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THE INFLUENCE OF CHEMICAL COMPOSITION OF STEEL ON STEEL DESULPHURIZATION

WPŁYW SKŁADU CHEMICZNEGO STALI NA PROCES ODSIARCZANIA

The steel desulphurization in ladle furnace depends on temperature, oxygen and sulphur content in the steel, but mainly on chemical composition and physical properties of slag. Necessary requirement for effective desulphurization is also minimum content of easily reducible oxides in the slag. There are many correlations for expression of slag desulphurization capability, where their functional dependency on each other can be found, mainly between sulphur distribution coefficient, optical basicity, basicity, sulphide capacity, desulphurisation potential of slag and also calcium - aluminate ratio of oxides in slag or content of easily reducible oxides in slag. This work presents statistical and graphical correlation between manganese and slag parameters using the set of approximately 768 heats and based on these, the optimal parameters for slag desulphurization capability are expressed especially for steel grades internally marked as OR1, OR3 in Železiarne Podbrezová, a.s. Steel grades OR1 and OR3 were chosen because of difference in manganese content with similar chemical composition of other elements. The MnO content in the slag is one of the most important parameters. Despite the higher scatter of obtained values, the distribution coefficient of sulphur (Ls) is one of the wide range of parameters for whom exists very close dependence on MnO content in slag.

Keywords: steel desulphurization, ladle furnace, sulphur distribution coefficient, slag

Odsiarczanie stali zależy od temperatury, zawartości tlenu i siarki w stali, ale przede wszystkim od składu chemicznego i właściwości fizycznych żużla. Dla skutecznego odsiarczania konieczna jest również minimalna zawartość łatwo redukowalnych tlenków w żużlu. Istnieje wiele zależności do wyrażenia zdolności żużla do odsiarczania, dla których można znaleźć funkcyjną zależność pomiędzy współczynnikiem podziału siarki, optyczną zasadowością, zasadowością, zawartością siarczków, potencjałem odsiarczania żużla, a także stosunkiem tlenków wapnia do glinu w żużlu lub zawartością łatwo redukowalnych tlenków w żużlu. W pracy przedstawiono statystyczną i graficzną korelację pomiędzy zawartością manganu i parametrami żużla uzyskaną z około 768 wytopów, i na ich podstawie optymalne parametry zdolności żużla do odsiarczania przedstawione zostały dla stali wewnętrznie oznaczonych jako OR1, OR3 w Železiarne Podbrezová, a.s. Gatunki stali OR1 i OR3 zostały wybrane ze względu na różnice w zawartości manganu przy podobnej zawartości innych składników. Zawartość MnO w żużlu jest jednym z najważniejszych parametrów. Mimo większego rozrzutu uzyskanych wartości, współczynnik podziału siarki (Ls) jest jednym z wielu parametrów, dla których istnieje bardzo ścisła zależność od zawartości MnO w żużlu.

1. Introduction

Correct and optimal slag management in the ladle furnace allows effective production of steel with required chemical composition and properties [1]. Very significant influence of MnO content on the desulphurization capability of ladle slag could be observed during the steel desulphurization [2]. The analysis of this work is based on the parameters from mini-mill, where steel is produced in electric arc furnace, then refined in the ladle furnace and finally casted in the continuous casting machine [3, 4, 5].

2. Results and their analysis

Steel with basic chemical composition shown in **Table 1** was chosen in order to the MnO influence on slag desulphurization capabilities.

Many parameters of slag and their mutual relations were investigated [6]. The binary basicity and the quaternary basicity were calculated:
binary basicity:

$$B_1 = \frac{(CaO)}{(SiO_2)} \tag{1}$$

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quaternary basicity

$$B_2 = \frac{(CaO) + (MgO)}{(SiO_2) + (Al_2O_3)} \quad (2)$$

The relationships for the calculation of other parameters are presented in [7-13]. **Table 2** was constructed based on the statistical treatment of the slag composition and its parameters.

TABLE 1

Basic composition of investigated steel internally marked as OR1, OR3

Element	C	Mn	Si	P	S	Al	Ti	Cr
Content [%] OR1	0.08-0.1	0.4-0.5	0.15-0.25	0.025	0.02	0.02-0.03	0.01	0.15
Content [%] OR3	0.17-0.2	1.15-1.3	0.15-0.35	0.025	0.02	0.02-0.03	0.01	0.3

TABLE 2

Composition and parameters of slag samples from ladle furnace

Slag constituent	Average content [%]		Parameter	Value [-]	
	OR1	OR3		OR1	OR3
CaO	60.33	59.64	R – desulphurization level	0.47	0.61
Al_2O_3	21.39	20.19	OB – optical basicity	0.83	0.83
MgO	8.56	8.23	CA – calcium – alumina ratio	2.84	2.97
MnO	0.27	0.68	Ls – sulphur distribution coefficient	22.22	26.18
FeO	0.89	0.81	SO – sum of easily reducible oxides	1.21[%]	1.53[%]
SiO_2	8.92	10.38	B_1 – binary basicity	6.99	5.99
(S) slag	0.29	0.31	B_2 – quaternary basicity	2.28	2.23
			DP – desulphurization potential	1.82	2.88
			Cs – sulphide capacity	0.08	0.06

