Research on the Use of Waste to Reducing Slag Formation

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Abstract —. The paper introduces the results of industrial experiments on the use of synthetic slags resulted from melting mechanical mixtures of industrial wastes, used in steelmaking in order to refine steel inside the ladle. The industrial experiments we performed consisted in adding the waste mechanical mixture at the bottom of the ladle, its melting leading to the formation of synthetic slag. The use of such industrial wastes in order to form slag reducing, economical, as well as ecological effects. To determine the efficiency of working with synthetic slags, we performed a series of correlation between the efficiency of desulphurization and deoxidation considered as independent parameters and specific amount of synthetic slag and CaO content. Results obtained by processing data are expressed as MATLAB graphical and analytical form. On the graphics could determine the most representative areas of variation of dependent parameters. Also determined a correlation equation between desulphurization and deoxidation efficiency of steel.

Keywords — waste, slag, steel, ladle, recovery

I. INTRODUCTION

The large scale introduction of liquid steel refining with synthetic slags inside the ladle is conditioned by the high costs and the lack of technical alumina, obtained from bauxite, a component of the synthetic slag.

The possibility of improving steel purity by refining with synthetic slags is based on [1]:

- the achieving – during the steel and slag mixing process – of a contact, interaction surface about 300 times larger than in the electric arc furnace;

- the physical-chemical properties of the slags adequate to the simultaneous reduction of the sulphur and oxide inclusions;

- in order to meet these requirements it is mandatory to know the physical and chemical reactions in the system metal-slag, under the conditions of an intense overlapping of the two phases.

The degree of steel mixing with the synthetic slag is determined by the possibility of its turning into the smallest possible particles, by the physical and chemical properties of the slag and steel, as well as by the hydrodynamic process taking place during steel tapping.

The contact surface increases significantly up to a certain value of the jet falling height, after which it practically stays constant. Usually, the falling height is 5 - 7 m.

As to the quantity of synthetic slag, its magnitude goes hand in hand with the growth of the quantity of emulsion slag in the steel and with the specific contact area, while the average dimensions of the slag particles stay practically unchanged. Normally, the quantity of synthetic slag is 30…50 kg/t of steel. Synthetic slag, as mechanical mixture has a composition of the type $CaO: SiO_2 : Al_2O_3 = 40:40:20$, and is characterized by a low melting temperature, a high fluidity and a high absorption capacity [2].

Steel refining with synthetic slag represents a possibility of diminishing steel impurification with non-metallic inclusions, due to the fact that, under certain conditions, the drops of slag emulsion in the steel can assimilate non-metallic suspensions, being decanted alongside with them.

Steel processing with synthetic slags leads to low-sulphur steel, low impurification (particularly) with sulphidic, oxidic inclusions, and with a lower content of oxygen.

On steel elaboration in electric arc furnaces and treating it with synthetic slags, the content of sulphur is 1,5-2 times lower than in steel obtained by the usual technology.

The data in reference literature [3-6] show that the use of synthetic slags with 52-55% CaO and 38-42% Al_2O_3 overheated to 1680-1750 ^oC, in a quantity of 10-60kg/t leads to desulphurizing degrees of 40-60%.

The use of synthetic slags corresponding to the ternary system $CaO-Al_2O_3-SiO_2$, with up to 15% SiO_2 is widely used as it a grants a high fluidity at the temperature of the molten steel. These slags are used in quantities of 40-50 kg/t, which make for desulphurizing degrees of 45-70 %.

Sulphur removal by means of synthetic slag depends, besides the charge deoxidizing degree, on the chemical composition, on the grain size and on the quantity of desulphurizing agent, as well as on the degree of steel-slag mixing.

II. PROBLEM FORMULATION

These slags can be added to the steel into the ladle both under a liquid state or a solid one. During our industrial experiments we opted for the latter variant, as there was no slag melting furnace on the work platform. The variant of choice is more economical and simpler from the point of view of the technological flux.

On synthetic slag formation, we chose two types of waste: aluminous slag (resulted in the process of aluminum elaboration) and lime powder and, in order to increase the fluidity of the newly formed slag, we added fluorine. The chemical composition of the aluminous slag is shown in fig.1. The synthetic slag results from the melting of the mechanical mixtures of industrial wastes (lime dust and aluminous slag) according to the recipe shown in fig.2.
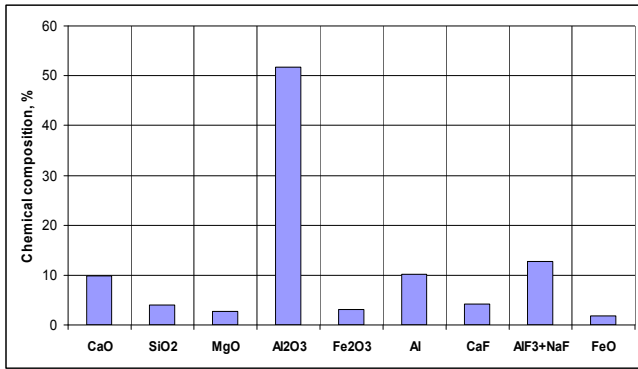
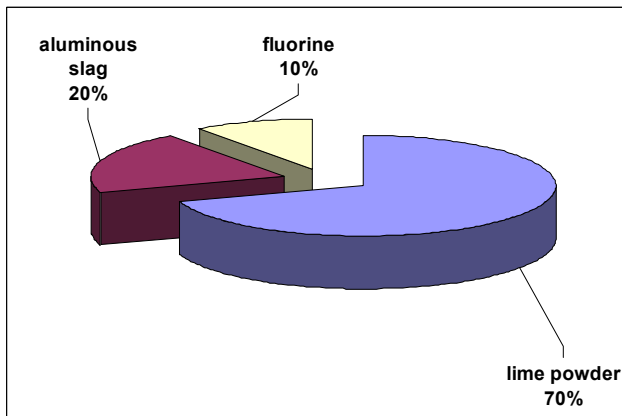**Fig.1.** Chemical composition of aluminous slag

