Influence of steel vacuuming on the reduction of hydrogen content

M Radu, S Serban, E Popa and T Heput
Politehnica University of Timisoara, Engineering and Management Department, 5 Revolution Street, Hunedoara, 331128, Romania

E-mail: mihairadu_66@yahoo.com

Abstract. Under the current technological development, steel consumers are increasingly demanding high quality steels, one of the conditions imposed is the content of gases (hydrogen and nitrogen). At the world level in the technological process of steel production, there are provided facilities for the processing of liquid steel in ladle, at least of type LF-ladle furnace and VD- vacuum degassing. In the researches and experiments carried out the possibilities of the advanced reduction of the hydrogen content, respectively the increase of the elimination level, were considered. As a factor of influence on the aforementioned parameters were chosen: the total duration of the vacuum, the duration of deep vacuum, the vacuum pressure, the inlet-outlet temperatures in the vacuum degassing installation and the distributor. The data obtained were processed in the EXCEL and MATLAB, and on the basis of the technological analysis of the obtained results the optimal limits of variation of the technological parameters were set in order to achieve the aim pursued.

1. Introduction
At the contact of liquid steel with the atmosphere of the elaboration aggregate takes place, on the one hand, a process of gas diffusion into the metal bath, by means of the slag, and on the other hand, its passage from the bath into the atmosphere of the aggregate. The direction of these processes is determined by several factors, namely: the quality of the raw and auxiliary materials (the degree of humidity, the oils, the plastic materials etc), the characteristics of the slags in use, the intensity and duration of the smelting, the temperature of the metal bath, the gas content in the metal bath and in the atmosphere of the aggregate, the duration of tapping, the duration of stay in the ladle, the values of the processing parameters in the ladle (LF, VD) etc. [1]

Irrespective of the steel elaboration, casting or rolling process, its structure traps, even if in small quantities, impurities consisting, besides non-metallic inclusions, in gases, the most representative ones being hydrogen, nitrogen and oxygen.

As to hydrogen, which represents an impurity in steel making processes, its negative influence is manifested by: the generation of bubbling in killed steels, the reduction of steel plasticity and tenacity, making for the flaw called “flakes” in chrome and nickel alloyed steels, which diminishes resistance to fatigue of steel parts and has an impact upon the electric and magnetic properties of steels. In order to produce steels with a minimum content of hydrogen, steps have to be taken during the flow process, such as [2], [3]: the use of a high quality charge, with no humidity, oil and plastic materials, calcined additives, fresh quick lime; steel vacuum processing, the proper heating up of the casting installation (the ladle, the tundish), the use of high quality casting powders, made of calcined components (tundish and crystallizer).
A most important aspect in steel degassing is the process of molten metal bubbling, generated by the release of (CO) bubbles. At the moment these (CO) bubbles appear, partial hydrogen pressure is practically null and this is why it diffuses inside these bubbles, under the force of the concentration gradients, being later removed from the bath. In order that the rate of hydrogen (gases) removal from the steel bath be higher than the rate of their passage through the slag into the metal bath and therefore its content diminish, the decarburization rate must be high enough to surpass a certain critical value, meant to trigger pressures in the (CO) bubble, superior to the Ferro static ones [4], [5].

As to the electric steel plants endowed with EBT-type furnaces (Eccentric Bottom Tapping), they offer very good conditions for the reduction and absorption of gases, that is hydrogen, in the steel bath, a high rate of smelting by intense oxygen blowing, slag foaming and the possibility of argon bubbling in the furnace [1], [6], [7].

The introduction in the steel making flow process of the so-called “Ladle metallurgy” (also known as “Secondary steelmaking) has triggered a real technical revolution, part of the processes that used to take place into the elaboration installations being transferred into the casting ladle, particularly in the L.F.-type (Ladle-Furnace) installations, in the vacuum with no thermal gain installations (R.H.-Ruhrstal Haerus, V.D.-vacuum degassing) and with thermal gain (V.A.D.- Vacuum Arc Degassing, V.O.D. Vacuum Oxygen Decarburization etc.) in the case of alloyed and particularly high alloyed steels [8].

As a result of these changes in the flow process, besides a significant quality improvement, there is an important increase of productivity, respectively the reduction of the specific consumption of electric energy.

