ESTIMATE OF DESULPHURIZING ABILITY OF SLAGS WITH THE USE OF INTEGRAL TESTS WHICH CHARATCERISES MELTED SLAG AS A CHEMICALLY UNIFORM SYSTEM

Kamkina L.V.[1], Togobitskaya D.N.[2] and Sokur Yu.I.[3]

[1] NMetAU, 49000 Dnipropetrovsk, Gagarina Ave., 4. Ukraine, lydmila_kamkina@ukr.net
[2] HMI named after Z.I.Nekrasov, NAS of Ukraine, 49050 Dnipropetrovsk, Academika Starodubova Sq., 1. Ukraine
[3] NMetAU, 49000 Dnipropetrovsk, Gagarina Ave., 4, Ukraine

Introduction

A special role in metal refining is paid to the melted slag, especially to ensuring its physico-chemical properties: desulphurizing ability, viscosity, surface tension. Forecasting of these properties is the objective of the present study.

Current state of the problem.

Metal desulfurization process is the most effective during the contact of metal with slag which has good portability (slag viscosity) and relative desulfurizing ability (C_S). There are several approaches to calculation of desulfurizing ability of slags. In the work [1] the options for assessing of desulfurizing ability of slags are discussed:

$$C_S = \left(P_{O_2} / P_{S_2}\right)^{1/2}(S) \qquad (1)$$

- desulphurising ability accepted by the foreign authors [2, 3].

$$C_S^{'} = a_{[O]} / f_{[S]} . (S)/[S] \qquad (2)$$

- desulphurising ability accepted by the authors [4],

$$C_C = P_{CO} / f_{[S]} . (S)/[S] \qquad (3)$$

- desulphurising ability accepted by the authors [5, 6],

where $f_{[S]}$ and $a_{[O]}$ - reactivity factor and sulfur reactivity in metal; P_{O_2} and P_{S_2} - oxygen and sulfur partial pressures; $[S]$ and (S) - sulfur content in steel and slag, respectively.

The main ways to reduce sulfur content in the melt are the use of non-sulfur charge materials, cast iron desulphurizing if it is used for steelmaking, steel desulphurization operation during its melting, out-of-furnace steel desulphurization.

Summary of the reserch basic material.

Melt desulphurization process is usually described by equations:

[FeS]+(CaO)=(CaS)+(FeO), $$\lg K_S = \lg \frac{a_{(FeO)} a_{(CaS)}}{a_{[FeS]} a_{(CaO)}} = -\frac{2047}{T} - 0.337 \quad (4)$$

[FeS]+(MnO)=(MnS)+(FeO) $$\lg K_S^{''} = \lg \frac{a_{(FeO)} a_{(MnS)}}{a_{[FeS]} a_{(MnO)}} = -\frac{4234}{T} - 0.271 \quad (5)$$

[FeS]+(MgO)=(MgS)+(FeO) $$\lg K_S^{''} = \frac{a_{(FeO)} a_{(MgS)}}{a_{[FeS]} a_{(MgO)}} = -\frac{7573}{T} - 0.337 \quad (6)$$

The numerical values of the equilibrium constants of the above reactions are indicative of the influence of free lime in slag on achieving maximum degree of sulfur redistribution from metal into slag. The following factors contribute to desulphurization of steel by slag: reduced reactivity of iron oxide in slag, increased reactivity of lime in slag, elevated temperature, decreased reactivity of sulfide compounds in slag.

In practice, the process of desulphurization is more active in a recovery period of electric melting when the metal temperature is the highest. For the intensification of this process, a high-calcium (free CaO) deoxidized white or carbide (having low iron oxide content) slag is prepared, and the higher its weight, the higher the degree of metal desulphurization.

In practice the main integral criterion of chemical reactivity of slags is considered to be basicity (B). To determine its value different ratios between the concentrations of major and acidic oxides in slag are used - starting with CaO/SiO_2 and ending with more complex than $(CaO + MgO + FeO + MnO)/(SiO_2, Al_2O_3)$. Numerous attempts to find a universal indicator of “chemical” basicity in the form of remainder or ratio of “basic” and “acid” components to the mathematically solid expression have failed.