Fig.2. Recipe for synthetic slag formation

The industrial experiments were done on 16 steel charges (4 charges/recipe) elaborated into a 100 ton electric arc furnace, steel to be used in the production of pipes. Steel secondary treatment with synthetic slag is done inside the ladle. In this case, considering that steel tapping is done into a single pot, the comparison was drawn with other charges of steel having the same grade and being elaborated under similar conditions.

In order to obtain the reducing slag, we introduced at the bottom of the ladle, 30 min before tapping, a mixture of 4-14,5 kg/t steel, made of: 68-75% lime dust (grain size below 40mm), 14-17% calcium fluoride (grain size below 35mm) and 11-20% aluminum slag (grain size below 25mm). In order to compensate the heat loss resulting from the melting of the mixture, the tapping temperature was 20-40ºC higher than the normal one. The average chemical composition of the resulting synthetic slag is shown in fig.3.
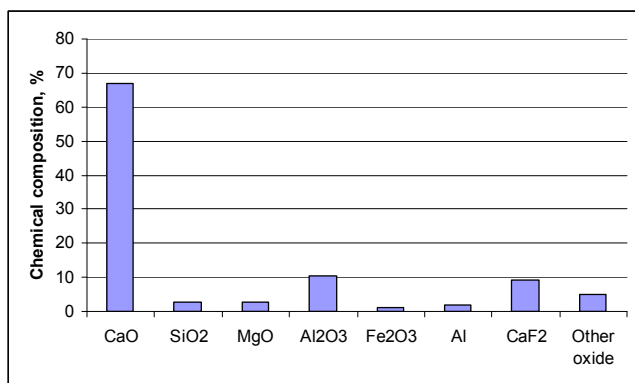

Fig.3. Average chemical composition
of synthetic slag

For all the experimental variants we collected samples from the tapped steel jet and also from the ladle, 15 min after it was filled up, as well as slag samples, right after the filling of the ladle. The analysis of the samples helped us determine the chemical composition of the steel and slag and, implicitly, we could calculate the desulphurizing degree.

In order to calculate the desulphurizing degree when treating with synthetic slags into the ladle ($\eta_{S\ ladle}$), we used the relation:

$$\eta_{S\,ladle} = \frac{S_{initial-ladle} - S_{final-ladle}}{S_{initial-ladle}} \cdot 100,\ [\%] \qquad (1)$$

$\eta_{S\ ladle}$ - steel desulphurizing degree inside the ladle, %;
$S_{initial-ladle}$ − the sulphur content in the ladle before treatment, %;
$S_{final-ladle}$ − the sulphur content in the ladle at the end of the treatment, %.

The total desulphurizing degree when treating with synthetic slags inside the ladle (η_S) is calculated by means of the relation:

$$\eta_S = \frac{S_{melting-furnace} - S_{final-ladle}}{S_{melting-furnace}} \cdot 100,\ [\%] \qquad (2)$$

η_S - total steel desulphurizing degree, %;
$S_{melting-furnace}$− the content of sulphur in the furnace at the end of steel smelting, %;
$S_{final-ladle}$ − the content of sulphur in the ladle at the end of the treatment, %.

In order to calculate the deoxidation degree when treating with synthetic slags into the ladle ($\eta_{O\ ladle}$), we used the relation:

$$\eta_{O\,ladle} = \frac{O_{initial-ladle} - O_{final-ladle}}{O_{initial-ladle}} \cdot 100,\ [\%] \qquad (3)$$

$\eta_{O\ ladle}$ - steel deoxidation degree inside the ladle, %;
$O_{initial-ladle}$ −the oxygen content in the ladle before treatment, %
$O_{final-ladle}$ − the oxygen content in the ladle at the end of the treatment, %

