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RESEARCHES REGARDING THE ELEMENTS LOSS THROUGH VAPORIZATION DURING THE ELABORATION PROCESS IN LD CONVERTER

Alexandru IVANESCU, Ana DONIGA,
Elisabeta VASILESCU, Lilica IVANESCU
“Dunărea de Jos” University of Galati

ABSTRACT

The paper presents a series of researches regarding the vaporization of the component elements of the metallic bath and slag during refining in LD converter. Also, the main factors which influence the vaporization process during steel making in LD converter are studied: the converter atmosphere; the carbon content of the metallic bath; the speed of the oxygen jet; the temperature of the metallic bath; the blowing diagram. Based on these researches we sought to obtain a technology of steel making in LD converter so that the percentage of losses by vaporization is minimum.

KEYWORDS: *oxygen converter, vaporization, sludge, slag, oxygen jet speed, critical carbon content.*

1. Introduction

During steelmaking in oxygen converters, in the impact zone of oxygen jet with the metallic bath, a local temperature of 3000^{0}C is created. As a result, the boiling points of the metallic bath components are exceeded, so that a part (0.6-1.2%) of the metallic charge is volatilized as a red smoke made of fine particles having a size of approximately 1μm [1-3].

1.1. Vaporisation of the elements from the metallic bath

In Fig. 1 is presented the temperature dependence of the vapor pressure for some metals.

The greater is the temperature of the metallic bath in the impact zone of the jet, the greater are the vapor pressures of the component elements Mn, Cr, Cu, Si, Fe, Ni, Co, Ti and the stronger the emission of gases and metallic vapors.

These vapors are entrained by the relaxing of the CO bubbles resulted from the metallic bath decarburization. Also, as a result of the bubbles action and of the oxygen jet impact with the slag-metal emulsion surface, an entrainment of the flux fine particles is achieved, especially during slag formation. At the level of the oxygen jet impact zone, the ascending gas flow has the pressure P_t corresponding to a temperature T_1 with which the gas-vapor mixture enters the recovery unit (approx. 1923 K):

$$P_t = P_{t_1} + P_{t_2} \ , \qquad (1)$$

$$P_{t_1} = P_{Fe} + P_{Si} + P_{Mn} + P_{Al} + \dots\dots \qquad (2)$$

$$P_{t_2} = P_{CO} + P_{CO_2} + P_{O_2} + P_{H_2O} + P_{H_2} \qquad (3)$$

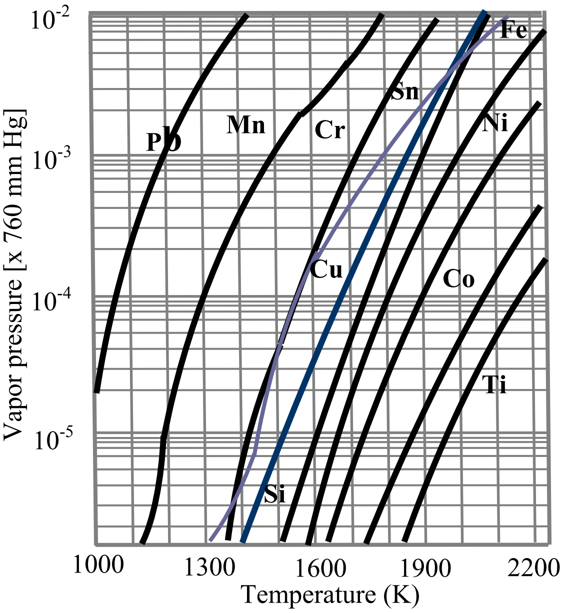


Fig. 1. *Variation of the vapor pressure with temperature*

Because of the oxidizing conditions in the recovery unit (false air excess) the elements vapors are oxidized and condensed at the temperature T_2 corresponding to the dew point (Fig. 2), being recovered in a proportion of 98% in the resulted sludge from the wet cleaning unit. T_3 is the temperature of condensation of the Fe, Mn and Al vapors, which were cooled with the aid of cooling water in Venturi tubes. Of the evaporated elements, Fe has an important weight and influences the level of the steel taking out [4].