In the works of G.I. Zhmoydin and I.S. Kulikov during the experimental study of desulphurizing ability of slag, the following expression was used:

$$C_S = L_S / f_{[S]} \tag{7}$$

where L_S is the equilibrium sulphur distribution coefficient between metal and slag.

For the forecast calculations of aluminosilicate melts the following expression is used:

$$\lg C_S = 1{,}7CaO/SiO_2 - 1.07 \tag{8}$$

(the basic composition is $CaO\text{-}SiO_2$ with the impurity of up to 30% Al_2O_3),

$$\lg C_S = 1{,}3CaO/Al_2O_3 + 1.07 - (0.04 + 0.01CaO/Al_2O_3)\cdot SiO_2 \tag{9}$$

(the basic composition is $CaO\text{-}Al_2O_3$ with the impurity of up to 30% SiO_2).

At the stage of slag analysis as a chemically uniform system which allows for the simultaneous contributions of all components is the use of optical basicity to forecast desulphurizing ability of C_S of the slag, which concept was developed in the work on glass chemistry by Duffy and Ingram and transferred into the field of studying metallurgical slags by many researchers [7, 8, 9]. It is interpreted by using the term “donor e-power” of oxygen ions in the slag which are defined by experimental spectroscopic methods in transparent slags. For other elements, optical basicity is determined by empirical dependence as a function of the electronegativity of cations by Polling scale: $\lambda_i = 0{,}74(X - 0{,}26)$, it allows representing λ of complex oxide systems as an integral parameter of the composition “compression”:

$$\lambda = \sum_{i=1}^{m} \lambda_i (v_i k_i P_i \big/ M_i)/(\sum_{j=1}^{m} v_j k_j P_j / M_j), \tag{10}$$

where v_i is the valence of the anion with the number *i*; k_i is its amount in the oxide formula; P_i is % by weight; M_i is molecular weight.

The use of optical basicity values is correct only if there is no chemical interaction between the components of the system and energy characteristics of melts formation of the inputs can be neglected. As a result, the use of this criterion provides good results for groups of slag melts identical in their composition.

Research findings.

In this work the experiment of HMI NAS of Ukraine is used for assessing desulphurizing ability of slags [10]. As integral criteria which characterize slag melt as chemically uniform system special parameters which characterize interatomic interaction in melts were used - stoichiometry indicator ρ equal to the cations (K) and anions (A) ratio, Δe - the number of electrons localized towards K-A bond, as well as the average charge Z_{K-A} in K-A bond. These parameters are used by the authors in assessing desulphurizing ability of slags as a pattern ones:

$$\lg Cs = 2.97\Delta e + 12.07\rho - 3.17Z_{(k-a)} - 2.06 \tag{11}$$

Some arguments in their rationale are close correlation of ρ and optical basicity parameter λ (Fig. 1), as well as the results of classification of refining slags used in out-of-furnace steel treatment in ladles (Fig. 2).

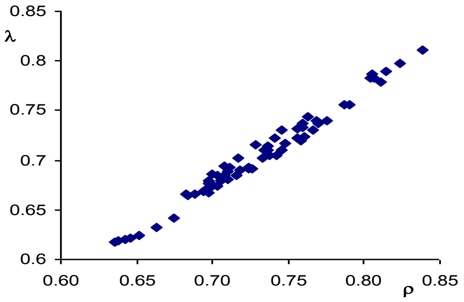


Fig. 1. Correlation between optical basicity and ρ parameter for CaO-SiO_2-Al_2O_3 system

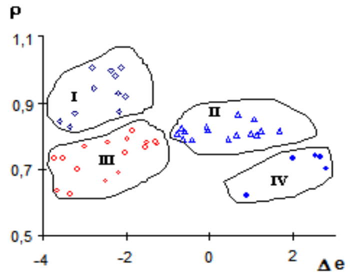


Fig. 2. Correlation between Δ*e* and ρ for synthetic refining slags

Analysis of the information available in literature about suggested refining synthetic refinery slag [11-18] (Table 1) showed that the composition of slags in zone I and III is commonly used for deep and partial desulphurization of metal, in zone II - for desulphurisation and partial dephosphorization, and in zone IV - for remelting and welding slags.