III. PROBLEM SOLUTION

The data obtained as a result of industrial experiments were processed in EXCEL and thus we obtained the variation of the desulphurizing degree with synthetic slags inside the ladle (fig.4) respectively the variation of the total desulphurizing degree on experimental charges (fig. 5).
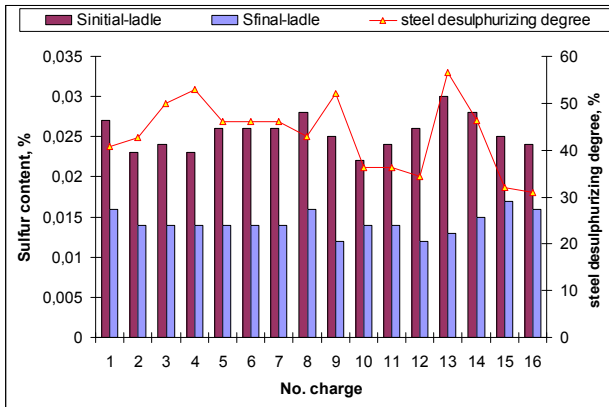
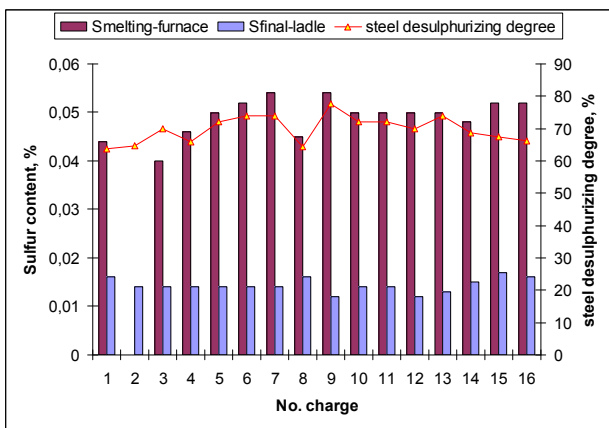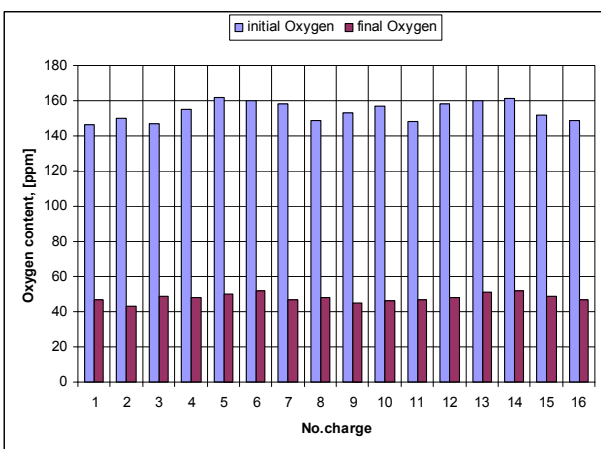**Fig.4.** Ladle steel desulphurizing degree.

Fig.5. Total steel desulphurizing degree.

Fig.6. Ladle steel deoxidation degree

Fig.7. Degree of deoxidation

Fig.8. Degree of removal of inclusions

The analysis of the diagrams shows that the degree of desulphurizing in the ladle with synthetic slags ranged within the limits 30-60%, respectively the total desulphurizing degree varied within the limits 60-80%, so the sulphur content at the end of the treatment was about 0,015%S.

The data obtained as a result of industrial experiments were processed in EXCEL and thus we obtained the variation of the deoxidation degree with synthetic slags inside the ladle (fig.6) respectively the variation of the total desulphurizing degree on experimental charges (fig. 5).
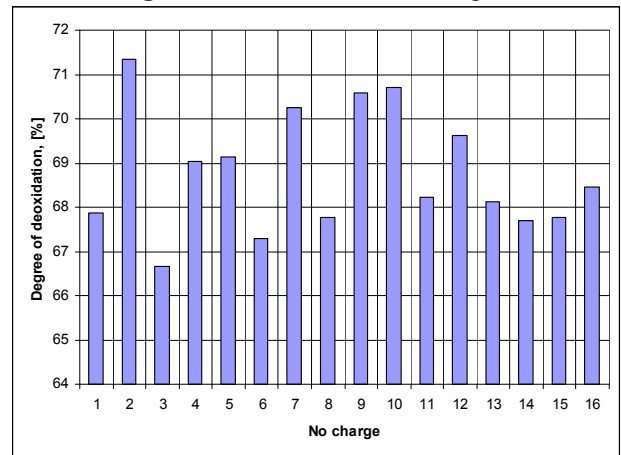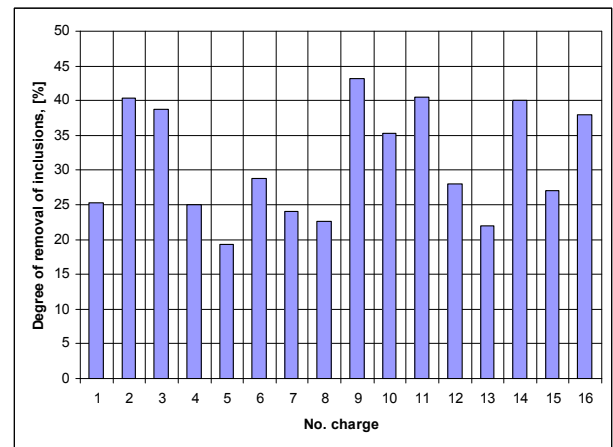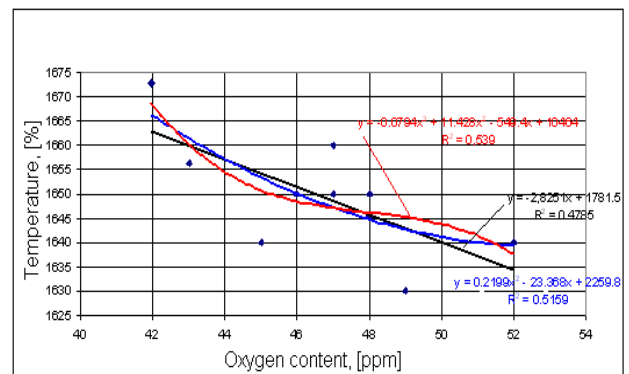

Fig.9. Oxygen variation with temperature from experimental batches

In the following the results of processing the computer program MATLAB.
Regression equations surfaces (η_S (i) in correlation with efficiency desulphurization degree (s)).

