

# THERMODYNAMICS OF $\text{CaO}(\text{BaO})\text{-Al}_2\text{O}_3(\text{SiO}_2)\text{-CaCl}_2(\text{CaF}_2, \text{BaF}_2)$ MOLTEN FLUXES IN PROCESS SIMULTANEOUS DEPHOSPHORIZATION AND DESULPHURIZATION OF IRON- CARBON MELTS.

I.A. MINAEV, V.T. BURTSEV

## Abstract

Selection of the fluxes for simultaneous dephosphorization and desulphurization of a pig iron require fundamental understanding of the processes or phenomenon, which define the thermodynamical forces are forming the slag capacity for sulphur or phosphorus. As a main for the method election of the sulphide or phosphide capacity discription we focus on the thermodynamical properties of fluxes as ionic melts. For the processes discription on basis of the experimental data the phosphid and phosphate capacity calculation has been used. It has been suggested that the influence of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaF}_2$  and  $\text{BaF}_2$  additions on the degree of dephosphorization is due to oxygen, aluminate and silicate ions concentration change. The experimental study of phosphorus and sulphur transfer from iron-carbon melt into fluxes has been carried out by separate pendant drop method and in industrial scale. The relationship between theoretical optical basicity and phosphorus phosphide or phosphate capacity and temperature was discussed.

**1-Moscow State Steel & Alloys Institute-Technology University, Leninsky prt.4, Moscow 117936, Russia.**

**2-Institute of Metallurgy of Russia Academy of Science Leninsky prt.49, Moscow 117911, Russia**

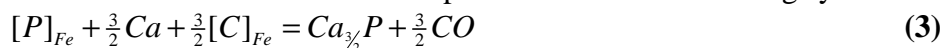
## Phosphide capacity.

On the basis of the preliminary thermodynamic analysis we have come to the conclusion that the dephosphorization of pig iron by fluxes of  $\text{CaO} - \text{CaCl}_2 - \text{Al}_2\text{O}_3$  system is performed according to the phosphide mechanism [1]. The chemical analysis show that P presence in slag as  $\text{Ca}_3\text{P}_2$ . The mass-spectrometric analysis show a low partial oxygen pressure ( $10^{-13} \div 10^{-15}$  Pa) at 1600 °C. The index of slag dephosphorating ability in the reducing atmosphere is phosphide capacity which is introduced by analogy with phosphate capacity for the following reaction mechanism



$$C_{(P^{3-})} = \frac{(\% P) \cdot P_{O_2}^{3/4}}{P_{P_2}^{1/2}} = K_1 \frac{a_{(O^{2-})}^{3/2}}{f(P^{3-})} \quad (2)$$

The equilibrium of the reaction is studied in our experiments on the metal-slag system:



The thermodynamic data of this reaction can be obtained from following equations [2] :

$$\frac{1}{2} P_2 = [P]_{Fe} : \Delta G_{10} = -29200 - 4,6T, [6] \quad (4)$$

$$\frac{3}{2} [C]_{Fe} + \frac{3}{4} O_2 = \frac{3}{2} CO_2 : \Delta G_{11} = -49650 - 15,788T, [7] \quad (5)$$

If the slag melt is saturated with  $\text{CaO}$  and the metallic one with carbon then  $a_c = 1$  and  $a_{CaO} = 1$ . Then phosphide capacity is defined by the equation:

$$C_{(P^{3-})} = \frac{K_{10}}{K_{11}} \cdot \frac{(\%P)P_{CO}^{3/2}}{[\%P]f_{[P]}} \quad (6)$$

Such interpretation gives a possibility to determine phosphide capacity directly from thermodynamic data ( $K_4$ ,  $K_5$ ,  $f_{[P]}$ ) and experimental data ( $P_{CO}$ ,  $[\%P]$ ,  $(\%P)$ ). The  $f_{[P]}$  value in our experiment have been derived for each pig-iron melt with take into account of Vagner parameters:  $\lg f_{[P]} = \sum e_P^{(i)} [\%i]$ .

The rate of P and S mass transfer from pig iron (with initial contents of P - 0,28%, S - 0,035%) into CaO–CaCl<sub>2</sub> fluxes with small addition of Al<sub>2</sub>O<sub>3</sub> (7 - 20 mol.%) has been studied by separate pendant drop method (in quasi-weightlessness conditions).