Table 1. Chemical compositions and pattern parameters of some slags for out-of-furnace treatment

Chemical composition of synthetic slag, %								Pattern parameters		Sourse
CaO	Al_2O_3	Na_2O	CaF_2 NaF	SiO_2	FeO	MgO	MnO	ρ	Δ*e*	
49	1		50					0.702	2.8	[11]
60	35		5					0.817	1.237	[12]
49	30	4.6	1	16				0.791	-1.98	[12]
45	5	9.2	10	32				0.768	-3.006	[12]
	30	9	30	32				0.627	-3.339	[12]
54	5		40	1				0.733	1.996	[12]
69	21			10				0.829	-0.074	[13]
65	20	3	10					0.866	-0.678	[14]
59	14	12	5					0.996	-2.359	[14]
10			65	20	5			0.548	-1.499	[15]
64	20		3	10		5		0.823	-0.656	[16]
55	20	5		10		10		0.874	-2.179	[17]
20	35	15		20		10		0.829	-3.362	[16]
61	5			5	20	5	4	0.929	-2.193	[17]
29	1			35	30		5	0.731	-3.726	[18]

Of course, this division is arbitrary to some extent, since it does not take into account the change in slag composition resulted from the interaction of metal in the ladle. Being guided by the taxonomy in Figure 3, one can assess in the first approximation the usefulness and direction of influence of synthetic slags chemical composition adjustments. Suggested evaluation method of desulphurizing ability of real steelmaking slags is also tested on the basis of industrial data of steel heat finishing at the limit: converter operation→ steel heat finishing in a ladle → casting. As an analysis of current melting operations which are different in mixing technology has shown, the ladle No. 36 had upgraded arrangement of tuyere plugs for more intensive mixing of melts to get the expected improvement of macro- and microstructural heterogeneity. However, statistical analysis of chemical composition of finished steel shows the change in the elements concentration in relatively wide ranges (Mn=0.36-1,57; S=0.005-0.05; P=0.011-0.041; Mn/S=12.1-240).

Figure 3 presents the integral curve of distribution of sulfur, manganese, phosphorus and Mn/S for the ladles No. 8 and No. 36 for their comparative analysis. Data of the analysis demonstrate that steel production in the ladle No. 36 has a higher ratio of Mn/S providing homogeneous macro- and microstructure of the finished product. It follows from Figure 4 that converter slags has a higher desulphurizing capacity than that of LF ladle furnace due to higher charge sulphur content.