$\eta_{S(1)}= 7.9045q+0.5967CaO-1.3523$

$\eta_{S(2)}=-6.0301q^2+0.20637qCaO-1.0365CaO^2+16.2102q+108.1063CaO-2792.0353$

$\eta_{S(3)}=0.7505q^3-0.02503q^2CaO-0.019234qCaO^2-0.050357CaO^3-8.2814q^2+2.2733qCaO+6.8522CaO^2-34.3192q-303.169CaO+4341.9126$

$\eta_{S(4)}=0.81909q^4-0.093178q^3CaO+0.11538q^2CaO^2+0.034706qCaO^3+0.050862CaO^4+0.51644q3-11.6308q^2CaO^2-5.7909qCaO^2-10.687CaO^3+292.9689q^2+320.0399qCaO+840.2787CaO^2-5837.4667q-29301.0791CaO+382355.9834$

Correlation coefficient $R_{S.1}$ = 0.6395
Deviation from the regression surface S_{S1}= 7.8145
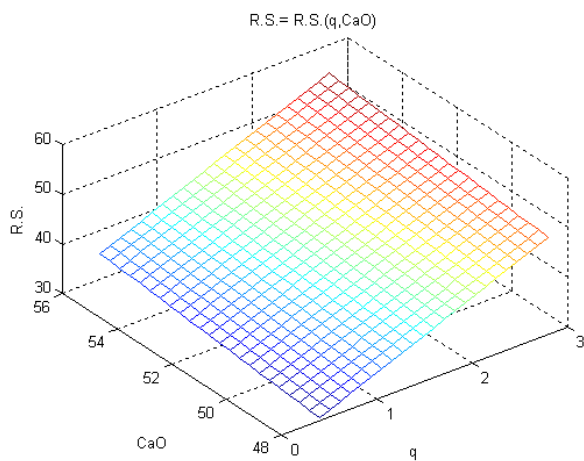Correlation coefficient $R_{S.2}$ = 0.9822
Deviation from the regression surface $S_{S.2}$ = 1.9110
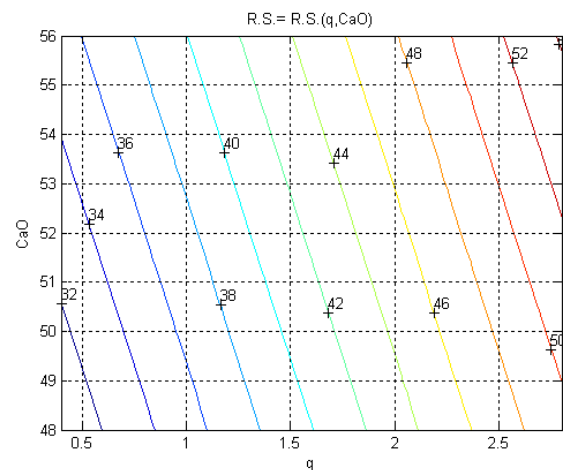Correlation coefficient $R_{S.3}$ = 0.9848
Deviation from the regression surface S_{S3}= 1.7647
Correlation coefficient $R_{S.4}$ = = 0.9917
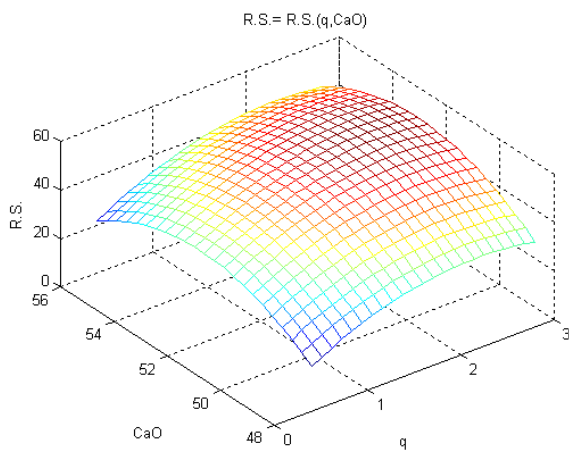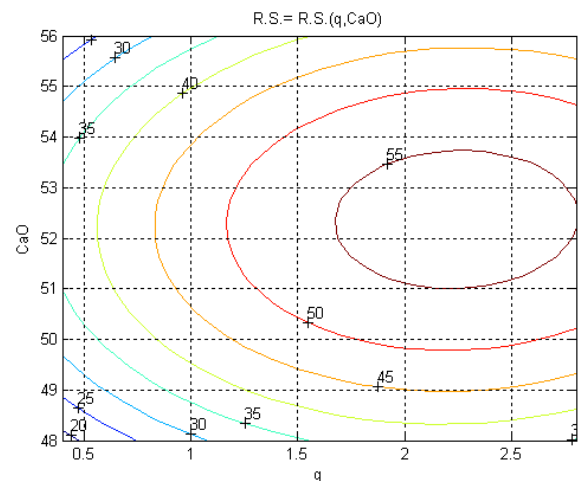Deviation from the regression surface $S_{S.4}$= 1.3053

a)   b)