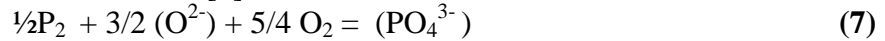
The kinetic regularities and the thermodynamic characteristics of the studied processes has been obtained, and it is presented on fig 1, 2. On fig.1 it is displayed the results of the industrial process in a 100 t ladle. The possibility of simultaneous high dephosphorization and desulphurization has been found. The degree of dephosphorization of the pig iron containing % weight: C 4,0-4,5; P 0,074-1,4; S 0,008-0,35 by mixture of optimal composition made up 75%.

The value of  $C_{(P^{3-})}$  obtained from an experimental data of the table 1 and fig.2 for slags of CaO–CaCl<sub>2</sub>– Al<sub>2</sub>O<sub>3</sub> system was permitted to construct the relation between  $\lg C_{(P^{3-})}$  and optical basicity at 1600 °C as represented on fig.3.

The extremal value of phosphide capacity logarithm was obtained for the slag of CaO – CaCl<sub>2</sub> system (CaO - saturated slag without Al<sub>2</sub>O<sub>3</sub> ) with 33% mol CaO,  $C_{(P^{3-})} = -9,69$ .. Decrease of dephosphorization along with increase of Al<sub>2</sub>O<sub>3</sub> content may be explained by aluminate-ions AlO<sub>2</sub> formation and decrease of oxygen activity in the flux.

#### Phosphated capacity.

Some author stated that phosphate capacity is a more excellent measure of the dephosphorization property of a slags. In recent study the dephosphorization have been described by the equilibrium of reaction[3]:



$$K_P = \{ (PO_4^{3-} \%) / P_{P_2}^{1/2} P_{O_2}^{5/4} \} (f_{PO_4^{3-}} / a_{O_2}^{3/2}) = C_{PO_4^{3-}} (f_{PO_4^{3-}} / a_{O_2}^{3/2}) \quad (8)$$

The phosphate capacity was derived from the equilibrium value of phosphorus in slag and partial pressure  $P_{P_2}$  , which was derived from equilibrium constant of reaction:

$$\frac{1}{2}P_2 = [P], \Delta G_9^0 = -125087 + 0,54T \quad (9)$$

The  $P_{O_2}$  was derived from experimental electrochemical measurement. The used slags characteristic and the results of calculations using experimental and theoretical data is represented in the table 1. Application of the theoretical optical basicity to characterization of the dephosphorization property for a wide range of metallurgical slags stated by Bergman and Gustafsson [4,5]. Theoretically the optical basicity of a slag is a measure of the electron donor power of the slag oxygen and empirically correlated to the Pauling electronegativity of the cation. But it is contrary to the thermodynamic conception of the theory of ionic solution. For example, the equilibrium phosphorus contents in slag are increase due to addition to slag of a fluoride or chloride compounds. According Samarin-Shvarcman-Temkin theory of a dilute ideal ionic solution the effect occurs due to oxygen activity and mole fraction decrease [6]. In the frame of the concept of optical basicity is not possible to reflex this fact: the experimental data has a considerable deviation from a line fitting [7,8].

Taken into account the discussed aspects of the ionic dilute solution theory and the thermodynamic reason of a slags phosphorus capacity change due to addition to slags a fluorine and chlorine contained compounds it may be offered the following. The value of optical basicity, with purpose to relate to slag composition, may be written as difference between the optical basicity of cation and anion formed oxides. In recent paper this “effective” basicity ( $\Lambda_{ef}$ ) is then derived as:  $\Lambda_{ef} = \sum \Lambda_C X_C - \sum \Lambda_A X_A$  (where indexes are relating to: C-cation, A – anion forming oxides). In this case  $\Lambda_{ef}$  may be negative value for slags with big  $Al_2O_3$  content. The results displayed on fig.3, 4 and its are showing the better correlation to linear function. For slags not contained  $Al_2O_3$  and  $SiO_2$  the value  $\Lambda_{ef}$  automatically is transforming into traditional optical basicity