2. Industrial experiments. Data processing

The research whose results are given in this paper aimed at reducing the hydrogen content of the steels meant for the manufacturing of pipes used in mineral oil transport.

The investigations focused on steel grade G52S (N), elaborated in an electric steel plant, by means of an EBT-type electric furnace, LF installation, VD installation and a 5-strand continuous casting machine. 51 charges were surveilled along the flow process, step by step, as follows:

- Furnace elaboration: high quality charge, no scrap with oils or humidity, rust under about 2%, fresh quick lime, the casting ladle heated up accordingly;
- Treatment in the LF and VD installations: the variation limits of the technological parameters were observed (heating up, bubbling), no humidity additives (for the formations of slag and alloying), chemical and thermal homogenizing by argon bubbling, followed by the treatment in the vacuum installation, with no thermal gain VD, on casting, the ladle was heated up accordingly and so was the tundish;
- Observance of the continuous casting parameters: casting rate correlated with the casting temperature, the cooling water flow rate and pressure along each cooling zone.

From the technological analysis were selected 45 charges, the parameters under analysis, the variation limits as well as their average values being given in Table 1.

Processing the data in EXCEL and MATLAB, resulted in simple and multiple correlation equations between the dependant and independent parameters, which were given in both analytical and graphical form.
Table 1. Parameters

| No. | Parameters                                      | Units of measurement | Value       |
|-----|-------------------------------------------------|----------------------|-------------|
|     |                                                 | min. | max. | average |
| 1.  | Hydrogen content final, $|H|_f$              | ppm  | 1,7  | 2,1  | 1,82 |
| 2.  | The yield hydrogen removed, $R_H$               | %    | 57,78| 68,52| 64,84|
|     | Independent parameters                          |         |     |       |      |
|     | The duration of the vacuum, $D_{t.v.}$          | min.  | 17   | 30   | 22,89|
|     | The duration of the vacuum under advanced vacuum, $D_{v.a.}$ | min. | 10   | 17   | 13,76|
| 3.  | Advanced vacuum pressure, $P_{v.a.}$            | m Bar | 0,8  | 1,9  | 1,06 |

By processing the data in EXCEL, the resulting correlations were given both in analytical and graphical form, by means of logarithmic and exponential ($2^{nd}$ and $3^{rd}$ degree) polynomial functions. For each correlation, the value of the correlation coefficient is also shown. Figure 1 and Figure 2 show that increasing the vacuum duration (total and advanced vacuum) leads to a reduction of the final hydrogen content (at the end of the vacuum process). These correlations can be technologically explained by the sufficient time given for the hydrogen to be removed from the (molten steel) solution, its diffusion into the argon bubbles and their removal from the metal bath into the vacuum space. The decrease of hydrogen content is more intense in the first 25 minutes and under advanced vacuum up to 15 min.

Figure 3 shows that lower pressure in the vacuum space leads to a lower concentration of hydrogen from the molten steel, as a result of a higher rate of argon bubbles (into which hydrogen diffused) being removed. Argon bubbles can also be removed when the pressure in the vacuum installation is lower, as they have to overcome lower total pressures (steel, capillary and vacuum space pressure). Hydrogen content reduction is more intense at pressures under 1mBar.

The yield of hydrogen removal from the metal bath increases with the total vacuum duration, respectively with the deep vacuum (Figure 4 and Figure 5). When it comes to the total duration, the influence is more significant up to 25min, while for the advanced vacuum, up to 15 min. The duration of these operations depends firstly on the steel temperature when it enters the vacuum installation (VD), considering that this is not done by thermal gain.

The graphical representation given in Figure 6 shows that if pressure in the vacuum installation is reduced, the hydrogen removal yield increases, the correlations being significant both mathematically and technologically (lower pressure triggers a larger quantity removed). A significant increase of the yield is manifest at pressures under 1mBar.