The iron vaporization is influenced by the converter atmosphere, the carbon content of the iron bath; the speed of the oxygen jet, the decarburizing rate.

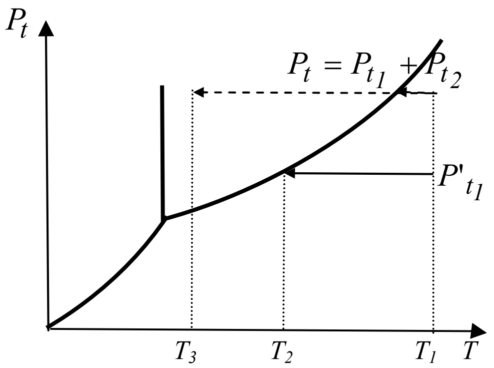


Fig. 2. *Diagram of the vapors condensation of a gaseous mixture*

2. The influence of the converter atmosphere upon the elements vaporization

For example it is considered the iron vaporization because Fe is quantitatively predominant in the heterogeneous system subjected to the process.

As a result of the oxygen blowing, a Fe vapors counter-flow appears and determines at a distance δ from the surface of the metallic bath the formation of a fog layer of FeO, the following reaction being produced:

$$\{Fe\} + \frac{1}{2}\{O_2\} \rightarrow \{FeO\}$$

resulting for the fluxes of the Fe vapors, F_{Fe}, and of oxygen, F_{O_2}:

$$F_{Fe} = -2F_{O_2} \qquad (4)$$

In conformity with Fick’s law, the flux of the Fe vapors is given by the relation

$$F_{Fe} = -CD_{Fe}\frac{\partial X_{Fe}}{\partial y} + X_{Fe}(F_{Fe} + F_{O_2}) \qquad (5)$$

From the relations (4) and (5) it is obtained:

$$F_{Fe}(2 + X_{Fe}) = -2CD_{Fe}\frac{\partial X_{Fe}}{\partial y} \qquad (6)$$

$$\int_0^{\delta} F_{Fe}\,dy = -2CD_{Fe}\int_{X_{Fe}^0}^{X'_{Fe}} \frac{dX_{Fe}}{2 + X_{Fe}} \qquad (7)$$

$$F_{Fe} = -\frac{2CD_{Fe}}{\delta}\ln\frac{2 + X'_{Fe}}{2 + X_{Fe}^0} \qquad (8)$$

where: F_{Fe} the flux of the Fe vapors, in mol/m^2.s; D_{Fe} – the diffusion coefficient of Fe in oxygen, in m/s; X_{Fe}^0 – the molar fraction of Fe at the distance *y=0*;

X'_{Fe} – the molar fraction of Fe at the distance *y=δ*; *C* – the molar concentration of the Fe vapors, in mol/m^3,

$$C = \frac{n}{V_{Fe}} = \frac{P_{Fe}}{RT} \qquad (9)$$

n – the number of moles of Fe which vaporize;

V_{Fe} – the molar volume of Fe;

P_{Fe} – the pressure of Fe vapors. In conclusion, the flux of the Fe vapors is twice the flux of oxygen and it is determined by the oxygen partial pressure P_{O_2} which characterizes the converter atmosphere.

3. The influence of the carbon content from the bath subjected to the vaporization

It is observed that during the decarburizing of a metallic bath with upper oxygen jet, the carbon content has a strong influence upon the decarburizing process. Thus, for a carbon content of less than 2% C (Fig. 3), the Fe vaporization becomes much weaker and tends to zero as the carbon content decreases. In industrial practice the medium decarburizing rate in LD converter is 10% C/h, at a bath depth of 100 mm. The disappearance of the flame at the converter mouth and the observation of the lance are realized at a carbon content of approximately 0.05% in the metallic bath, when the vaporization is minimum. It is important to determine the critical content of carbon from which the vaporization begins to decrease.

