Kinetics of gas removal from steel smelts with advanced characteristics

M. NICOLAE, C. PREDESCU*, I. VILCIU, M. SOHACIU, A. NICOLAE
University "Politechnics" of Bucharest, Faculty "Science and Engineering of Materials", Romania

The high quality of steels depends to a great extent on gaseous inclusions, their amount and dispersion being influenced by two possible methods of degassing smelts: vacuumizing and bubbling with inert gas. Taking into account this topic, the paper emphasizes experiments concerning: The explanation of scientific dilemmas on kinetics of hydrogen removal; Establishing optimal values for the hydrogen and nitrogen removal rate; Role of bubbling smelts with argon.

1. Introduction

The making of steels having advanced properties requires the using of modern steelmaking technologies, a very important one being degassing, namely the removal of gas as hydrogen, nitrogen, oxygen [1, 2]. At present, the steel industry is confronted on this field with two problems, namely that of:
- Finding a new method to exhaust gas from metallic smelts [4 - 6];
- Retechnologization by upgrading the existent installations in metallurgical plants [3].

Taking into account Romania, the last mentioned aim is of great importance, thus, one has to undertake researches which shall generate efficient measures of improving the performances of the current equipment, especially of vacuum degassers of VAD-VOD type.

2. Researches concerning the kinetics of hydrogen removal from smelts

2.1. Aim and conditions for researches performing

The first part of experiments referred to the study of processes of hydrogen degassing.

The programmed researches had in view simultaneously two targets:

A. First, there was necessary to obtain data concerning the degassing rate as important parameter for the characterization of installations productivity.

B. Second, one proposed to explain the scientific dilemma from literature. Thus, one considers that the removal of hydrogen is the complex consequence of two sub-processes, namely:

• The diffusion of hydrogen atoms from the smelt to the separation surfaces (s.s) determined by the gas bubbles from bubbling or by the surface of the hot metal during the contact with the medium of the aggregate; when bubbling is used, then one obtains both types of surfaces; in the case of vacuum degassing, only the second surface is provided;

• The molecularization phenomenon at the separation surface of hydrogen atoms:

$$[H]_{s,s} + [H]_{s,s} = [H_2]_{s,s} \qquad (1)$$

Due to the interest for performances concerning the efficiency of the equipment, the present paper includes researches for the determination of the degassing rate calculated in the case of hydrogen by using v_H [ppm/min]:

$$v_H = \frac{[H]_i - [H]_f}{\tau_d} \qquad (2)$$

The above relation $[H]_i$ is the primary hydrogen percentage (before the start of the vacuumizing process), $[H]_f$ – the hydrogen percentage after vacuumizing and τ_d – the vacuum degassing time in minutes.

In order to reduce the number of parameters exerting a real influence to only three ones ($[H]_i$, $[H]_f$ and τ_d), one selected batches, which are characterized by following relatively constant indicators, as:
- C ....…...0.47 – 0.52%
- S..............................………0.018 – 0.022%
- P.............................……......0.011 – 0.014%
- Ladle capacity ………………………50 t
- Temperature at the beginning of the treatment ……………………….…......1655 – 1670 °C
- Temperature at the end of the treatment………………………….....1570 – 1590 °C
- Pre-advanced vacuum………..42 – 46 Torr
- Advanced vacuum……………….1-2 Torr.

2.2 Experimental data processing

Experimental data are shown in table 1 $[H]_i$ is the concentration of the analyzed hydrogen.

Correlations such as $v_H = f[H_i]$ and $v_H = f([H_i]^2)$ were of interest. The graphic processing of experimental data from Table 1 is emphasized in Fig. 1 and Fig. 2.

Table 1. Data referring to researches aiming the hydrogen removal.

