_{1(CaO\ med)} = fc(Al_2O_3, Me_xF)$.

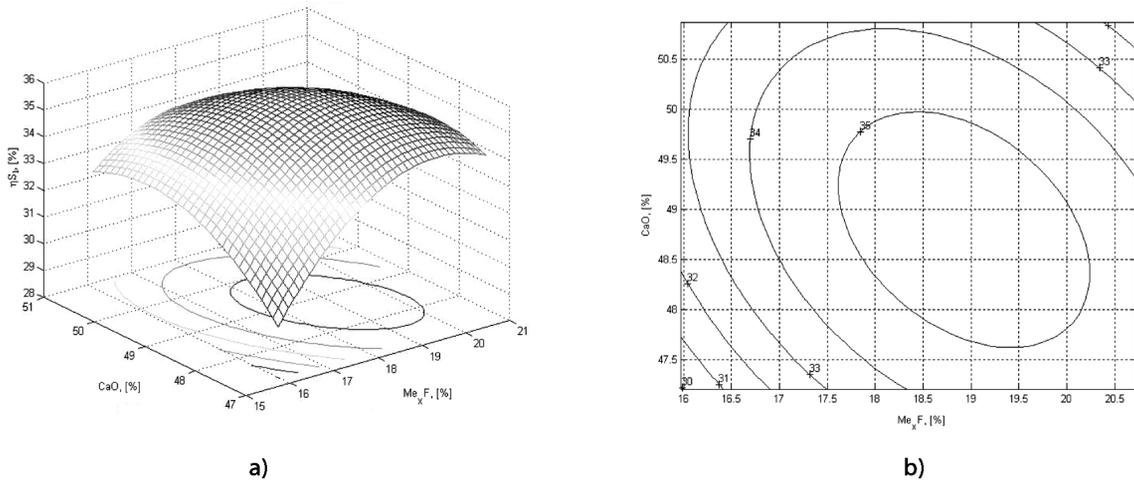


Figure 3. The regression surface (a) and the contour lines (b) for the dependency $\eta S_{1(Al_2O_3\ med)} = fc(Me_xF, CaO)$

Figura 3. Superficie de regresión (a) y las curvas de nivel (b) para la dependencia $\eta S_{1(Al_2O_3\ med)} = fc(Me_xF, CaO)$.

The correlation coefficient is: $R^2_2=0.3941$ and the coordinates of the saddle point are:

$$\begin{aligned}
 &CaO=50.1927\%; Al_2O_3=23.9571\%; \\
 &Me_xF=18.7424\%; \dot{E}S_1=39.1253\%. \\
 &\eta S_3=2.2002 \cdot CaO^2 - 3448.869 \cdot Al_2O_3^2 \\
 &\quad - 3.476 \cdot Me_xF^2 - 14.6779 \cdot CaO \cdot Al_2O_3 \\
 &\quad + 108.8589 \cdot Al_2O_3 \cdot Me_xF \\
 &\quad - 0.59388 \cdot Me_xF \cdot CaO - 265.3381 \cdot CaO \\
 &\quad + 5073.9529 \cdot Al_2O_3 + 113.8885 \cdot Me_xF \\
 &\quad + 4896.2141
 \end{aligned} \tag{4}$$

The correlation coefficient is: $R^2_3=0.8386$ and the coordinates of the saddle point are: $CaO=67.2368\%$; $Al_2O_3=1.01\%$; $Me_xF=26.454\%$; $\eta S_1=44.7586\%$.

As hypersurfaces cannot be represented in a 4-dimensional space. We resorted to successively replacing an independent value by its mean value. These surfaces whose equations are given in relations (5-13) belong to the 3-dimensional space and can be represented (figs. 2-10) and interpreted technologically.

$$\begin{aligned}
 \eta S_{1(CaO\ med)} &= 0.9087 \cdot Al_2O_3^2 - 0.35423 \cdot Me_xF^2 \\
 &\quad - 0.58185 \cdot Al_2O_3 \cdot Me_xF - 32.5629 \cdot Al_2O_3 \\
 &\quad + 26.7633 \cdot Me_xF + 177.6185
 \end{aligned} \tag{5}$$