Fig.10. Graphical representation of correlation $\eta_{S(1)} = f(q,CaO)$:
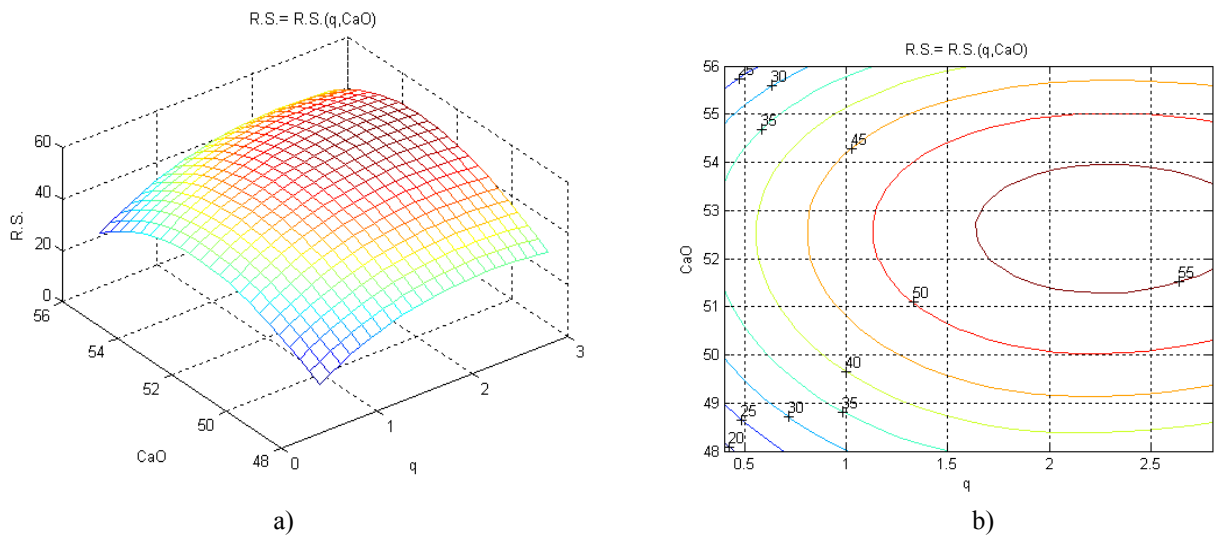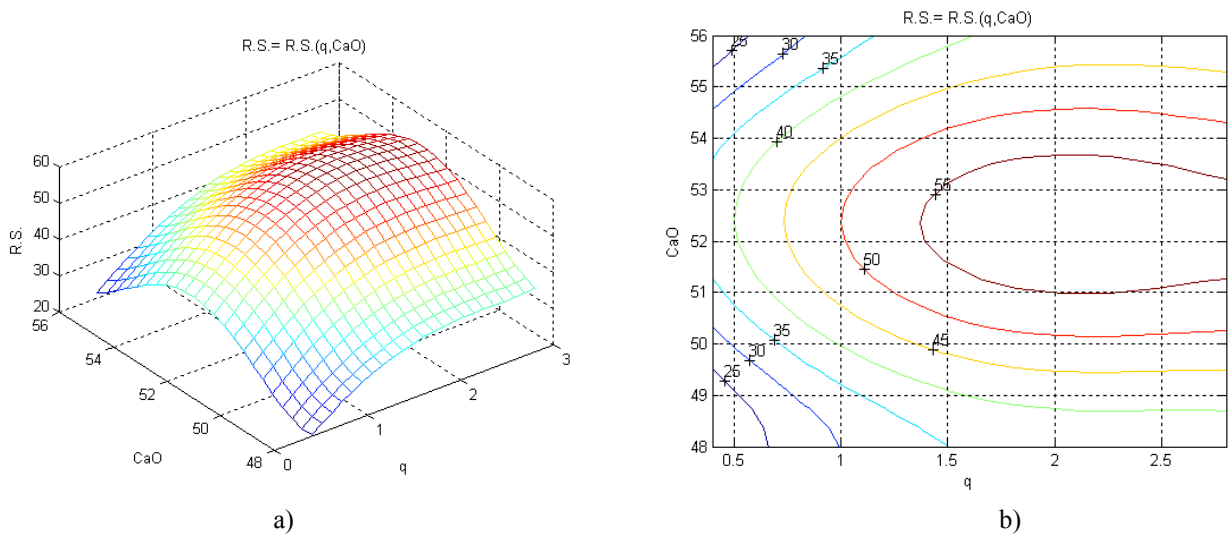a) surface; b) contour lines

a)   b)

Fig.11. Graphical representation of correlation $\eta_{S(2)} = f(q,CaO)$:
a) surface; b) contour lines

Fig.12. Graphical representation of correlation $\eta_{S(3)}$ = f(q,CaO):
a) surface; b) contour lines

Fig.13. Graphical representation of correlation $\eta_{S(4)}$ = f(q,CaO)
a) surface; b) contour lines

In the following the results representing the degree of deoxidation.

Regression equations surfaces (RO (i) in correlation with efficiency deoxidation degree (s))

$\eta_{O(1)}$ =9.5595q+0.65719CaO-9.4922

$\eta_{O(2)}$ =-5.9673q^2+0.058127qCaO-0.88098CaO^2+25.3982q+92.2249CaO-2392.9577

$\eta_{O(3)}$ =-1.6828q^3+0.084784q^{2}CaO-0.091653qCaO^2-0.054339CaO$_3$-2.4129q^2+9.3543qCaO+7.7363CaO^2-220.1836q-362.308CaO+5584.8113

$\eta_{O(4)}$ =1.4644q^4-0.19409q^{3}CaO-0.0089778q^{2}CaO^2 +0.040877qCaO^3 +0.03687CaO^4 -0.90261q^3+1.917q^{2}CaO^2-6.4304qCaO^2-7.7903CaO^3-53.3119q^2+335.2318qCaO+615.6833CaO^2-5790.5411q-21570.3208CaO+282676.3832

