ISSN 1330-3651 (Print), ISSN 1848-6339 (Online)
DOI: 10.17559/TV-20140204114421

RESEARCHES ON THE REDUCTION OF STEEL HYDROGEN CONTENT BY ITS SECONDARY TREATMENT INSIDE THE LADLE

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Original scientific paper
The paper introduces the results obtained in the determination of the variation domains of the technological parameters used for steel secondary treatment in LF-type installations, in view of improving its quality. The use of the resulting technological parameters allows the production of low-gas steel (particularly low-hydrogen) and brings new information pertaining to steel degassing in the steel secondary treatment installations.

Keywords: *argon; bubbling; hydrogen; mathematical modelling; refining; steel; yield*

Istraživanje smanjenja sadržaja vodika u čeliku njegovom sekundarnom obradom unutar ljevačkog lonca

Izvorni znanstveni članak
U radu se daju rezultati dobiveni određivanjem područja varijacije tehnoloških parametara primijenjenih kod sekundarne obrade čelika u instalacijama LF-tipa u svrhu poboljšanja njegove kvalitete. Primjena dobivenih tehnoloških parametara omogućuje proizvodnju čelika s malom količinom plina (naročito vodika) i pruža nove spoznaje u odnosu na otplinjavanje čelika u instalacijama za sekundarnu obradu čelika.

Ključne riječi: *argon; čelik; korist; matematičko modeliranje; mjehuranje; pročišćavanje; vodik*

1 Introduction

Steel purity, respectively its high quality, starts as early as its elaboration stage where, besides an appropriate charge, the process itself has to be carried out accordingly. This involves the observance of the elaboration technology according to the specific aggregate in use, the steel grade and the purity requirements referring to the content of non-metallic inclusions and the gas content, as specified by standards and/or by the beneficiary [1].

Along the years, in spite of the various analyses of steel refining and gas content, there are still aspects that are worth being looked into.

During steel secondary treatment in an LF-type installation, chemical composition is corrected and an adequate (active) slag is obtained in order to have a good degassing, desulphurization and deoxidizing; at the same time, steel temperature is kept within the technological limits required by continuous casting.

Steel refining in the LF-type installation is supposed to lead to the following metallurgical effects [2 ÷ 5]:
- temperature adjusting and diminishing its variations;
- adjustment of the metal bath chemical composition;
- deoxidizing and desulphurization with or without synthetic slags;
- reduction of the gas and non-metallic inclusions in the steel content.

Between the metallurgical effects and the factors that condition them, there is a close interdependency, also reflected by the succession of the process stages [5÷7]. Thus:

a) synthetic slag addition leads to:
- screening the electric arc, with beneficial effects on the thermal output and the wear of the furnace – ladle refractory material;
- less contact between the metal bath and the oxidizing atmosphere;
- desulphurization;
- increase of inclusionary purity.

b) steel heating up at a rate of 3 ÷ 5 °C/min. allows:
- lime and fluorine melting and obtaining a fluid and active slag;
- pulverous material injection;
- addition of special deoxidizing-alloying elements, aluminium wires or those filled with deoxidizing or modifying elements.

c) argon injection leads to:
- homogenizing the chemical composition and the temperatures of the metallic melting;
- stimulation of the reactions slag – melting, particularly in case of desulphurization;
- flotation and decanting of non-metallic inclusions and, as a result, a higher steel inclusionary purity.

The economical effects resulting from the process of steel elaboration – refining considered for the metallurgical duplex ensemble CAE – LF are shown in [6, 8 ÷ 11]:
- cutting down the tapping temperature in the primary aggregate by 40 ÷ 80 °C;
- reduction of the elaboration times in the primary aggregate;
- reduction of wear and refractory material consumption by 10 ÷ 20 %, due to the lower functioning temperature;
- lower electric power consumption by 20 ÷ 50 kWh/t and lower electrode consumption by 0,1 ÷ 0,2 kg/t.

Inside the LP installation, the main factors that can influence the hydrogen and particularly the nitrogen content are the parameters of the bubbling gas, the pressure and flow rate (argon), the humidity of the lime and bauxite.

2 Laboratory experiments

In order to study the influence of steel processing parameters inside the LF installation upon the rate of hydrogen removal from the metallic bath, research and industrial experiments have been carried out on the electric furnace-LF installation-continuous casting flux of an electric steel plant.