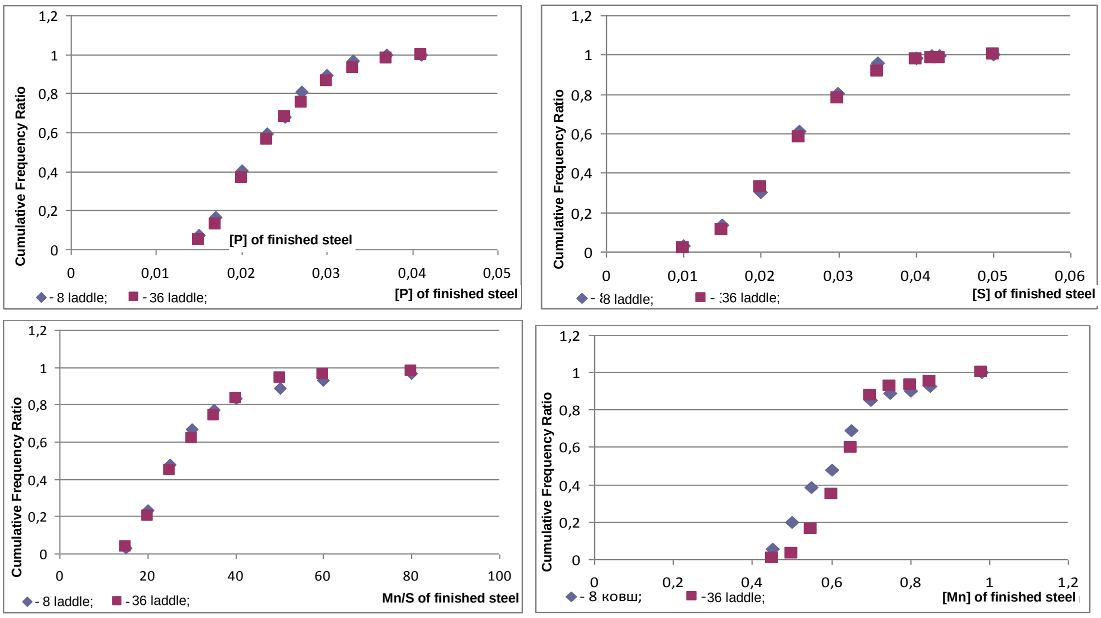
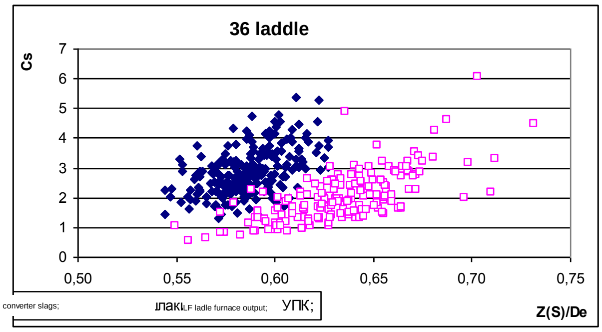


Fig. 3: Integral distribution curves of finished steel components of ladles No. 8 and No. 36



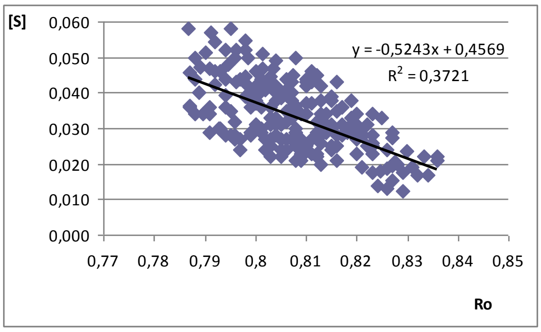


Fig. 4:
The influence of the charge state of sulfur in slag on its desulphurizing ability

Fig. 5:
Dependence of sulfur content in finished steel on slag stoichiometry coefficient

Stoichiometry coefficient R_o estimates in the most complete manner slag desulphurizing ability. This value is recommended to be used for the preparation of desulfurator slag which ensures the required level of sulfur content in steel at all melting limits. For example, as can be seen from Fig. 5, to ensure sulfur content in steel at the level of $S \leq 0.03$ it is necessary to prepare slag with stoichiometry coefficient of $R_o \geq 0.81$.

In the final period of converter smelting and the ratio of basicity and oxidation of steel is crucial for metal desulphurization. Figure 6 demonstrates a cartogram of deviations of the sulphur content in steel from $CaO/SiO_2/Al_2O_3$ ratios and of slag oxidation ($FeO+MnO$), the optimal values are selected for slag preparation that provides the appropriate level of sulfur.