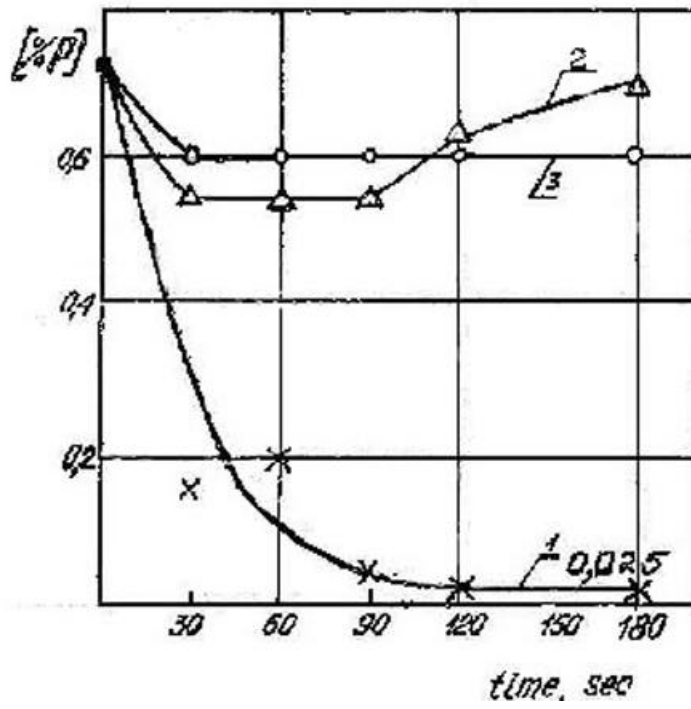
Considerable massive of the dephosphorization data [7,8,9] for fluorine contained slags at the temperature range 1180 – 1640°C allow to calculate a slag phosphate capacity related to temperature and theoretical optical basicity. Using the sets of Burtsev data for slag composition showed in table 2 and Nassaralla [9], and Sano [7] data for computer calculation (program SURFER Access.system) it has been obtained the results displayed on fig.5. Such interpretation of data allow to composed the dephosphorization fluxes on more reasonable basis.

## References

1. Minaev, Y.A.; Burtsev, V.T.; Bajtenev, N.A.; Abisev, G.D.; Izv. Vuz. Chernaya Metallurgia {1989).No.7, p.1.
  2. Kubashevsky, O.; Alcock, K.B.; Metallurgical Thermochemistry, Moscow, Metallurgia Ed., 1982.
  3. Wagner, C.; Met. Trans. 6B (1975) No.9, p.405.
  4. Bergman, A.; steel. Res. 61 (1990) No.9, p.347
  5. Bergman, A.; Gustafsson, A.; 3<sup>rd</sup> Int. Symp. on Met. Slags and Fluxes, Glasgow, 27-29 June 1988.
  6. Samarin, A.; Shvarcman, A.; Temkin, A.; Acta Phisikochemica USSR 20 (1945), p.421.
  7. Sano, N.; 4<sup>th</sup> Int. Conf. On Molten Slags and Fluxes, Tokio, Senday, ISIJ (1992), p.179.
  8. Burtsev, V.T.; Izv. RAS, Metals (1995) No.4, p.9.
  9. Nassaralla, C.; Fruehan, R.J.; Min, D.J.; Met. Trans. 22B (1991) No.2, p.33.
- Paper No. 0-2-383

<i>N</i>	<i>CaCl<sub>2</sub></i>	<i>CaO</i>	<i>SiO<sub>2</sub></i>	<i>MgO</i>	<i>Al<sub>2</sub>O<sub>3</sub></i>	<i>%mol</i>
1	68	33	—	—	—	
2	48	20	20	36	8,3	
3	48	50	22	—	—	

Fig.1. Kinetics of dephosphorization and desulphurization of the hig-iron.