The Fick’s first law is applied to the carbon transport through a thin diffusion layer at the metal-gas interface:

$$-\frac{d[C]}{dt} = \frac{1}{L}\frac{D_C}{g_0}(C_0 - C_{cr}) \qquad (10)$$

where: L – the depth along which the boiling of the metallic bath takes place (~ 100 mm); D_C – carbon diffusion coefficient in iron [3.10^{-8} m^2/s]; g_0 – the thickness of the limit diffusion layer [3.10^{-5} m]; C_0 – the carbon content at the interface (~ 0.03%); C_{cr} – the critical carbon content when the vaporization is reduced.

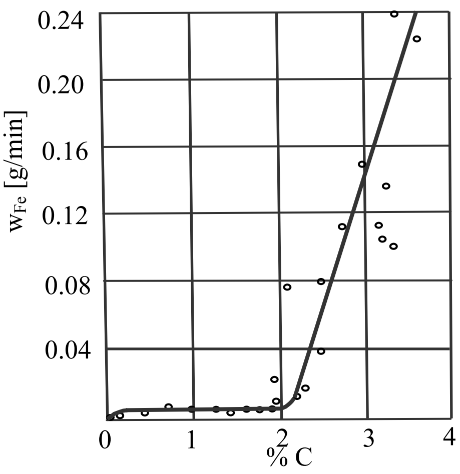


Fig.3. *Variation of Fe vaporization speed with the carbon content [C]*

From the relation (10) it results the value $C_{cr} = 0.31\,\%$ which corresponds to the practical values: 0.20-0.40 %C.

4. The influence of the oxygen jet speed upon the elements vaporization

In Fig. 4 is presented the variation of the oxygen jet speed as a function of the carbon content of the metallic bath.

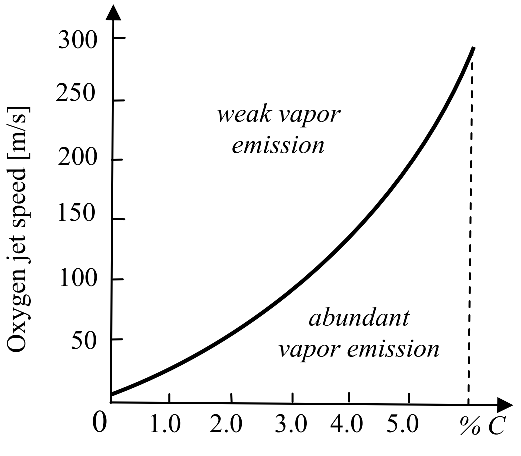


Fig. 4. *Variation of oxygen jet speed with [C]*

If the oxygen jet speed is bigger than the value given by this curve for all the carbon contents, the vapors emission is weak.

If the oxygen jet speed is smaller than the critical value, Fe is vaporized at a rate close to its maximum value:

$$w_{O_2} = K[C]^2 \qquad (11)$$

where: w_{O_2} – the oxygen jet speed; *[C]* – the carbon concentration in the metallic bath; K – proportionality constant. The relation (11) is established on the basis of the relation:

$$2F_{O_2} = F_{CO_2} > F_C \qquad (12)$$

obtained when the vapors release ends, from the reaction:

$$\{CO\} + \frac{1}{2}\{O_2\} \rightarrow \{CO_2\} \qquad (13)$$

with F_{O_2}, F_{CO_2} and F_C – the oxygen, CO_2 and carbon fluxes. The domain upon the curve from the Fig. 4 corresponds to the case in which the steel making takes place with minimum emissions of red gases and the domain under the curve corresponds to the case in which the steel making takes place with maximum emissions.

It is concluded that during iron decarburization by oxygen blowing through the upper side, in order to obtain a reduced vaporization, the oxygen speed at the lance nozzle exit must be as great as possible in the case that the metallic bath has great carbon contents. As the decarburization advances, the iron oxidation must be maintained to a minimum value in order to suppress the smoke formation.