It results from Fig. 1 and Fig. 2 that sulphur distribution coefficient exceeded value 50 in exceptional cases, while average value were: Ls = 22.22 for grade OR1 and Ls = 26.18 for grade OR3. It is evident that sulphur distribution coefficient decreases with increase of easily reducible oxides concentration in the slag. Presented graphical relationships were created and calculated using statistical program StatSoft Statistica 7.0. Red curves within all the graphs are quadratic polynomial functions.

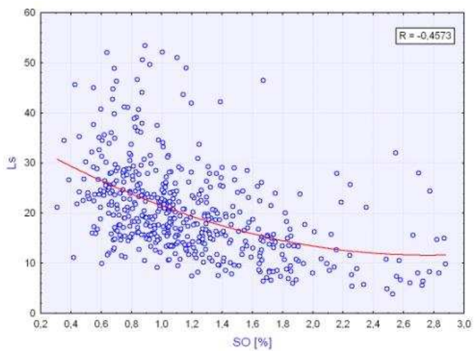

Fig. 1. Relation between sulphur distribution coefficient and the sum of easily reducible oxides SO (539 heats, steel grade OR1)

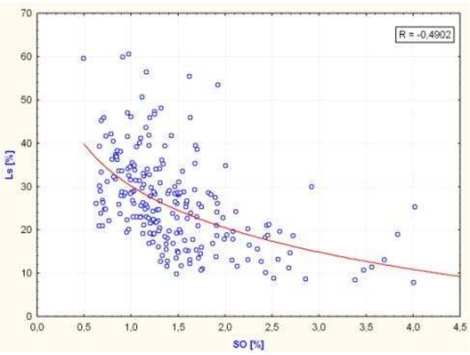

Fig. 2. Relation between sulphur distribution coefficient and the sum of easily reducible oxides SO (229 heats, steel grade OR3)

Significant influence of MnO on the sulphur distribution coefficient was revealed for both steel grades. Higher contents of MnO in the ladle slag were observed for OR3 grade production, which was caused by higher contents of Mn in OR3 grade (1.15-1.3% Mn) as compared to OR1 grade (0.4-0.5% Mn), see Fig. 3 and Fig. 4.

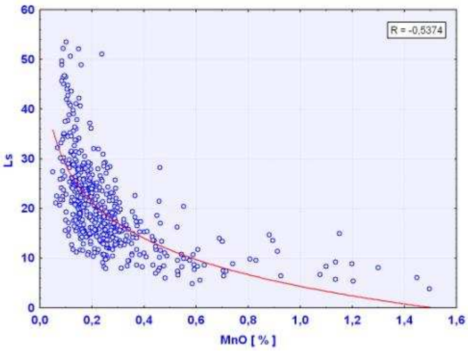

Fig. 3. Relation between sulphur distribution coefficient and MnO content in slag (539 heats, steel grade OR1)

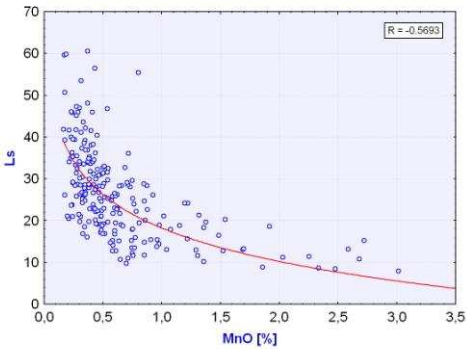

Fig. 4. Relation between sulphur distribution coefficient and MnO content in slag (229 heats, steel grade OR3)

Manganese distribution between slag and steel can significantly affect the steel oxidation [14]. This can be shown as a relation between MnO/Mn and sulphur distribution coefficient, presented in the Figure 5, 6. Especially strong influence of manganese distribution is visible in the region (MnO)/[Mn]<1 [15].