Correlation coefficient $R_{O.1}$ =   0.7515

Deviation from the regression surface S_{O1}= 6.8618
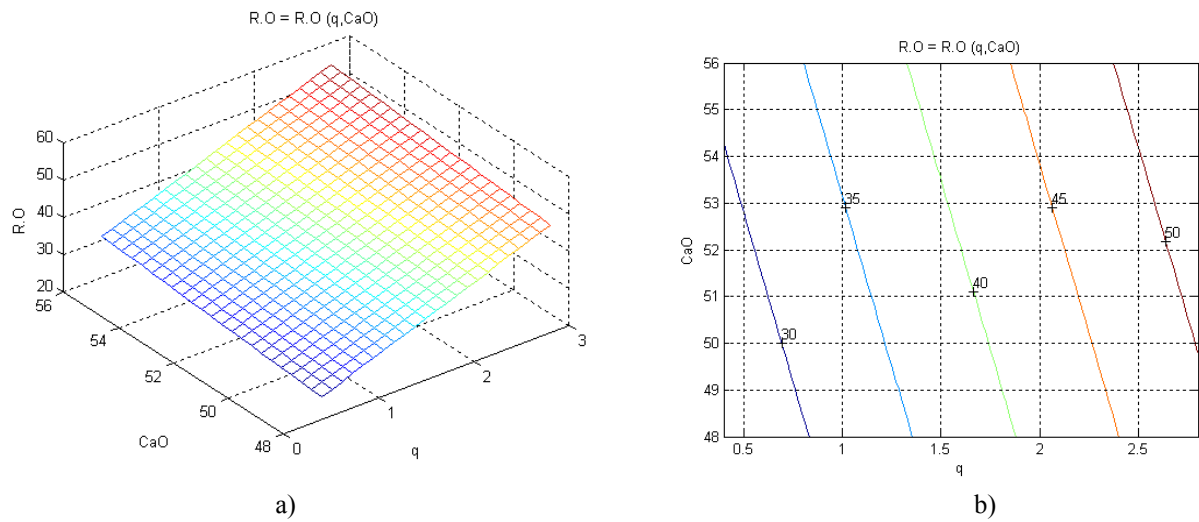
Correlation coefficient $R_{O.2}$ =   0.9858

Deviation from the regression surface S_{O2}= 1.7473

Correlation coefficient $R_{O.3}$ =   0.9909

Deviation from the regression surface S_{O3}= 1.3983

Correlation coefficient $R_{O.4}$ =   0.9951

Deviation from the regression surface S_{O4}= 1.0266

Fig.14. Graphical representation of correlation $\eta_{O(1)}$ = f(q,CaO):
a) surface; b) contour lines
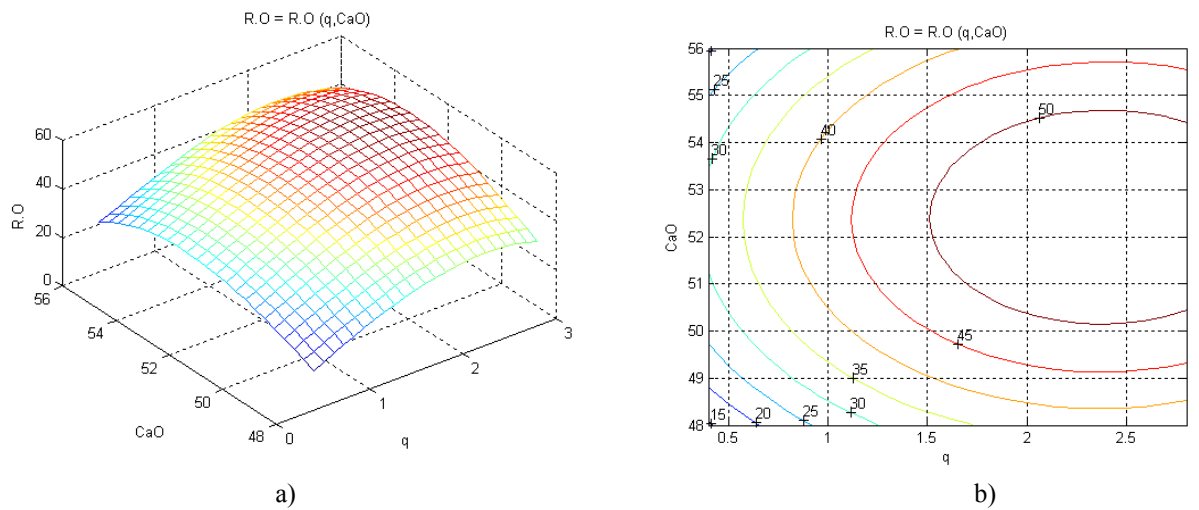
Fig.15. Graphical representation of correlation $\eta_{O(2)}$ = f(q,CaO):
a) surface; b) contour lines

Fig.16. Graphical representation of correlation $\eta_{O(3)}$ = f(q,CaO):
a) surface; b) contour lines

Fig.17. Graphical representation of correlation $\eta_{O(4)} = f(q, CaO)$:
a) surface; b) contour lines