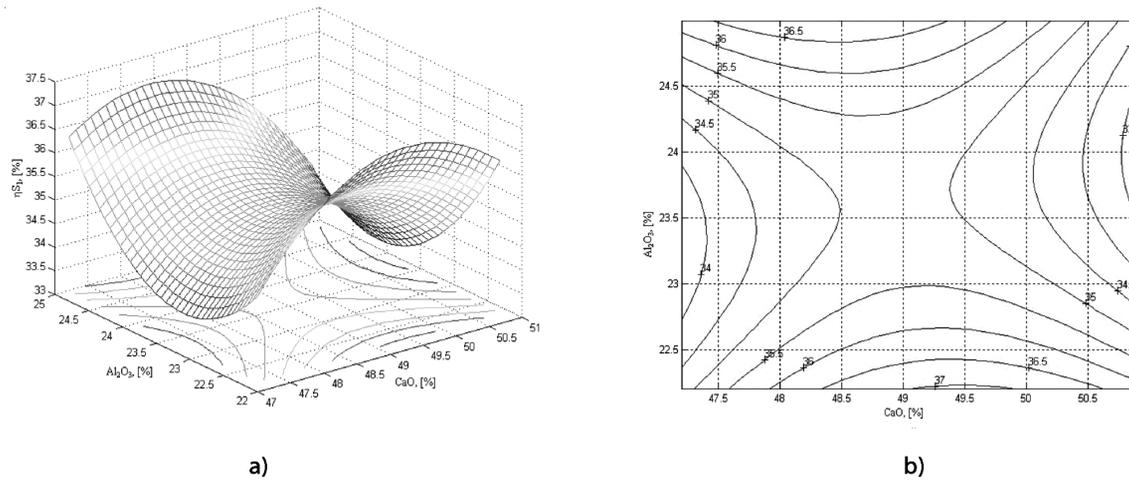


Figure 4. The regression surface (a) and the contour lines (b) for the dependency $\eta S_{1(MexFmed)} = fc(CaO, Al_2O_3)$.

Figura 4. Superficie de regresión (a) y las curvas de nivel (b) para la dependencia $\eta S_{1(MexFmed)} = fc(CaO, Al_2O_3)$.

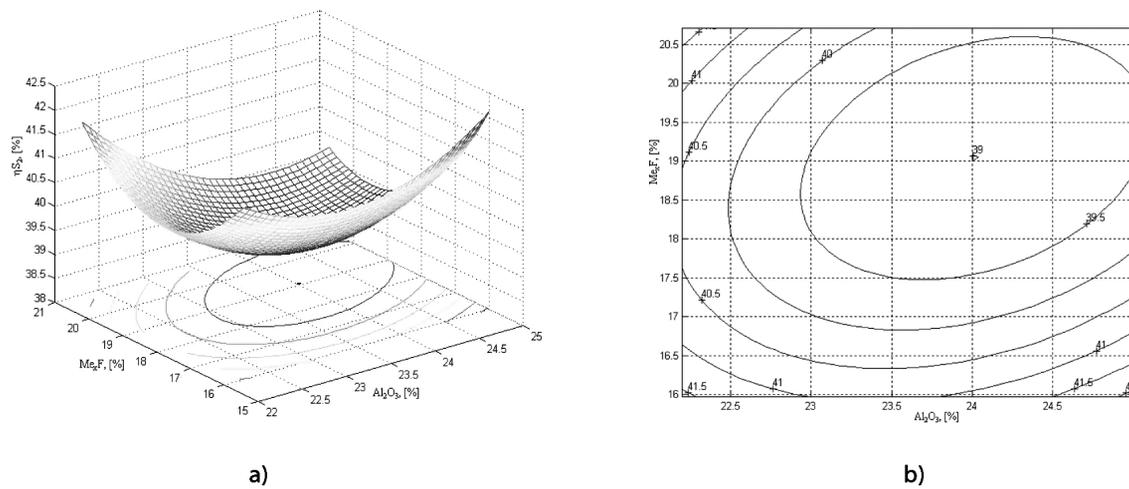


Figure 5. The regression surface (a) and the contour lines (b) for the dependency $\eta S_{2(CaO med)} = fc(Al_2O_3, Me_xF)$.