5. Experimental researches

The sludge samples were taken from the sludge funnel every two minutes of blowing from nine charges. The chemical composition of the converter dust (dry sludge) is presented in Tab. 1 from which some aspects concerning the vaporization process in the LD converter can be highlighted:

- the Fe content from the red smokes is a maximum in the minute 4 of blowing and corresponds to the maximum content of Fe_2O_3;
- the SiO_2 content is a maximum in the minutes 8-10 of blowing;
- the Al_2O_3 content variation is a maximum in the minute 4 of blowing, as the Fe content;
- the CaO content variation is a maximum in the minute 14 of blowing;
- the MgO content variation is a maximum in the first two minutes of blowing and a maxim in the last minutes;
- the Mn content variation presents a loop in the minute 20 of blowing;

- the calcination losses (PC) variation is a maximum in the minute 14 of blowing, as CaO;

Using a statistical program, from the data in Tab. 1 there were obtained the histograms of the main parameters of the vaporization process as well as the simple and multiple correlations between them [5]. Out of these, we have selected the Fe content histogram_(Fig.5). From the histograms the following conclusions can be drawn:

- the Fe content in the red smokes varies in the range 20-60% and the maximum frequency of 40% is obtained for a 42-50% Fe content (fig. 5);
- the FeO content in the dry sludge varies in the range 6-27% and the maximum frequency of 28% is obtained for a 18-20% FeO content;
- the CaO content in the in the dry sludge varies in the range 10-30% and the maximum frequency of 43% is obtained for a 15-20% CaO content;
- the quantity of dry substance SU varies between 5 and 35 g/l and has a maximum frequency of 40% for a concentration of 17-23 g/l;
- the dry substance (SU) variation has a maximum concentration in the minute 12 of blowing.
- the calcinations losses PC vary in the range 5-28% and the maxim frequency of 28% is obtained for a 17-20% PC;
- the vaporized elements Ca, Si, Al, Mg pass as oxides CaO, SiO_2, Al_2O_3 and MgO, respectively;
- the SiO_2 content in the dry sludge varies in the range 0-2.4% and the maximum frequency of 37% is obtained for a 1.3-1.5% SiO_2 content;
- the Al_2O_3 content in the dry sludge varies in the range 0-3.8% and the maximum frequency of 42% is obtained for a 0.7-1.2% Al_2O_3 content;
- the MgO content in the dry sludge varies in the range 0-4.2% and the maximum frequency of 38% is obtained for a 0-0.8% MgO content;
- the Mn content in the dry sludge varies in the range 0.5-2.5% and the maximum frequency of 42% is obtained for a 1.3-1.5% Mn content.