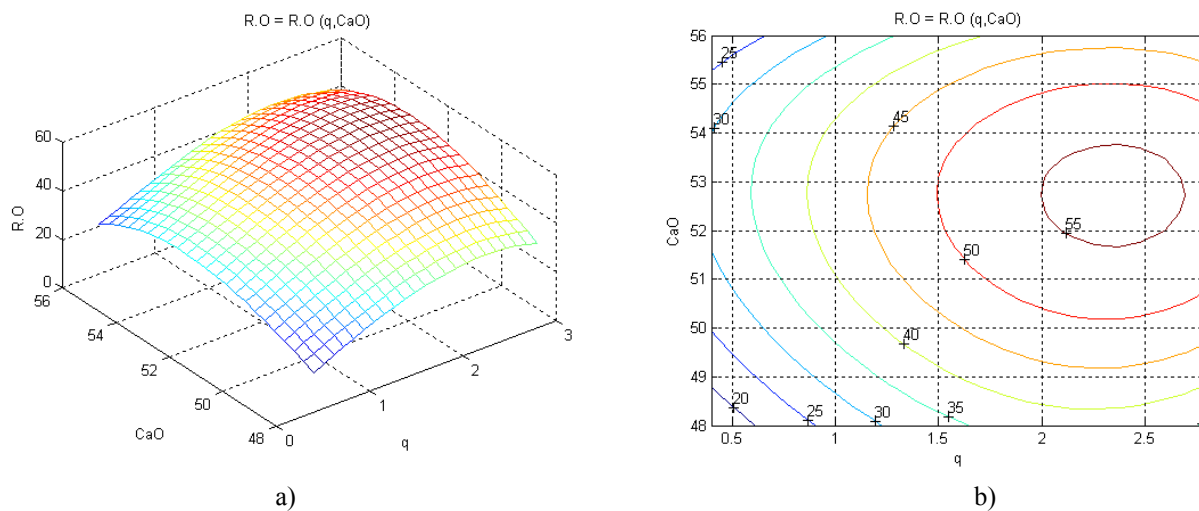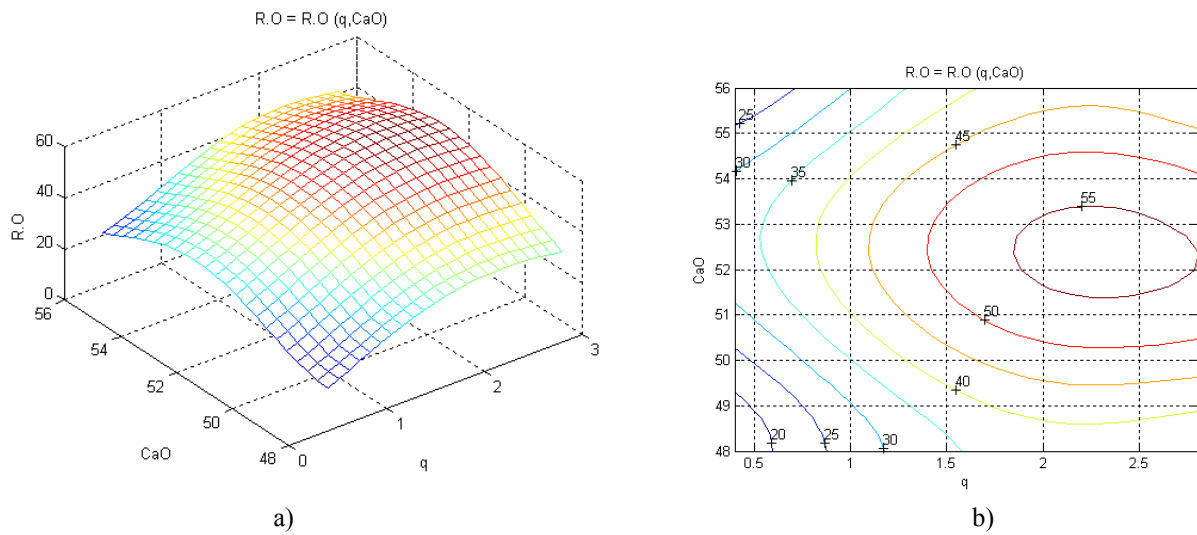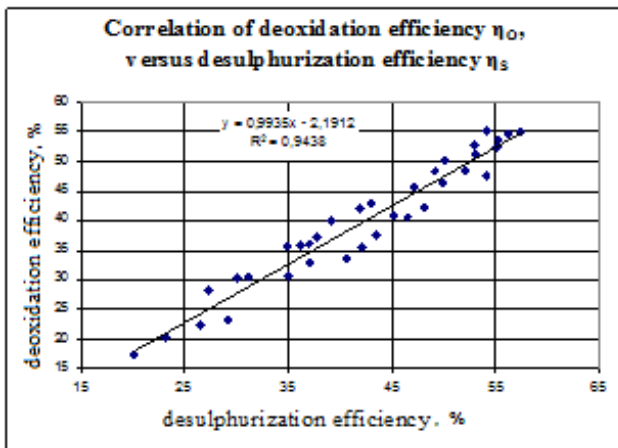**Fig.18.** Correlation of deoxidation efficiency η_O, versus desulphurization efficiency η_S

IV. CONCLUSION

The data obtained as a result of industrial experiments were processed in EXCEL and thus we obtained the variation of the desulphurizing degree with synthetic slags inside the ladle (fig.4) respectively the variation of the total desulphurizing degree on experimental charges (fig. 5).

The analysis of the diagrams shows that the degree of desulphurizing in the ladle with synthetic slags ranged within the limits 30-60%, respectively the total desulphurizing degree varied within the limits 60-80%, so the sulphur content at the end of the treatment was about 0,015%S.

Reintroducing small size and powdery industrial wastes in the economical flux, preferably if they have a low content of iron, whether they come from current technological fluxes or from waste dumps, may lead to a reduction of pollution in the air, soil and water in areas adjacent to the generators of such wastes.