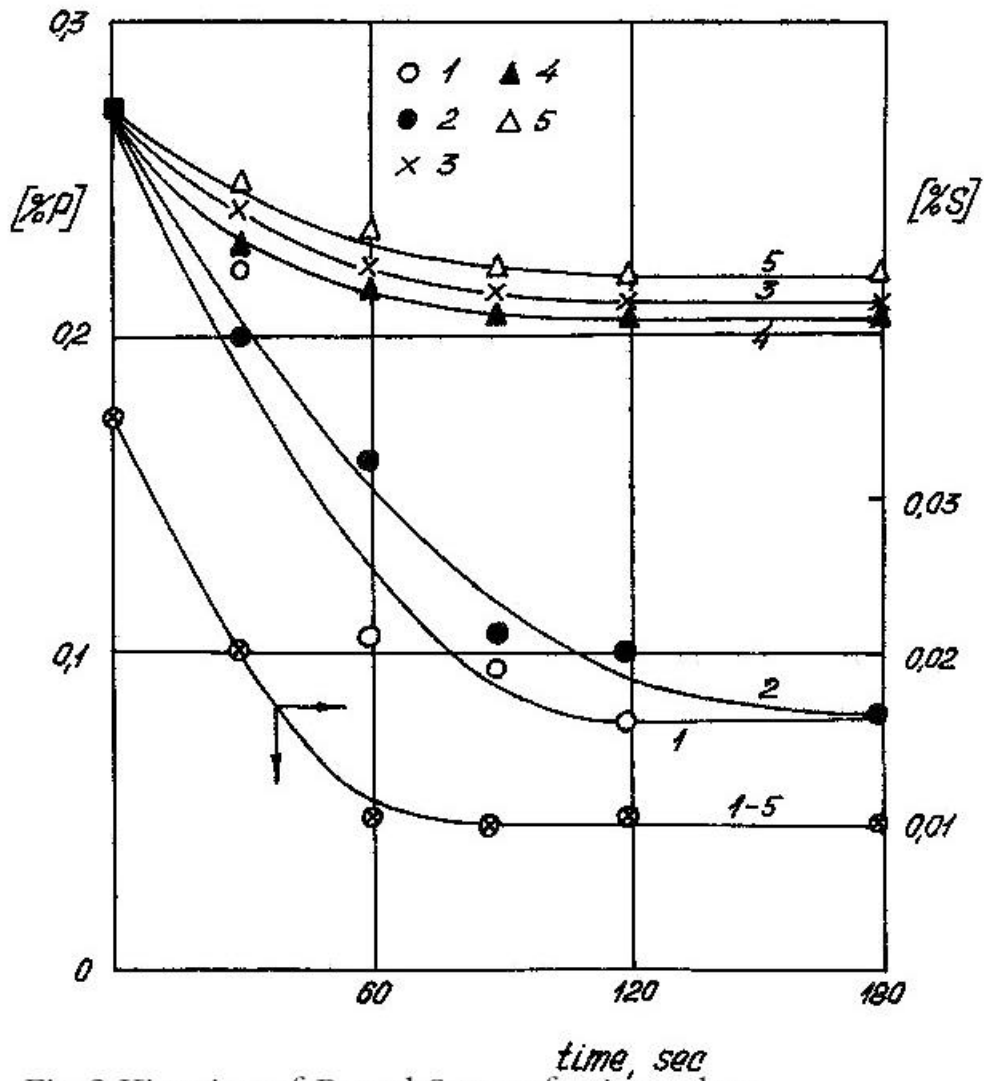


Fig.2. Kinetics of P and S transfer into slags.

Composition of used slags .

1. 33%CaO, 67%CaCl<sub>2</sub>
2. 42%CaO, 51%CaCl<sub>2</sub>, 7%Al<sub>2</sub>O<sub>3</sub>
3. 60%CaO, 20%CaCl<sub>2</sub>, 20%Al<sub>2</sub>O<sub>3</sub>
4. 41%CaO, 41%CaCl<sub>2</sub>, 18%Al<sub>2</sub>O<sub>3</sub>
5. 19%CaO, 63%CaCl<sub>2</sub>, 18%Al<sub>2</sub>O<sub>3</sub>

Fig.3.The variation of  $\lg C_{P3-}$  with optical basicity (effective).