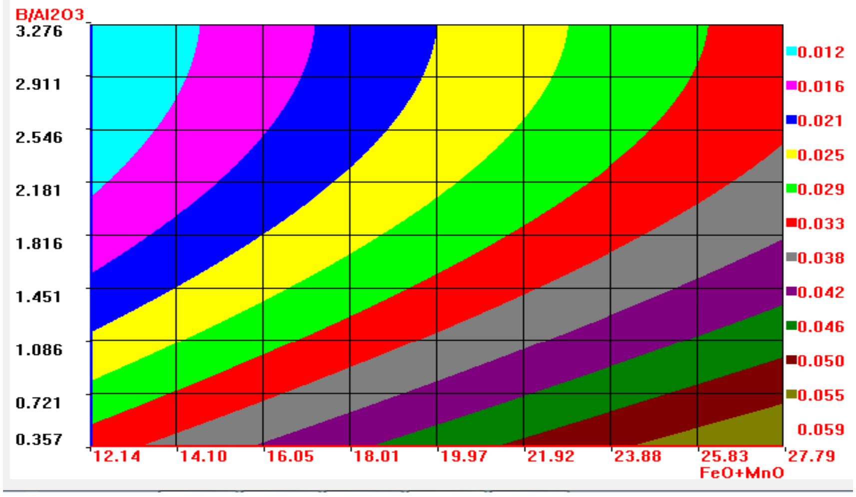


Fig. 6: Cartogram of sulfur reaction in steel from its oxidation and $CaO/SiO_2/Al_2O_3$ ratio

4. Conclusions

1. The analysis of available approaches to evaluation of desulphurizing ability of steelmaking slags is carried out. For the estimation of desulphurizing ability of melts it is recommended to use the components interaction parameters and the established physic-chemical criteria.
2. The method of classification of synthetic slags refining abilities on the basis of interatomic interaction parameters. Based on the analysis of current melts in steel production, the method their statistical analysis and the use of interatomic interaction parameters for estimation of desulphurizing ability of real slags and selection of optimal desulfator slag is provided.

References

[1] Zhmoydin G.I., Sulphur removal ability and sulfur content in slags
[2] /G.I. Zhmoydin // Fam. Academy of Sciences of USSR. Metals. - 1982. – No. 2. –pp. 3-9.
[3] Fincham C.J., Sulphur in silicate and aluminate glags. - 1954, 223, Pp. 40-60.
[4] Abraham K.P., Sulphide capacities of silicate melts. - 1960, 196, Pp. 313-317.
[5] Carter P.T., Thermodynamycs of slag systems. - 1957 ,185, Pp. 54-56.
[6] Sharma R.A., Richardson F.D., Activities of manganese oxide, sulfide capacities, and activity coefficients in aluminate and silicate melts, Transactions of the metallurgical society of AIME, Volume 233, August 1965, Pp. 1586-1592.
[7] Schenk H., 1960, Pp. 386-390.
[8] Melnik S.G., Sulfide content of active refinery slags in Bessemer steel production with the application of solid slag mix/ S.G. Melnik // Metal and foundry of Ukraine. - 2000. – No. 3-4. – Pp. 30-31.
[9] Kazachkov E.A., The structure of melted slags and their physical properties (dedicated to the 110th anniversary of P. Gerasimenko) / E.A. Kazachkov // Metallurgical and metal mining industry. - 2010. – No. 6. – C. 28-30.
[10] Togobitska D.N., Fundamental and applied problems of the steel industry, Sat saince. work., 2011, Vol. 24., Pp. 136–144.
[11] Togobitska D.N., The 10th Russian seminar “Modelling of metallurgical melts”. – Ekaterinburg. - 2012. – Pp.49-50.
[12] Slag forming compound. USSR №497344.
[13] Slag forming compound for liquid metal treatment. USSR №553295.
[14] Abstract Journal 1976. A149.
[15] The compound of fluxing agent for liquid metal desulphurization. Patent. Great Britain No. 1482458.
[16] Synthetic slag for steel refining. USSR №280508.
[17] Slag for steel fining. USSR №443913.
[18] Complex slag-forming material. USSR №536232.
[19] Slag for out-of-furnace refining. USSR №5300