The evolution of the oxygen content has been analyzed along the process of steel elaboration and casting, for a number of 20 unalloyed charges, meant for pipe manufacturing. During the industrial experiments, we measured the level of hydrogen in the metal bath after steel tapping from the ladle, at the entrance of the ladle into the LF installation, when the first steel sampling was made, at the end of the treatment into the LF installation, when steel temperature and the hydrogen level were gauged, and the final steel sampling was made in the tundish of the continuous casting machine. In the LF installation new slag is formed, its role being to achieve desulphurizing, and whose characteristics should be optimal in terms of viscosity and basic character in order to boost processes of inclusion degasification and decanting.

The parameters under consideration were: the structure of the metallic charge and additives, the humidity of the charge, the characteristics of the slag, the parameters of melting and oxidizing, the purity of the oxygen blown into the furnace, the temperature of the metallic bath inside the furnace, the additives used in the furnace and in the ladle, the ladle additives during the treatment inside the LF installation, the content of hydrogen in the steel at different stages of the elaboration process, the parameters of argon bubbling inside the LP installation (flow rate, pressure, duration, temperature of the metallic bath) as well as the chemical composition of the slag inside the LF installation. The values of the above-mentioned parameters have been obtained both directly, by means of the gauging and control apparatus and by laboratory analyses of the steel and slag samples collected at different stages of the technological flux.

Taking into consideration the overwhelming influence of steel processing inside the LF installation upon the steel hydrogen content as well as upon the rate of its removal, the processing of the resulting data has lead to correlations between the significant parameters of steel treatment inside the LF installation and the rate of hydrogen removal.

The independent parameters of choice were: the argon flow rate (D_b/Nm^3/h); the duration of argon bubbling (t_b/min); the pressure of argon when bubbled (p_b/bari); and steel temperature (T/°C).

The dependent parameter of choice was the rate of hydrogen removal (η_H/%). The data were processed in MATLAB, which resulted in a series of double and multiple correlations. The regression surfaces (1st, 2nd and 3rd degree) respectively the level curves for the variation of the hydrogen removal rate and argon pressure inside the LF installation are shown in Fig. 1 ÷ 3.

Correlation equations, correlation coefficients and deviation from regression surface $\eta_H = f(D_b, p_b)$ are:

$$\eta_H = -0{,}05 \cdot D_b + 12{,}43 \cdot p_b + 20{,}02 \ \% \quad (1)$$

Correlation coefficient: R = 0,38; deviation from the regression surface: S = 7,76.

$$\eta_H = -0{,}005 \cdot D_b^2 + 0{,}02 \cdot D_b \cdot p_b - 0{,}02 \cdot p_b^2 + 5{,}59 \cdot D_b + 699{,}44 \cdot p_b - 3081{,}35 \ \% \quad (2)$$

Correlation coefficient: R = 0,92; deviation from the regression surface: S = 3,25; point of maximum: p_b = 4,48 bar; D_b = 555,39 Nm^3/h; η_H = 55,39 %.

$$\eta_H = 6{,}15 \cdot e^{-0{,}07} \cdot D_b^3 - 0{,}007 \cdot D_b^2 \cdot p_b + 1{,}63 \cdot D_b \cdot p_b^2 - 123{,}59 \cdot p_b^3 + 0{,}025 \cdot D_b^2 - 6{,}15 \cdot D_b \cdot p_b + 621{,}14 \cdot p_b^2 + 1{,}76 \cdot D_b - 610{,}01 \cdot p_b - 463{,}61 \ \% \quad (3)$$

Correlation coefficient: R = 0,96; deviation from the regression surface: S = 2,23; point of maximum: p_b = 4,50 bar; D_b = 556,32 Nm^3/h; η_H = 55,62 %.

The regression surfaces (1st, 2nd, 3rd and 4th degree) respectively the level curves for the variation of the hydrogen argon pressure and temperature inside the LF installation are shown in Fig. 4 ÷ 7.

Correlation equations, correlation coefficients and deviation from regression surface $\eta_H = (p_b, t_b)$ are:

$$\eta_{|H} = 13{,}78 \cdot p_b + 0{,}11 \cdot t_b - 24{,}37 \ \% \quad (4)$$

Correlation coefficient: R = 0,44; deviation from the regression surface: S = 7,51.