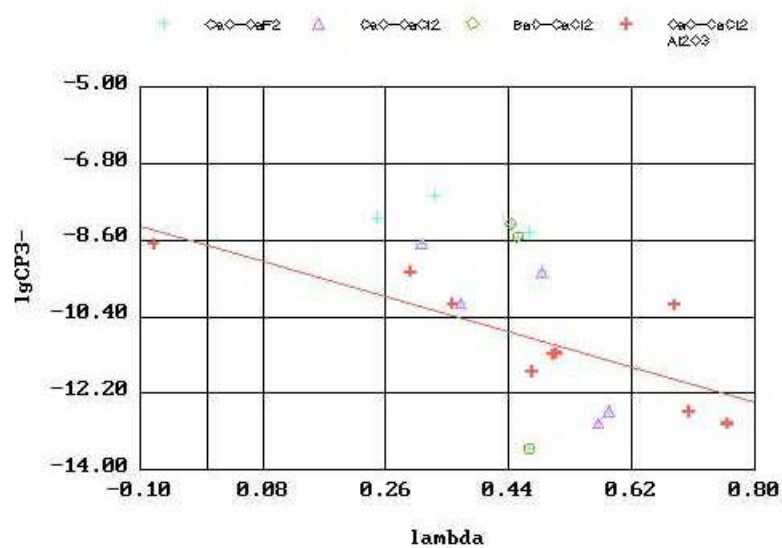


Fig.4.Variation of phosphate capacity with basicity (effective).

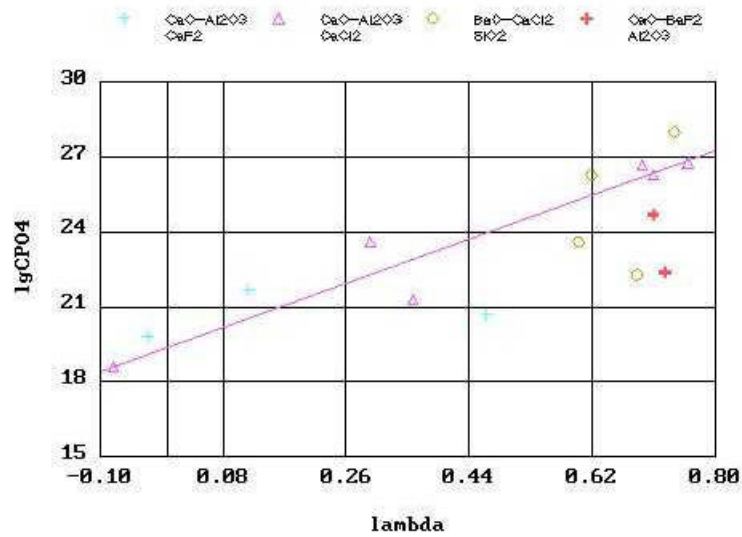


Fig 1. Variation of phosphate capacity with temperature and theoretical optical basicity

