Researches on the influence of slag addition and secondary treatment duration on steel quality

E Ardelean, M Ardelean, A Socalici, V Puțan and A Puțan

Politehnica University of Timisoara, Engineering and Management Department, 5 Revolution Street, Hunedoara, 331128, Romania

E-mail: erika.ardelean@fih.upt.ro

Abstract. Steel physical, mechanical and usage characteristics are influenced by its elaboration, secondary treatment, casting and further treatment. But if elaboration and secondary treatment do not benefit from the appropriate qualitative technological steps, it will not be possible to correct the resulting fails during the casting and processing stages. This paper introduces some laboratory researches related to the way steel quality can be influenced (in terms of sulphur and oxygen content) by the variation of the secondary treatment duration (inside the ladle) and that of the quantity of the reducing mixture in use (depending on the targeted metallurgical effect). The result consists in recommendable optimal variation intervals for the two parameters; these results can be easily implemented in industrial practice and therefore, with minimum costs, one can obtain maximal technological and economical effects.

1. Introduction
In order to obtain a high quality steel one should pay particular attention to the elaboration process, starting from the furnace load composition and going on through the economically appropriate means of melting, reducing to a minimum the alloy elements loss [1]. After melting and phosphorous oxide slag removal, the refining process makes for the increase of steel purity, by reducing the oxides resulted from the oxidizing of the accompanying element. Deoxidizing and desulphurization, operations that precede the refining stage, are meant to remove two of the elements that can damage steel quality: oxygen and sulphur [2].

Oxygen negatively affects quality by:
- causing hot steel brittleness, which makes it likely to overheat and leads to the appearance of cracks during hot plastic deformation, as a result of the oxide and oxide-sulphide deposits at the limits of the structural grains;
- the formation of blowholes during the solidification of the continuous cast ingots or semi-finished parts [2].

As a result, the content of oxygen dissolved in the steel may not exceed the limits of 40-80ppm (for calming steels).

Sulphur can cause red brittleness under 988°C (respectively 960°C) – when the products become brittle, or hot embrittlement, over 988°C (respectively 960°C), when sulphur rich products are melting and suppressing metallic continuity [3].

The contents of sulphur and oxygen can be cut down inside the elaboration aggregate, but not up to the prescribed standard limits. That is why modern technologies envisage advanced processing outside
the elaboration aggregate [4], by means of synthetic slag [5], inert gas bubbling [6], [7], electromagnetic stirring and/or vacuum treatment [8], [9].

The paper intends to go deeper into the influence of synthetic slag addition [10] and duration of secondary treatment upon the rate of oxygen and sulphur removal from the steel meant for pipe production.

2. Laboratory experiments

The experiments have been done on steel elaborated in a 10kg electric induction furnace, during 16 charges. The charges consisted in pipe steel waste, more exactly samples from the steel load determination related to pipe steel elaboration in EBT-type electric arc furnaces [1].

After melting determination, steel was deoxidized by precipitation with FeMn (25g), FeSi (30g), SiMn (50g) and carburizing graphite (10g) after which, the reducing mixture was added. This was introduced into a metal plate cartridge, attached to a wooden pole and immersed down to the bottom of the furnace [1].

It was considered that after the deoxidizing stage, the furnace worked in a ladle-furnace regime (similar to LF). Steel casting was done into 2kg ingots, the casting scheme being shown in Table 1.

Table 1. Experimental ingot casting, depending on the duration of the secondary treatment

| Charge | Duration of the secondary treatment with reducing mixture/min |
|--------|-------------------------------------------------------------|
|        | 4   | 6   | 8   | 10  | 11  | 12  | 13  | 14  | 15  | 16  | 17  |
| 1      | X   | X   | X   | X   |     |     |     |     |     |     |     |
| 2      | X   |     |     | X   |     |     | X   |     |     |     |     |
| 3      |     | X   | X   |     | X   |     |     |     |     |     |     |
| 4      |     |     |     |     | X   | X   |     |     |     |     |     |
| Total ingots | 1   | 1   | 4   | 1   | 1   | 2   | 1   | 2   | 1   | 1   | 1   |

At the end of the melting process, we sampled the steel in order to determine its chemical composition (the content of sulphur and oxygen is mandatory); another sampling was done before casting, which allowed the determination of the sulphur, respectively oxygen removal extent. On treatment completion, slag was also sampled in order to determine its chemical composition, particularly the content of CaO.

During tapping, respectively during ingot casting, ferrous alloys were added to the jet, as follows: FeMn (8g), SiMn (8g), FeSi (8g), aluminum (6g), SiCa (8g), respectively for one ingot: FeMn (2g), SiMn (2g), FeSi (2g), aluminum (1.5g), SiCa (2g).