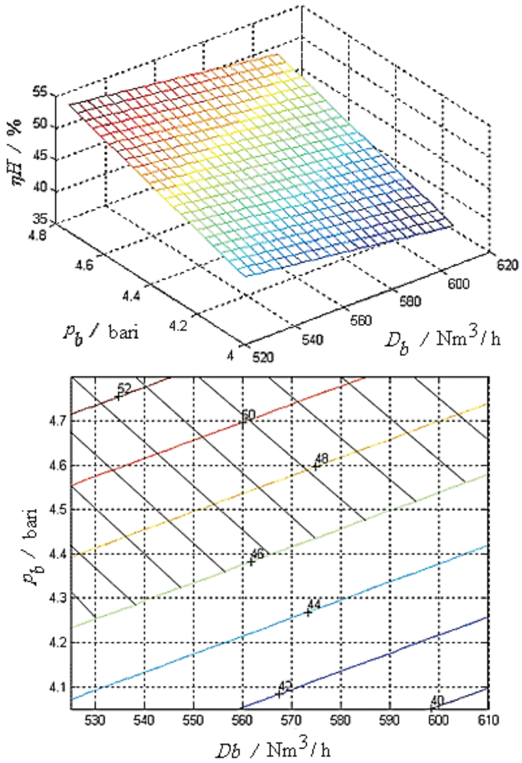

Figure 1 $\eta_H = f(D_b, p_b)$ – correlation 1st degree

$$\eta_H = -66{,}55 \cdot p_b^2 + 0{,}08 \cdot p_b \cdot t_b - 0{,}009 \cdot t_b^2 + 589{,}37 \cdot p_b + 1{,}31 \cdot t_b - 1324{,}45 \ \% \quad (5)$$

Correlation coefficient: R = 0,95; deviation from the regression surface: S = 2,49; point of maximum: p_b = 4,49 bari; t_b = 88,12 min; η_H = 55,06 %.

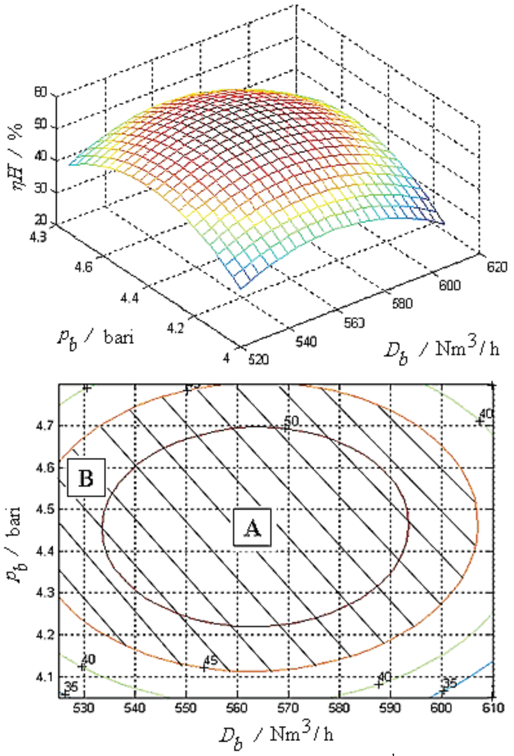

Figure 2 $\eta_H = f(D_b, p_b)$ – correlation 2[nd] degree

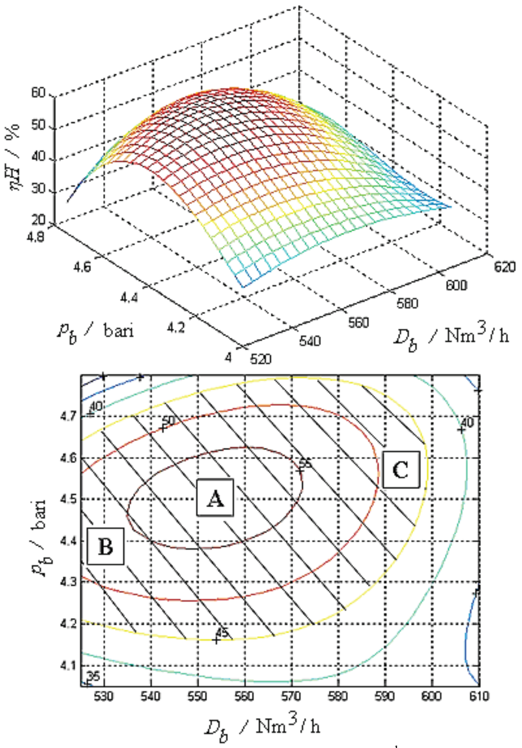

Figure 3 $\eta_H = f(D_b, p_b)$ – correlation 3[rd] degree

$$\eta_H = -85{,}78 \cdot p_b^3 - 0{,}32 \cdot p_b^2 \cdot t_b - 0{,}021 \cdot p_b \cdot t_b^2 - 0{,}0003 \cdot t_b^3 + 1097{,}54 \cdot p_b^2 + 6.52 \cdot p_b \cdot t_b + 0{,}16 \cdot t_b^2 - 4800{,}35 \cdot p_b - 27{,}30 \cdot t_b + 7331{,}34 \ \% \quad (6)$$

Correlation coefficient: R = 0,97; deviation from the regression surface: S = 2,24; point of maximum: p_b = 4,58 bari; t_b = 91,88 min; η_H = 55,15 %.

