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Experimental determination of sulphide capacities of blast furnace slags with higher MgO contents

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ABSTRACT

Sulphide capacity measurements of slag with MgO content up to 18 mass% were carried out at 1713, 1743 and 1773 K to obtain reliable data for the blast furnace process. In the measurement, the slag is equilibrated with copper at a controlled oxygen partial pressure for 24 h. The sulphide capacities are calculated based on the sulphur analyses for both slag and copper.

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The increasing demand on improvement of steel cleanness and process optimisation has drawn a great attention on the desulphurisation of hot metal before the BOF process [1–15]. If the capacity of the blast furnace slag to capture sulphur can be optimally utilised, it would have a big impact on the process optimisation and material saving [5,6,8]. Despite of the tremendous effort and a huge number of publications, there are still only a few data of sulphide capacity for the CaO–SiO₂–Al₂O₃–MgO slag system with magnesia content above 15 mass%. In the modern steel plants, the slag composition varies with the blast furnace. In some of the furnaces, slags containing higher MgO contents are used. For instance, the blast furnaces at Oxelösund-SSAB use slag having higher MgO contents ranging from 14 to 18 mass%. To optimise the blast furnace process, the sulphide capacity data for slags are essential. The main objective of this work is to determine the sulphide capacities of the blast furnace slags with MgO contents up to 18 mass%.

The details of the experimental setup can be found in previous publications [2,16]. As shown in Figure 1, a high temperature furnace with graphite heating element was employed. The Al₂O₃ reaction tube was internally connected to a water-cooled quenching chamber. 1–3 Mo crucibles containing the samples were kept in the Mo crucible holder that was connected to a lifting system using a Mo rod. It took less than 2 s to lift the sample from hot zone to the quenching chamber for quenching.

In a typical run, copper powder (purity >99.8%) was well mixed with Cu₂S (99.5%) and placed in a Mo crucible. Thereafter, the slag components were well mixed and put on the top of the copper layer in the molybdenum working crucible (18 mm, IH: 49 mm). After positioning the samples in the even temperature zone of the furnace, the whole system was completely sealed using O-rings. The reaction chamber was evacuated for 30 min and then refilled with the reaction gas. Different mixtures of CO–CO₂ were used to set the partial pressures of oxygen at three different temperatures. To ensure that the equilibrium would be attained, samples

were kept at respective temperature for 24 h [16]. The samples were quenched when the equilibration time was reached. The quenching was done by fast moving of the assembly to the quenching chamber and at the same time blowing argon with high flow rate on the samples. The analyses of sulphur contents in the copper and slag were made by combustion method using a LECO CS-600 analyser. The samples along with their containers were weighed before and after the experiments. No appreciable weight loss was noticed indicating thereby that the mass exchange between the sample and gas phase was negligible. The results of the XRF analysis confirmed that the fractions of the weighed-in oxides were maintained throughout the equilibrating time.

A mixture of 98.1% CO–1.9% CO₂ was used for the experiment at 1713 K to generate an oxygen partial pressure of 2.16×10^{-12} atm, a gas mixture of 98.7% CO–1.3% CO₂ at 1743 K to generate an oxygen partial pressure of 1.97×10^{-12} atm and a gas mixture of 99.0% CO–1.0% CO₂ to generate an oxygen partial pressure of 2.23×10^{-12} atm at 1773 K. All the slag compositions are chosen within the homogeneous liquid region according to phase diagram of the CaO–SiO₂–MgO–Al₂O₃ system [17,18]. It is worthwhile to mention that all the samples were glassy after quenching, indicating that the samples were liquid during the experiments. The experimental results are shown in Table 1. To examine the reliability of the experiments, some experiments were repeated. As shown in Table 1, the agreements between the results of the two runs for different pairs of samples, for example, SC7 and SC7*, SC8 and SC8*, SC9 and SC9* and so on are excellent.

Richardson and Frincham [1] defined the sulphide capacity as

$$C_S = \frac{K \times a_{O^{2-}}}{f_{S^{2-}}} = (\text{mass\% } S^{2-}) \times \sqrt{\frac{p_{O_2}}{p_{S_2}}} \quad (1)$$

where K stands for equilibrium constant, $f_{S^{2-}}$ is the activity coefficient of sulphur ions in the slag, $a_{O^{2-}}$ is the activity of oxygen ions in the slag, p_{O_2} and p_{S_2} are the partial pressures of oxygen and sulphur, and (mass % S²⁻) is the concentration of sulphide

Figure 1. Scheme of the experimental setup.

ions in the slag. Using Equation (1), the sulphide capacity can be calculated by the concentration of sulphur in the slag knowing the partial pressure of oxygen and sulphur. While the oxygen partial pressure is controlled by the CO–CO₂ gas mixture, the sulphur partial pressure can be evaluated using the activity of sulphur in copper based on reaction (2) using the literature data [19,20]:

The calculated C_S values of the slags are included in Table 1. In order to compare the present values with the literature data, the sulphide capacities obtained in the present study are plotted in Figures 2 and 3 along with the literature data [3,7,9,11,15] at 1773 K. Nzotta et al. [3], Kärsrud [7], Kalyanram et al. [9], Seo and Kim [11] and Ma et al. [15] have measured the sulphide capacities of the CaO–SiO₂–MgO–Al₂O₃ system with compositions close to the blast furnace slags at 1773 K. For the comparison, the experimental points having alumina contents differing less than 2 mass% from either 10 or 15 mass% are plotted in the two figures. Figures 2 and 3 show that the present results are in good agreement with the data reported by Kärsrud [7], and Kalyanram et al. [9], and reasonable agreement with the data from Seo and Kim [11] and Ma et al. [15]. On the other hand, the data by Nzotta et al. [3] appear to be somewhat lower.