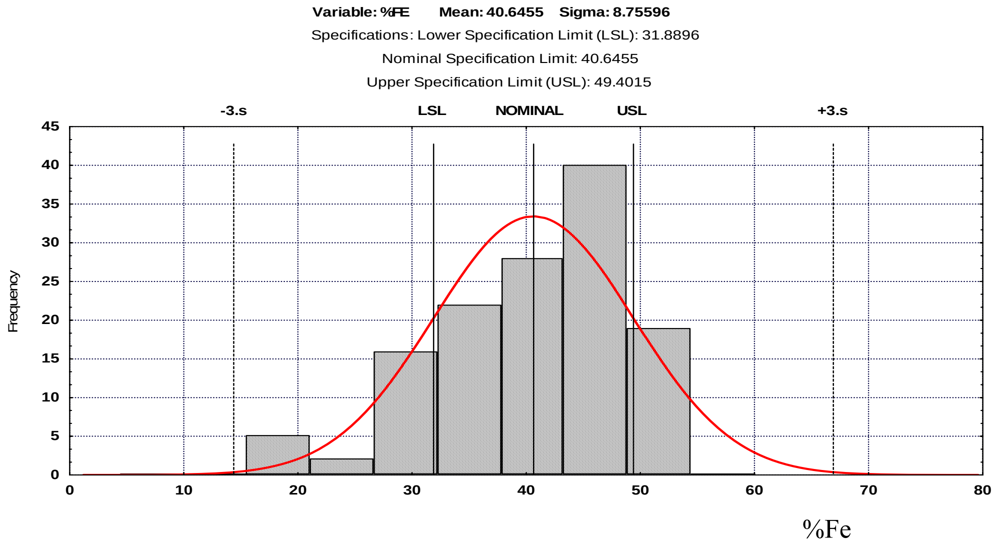


Fig. 5. *The histogram of the absolute frequencies of % Fe*

Table 1. *Chemical analyses of the sludge samples*

Minute of blow	Fe	FeO	Fe_2O_3	SiO_2,	Al_2O_3	CaO	MgO	Mn	PC	SU	Remarks
	[%]									[g/l]	
2	41.98	5.34	54.50	1.57	0.63	18.96	0.12	0.57	17.46	11.74	Charge 1 (923654)
4	53.60	11.04	65.05	1.39	0.91	13.02	1.07	1.28	9.32	28.94	
6	45.65	18.37	45.95	1.94	0.49	18.43	0.12	1.13	13.62	13.74	
8	53.19	26.02	49.72	1.61	0.77	12.33	0.75	1.31	5.42	14.74	
10	50.77	18.81	52.88	1.59	0.89	12.33	0.11	1.36	13.90	27.04	
12	47.03	16.16	50.34	1.33	0.49	18.82	0.13	1.51	15.05	29.94	
14	17.13	7.22	17.03	0.81	1.46	49.31	0.37	0.70	26.02	27.44	
16	32.73	22.01	24.30	1.25	0.34	27.25	0.16	1.42	22.31	11.04	
18	39.46	21.08	34.35	0.82	1.96	20.53	0.12	1.99	19.74	20.34	
20	35.40	17.89	31.91	0.63	1.33	14.93	1.87	2.35	21.18	9.74	
22	27.45	5.34	33.75	0.55	2.58	30.82	5.14	1.32	13.83	8.94	
2	42.79	5.43	55.63	1.70	0.69	19.06	0.20	0.64	18.33	12.71	Charge 2