$$\eta_{|H} = 899{,}49 \cdot p_b^4 + 2{,}74 \cdot p_b^3 \cdot t_b + 0{,}03 \cdot p_b^2 \cdot t_b^2 + 0{,}0003 \cdot p_b \cdot t_b^3 + 9{,}04 \cdot e^{-0{,}06} \cdot t_b^4 - 16228{,}03 \cdot p_b^3 - 40{,}15 \cdot p_b^2 \cdot t_b^2 - 0{,}43 \cdot p_b \cdot t_b^2 - 0{,}005 \cdot t_b^3 + 109608{,}44 \cdot p_b^2 + 204{,}93 \cdot p_b \cdot t_b + 1{,}69 \cdot t_b^2 - 328823{,}45 \cdot p_b - 387{,}16 \cdot t_b + 370691{,}99 \ \% \quad (7)$$

Correlation coefficient: R = 0,99; deviation from the regression surface: S = 0,66; point of maximum: p_b = 4,55 bar; t_b = 89,92 min; η_H = 55,63 %.

The regression surfaces (1[st] and 2[nd] degree) respectively the level curves for the variation of the hydrogen argon flow rate and temperature inside the LF installation are shown in Fig. 8 ÷ 9.

Correlation equations, correlation coefficients and deviation from regression surface $\eta_H = f(t_b, D_b)$ are:

$$\eta_H = 0{,}09 \cdot t_b - 0{,}053 \cdot D_b + 68{,}11 \ \% \quad (8)$$

Correlation coefficient: R = 0,25; deviation from the regression surface: S = 8,12.

$$\eta_H = -0{,}004 \cdot t_b^2 - 0{,}002 \cdot t_b \cdot D_b - 0{,}008 \cdot D_b^2 + 2{,}32 \cdot t_b + 9{,}41 \cdot D_b - 2688{,}05 \ \% \quad (9)$$

Correlation coefficient: R = 0,92; deviation from the regression surface: S = 3,25; point of maximum: t_b = 86,12 min; D_b = 560,42 Nm^3/h; η_H = 56,17 %.

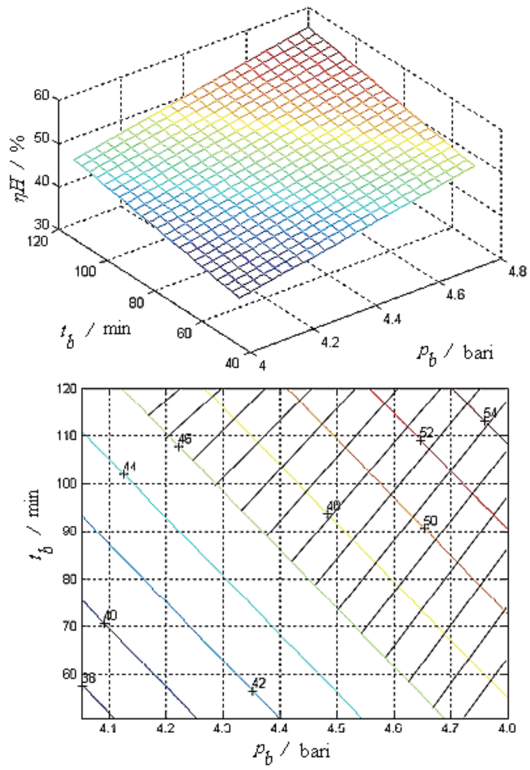

Figure 4 $\eta_H = f(p_b, t_b)$ – correlation 1[st] degree

In order to determine the most significant industrial variation domains of the independent parameters, the

MATLAB program also gave multiple (triple) correlations. In the case of establishing some correlations between a dependent parameter and three independent parameters, the resulting correlations were represented as 2nd degree polynomial functions.