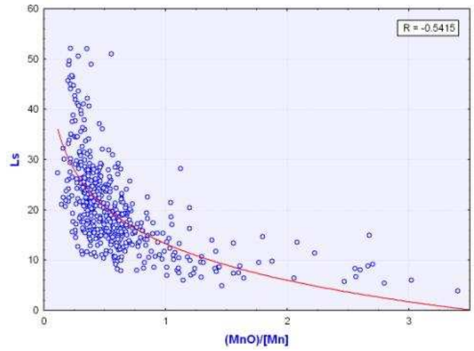

Fig. 5. Sulphur distribution coefficient as the function of Mn distribution between slag and steel, steel grade OR1

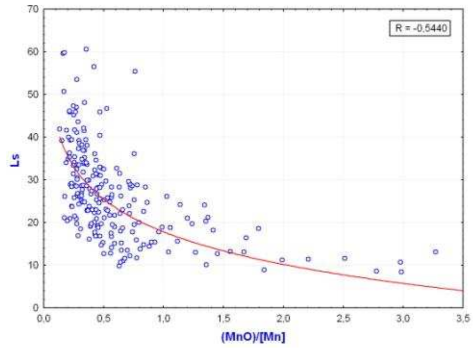

Fig. 6. Sulphur distribution coefficient as the function of Mn distribution between slag and steel, steel grade OR3

The dependence exists also between MnO and FeO contents in slag [16, 17]. There is a visible relationship between manganese distribution ratio and a FeO content in the slag despite the relatively low value of R as can be seen in Fig. 7. Distribution coefficient of manganese is increasing with FeO content in the slag. When FeO content of the slag is increasing, it results in decline of manganese content in the steel.

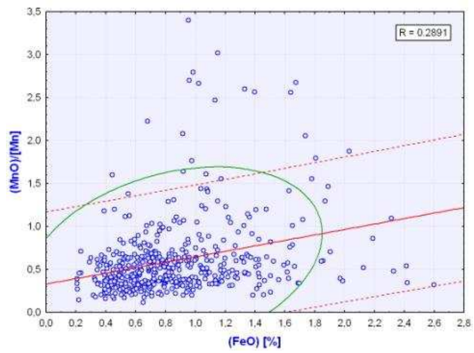

Fig. 7. Distribution of Mn between slag and steel as the function of FeO content in slag (Steel grade OR1)

The green prediction interval ellipse shows the area where are 95% of all points. Two red dashed lines showing the confidence interval for the regression line and confidence interval around the regression line are shown for the regression line.

From the data presented in Fig. 7 the linear equation describing the relationship of sulphur distribution ratio and MnO-content in the slag was evaluated:

$$L_s = 26.8811 - 24.6379(\%MnO) \quad (3)$$

The average absolute error for this equation was found to be 57.82%, so the accuracy of this equation is 57,82%. This is relatively low accuracy, which is mainly caused by:

– different mass of slag which overflowed from EAF to the LF in particular heats,
– too short process time in LF – approximately 20 minutes, which was insufficient to reach the equilibrium between slag and metal, in contrary to converter process.

3. Conclusions

Based on given data, optimal values of slag parameters for steel grades OR1 and OR3 according to the best desulphurization in the ladle furnace was formulated, see Table 3. It can be very complicated to respect these parameters in steelmaking practice, but in principle it is possible to reach them [19].

TABLE 3
Optimal parameters of desulphurization slag for steel grades OR1 and OR3

Parameter	Steel grade OR1	Steel grade OR3
Binary basicity B_1	8	6.17
Quaternary basicity B_2	2.4	2.3
Calcium-alumina ratio CA	2.8	3.03
Sum of easily reducible oxides SO	<1.5%	<2%
Sulphur distribution coefficient Ls	58	38
Sulphide capacity Cs	0.18	0.07
Content of MnO	<0.3%	<0.8%
Desulphurization potential DP	4.55	4.32
Optical basicity OB	0.81-0.86	0.83-0.86

The best results of desulphurization were reached at the MgO-content: 10.54% in average for grade OR1 and 8.45% in average for grade OR3. Very strong effect of easily reducible oxides ($FeO, Fe_2O_3, MnO, P_2O_5$) on the slag desulphurization ability was confirmed too.

The best results of desulphurization were reached in the SiO_2-content: 7.65% in average for grade OR1 and 9.94% in average for grade OR3. The rank of individual factors affecting the sulphur distribution coefficient L_s was formulated based on the shown figures and calculated relations of R^2, Table 4 and Table 5.

The most important is influence of MnO in slag with value R^2=28.88% for grade OR1 and R^2=32.41% for grade OR3, what is confirmed by Figure 5 and Figure 6.

The second most important oxide under determination coefficient R^2 for grade OR1 is FeO with the value of R^2 = 9.2% and for grade OR3 it is Al_2O_3 with a value of R^2 = 7.15%, which further emphasizes the effect of MnO on the partition coefficient of sulphur.

TABLE 4
The order of individual factors affecting the sulphur distribution coefficient Ls for steel grade OR1

Rank	Factor	R^2[%]
1	MnO	28.88
2	FeO	9.2
3	Temperature	2.97

TABLE 5
The order of individual factors affecting the sulphur distribution coefficient Ls for steel qrade OR3

Rank	Factor	R^2[%]
1	MnO	32.41
2	Al_2O_3	7.15
3	P_2O_5	5.24

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