Figura 5. Superficie de regresión (a) y las curvas de nivel (b) para la dependencia $\eta S_{2(CaO med)} = fc(Al_2O_3, Me_xF)$.

$$\eta S_{1(Al_2O_3 med)} = -0.35423 \cdot Me_xF^2 - 0.44015 \cdot CaO^2 - 0.2952 \cdot Me_xF \cdot CaO + 27.8143 \cdot Me_xF + 48.5457 \cdot CaO - 1412.1937 \quad (6)$$

$$\eta S_{2(Al_2O_3 med)} = 0.22471 \cdot Me_xF^2 - 0.12669 \cdot CaO^2 + 0.13077 \cdot Me_xF \cdot CaO - 14.84 \cdot Me_xF + 10.2679 \cdot CaO - 80.6125 \quad (9)$$

$$\eta S_{1(MexF med)} = -0.44015 \cdot CaO^2 + 0.9087 \cdot Al_2O_3^2 - 0.33658 \cdot CaO \cdot Al_2O_3 + 51.0275 \cdot CaO - 26.473 \cdot Al_2O_3 - 900.573 \quad (7)$$

$$\eta S_{2(MexF med)} = -0.12669 \cdot CaO^2 + 0.46838 \cdot Al_2O_3^2 - 0.0010206 \cdot CaO \cdot Al_2O_3 + 12.6497 \cdot CaO - 22.2552 \cdot Al_2O_3 - 10.9359 \quad (10)$$

$$\eta S_{2(CaO med)} = 0.46838 \cdot Al_2O_3^2 + 0.22471 \cdot Me_xF^2 - 0.19129 \cdot Al_2O_3 \cdot Me_xF - 18.856 \cdot Al_2O_3 - 3.9615 \cdot Me_xF + 303.1306 \quad (8)$$

$$\eta S_{3(CaO med)} = -3448.869 \cdot Al_2O_3^2 - 3.476 \cdot Me_xF^2 + 108.8589 \cdot Al_2O_3 \cdot Me_xF + 4107.5885 \cdot Al_2O_3 + 74.7883 \cdot Me_xF - 3035.8812 \quad (11)$$

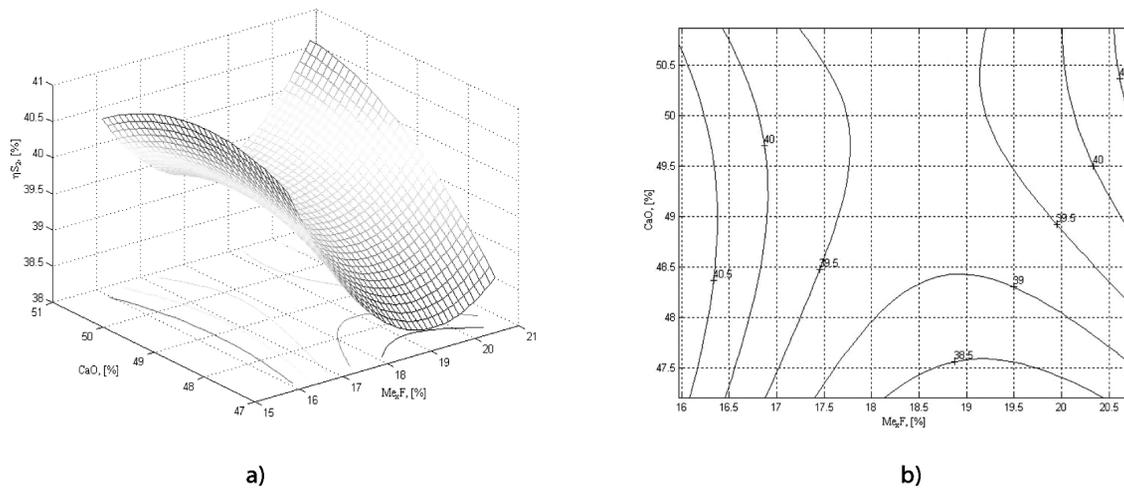


Figure 6. The regression surface (a) and the contour lines (b) for the dependency $\eta_{S_{2(Al_2O_3 \text{ med})}} = f_c(Me_xF, CaO)$.

Figura 6. Superficie de regresión (a) y las curvas de nivel (b) para la dependencia $\eta_{S_{2(Al_2O_3 \text{ med})}} = f_c(Me_xF, CaO)$.