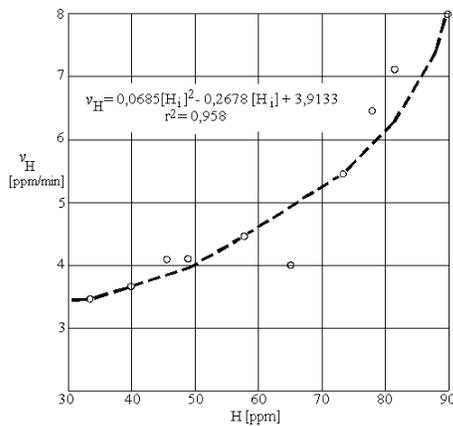| Crt. no.	H_i [ppm]	H_f [ppm]	τ_d [min]	v_H [ppm/min]	$[H_i]^2$
1	34.18	1.28	9.20	3.58	1170
2	40.08	1.11	10.80	3.62	1600
3	46.02	1.82	10.80	4.08	2120
4	48.12	0.98	11.50	4.10	2315
5	57.50	2.21	13.00	4.23	3300
6	64.20	1.21	15.80	4.00	4120
7	73.70	2.82	12.60	5.62	5430
8	78.80	1.24	11.90	6.52	6210
9	80.42	3.16	11.00	7.02	6470
10	90.00	1.96	11.00	8.00	8100

Fig. 1. Degassing rate variation function primary hydrogen concentration.
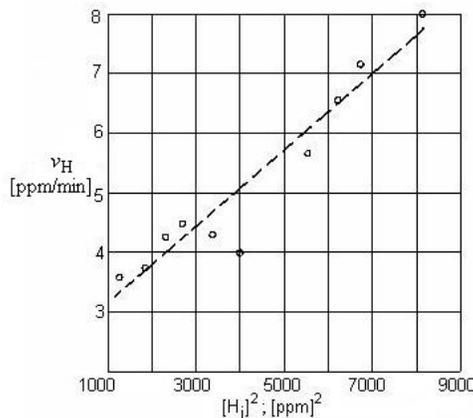

Fig. 2. Degassing rate variation function square value of hydrogen concentration.

2.3 Conclusions

As concern function number one, which has also a practical importance because it characterizes the efficiency

of the equipment, one determined by the processing of information the mathematical model such as:

$$v_H = 0.0685\,[H_i]^2 - 0.2678\,[H_i] + 3.9133 \qquad (3)$$

Because the rate v_H variates exponentially function of the hydrogene concentration, but linearly to the square of the concentration value, one can be led to an important conclusion: *in the analyzed case, the limiting phase for hydrogen removal is not its diffusion, but the formation of hydrogen molecules on the separation surfaces.*

3. Nitrogen removal from smelts by bubbling with argon

Bubbling was used for nitrogen removal.

3.1. Aim of researches

If one has to design or to redesign an equipment aiming its upgrading, he must take into account a very important technological parameter, namely the *flow rate* D_{Ar} *[Nl/min] of argon blown for smelts bubbling*. In such a context one can consider also the *argon blowing time τ_{Ar} [min]* as a pre-vacuumizing phase.

In order to know and to characterize both parameters one programmed and performed investigations aiming the identification of denitrizing processes based on mathematical models like:

$$v_H = f(D_{Ar});$$

$$v_H = f(\zeta_{Ar});$$

$$v_H = f(D_{Ar},\, \tau_{Ar});$$

$$v_H = \frac{[N]_i - [N]_f}{\tau_{Ar}}. \qquad (4)$$

$[N_i]$ from the relation above, represents the nitrogen content of steel after tapping, $[N_f]$ the nitrogen content after bubbling and v_N the removal rate of nitrogen.

Batches belonging to the other category with constant parameters, were analyzed, namely:

- C………………………………..0.12-0,18%
- S…………………………...0.009-0,014%
- P……………………………….0.01-0.018%
- Ladle capacity………………………..50 t
- Temperature at the beginning of treatment ………….1660-1675 °C
- Temperature at the end of treatment…………………………...1563-1572 °C
- Pre-advanced vacuum ………...40-45 Torr
- Advanced vacuum ……………….1-2 Torr

3.2. Experimental data processing

Tabellary processed data are emphasized in Table 2 and graphically processed ones in Fig. 3.

Table 2. Experiments concerning the kinetics of denitrizing.

Crt. no.	D_{Ar} [Nl/min]	N_i [ppm]	N_f [ppm]	v_N [ppm/min]	
$\tau_{Ar} = 5$ min					
1	40	624	520	20,8	
2	52	632	502	26,0	
3	58	629	485	28,8	$(v_N)_{\tau_{Ar=5\,min}} = f(D_{Ar})$
4	64	598	443	31,0	
5	72	617	441	35,2	
6	78	642	428	42,8	
$\tau_{Ar} = 6$ min					
1	40	570	439	22,0	
2	51	580	421	26,5	$(v_N)_{\tau_{Ar=6\,min}} = f(D_{Ar})$
3	56	618	418	33,3	
4	64	634	396	40,0	
$\tau_{Ar} = 7$ min					
1	38	574	401	24,7	
2	52	567	383	26,3	
3	58	593	380	30,4	$(v_N)_{\tau_{Ar=7\,min}} = f(D_{Ar})$
4	74	614	379	37,8	
5	76	592	348	34,8	
$\tau_{Ar} = 8$ min					
1	38	528	352	22,0	
2	51	539	341	24,7	
3	58	537	332	25,6	$(v_N)_{\tau_{Ar=8\,min}} = f(D_{Ar})$
4	75	540	322	27,2	
5	79	535	306	28,6	