![Figure 1](image1.png)  ![Figure 2](image2.png)
2.1. Correlations obtained in MATLAB

The data obtained during the experiments were processed by means of three types of polynomial equations for the double correlations and one for the triple correlations.

\[ y = a_1 + a_2 x_1 + a_3 x_1^2 + a_4 x_1^3 + a_5 x_2 + a_6 x_2^2 + a_7 x_2^3 + a_8 x_2^4 + a_9 x_2^5 \]  \hspace{1cm} (1)

\[ y = a_1 + a_2 \log x_1 + a_3 \log x_1^2 + a_4 \log x_1^3 + \frac{a_5}{x_2} + \frac{a_6}{x_2^2} + \frac{a_7}{x_2^3} + \frac{a_8}{x_2^4} + \frac{a_9}{x_2^5} \]  \hspace{1cm} (2)

\[ y = a_1 x_1^2 + a_2 x_2^2 + a_3 x_1 x_2 + a_4 x_1 + a_5 x_2 + a_6 \]  \hspace{1cm} (3)

The results were given both analytically and graphically (the correlation surface and the plan-projected level curves).
Figure 7. \( H_f = f(D_{t.v.}, D_{v.a.}) \), EC1

\[
\begin{align*}
R^2 &= 0.561399; a_1 = -9.806554; a_2 = -0.912767; a_3 = 0.037333; a_4 = -0.000512; \\
a_5 &= 5.244260; a_6 = -0.456043; a_7 = 0.007273; a_8 = 0.000768; a_9 = -2.688622.
\end{align*}
\]

Figure 8. \( H_f = f(D_{t.v.}, P_{v.a.}) \), EC1

\[
\begin{align*}
R^2 &= 0.646031; a_1 = 115.116788; a_2 = -0.840732; a_3 = 0.035726; a_4 = -0.000505; \\
a_5 &= -465.102396; a_6 = 793.509140; a_7 = -662.114066; a_8 = 270.007113; a_9 = -43.001559.
\end{align*}
\]

Figure 9. \( R_H = f(D_{t.v.}, D_{v.a.}) \), EC1

\[
\begin{align*}
R^2 &= 0.543460; a_1 = -1705.214048; a_2 = 13.794885; a_3 = -0.544740; a_4 = 0.007210; \\
a_5 &= 682.386316; a_6 = -112.015261; a_7 = 9.125437; a_8 = -0.368294; a_9 = 0.005883.
\end{align*}
\]
\[ R^2 = 0.561325; a_1 = -1880.850806; a_2 = 20.031922; a_3 = -0.847037; a_4 = 0.011883; \\
\quad a_5 = 7742.791479; a_6 = -13117.596460; a_7 = 10870.091880; a_8 = -4403.981984; a_9 = 697.285802. \\
\]

**Figure 10.** \( R_{D_2} = f(D_{v,a}, P_{v,a}), \) EC1

\[ R^2 = 0.554746; a_1 = 21.589078; a_2 = -140.902524; a_3 = 44.473090; a_4 = 4.685751; a_5 = 8156.568184; \\
\quad a_6 = -202991.513023; a_7 = 2491309.658675; a_8 = -15089768.666007; a_9 = 36118097.229185. \\
\]

**Figure 11.** \( |H| = f(D_{v,a}, D_{v,a}), \) EC2

\[ R^2 = 0.547101; a_1 = -2943.222250; a_2 = 3890.568937; a_3 = -1233.661426; a_4 = 130.354016; \\
\quad a_5 = -6691.885363; a_6 = 16157.747581; a_7 = -19055.509913; a_8 = 10993.983287; a_9 = -2485.330618. \\
\]

**Figure 12.** \( H_{\mathbf{i}} = f(D_{v,i}, P_{v,i}), \) EC2
The analysis of the results leads to the following findings:

- The correlation surfaces, the plan projection of the level curves lead to quite similar results, confirms the validity of the results;
- In the case of the triple correlations, by turning them into double correlations, the resulting graphical representations are quite similar for the same parameters as in the double correlations;
- The analysis of the graphical representation from Figure 7.b. shows that for a total steel processing duration of 18 – 24 min and under advanced vacuum of 12-15 min, once these durations increase, the content of hydrogen is significantly diminished at the end of the vacuum process;
- In order to obtain the desired values for the dependent parameter, the graphical representations help in establishing the values of the independent parameters for each correlation (Figure 8- Figure 14).
3. Conclusions
Considering the target of cutting down hydrogen content and increasing the yield, the analysis of the experiments and of the results obtained after data processing leads to the following conclusions:
- The total duration of treatment must be within the limits 20-25min;
- The duration of treatment under advanced vacuum must be within the limits 15-18min;
- Pressure in the advanced vacuum installation must be under 1mBar;
- Steel temperature on entering the vacuum installation should range between 1620 and 1650°C.

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