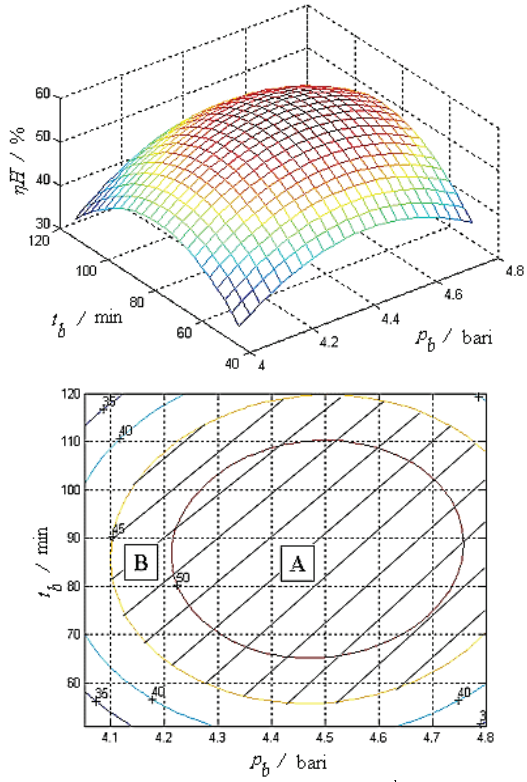

Figure 5 $\eta_H = f(p_b, t_b)$ – correlation 2nd degree

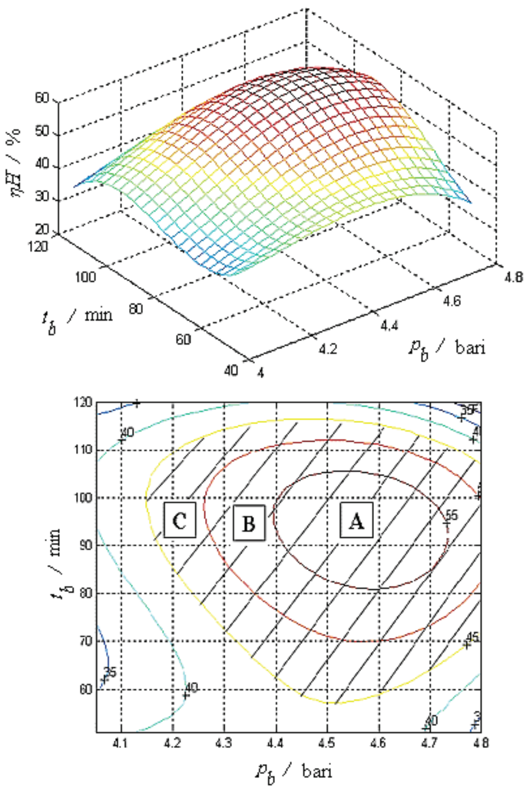

Figure 6 $\eta_H = f(p_b, t_b)$ – correlation 3rd degree

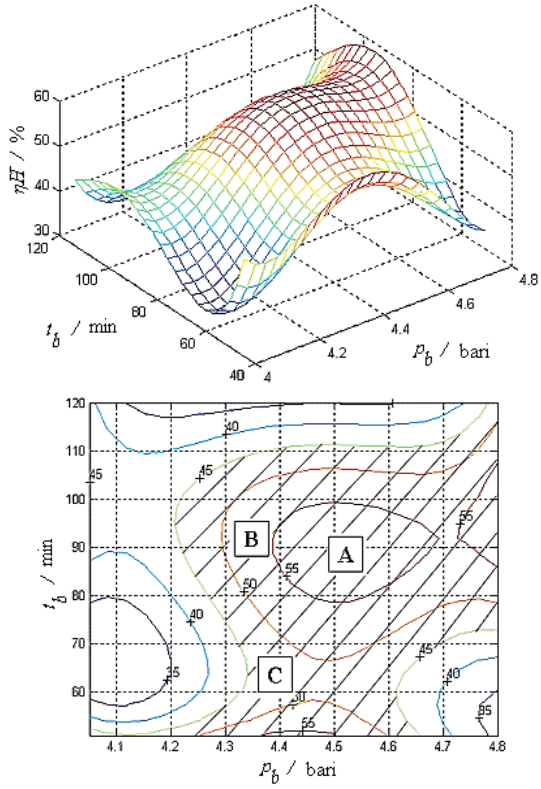

Figure 7 $\eta_H = f(p_b, t_b)$ – correlation 4th degree

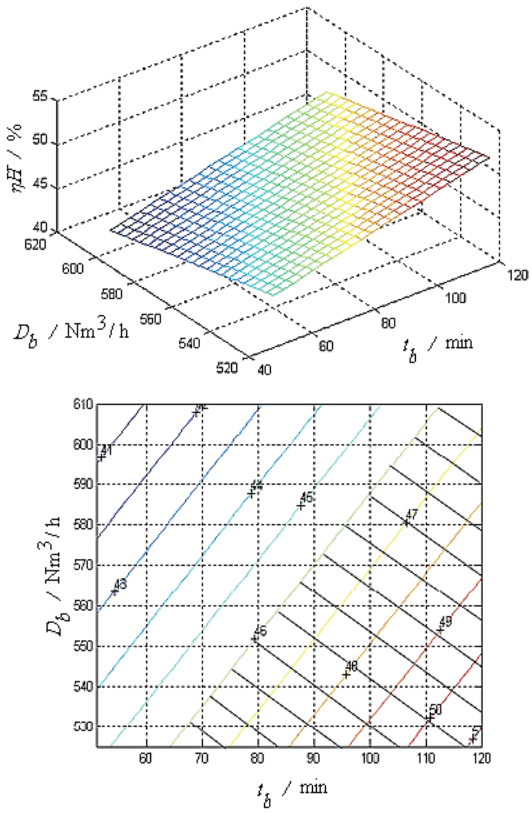

Figure 8 $\eta_H = f(t_b, D_b)$ – correlation 1st degree

Hypersurfaces regression equation obtained is:

$$\begin{aligned}\eta_{\mathrm{H}} &= -0{,}003\cdot D_{\mathrm{b}}^2 - 60{,}25\cdot p_{\mathrm{b}}^2 - 0{,}005\cdot t_{\mathrm{b}}^2 - \\ &- 0{,}08\cdot D_{\mathrm{b}}\cdot p_{\mathrm{b}} + 0{,}10\cdot p_{\mathrm{b}}\cdot t_{\mathrm{b}} - 0{,}002\cdot t_{\mathrm{b}}\cdot D_{\mathrm{b}} + \\ &+ 3{,}99\cdot D_{\mathrm{b}} + 581{,}39\cdot p_{\mathrm{b}} + 1{,}83\cdot t_{\mathrm{b}} - 2442{,}05\ \%\end{aligned} \tag{10}$$

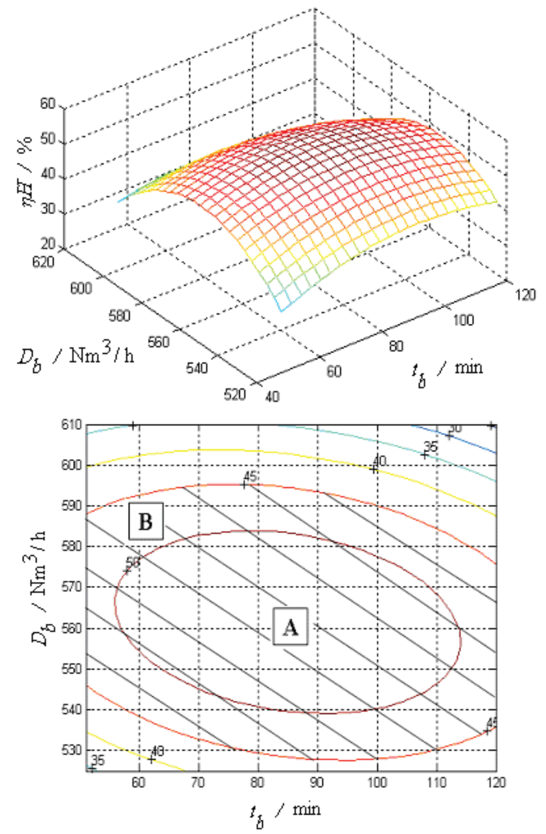

Figure 9 $\eta_H = f(t_b, D_b)$ – correlation 2nd degree

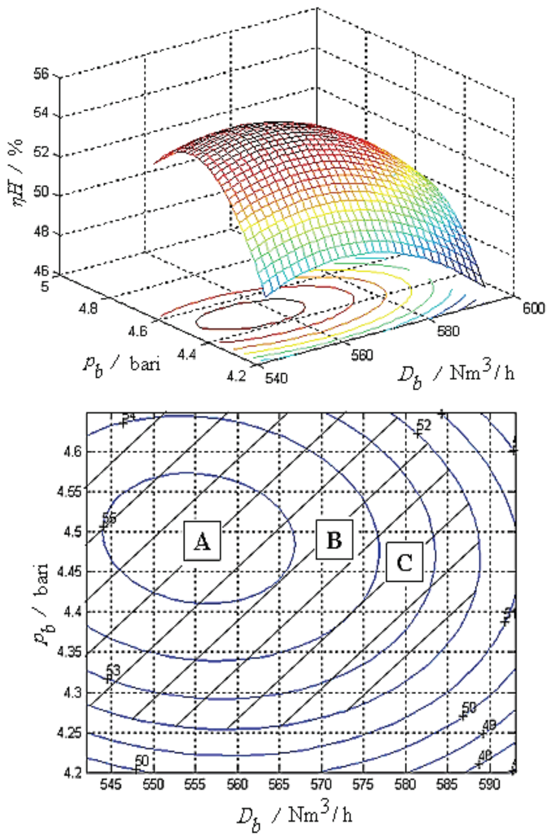

Figure 10 $\eta_H = f(D_b, p_b, t_b = t_{b\,med})$ – correlation 2nd degree

Correlation coefficient: R = 0,97; deviation from the regression surface: S = 2,03.