This experimental method was chosen in order to allow the practical implementation of the results for pipe steel elaboration in EBT-type electric furnaces; the steel was treated in an LF-type installation and was continuously cast.

3. Results, discussions

The resulting experimental data have been processed in EXCEL, in order to obtain the influence of the duration of treatment with synthetic slag and the specific reducing mixture added, upon the desulphurization and deoxidizing rate, for various contents of CaO into the slag (with various chemical compositions). Further on, the results of data processing meant to give the simple correlations are given in analytical and graphical form (Figures 1-4).
Figure 1. The influence of treatment duration upon the desulphurization rate

Figure 2. The influence of treatment duration upon the deoxidizing rate

Figure 3. The influence of quantity of reducing mixture upon the desulphurization rate
Figure 4. The influence of quantity of reducing mixture upon the deoxidizing rate

A global analysis of the resulting correlations shown above leads to the following results:
- for the cases under analysis, the 2nd degree polynomial correlations were studied, as it was considered that they are the most significant, since they have a maximum point, their coordinates being given for each equation describing the curve;
- both the desulphurization ($\eta_S$) and deoxidizing ($\eta_O$) output are directly proportional to the synthetic slag treatment duration ($t$) and also to the specific addition of reducing mixture ($q$) meant to form the synthetic slag;
- in all cases, a maximum point was obtained for each correlation; its coordinates range within the technological variation limits of the parameters under analysis;
- as to the duration of the treatment, it was found that the best values of the desulphurization, respectively deoxidizing output are obtained if the duration of this technological operation is ranging between 13.75-15.25 min (interval in which the output maximal values are reached: (13.973; 56.959) for $\eta_S$ and (15.216; 55.406) for $\eta_O$);
- for the same duration of the treatment, the desulphurization and deoxidizing output values are also influenced by the content of CaO in the slag, as follows: the best values are obtained for 52%CaO, followed by 54%CaO and the lowest values, for 48%CaO;
- as to the specific addition of reducing mixture (g/kg of steel) it was found that the best values for the desulphurization and deoxidizing output are obtained if it ranges within the limits 2.0–2.5 (interval in which the maximal output value is reached);
- for the same reducing addition, the value of the desulphurization and deoxidizing output is also influenced by the content of CaO in the slag, as follows: the best values are obtained for 52%CaO, followed by 54%CaO and lower values for 48%CaO.

The conditions shown above can be observed technologically and $\eta_S$, respectively $\eta_O$ can be granted values within the interval 30-58%.

The data processed in Excel were also processed in Matlab in view of obtaining the double, 1st, 2nd, 3rd and 4th degree correlations, the results being shown in Figures 5-20. After having processed the results, they will be analysed technologically.
Figure 5. Correlation $\eta_S = f(t; \%\text{CaO})$ – 1st degree
The correlation equation: $\eta_S = 1.271 \times t + 0.641 \times (\%\text{CaO}) - 4.397$
The correlation coefficient: $R_1 = 0.592$; Deviation: $S_1 = 7.984$

Figure 6. Correlation $\eta_S = f(t; \%\text{CaO})$ – 2nd degree
The correlation equation: $\eta_S = -0.227 \times t^2 + 0.031 \times t \times (\%\text{CaO}) - 1.026 \times (\%\text{CaO})^2 + 4.468 \times t + 106.998 \times (\%\text{CaO}) - 2773.92$
The correlation coefficient: $R_2 = 0.983$; Deviation $S_2 = 1.814$
Maximum point deviation: $(\%\text{CaO}) = 52.351\%$; $t = 13.620$ min; $\eta_S = 57.231\%$

Figure 7. Correlation $\eta_S = f(t; \%\text{CaO})$ – 3rd degree
The correlation equation: $\eta_S = 0.006 \times t^3 - 0.002 \times t^2 \times (\%\text{CaO}) - 0.0004 \times t \times (\%\text{CaO})^2 - 0.047 \times (\%\text{CaO})^3 - 0.322 \times t^2 + 0.116 \times t \times (\%\text{CaO}) + 6.402 \times (\%\text{CaO})^2 + 3.058 \times t - 279.051 \times (\%\text{CaO}) + 3900.427$
The correlation coefficient $R_3 = 0.985$; Deviation $S_3 = 1.658$
Maximum point deviation: $(\%\text{CaO}) = 52.391\%$; $t = 13.710$ min; $\eta_S = 57.102\%$
Figure 8. Correlation $\eta_S = f(t; \%\text{CaO})$ – 4th degree
The correlation equation: $\eta_S = 0.0005 \cdot t^4 + 0.0002 \cdot t^3 \cdot (\%\text{CaO}) + 0.003 \cdot t^2 \cdot (\%\text{CaO})^2 + 0.006 \cdot t \cdot (\%\text{CaO})^3 + 0.044 \cdot (\%\text{CaO})^4 - 0.004 \cdot t^2 - 0.338 \cdot t \cdot (\%\text{CaO})^2 - 1.079 \cdot t \cdot (\%\text{CaO})^2 - 9.387 \cdot (\%\text{CaO})^3 + 8.557 \cdot t^2 + 59.722 \cdot t \cdot (\%\text{CaO}) + 739.948 \cdot (\%\text{CaO})^2 - 1089.643 \cdot t - 25864.41 \cdot (\%\text{CaO}) + 338292.863$