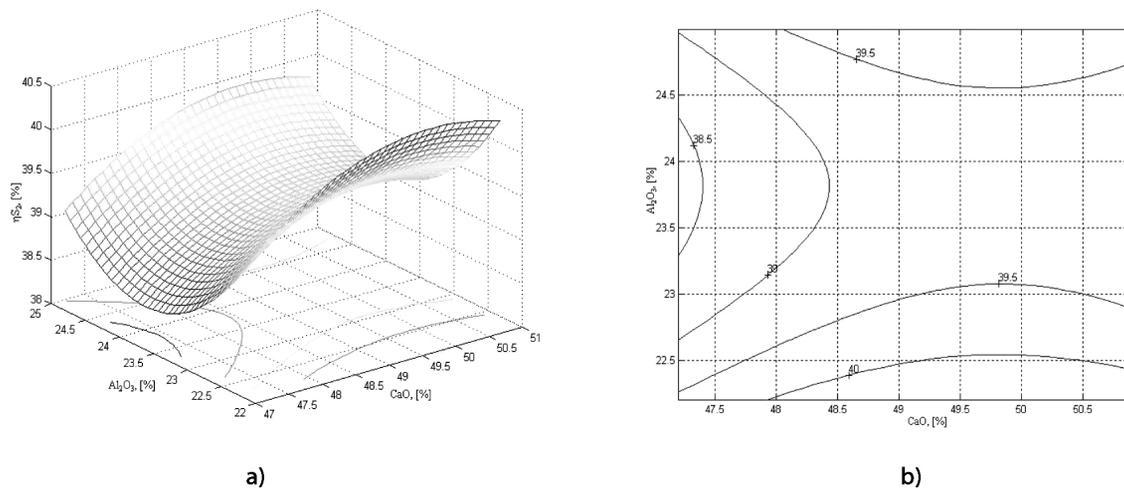


Figure 7. The regression surface (a) and the contour lines (b) for the dependency $\eta_{S_{2(MexFmed)}} = f_c(CaO, Al_2O_3)$.

Figura 7. Superficie de regresión (a) y las curvas de nivel (b) para la dependencia $\eta_{S_{2(MexFmed)}} = f_c(CaO, Al_2O_3)$.

$$\eta_{S_{3(Al_2O_3 \text{ med})}} = -3.476 \cdot Me_xF^2 + 2.2002 \cdot CaO^2 - 0.59388 \cdot Me_xF \cdot CaO + 221.1145 \cdot Me_xF - 279.7958 \cdot CaO + 6547.8788 \quad (12)$$

$$\eta_{S_{3(MexF \text{ med})}} = 2.2002 \cdot CaO^2 - 3448.869 \cdot Al_2O_3^2 - 14.6779 \cdot CaO \cdot Al_2O_3 - 280.8719 \cdot CaO + 7921.2935 \cdot Al_2O_3 + 5497.0294 \quad (13)$$

An analysis of the equations of regression hypersurfaces from the point of view of the values of correlation coefficients R, may lead to the conclusion that they are representative. The presence of a graphical

form of correlations allows a more eloquent interpretation of the influence of slag chemical composition upon the desulphurization degree.

From the interpretation of the graphics one can determine the domains of chemical composition for which the degree of desulphurization has values above the mean, these domains belonging to the technological ones.

An analysis of figures 2, 3 and 4 (the variation of the degree of desulphurization according to the chemical composition of the slag, for the steel elaborated in the Siemens-Martin furnace and not bubbled in the casting ladle), proves that for a ranging of the contents