Maximum point coordinates are: D_b = 552,61 Nm^3/h; p_b = 4,5 bar; t_b = 91,84 min; η_H = 55,62 %.

Behaviour in the vicinity of hypersurfaces middle: $D_{b,\ med}$ = 569,15 Nm^3/h; $p_{b,\ med}$ = 4,37 bar; $t_{b,\ med}$ = 84,95 min; $\eta_{H,\ med}$ = 45,58 %.

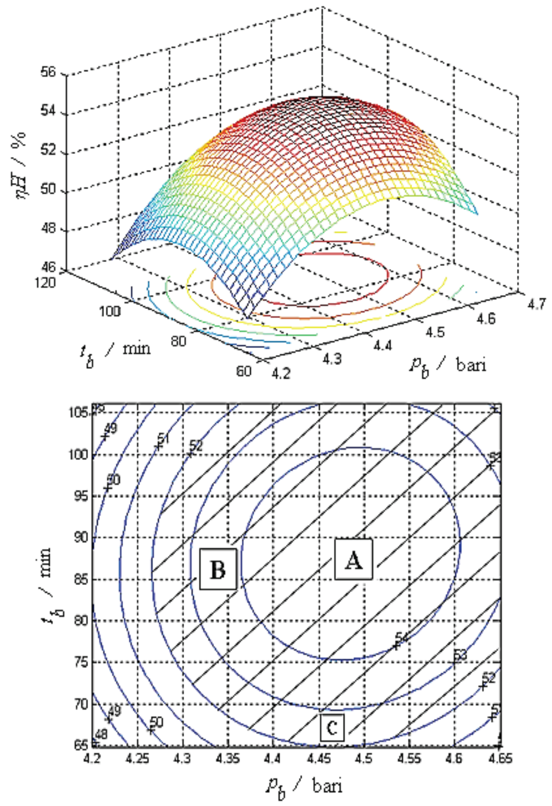

Figure 11 $\eta_H = f(p_b, t_b, D_b = D_{b\,med})$ – correlation 2nd degree

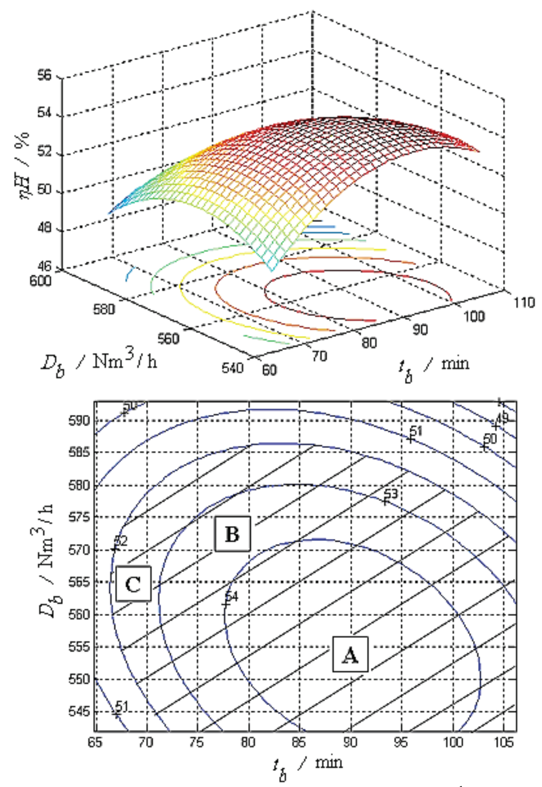

Figure 12 $\eta_H = f(t_b, D_b, p_b = p_{b\,med})$ – correlation 2nd degree

As this hypersurface cannot be represented in the 4 - dimensional space, each independent variable has been successively replaced by its mean value, which allowed their representation in the 3 - dimensional space, which allowed the interpretation of its graphical form.

Average values used are: D_b = 569,15 Nm^3/h, p_b = 4,37 bar, t_b = 84,95 min, η_H = 45,58 %.

The regression surfaces (2^{nd} degree) respectively the level curves for the variation of the hydrogen removal rate, argon pressure and temperature inside the LF installation are shown in Fig. 10 ÷ 12.