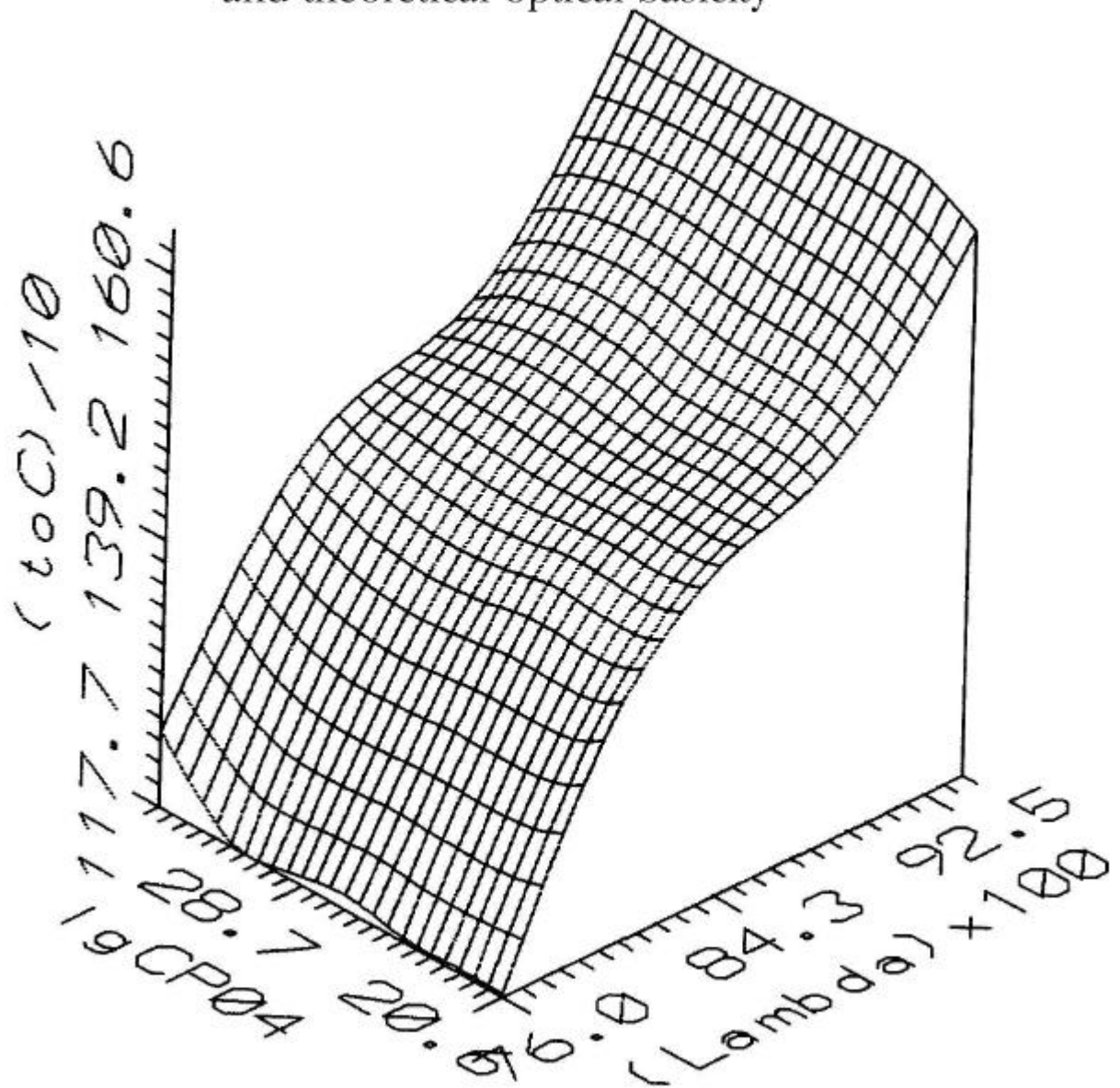




Table 1. Slags Characteristics.

N <sup>o</sup> slag	CaO	Al <sub>2</sub> O <sub>3</sub>	CaF <sub>2</sub>	lgC <sub>p04-</sub>	-lgC <sub>p3-</sub>	Λ 10 <sup>-3</sup>
1	36.6	54.2	9.2	19.8	8.06	-30
3 <sup>x</sup>	31.2	41.3	18.3	21.7	7.56	117
4 <sup>4x</sup>	32.1	6.0	25.6	24.7	9.62	709
2	32.0	21.1	46.9 BaF <sub>2</sub>	20.7	8.43	466
5	29.3	5.3	64.5	22.4	8.59	726
11	-	4.2	67.5	23.6	8.62	600
			CaCl <sub>2</sub>			
6	42.0	56.0	2.0	18.6	8.67	-80
7	40.3	31.4	28.3	23.6	9.33	295
8	19.8	22.8	57.4	21.3	10.08	357
9	26.0	4.0	70.0	26.3	12.62	708
10	20.0	-	80.0	26.8	12.9	759
12 <sup>2x</sup>	16.0	4.0	47.0	26.7	8.22	692
	BaO					
13	20.0	-	80.0	28.0	13.5	740
14 <sup>3x</sup>	38.0	-	53.0	26.3	8.52	618
15 <sup>4x</sup>	45.0	-	51.0	22.3	6.62	685

<sup>x</sup> 9.2%Na<sub>2</sub>O; <sup>4x</sup> 36.3%BaF<sub>2</sub>; <sup>2x</sup> 9%SiO<sub>2</sub>; 13%BaO; <sup>3x</sup> 7%SiO<sub>2</sub>; <sup>4x</sup> 4%SiO<sub>2</sub>.

Table 2. Slags compositions (% mass.)

slag	BaO	BaF <sub>2</sub>	CaF <sub>2</sub>	NaF
1	30	30	20	20
2	30	40	20	10
3	30	20	40	10
4	30	10	50	10