The correlation coefficient: $R_4 = 0.991$; Deviation $S_4 = 1.279$
Maximum point deviation: $\%\text{CaO} = 52.702\%$; $t = 13.805\text{ min}$; $\eta_S = 57.872\%$

Figure 9. Correlation $\eta_O = f(t; \%\text{CaO})$ – 1st degree
The correlation equation: $\eta_O = 1.514 \cdot t + 0.682 \cdot (\%\text{CaO}) - 11.526$

The correlation coefficient: $R_1 = 0.687$; Deviation $S_1 = 7.337$

Figure 10. Correlation $\eta_O = f(t; \%\text{CaO})$ – 2nd degree
The correlation equation: $\eta_O = -0.250 \cdot t^2 + 0.005 \cdot t \cdot (\%\text{CaO}) - 0.886 \cdot (\%\text{CaO})^2 + 6.564 \cdot t + 92.791 \cdot (\%\text{CaO}) - 2421.275$

The correlation coefficient: $R_2 = 0.986$; Deviation $S_2 = 1.655$
Maximum point deviation: $\%\text{CaO} = 52.355\%$; $t = 13.862\text{ min}$; $\eta_O = 56.241\%$
Figure 11. Correlation $\eta_0 = f(t; \%\text{CaO})$ – 3rd degree
The correlation equation: $\eta_0 = -0.010 \cdot t^3 - 0.0002 \cdot t^2 \cdot (\%\text{CaO}) - 0.013 \cdot t \cdot (\%\text{CaO})^2 - 0.051 \cdot (\%\text{CaO})^3 + 0.098 \cdot t^2 + 1.417 \cdot t \cdot (\%\text{CaO}) + 7.239 \cdot (\%\text{CaO})^2 - 33.368 \cdot t - 336.744 \cdot (\%\text{CaO}) + 5140.889$
The correlation coefficient: $R_3 = 0.991$; Deviation $S_3 = 1.328$
Maximum point deviation: $(\%\text{CaO}) = 52.681\%; t = 13.751\min; \eta_0 = 56.284\%$

Figure 12. Correlation $\eta_0 = f(t; \%\text{CaO})$ – 4th degree
The correlation equation: $\eta_0 = 0.002 \cdot t^4 + 0.001 \cdot t^3 \cdot (\%\text{CaO}) + 0.0004 \cdot t^2 \cdot (\%\text{CaO}) + 0.0074 \cdot t \cdot (\%\text{CaO})^3 + 0.033 \cdot (\%\text{CaO})^4 + 0.011 \cdot t^3 + 0.007 \cdot t^2 \cdot (\%\text{CaO})^2 - 1.191 \cdot t \cdot (\%\text{CaO})^3 - 6.998 \cdot (\%\text{CaO})^4 - 0.187 \cdot t^2 + 62.507 \cdot (\%\text{CaO}) + 554.933 \cdot (\%\text{CaO})^2 - 1087.221 \cdot t - 19503.508 \cdot (\%\text{CaO}) + 256355.498$
The correlation coefficient: $R_4 = 0.995$; Deviation $S_4 = 0.992$
Maximum point deviation: $(\%\text{CaO}) = 52.743\%; t = 13.710\min; \eta_0 = 56.621\%$

Figure 13. Correlation $\eta_S = f(q; \%\text{CaO})$ – 1st degree
The correlation equation: $\eta_S = 7.904 \cdot q + 0.596 \cdot (\%\text{CaO}) - 1.352$
The correlation coefficient: $R_1 = 0.639$; Deviation $S_1 = 7.814$
Figure 14. Correlation $\eta_S = f(q; \%\text{CaO})$ - 2nd degree

The correlation equation: 
$$\eta_S = -6.031q^2 + 0.206q(\%\text{CaO}) + 1.036(\%\text{CaO})^2 + 16.211q + 108.106(\%\text{CaO}) - 2792.035$$