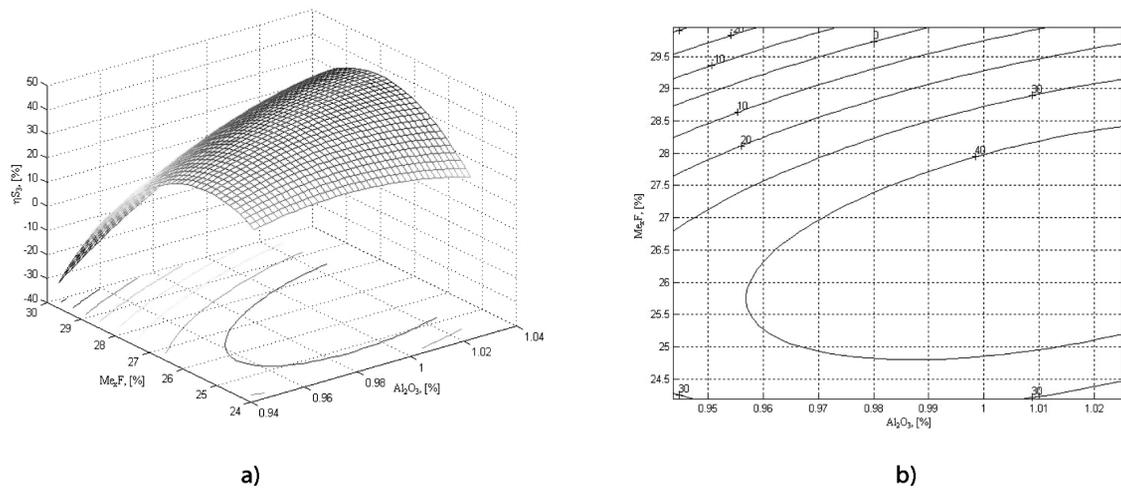


Figure 8. The regression surface (a) and the contour lines (b) for the dependency $\eta_{S_3(CaO\ med)}=fc(Al_2O_3, Me_xF)$.

Figura 8. Superficie de regresión (a) y las curvas de nivel (b) para la dependencia $\eta_{S_3(CaO\ med)}=fc(Al_2O_3, Me_xF)$.

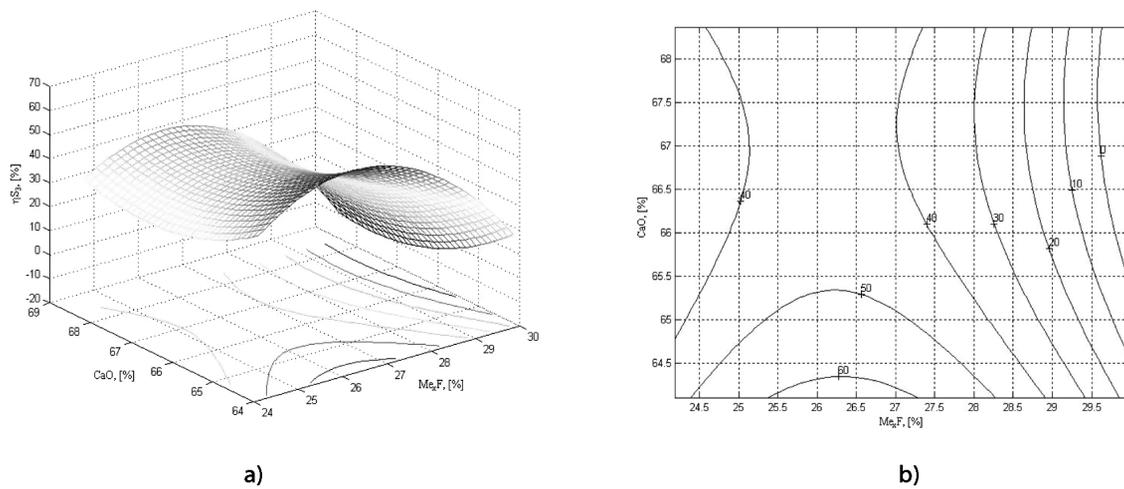


Figure 9. The regression surface (a) and the contour lines (b) for the dependency $\eta_{S_3(Al_2O_3\ med)}=fc(Me_xF, CaO)$.

Figura 9. Superficie de regresión (a) y las curvas de nivel (b) para la dependencia $\eta_{S_3(Al_2O_3\ med)}=fc(Me_xF, CaO)$.

in Al_2O_3 within the limits 22-23.5% ($Al_2O_{3\ mean} = 23.19\%$). CaO : 48-53% ($CaO_{\ mean} = 49.268\%$) and fluorides Me_xF : 17.5-20.5% ($Me_xF_{\ mean} = 18.33\%$) a degree of desulphurization above 35% (mean value 34.058%) can be obtained.

Figures 5, 6, 7 (the variation of the degree of desulphurization according to the chemical composition of the slag, for the steel elaborated in the Siemens-Martin furnace and bubbled in the casting ladle) show that for the same domain of chemical composition, with values close to the previous ones ($CaO_{\ mean} = 49.295\%$, $Al_2O_{3\ mean} = 23.12\%$ and $Me_xF_{\ mean} = 18.102\%$) one can obtain values for the degree of desulphurization above 41 %, the mean value being 40.104%.