4	54.41	11.13	66.18	1.52	0.97	13.12	1.15	1.35	10.19	29.91	(923655)
6	46.46	18.46	47.08	2.07	0.55	18.53	0.20	1.20	14.49	14.71	
8	54.00	26.11	50.85	1.74	0.83	12.43	0.83	1.38	6.29	15.71	
10	51.58	18.90	54.01	1.72	0.95	12.43	0.11	1.43	14.77	28.01	
12	47.84	16.25	51.47	1.46	0.55	18.92	0.13	1.58	15.92	30.91	
14	17.94	7.31	18.16	0.94	1.52	49.41	0.45	0.77	26.89	28.41	
16	33.54	22.10	25.43	1.38	0.40	27.35	0.16	1.49	23.18	12.01	
18	40.27	21.17	35.48	0.95	2.02	20.63	0.20	2.06	20.61	21.31	
20	36.21	17.98	33.04	0.76	1.39	15.03	1.95	2.42	22.05	10.71	
22	28.26	5.43	34.88	0.68	2.64	30.92	5.22	1.39	14.70	9.91	
2	42.24	5.09	54.86	1.47	0.67	18.97	0.18	0.52	17.77	12.05	Charge 3 (933944)
4	53.86	10.79	65.41	1.29	0.95	13.03	0.88	1.23	9.63	29.25	
6	45.91	18.12	46.31	1.84	0.53	18.44	0.18	1.08	13.93	14.05	
8	53.45	25.77	50.08	1.51	0.81	12.34	0.81	1.26	5.73	15.05	
10	51.03	18.56	53.24	1.49	0.93	12.34	0.11	1.31	14.21	27.35	
12	47.29	15.91	50.70	1.23	0.53	18.83	0.13	1.46	15.36	30.25	
14	17.39	6.97	17.39	0.71	1.50	49.32	0.43	0.65	26.33	27.75	
16	32.99	21.76	24.66	1.15	0.38	27.26	0.16	1.37	22.62	11.35	
18	39.72	20.83	34.71	0.72	2.00	20.54	0.18	1.94	20.05	20.65	
20	35.66	17.64	32.27	0.53	1.37	14.94	1.93	2.30	21.49	10.05	
22	27.71	5.09	34.11	0.45	2.62	30.83	5.20	1.27	14.14	9.25	
2	51.80	8.56	63.38	1.28	0.65	11.39	1.44	0.74	9.99	12.20	Charge 4 (923653)
4	50.75	12.79	57.52	1.28	0.52	13.76	0.70	0.85	11.24	14.71	
6	49.45	16.12	52.24	1.25	0.44	15.89	0.16	0.95	12.37	16.22	
8	47.90	18.53	47.54	1.19	0.43	17.78	0.00	1.04	13.38	16.70	
10	46.10	20.04	43.42	1.11	0.48	19.42	0.00	1.13	14.25	16.17	
12	44.06	20.63	39.88	1.00	0.59	20.81	0.00	1.21	15.00	14.62	
14	41.76	20.32	36.91	0.87	0.76	21.97	0.00	1.28	15.61	12.06	
16	39.22	19.10	34.53	0.71	1.00	22.87	0.44	1.35	16.10	8.47	
18	36.42	16.97	32.72	0.53	1.29	23.53	1.09	1.41	16.47	3.88	
20	33.38	13.93	31.50	0.32	1.65	23.95	1.94	1.46	16.70	19.20	
22	30.09	9.99	30.85	0.09	2.07	24.12	2.99	1.50	16.81	8.60	
2	48.53	7.73	61.16	1.46	0.76	13.21	1.54	0.75	9.86	13.29	Charge 5 (918798)
4	47.48	11.96	55.30	1.45	0.63	15.58	0.89	0.88	11.31	17.16	
6	46.18	15.29	50.02	1.42	0.55	17.71	0.44	0.99	12.62	20.01	
8	44.63	17.70	45.32	1.37	0.54	19.60	0.19	1.10	13.80	21.84	
10	42.83	19.21	41.19	1.29	0.59	21.24	0.14	1.21	14.85	22.66	
12	40.79	19.81	37.65	1.18	0.77	22.63	0.29	1.30	15.77	22.46	
14	38.49	19.49	34.69	1.05	0.87	23.78	0.63	1.39	16.55	21.24	
16	35.95	18.27	32.30	0.89	1.11	24.69	1.18	1.47	17.20	19.00	
18	33.15	16.14	30.50	0.71	1.40	25.35	1.93	1.54	17.71	15.75	
20	30.11	13.11	29.27	0.50	1.76	25.77	2.87	1.61	18.09	11.49	
22	26.82	9.16	28.63	0.26	2.18	25.94	4.02	1.67	18.34	6.20	
2	48.73	7.53	61.25	1.44	0.96	13.40	1.73	0.74	9.90	13.49	Charge 6 (923648)
4	47.88	11.56	55.39	1.41	1.03	15.97	1.28	0.85	11.40	17.56	
6	46.78	14.69	50.11	1.36	1.15	18.30	1.03	0.95	12.77	20.61	
8	45.43	16.90	45.41	1.29	1.34	20.39	0.98	1.04	14.00	22.64	
10	43.83	18.21	41.28	1.19	1.40	22.23	0.77	1.13	15.10	23.66	
12	41.99	18.61	37.74	1.06	1.45	23.82	0.90	1.21	16.07	23.66	
14	39.89	18.09	34.78	0.91	2.17	25.18	1.30	1.28	16.90	22.64	
16	37.55	16.67	32.39	0.73	2.32	26.28	1.40	1.35	17.59	20.60	
18	34.95	14.34	30.59	0.53	2.80	27.14	1.99	1.41	18.16	17.55	
20	32.11	11.11	29.36	0.30	2.95	27.76	2.60	1.46	18.59	13.49	
22	29.02	6.96	28.72	0.04	3.20	28.13	3.00	1.50	18.89	8.40	

From the ten simple correlations we have selected for presentation the regression curves of % FeO (Fig. 6a), and of SU (Fig. 6b), in g/l, as function of the blowing time, *t*. From the regression curves the following conclusions can be drawn:

- the FeO content presents two maxims in the minutes 8 and 20 and between them a minimum corresponding to the minute 14 when the decarburization is advanced (Fig. 6a);
- the quantity of dry substance SU presents a parabolic variation, presenting a maximum of 25 g/l in the minute 12 of blowing (Fig. 6b);
- the MgO content in the dry sludge presents a parabolic variation, presenting a minimum of 0.2% in the minute 12 of blowing;
- the Fe content presents a linear variation, descending from a maximum value of approx. 55% in the minute 4 of blowing to a value of approx. 30% in the minute 22 of blowing;
- the SiO_2 content variation is linear, descending from a maximum value of 1.8% in the first two minutes of blowing to a value of 0.2% in the minute 22 of blowing;
- the Al_2O_3 content variation is linear, ascending from a 0.5% minimum value in the minute 2 of blowing to a maximum value of 2.5% in the minute 22.

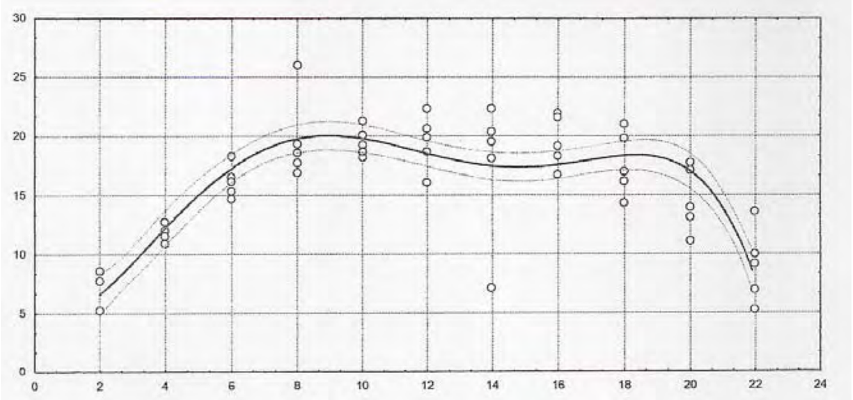
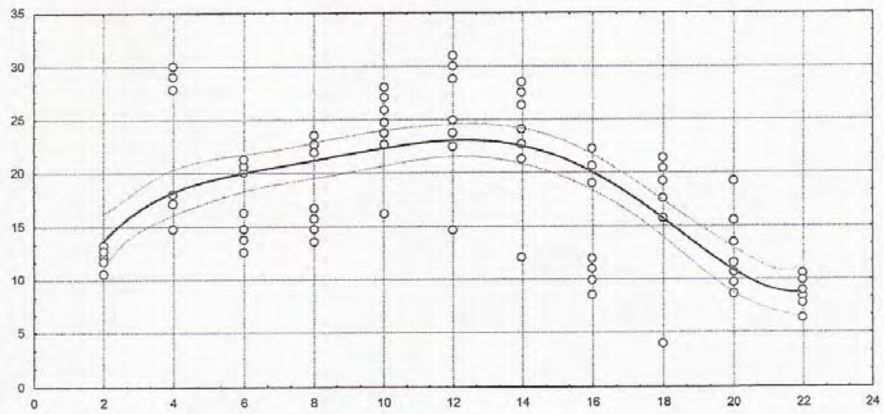
<table>
<tr><td></td><td>% FeO = 5.121 – 1.53 t + 1.53 t^2 - 0.219 t^3 + 0. 012 t^4; correlation : 0.1116470 ; N=132</td><td></td></tr>
<tr><td>[% FeO]</td><td>
</td><td>a</td></tr>
<tr><td></td><td>SU (g/l) = 2.062 + 8. 622 t - 1.73 t^2 + 0.178 t^3 – 0.009 t^4; correlation : -0.303229; N=132</td><td></td></tr>
<tr><td>SU [g/l]</td><td>
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Fig. 6. *Regression curves for % FeO and dry substance SU [g/l]*

From the multiple correlations we have selected for presentation the regression surfaces of % Fe=f(%CaO, %SiO_2) (Fig. 7) and of SU=f(%Fe, %CaO) (Fig. 8) and the following technological aspects can be detached:

- the Fe content in the red smokes depends to a great extent on the CaO and SiO_2 contents from the sludge obtained by the vaporization of Ca and Si and by the lime dust training in the converter. A maxim of 54-55% Fe is registered for a 15% CaO and 2.2% SiO_2 content. The greater the CaO content in the sludge, the smaller the Fe content. This fact conducts to the conclusion that the iron vaporization can be diminished with a great CaO content in slag;
- the quantity of dry substance is determined by an intense Fe and Ca vaporization, obtaining a maximum of 35% SU for 55% Fe and 35% CaO and a minimum of 2% SU for 10% Fe and 6% CaO;
- the calcination losses are influenced by the Fe and Si vaporization, obtaining a maximum of 28% PC for 8% Fe and 2.2% SiO_2 and a minimum of 6% PC for 55% Fe and 0.2% SiO_2.

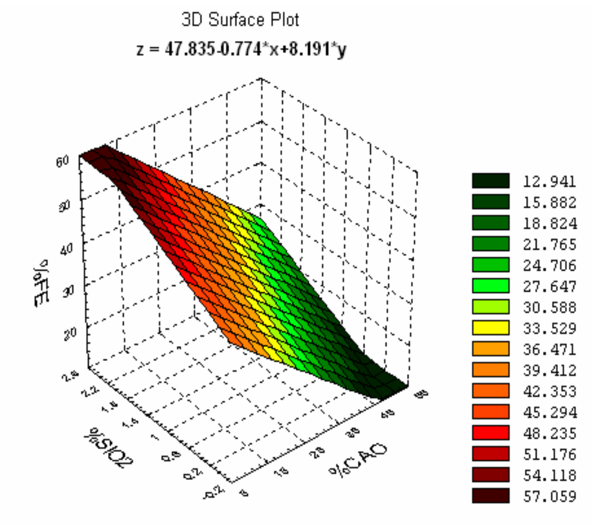

***Fig.7**. Correlation of %Fe as function of %CaO şi %SiO$_2$*

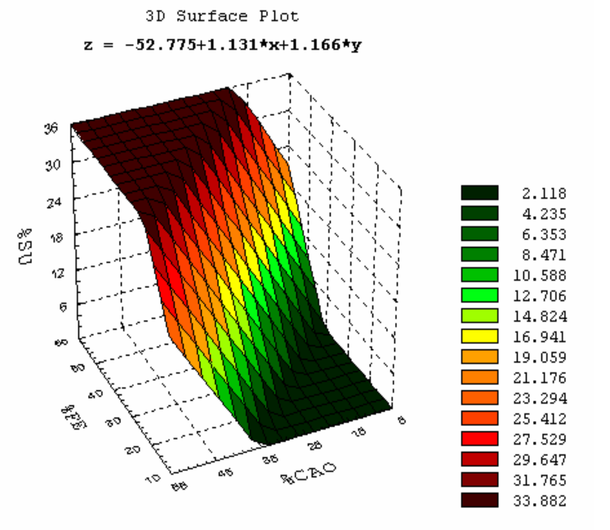

***Fig.8.** Correlation of %SU as function of %Fe şi %CaO*

6. Conclusions

The iron volatilization in the LD converters with oxygen blowing at top through lance is important because great iron quantities (0.6-1.2%) from the metallic charge are lost as fine particles having a size of approximately 1µm, mainly made of iron oxides. In order to diminish this loss it is necessary to achieve an intense oxygen blowing regime being able to ensure as greater oxygen jet speeds as the carbon content in the metallic bath is higher. The sludge obtained from the LD converter gases' purging represents an ore enriched in iron (approx. 50-55% Fe). The maintaining of a quantity of liquid slag from the previous charge determines, on one hand the faster formation of slag and, on the other hand, helps to obtain poorer emissions of vapors of Fe, Mn, Si, Mg, Al, Ca, etc at high carbon contents in the metallic bath. At small carbon contents (less than the critical one) the oxygen speed at the lance nozzle exit is the factor whose size influences the emission of metallic vapors: the greater the speed, the poorer emission of metallic vapors.

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