The correlation coefficient: $R_2 = 0.822$; Deviation $S_2 = 1.911$

Maximum point deviation: $\%\text{CaO} = 52.444\%$; $q = 2.251g/kg$; $\eta_S = 57.368\%$

Figure 15. Correlation $\eta_S = f(q; \%\text{CaO})$ - 3rd degree

The correlation equation: 
$$\eta_S = 0.751q^3 - 0.025q^2(\%\text{CaO}) - 0.019q(\%\text{CaO})^2 + 0.051(\%\text{CaO})^3 - 8.281q^2 + 2.73q(\%\text{CaO}) + 6.852(\%\text{CaO})^2 - 34.319q - 303.169(\%\text{CaO}) + 4341.912$$

The correlation coefficient: $R_3 = 0.984$; Deviation $S_3 = 1.764$

Maximum point deviation: $\%\text{CaO} = 52.671\%$; $q = 2.303g/kg$; $\eta_S = 57.629\%$

Figure 16. Correlation $\eta_S = f(q; \%\text{CaO})$ - 4th degree

The correlation equation: 
$$\eta_S = 0.819q^4 - 0.093q^3(\%\text{CaO}) + 0.115q^2(\%\text{CaO})^2 + 0.034q(\%\text{CaO})^3 + 0.051(\%\text{CaO})^4 + 0.516q^2 - 11.631q(\%\text{CaO})^2 - 5.791q(\%\text{CaO})^3 - 0.687(\%\text{CaO})^4 + 292.968q^2 + 320.039q(\%\text{CaO}) + 840.278(\%\text{CaO})^2 - 5837.466q - 29301.079(\%\text{CaO}) + 382355.983$$

The correlation coefficient: $R_4 = 0.991$; Deviation $S_4 = 1.305$

Maximum point deviation: $\%\text{CaO} = 52.384 \%$; $q = 2.431g/kg$; $\eta_S = 57.924\%$
Figure 17. Correlation $\eta_0 = f(q; \%CaO) – 1^{\text{st}}$ degree
The correlation equation: $\eta_0 = 9.559q + 0.657(\%CaO) - 9.492$
The correlation coefficient: $R_1 = 0.751$; Deviation $S_1 = 6.861$

Figure 18. Correlation $\eta_0 = f(q; \%CaO) – 2^{\text{nd}}$ degree
The correlation equation: $\eta_0 = -5.967q^2 + 0.058q(\%CaO) - 0.881(\%CaO)^2 + 25.398q + 92.224(\%CaO) - 2392.957$
The correlation coefficient: $R_2 = 0.985$; Deviation $S_2 = 1.747$
Maximum point deviation: $(\%CaO) = 52.513%$; $q = 2.463g/kg$; $\eta_0 = 56.473%$

Figure 19. Correlation $\eta_0 = f(q; \%CaO) – 3^{\text{rd}}$ degree
The correlation equation: $\eta_0 = -1.682q^3 + 0.084q^2(\%CaO) - 0.091q(\%CaO)^2 - 0.054(\%CaO)^3 - 2.412q^2 + 9.354q(\%CaO) + 7.736(\%CaO)^2 - 220.183q - 362.308(\%CaO) + 5584.811$
The correlation coefficient: $R_3 = 0.991$; Deviation $S_3 = 1.398$
Maximum point deviation: $(\%CaO) = 52.613%$; $q = 2.471g/kg$; $\eta_0 = 56.937%$
The correlation equation: \[ \eta_{O} = 1.464 \cdot q^4 - 0.194 \cdot q^3 \cdot (%CaO) - 0.009 \cdot q^2 \cdot (%CaO)^2 + 0.041 \cdot q \cdot (%CaO) + 0.036 \cdot (%CaO)^2 + 0.902 \cdot q^2 + 1.917 \cdot q \cdot (%CaO) - 6.431 \cdot q \cdot (%CaO)^2 - 7.791 \cdot (%CaO)^3 - 53.311 \cdot q^3 + 335.231 \cdot q \cdot (%CaO) + 615.683 \cdot (%CaO)^2 - 5790.541 \cdot q - 21570.321 \cdot (%CaO) + 282676.383 \]

The correlation coefficient: \[ R_4 = 0.995 \]; Deviation \[ S_4 = 1.026 \]

Maximum point deviation: \( (%CaO) = 52.702\% \); \( q = 2.476\)g/kg; \( \eta_{O} = 56.937\% \)

The analysis of the double correlation equations expressed analytically and graphically in Figures 5–20, leads to a series of observations and conclusions having both a general and a specific character, namely:

1. The variation of the independent parameters within the technological limits determines a variation of the dependent parameter also within the technological limits, it being located on a regression surface or in its vicinity, considering the standard dispersion, deviation and error.