Industrial implementation of the solution we suggested, consisting in using wastes in the secondary treatment of steel, leads to the following technological, economical and ecological advantages:

- the additives used to desulphurize steel allow us to obtain slag with high desulphurizing power, an important part being played by fluorides which grant a good fluidity, a highly important parameter in the slag deoxidizing capacity;
- desulphurization with synthetic slags is efficient, both in the case of using slags corresponding to the ternary system $CaO - Al_2O_3 - Me_xF$, and in the binary one: $CaO - Me_xF$;
- the quantity of slag positively influences the desulphurizing degree; thus, its increase from 4kg/t to 15kg/t leads to an increase of the desulphurizing degree by 6-9% for the electric arc furnace steel;
- the use of aluminous slag (resulting from the aluminum production lines) in the desulphurizing mixture used in the formation of the synthetic slag grants the turning into account and reintroduction in the economical circuit of dumped wastes and returning the respective area to the natural habitat.

The implementation of this technology and the use of the products we suggested leads to technological benefits (the recovery of useful elements from the wastes, the intensifying of the siderurgical processes), economical benefits (cutting down the costs with raw materials, financial benefits for the processing plants) and ecological ones (reducing the degree of pollution in the soil, air and water).

Analyzing the correlation equations and regression surfaces, both for efficiency desulphurisation and deoxidation as shows the following:

- regardless of rank correlation, in terms of correlation coefficient are representative:
- to increase the correlation equation, increase value for the correlation coefficient, and reduced value for deviations from the regression surfaces;
- for correlations of degree 2, especially for those of degree 3 and 4, the correlation surfaces allow easy determination of the relative variation (limits of variation) for independents parameters that lead to certain values required for dependent parameter (η_S or η_O);

- figure 18 shows that there is a very good correlation between the degree of deoxidation and desulphurization;
- in the technological point of view synthetic slag with reducing character acts both on sulfur and oxygen, in order to reduce them, influenced by the amount of slag used and chemical composition.

REFERENCES

[1] A. Ilie, *Research on materials high recovery from steel powder*, PhD thesis, Scientific supervisor: Prof.dr.eng. Dragomir I., University Politehnica Bucureşti, 1999.

[2] E. Ardelean, M. Ardelean, T. Heput, Research concerning the obtaining from industrial wastes of a cover powder used in steel continuous casting, *Advanced Materials Research, vol.23: Materials and Technologies*, 2007, pp.329-332.

[3] E. Ardelean, M. Ardelean, T. Heput, A. Socalici, Posibilities recycling the lime-dolomite plant dust, *Journal of Environmental and Ecology*, No.1, pp.217-226, 2010.

[4] N. Constantin, M. Nicolae, V. Geantă, I. Butnariu, *Alternative processes and technologies in steel,* Fundatia Metalurgia Romana Publishing House, 1997.

[5] I. Butnariu, M. Nicolae, N. Constantin, E. Rusu, *Metallurgical processes and technologies,* Tehnica Publishing House, 1995.

[6] I.Tripşa, C., Pumnea, *Steel deoxidation*, Tehnica Publishing House, Bucureşti, 1981.

[7] Project no. 31-098/2007: *Prevention and fighting pollution in the steel making, energetic and mining industrial areas through the recycling of small-size and powdering wastes,* Program PN2 – Consortium – CO. Responsable: Prof. dr. eng. Teodor Heput. Socalici Ana, Heput Teodor, Ardelean Erika, Ardelean Marius., Valorization of Powdery Ferrous Wastes in the Context of Sustainable *Development pp.153-157.*

[8] T. Heput, E. Ardelean, I. Kiss, Some influence of the viscosity of synthetic slags used in continuous steel casting, *Revista de Metalurgia* 41(3), Madrid, 2005, pp. 220-226

[9] C. Constantin, *Engineered to produce pig iron in blast furnace,* PRINTECH Publishing House, Bucuresti, 2002.

[10] Ghe. Amza, Z. Apostolescu, M.Iliescu, Z.Garac, S.Paise, M. Groza, Applied Ecotechnological Issues Recycling Cars *In Proceedings of WSEAS Conferences 2011/ Iasi/ DYMANOW*, pp. 33-38.

[11] E. Matei, C. Predescu, M. Sohaciu, A. Berbecaru, Method for Assessment of Potentially Pollution of Slag from Iron and Steel Industry, *In Proceedings of WSEAS Conference Greece, July 24-26, 2007, pg 22-27.*

[12] A. Socalici, T. Heput, E. Ardelean, M. Ardelean, Research regarding using the wastea with carbon content in siderurgical industry, *Journal of Environmental Protection end Ecology,* book 2, 2010, pp. 465-470.

[13] Socalici A., Heput T., Ardelean E., Ardelean M., Researches Regarding the Obtaining of Active Slag by Using Reactive Admixtures Produced from Ferrous and Basic Scrap, *In Proceedings of WSEAS Conference Timisoara, october 21-23, 2010, Selected Topics in Energy, Environment, Sustainable Development and Landscaping, pg.157-163.*

[14] Heput, T., Petre, D., Ardelean, E., Găvănescu, A., Ardelean, M.,*Researches on the viscosity of synthetic slags used in steel continous casting*, Rev. Metalurgia Internaţional, nr.2, 2002, pp.6/10

[15] Socalici A., Heput T., Ardelean E., Ardelean M., Researches Regarding the Recovery of Small and Powder Ferrous Wastes within Iron and Steel Industry, 6th IASME / *WSEAS International Conference on ENERGY &ENVIRONMENT (EE '11) , Cambridge, UK , February 23-25, 2011 pp 282-287.*