Correlation equations are:

$$\eta_H(t_{b\,med}) = -0{,}003 \cdot D_b^2 - 60{,}25 \cdot p_b^2 - 0{,}08 \cdot D_b \cdot p_b + 3{,}79 \cdot D_b + 589{,}98 \cdot p_b - 2324{,}63\ \% \quad (11)$$

Stationary points: D_b = 555,39 Nm^3/h; p_b = 4,49 bar; η_H = 55,39 %; point of maximum.

$$\eta_H(D_{b\,med}) = -60{,}25 \cdot p_b^2 - 0{,}005 \cdot t_b^2 + 0{,}10 \cdot p_b \cdot t_b + 531{,}57 \cdot p_b + 0{,}48 \cdot t_b - 1158{,}68\ \% \quad (12)$$

Stationary points: p_b = 4,48 bar; t_b = 88,04 min; η_H = 54,87 %; point of maximum.

$$\eta_H(p_{b\,med}) = -0{,}005 \cdot t_b^2 - 0{,}003 \cdot D_b^2 - 0{,}002 \cdot t_b \cdot D_b + 2{,}27 \cdot t_b + 3{,}61 \cdot D_b - 1051{,}55\ \% \quad (13)$$

The graphical and analytical analyses of the double correlation equation have lead to the following results:

- The correlations expressed by a 1^{st} degree polynomial and shown in Figs. 1, 4 and 8, allow the choice of steel treatment parameters inside the LF installation so that hydrogen removal rate is superior to the mean values resulting from the charges under analysis. In order to reach this target, the values of the processing parameters should be chosen so that η_H is always within the hatched domain;

- Correlation $\eta_H = f(p_b, D_b)$ shown in Fig. 2, which establishes by a 2^{nd} degree function the dependency between the hydrogen removal rate, the bubbling duration and the pressure of argon during bubbling, has its maximum value, of 55,39 %, located on the graphical representation within the hatched area - zone A.

- The graphical representation of correlation $\eta_H = f(p_b, D_b)$ by a 3^{rd} degree polynomial function is shown in fig.3. The correlation surface has a maximum point with value 55,62 %, located within the hatched domain A. As compared to the graphical representation of Fig. 2 one can notice the narrower domain in the vicinity of the maximum point. Whereas in the graphical representation shown in Fig. 2 the maximum point is located inside the level curve with the η_H value of 50 %, in Fig. 3 it is located inside the level curve with the η_H value of 55 %;

- For correlations $\eta_H = f(p_b, t_b)$ the conclusions are similar to those of the preceding correlation. For the correlation analyzed and defined by a 4^{th} degree function, one can notice that the surface shows a well defined sub-domain with the maximum point located within the level curve, with a value of 55,63 % and the other two partial sub-domains inside the level curve, with the value 55 %, but with a maximum point outside the variation interval of bubbling parameters (argon pressure and bubbling duration). Also, Fig. 7 shows that the surface also has three sub-domains where (probably minimum) points could be located, whose values for the hydrogen removal rate are below the mean ones; these sub-domains have to be avoided.

- Correlation $\eta_H = f(t_b, D_b)$ is expressed by two polynomial functions, one of the 1^{st} degree and the other of the 2^{nd} degree. In the case of the graphical representation shown in Fig. 9, the maximum point whose value is 56,17 can be found inside the level curve of value 55 (so in sub-domain A);

- The correlation shown in Fig. 10 has value 55,39 % for the η_H maximum point, located in the hatched area (A). Bubbling duration and argon pressure have to vary in such a way that the hydrogen removal rate should be within the sub-domain $\eta_H \geq 51$ % (domain A+B);

- In the case of the correlation shown in Fig. 11, the maximum point is located in sub-domain A; it is desirable that the independent parameters be located within this sub-domain, or at least in sub-domain B;

- For the correlation shown in Fig. 12, the maximum point is located in sub-domain A; it is desirable that the independent parameters be located within this sub-domain or in A+B.

3 Conclusions

The analysis of the data processed graphically and analytically leads to the following conclusions:

- The variation of the independent parameters within technological limits also determines for the dependent parameter a variation within technological limits, it being located on a regression surface or in its vicinity, considering the dispersion, the deviation and the standard error.
- The intersection of the correlation surfaces with level plans (parallel to the horizontal plan), resulted in obtaining level curves (level lines for 1^{st} degree polynomial functions), which allowed the establishing of variation limits for the independent parameters in the vicinity of the stationary point in case there is a saddle point. For each graphic representation the (hatched) sub-domains show the areas where the values of the dependent parameter should be, which, in fact, determines the variation limits for the independent parameters;
- Considering the value of the triple correlation coefficient R = 0,97 and the deviation S = 2,3, it is considered that this correlation expresses very accurately the correlation between the three parameters of steel treatment in the LF installation and the hydrogen removal rate.

In order to obtain over 50 % hydrogen removal from the steel, the optimal variation domains of the parameters under analysis are:

- the argon flow rate D_b = 540 ÷ 582 Nm^3/h
- the duration of argon bubbling t_b = 65 ÷ 110 min
- the pressure of argon when bubbled p_b = 4,2 ÷ 4,7 bar.

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