Higher values (by 4-6 %) for the degree of desulphurization in the case of the bubbled steel as compared to the non-bubbled one (for the same steel grade and ladle capacity) are due to an improvement of diffusion as a result of argon bubbling of the metal bath.

With respect to the steel elaborated in the electric arc furnace and bubbled in the casting ladle (Figs. 8-10), for which the bauxite in the additive was replaced by fluorine, one can notice that it is possible to obtain values of the degree of desulphurization above the mean one (41.435%) if the slag components range within the limits 64-68% CaO and 24.8-28.5% Me_xF (the influence of Al_2O_3 is negligible), in this case desulphurization being analyzed in the binary system,

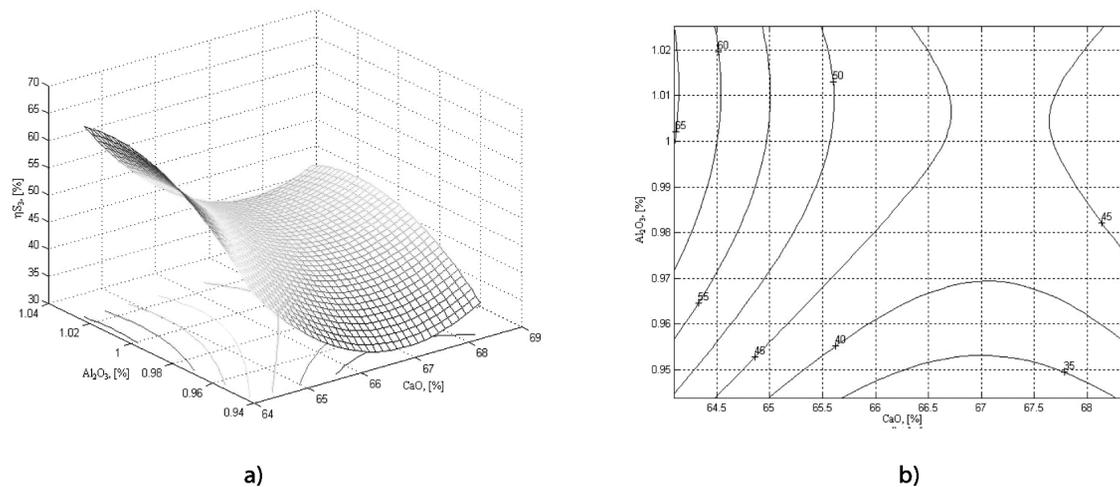


Figure 10. The regression surface (a) and the contour lines (b) for the dependency $\eta S_{3(MexFmed)} = fc(CaO, Al_2O_3)$.

Figura 10. Superficie de regresión (a) y las curvas de nivel (b) para la dependencia $\eta S_{3(MexFmed)} = fc(CaO, Al_2O_3)$.

CaO-Me_xF, with respect to the previous cases, when it was analyzed in the ternary system CaO-Al₂O₃-Me_xF.

4. CONCLUSIONS

Having studied the process of steel desulphurization in the casting ladle with synthetic slag obtained by melting the desulphurization mixture, we reached the following conclusions:

- the additives used for the desulphurization of steel allow the obtaining of slag with a high desulphurization power, an important role being played by fluorides, which ensure a good fluidity;
- desulphurization is efficient both in the case of the slag corresponding to the ternary system CaO-Al₂O₃-Me_xF, and in that of the binary system CaO-Me_xF;
- steel bubbling during the treatment with synthetic slag determines an increase in the desulphurization degree by 4-6 %;
- the quantity of slag has a positive influence upon the degree of desulphurization; thus, its increase from 4 kg/t to 15 kg/t leads to an increase of the desulphurization degree by 8-10% for the steel elaborated in the electric arc furnace (with bubbling inside the casting ladle), and for the steel elaborated in the Siemens-Martin furnace and unbubbled, by 2-3% respectively by 4-5% when bubbled in the ladle;

- establishing the multiple correlations and particularly the graphic representation of the regression hypersurfaces are particularly relevant in practice as they allow the determination of some domains for the slag chemical composition (achievable in practice), which ensure high values for the desulphurization degree;
- the use of aluminum slag in the desulphurization mixture ensures the turning into account and recycling of some waste to be found in the dump and returning that space to the natural environment.

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