2. The graphical representations of the analytical correlations expressed by 1st degree polynomial functions are plane surfaces and those expressed by 2nd, 3rd and 4th degree polynomial functions are non-plane surfaces.

3. The intersection of the correlation surfaces with the level planes (parallel to the horizontal) resulted in level curves (level lines for the 1st degree polynomial functions), which allowed setting the variation limits of the independent parameters.

4. The correlations expressed by a 1st degree polynomial function and shown in their graphical form in Figures 5, 9, 13 and 17, allow the choice of parameter values: \( t, q, (%CaO) \), so that for the desulphurization (\( \eta_{S} \)), respectively deoxidizing (\( \eta_{O} \)) output values obtained should be above the average values resulted for the charges under analysis.

5. The graphical representations of the 2nd, 3rd and 4th degree correlations show a maximum point, the values of all parameters (both independent and dependent) ranging within the technological limits. In order to obtain high values for the dependent parameter, it is desirable that these values be situated primarily within the sub-domain where the maximum point is located, and if this area is small (which means narrower limits for the independent parameters), in the nearby zones.

6. The analysis of the correlations \( \eta_{S} = f(t, CaO) \) shown in their analytical and graphical form in Figures 6, 7 and 8 leads to the conclusion that for all cases, there is a maximum point within the technological variation interval of the technologically independent parameters. For \( (%CaO) \) within the limits 49–56\% and for \( t = 8–17\)min. can be obtained for \( \eta_{S} \) values above the average obtained during the experiments (42.278\%), and for \( (%CaO) = 51–54\% \) and for \( t = 1–17 \) min. can be obtained for \( \eta_{S} \) values above 55\%.

7. As to correlations \( \eta_{O} = f(t, CaO) \) shown analytically and graphically in Figures 10, 11 and 12 it was observed that in all cases, there is a maximum point within the interval of technological variation of the technologically independent parameters. For \( (%CaO) \) and \( t \) within the same variation limits as for \( \eta_{O} \) values above the average, respectively for \( \eta_{O} \) above 55\% (up to the maximum point 56-57\%) for \( (%CaO) = 51.5–53.5\% \) and \( t = 1.5–15.5\)min.
8. The study of correlations $\eta_S = f(q, CaO)$ shown analytically and graphically in Figures 14, 15 and 16, proves they all have a maximum point. For the same variation limits of (%CaO) as in the previous case and for the specific synthetic slag consumption $q = 1-1.15g/kg$ the values of $\eta_S$ were above the average, while for %CaO= 51.0-53.5% and $q =1.5–2.8g/kg$ the values of $\eta_S$ were superior to 55% up to a maximum point.

9. As to correlations $\eta_O = f(q, CaO)$ shown analytically and graphically in Figures 18, 19 and 20, the situation and the technological analysis are similar to the previous ones, except for the fact that in order to obtain for $\eta_O$ values above 55% the variation domain is narrowed as follows: (%CaO)=51.5-53.5% and $q=2.0–2.8g$ synthetic slag/kg steel.

4. Conclusions
The experiments, the data processing and the technological analysis of the results allow the following conclusions:
- lime, alumina and titanium oxide-based mechanical mixtures, respectively the slag resulting from their melting, grant favorable conditions for steel refining inside the ladle, through the so-called method of “synthetic slag treatment”;
- obtaining a mechanical mixture having oxide values (respectively oxide summary) within the limits in the vicinity of the maximum point, leads to high values of $\eta_S$, respectively $\eta_O$;
- in the case of oxide ratio variation in the vicinity of the maximum point, it is possible to obtain for $\eta_S$, respectively for $\eta_O$ values close to the upper limit;
- the results lead to the idea of continuing the experiments using for the mechanical mixture the slag resulted from ferro-titanium production and, according to some data in the reference literature, of the reducing mixture containing vanadium oxides and a higher content of magnesium oxide;
- the results obtained are applicable in steel elaboration research and practice;
- in order to obtain an advanced rate of desulphurization and deoxidizing, it is desirable to treat steel with slag containing CaO = 50–56%, the treatment time $t = 10-17$ min and the specific addition of synthetic slag of 1.5-2.8 g/kg;
- the values of the independent parameters (CaO), t and q can be established graphically, by use of any of the graphical representations (2nd, 3rd or 4th degree), minding that the results should be checked both graphically and analytically (after the 2nd degree double correlation, desirably).

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