In accordance with the data of Kalyanram et al. [9], the present results show that the desulphurisation power of the slag will be far more affected by silica than that by alumina. A comparison of Figure 2 and Figure 3 reveals that an increase of Al₂O₃ from 10 to 15 mass% has minor effect on C_S , with C_S values being slightly lowered. On the other hand, both figures show an applicable decrease in sulphide capacity when the slag composition moves towards the SiO₂ corner. The variation of SiO₂ content from 40 to 35 mass% led to a sharp increase of sulphide capacity in both figures.

The blast furnace slag in Oxelösund-SSAB contains usually 14–15 mass% Al₂O₃ and 32–34 mass% SiO₂. As seen in Figure 2, at a constant SiO₂ content (32–34 mass%), the increase of

Table 1. Experimental results of sulphide capacity in CaO–SiO₂–MgO–Al₂O₃ slag system having 10 and 15 mass% Al₂O₃.

Sample	T [K]	Slag composition (weighed in/analysed) (mass%)				Sulphur [mass%]		$C_S \times 10^4$
		CaO	SiO ₂	MgO	Al ₂ O ₃	Slag	Copper	
SC1	1713	28	39	18	15	0.08	0.74	0.4
SC2	1713	35	36	14	15	0.14	0.60	0.9
SC3	1713	38	37	10	15	0.13	0.64	0.8
SC4	1713	34	38	18	10	0.15	0.58	0.9
SC5	1713	38	38	14	10	0.16	0.57	1.0
SC6	1313	42	38	10	10	0.17	0.58	1.1
SC7	1743	32	35	18	15	0.18	0.66	0.8
SC7*	1743	32	35	18	15	0.14	0.55	0.7
SC8	1743	38	33	14	15	0.26	0.45	1.6
SC8*	1743	38	33	14	15	0.26	0.45	1.6
SC9	1743	42	33	10	15	0.27	0.45	1.7
SC9*	1743	42	33	10	15	0.27	0.45	1.7
SC10	1743	37	35	18	10	0.31	0.41	2.2
SC11	1743	41	35	14	10	0.33	0.40	2.4
SC12	1743	45	35	10	10	0.34	0.36	2.7
SC13	1773	35/35.8	32/31.9	18/18.5	15/13.8	0.30	0.38	2.1
SC13*	1773	35	32	18	15	0.32	0.40	2.1
SC14	1773	40/40.4	31/31.3	14/14.4	15/13.9	0.39	0.36	2.8
SC14*	1773	40	31	14	15	0.39	0.36	2.8
SC15	1773	44/44.4	31/30.8	10/10.3	15/14.5	0.41	0.35	3.1
SC15*	1773	44	31	10	15	0.43	0.32	3.5
SC16	1773	37	35	18	10	0.31	0.34	2.4
SC16*	1773	37	35	18	10	0.34	0.38	2.3
SC17	1773	41	35	14	10	0.34	0.38	2.3
SC17*	1773	41	35	14	10	0.36	0.42	2.3
SC18	1773	45/44.2	35/34.5	10/11.5	10/9.8	0.36	0.35	2.7
SC18*	1773	45	35	10	10	0.37	0.38	2.6
SC19	1773	41/41.7	39/37.5	10/11.1	10/9.7	0.18	0.57	0.9
SC20	1773	32	35	18	15	0.18	0.61	0.8
SC21	1773	43/44	30/29.2	12/12.7	15/14.1	0.40	0.43	2.4
SC22	1773	43	34	13	10	0.41	0.31	3.4
SC23	1773	43	37	10	10	0.28	0.40	1.8
SC24	1773	43/42.7	27/25.1	20/21.9	10/10.3	0.52	0.27	4.9
SC25	1773	28	39	18	15	0.11	0.57	0.7
SC26	1773	35	36	14	15	0.21	0.57	1.0
SC27	1773	38	37	10	15	0.19	0.54	0.9
SC28	1773	34	38	18	10	0.22	0.47	1.2
SC29	1773	38/40.2	38/35.3	14/15.2	10/9.3	0.21	0.53	1.1
SC30	1773	42	38	10	10	0.21	0.41	1.4

Figure 2. Experimental and literature $C_S \times 10^4$ data in the CaO–SiO₂–MgO–Al₂O₃ (15 mass%) system at 1773 K.

Figure 3. Experimental and literature $C_S \times 10^4$ data in the CaO–SiO₂–MgO–Al₂O₃ (10 mass%) system at 1773 K.

MgO content above 14 mass% in the slag decreases the sulphide capacity. This observation shows clearly that slags with high magnesia content (>14 mass%) will be less efficient for sulphur removal inside the blast furnace in the case of usually used alumina and silica ranges. Hence, in the blast furnace operation, it is desired to keep the MgO lower than 14 mass%. Note that other parameters, e.g. the flux in the iron ore pellets, should also be taken into consideration when making the process optimisation.

Disclosure statement

No potential conflict of interest was reported by the authors.

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