Applying the mathematical statistics processing, one obtained following mathematical models, which can be used for the designing and upgrading of equipments:

$$(v_N)_{\tau_{Ar=5}} = 0.3143 D_{Ar}^2 + 1.7943 D_{Ar} + 19.72 \quad (5)$$

$$(v_N)_{\tau_{Ar=6}} = 0.5500 D_{Ar}^2 + 3.3300 D_{Ar} + 18.00 \quad (6)$$

Fig. 3. Modification of the denitrizing rate during primary bubbling function flow rate and duration of argon blowing.

$$(v_N)_{\tau_{Ar=7}} = 0.4214 D_{Ar}^2 + 5.6986 D_{Ar} + 18.34 \quad (7)$$

$$(v_N)_{\tau_{Ar=8}} = 0.1357 D_{Ar}^2 + 2.3843 D_{Ar} + 19.96 \quad (8)$$

3.3. Conclusions

After analyzing the results of researches mentioned above, we can draw following conclusions:

• When the blowing duration is not so long, there is an exponential dependency between V_N and the argon flow rate. The longer the blowing duration, the more evident will be the linearization trend of this dependency.

• Subsequent to the mentioned conclusion, one can state that the effect of the increasing argon flow rate is diminished if the blowing duration increases.

• Both observations from above *induce the very important recommendation for the designing and upgrading practice: if the aim is the obtaining of high nitrogen removal rates, there is a better way consisting in the increase of the blowing time as compared with the increase of the argon flow rate.*

• Based on the former statements, for the research practice following product will be of interest:
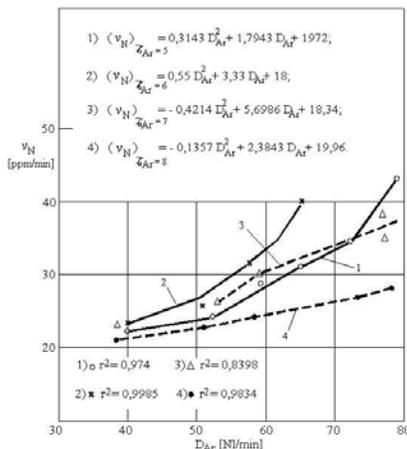
$$D_{Ar} \times \tau_{Ar} = [Nl/min] \times [min] = [Nl],$$

i.e., one should take into account the amount of blown argon. It must be mentioned, that in some specialty papers there are diagrams which emphasize the influence of the total blown argon volume [Nm^3] on the nitrogen content decrease.

 • But one has to consider that such a parameter can characterize this process only globally, in the case of further researches being recommended to use *the specific argon blowing flow rate,* $D_{s\ Ar}$, as a bulk related to the amount of treated steel and thus, measured in [Nm^3 argon/ t steel]. One could expect better results but using *the specific argon blowing flow rate,* $D_{s\ Ar}$, defined on the basis of the unit of measurement [Nm^3 argon/ t steel x min].

References

[1] I. Dragomir – "Teoria proceselor siderurgice", Editura Didactica si Pedagogica, Bucuresti, 1985.
[2] M. Nicolae, I. Dragomir, C. Dobrescu – "Teoria proceselor de la elaborarea fontei si feroaliajelor", Editura Politehnica Press, Bucuresti, 2006.
[3] F. Zaman – Met. and New Mat. Rev., **6**, 2, 12 (1998).
[4] R. J. Fruehan – "Ladle Metallurgy Principles and Process", ISS Warrendall, Pitsburg, 1985.
[5] M. S. Mielman – Ironmak and Steelmak, **47**(3), 48 (1999).
[6] R. Teworte – MPT Int, **20**, 3, 42 (2004).

_____
[*]Corresponding author: predescu@ecomet.pub.ro