EFFECT OF A FOURTH COMPONENT (Na_2O, SrO, MgO AND BaO) ADDITION TO $CaO-Al_2O_3-SiO_2$ SYNTHETIC SLAG ON SULFUR REMOVAL FROM PLAIN CARBON STEEL

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Abstract: *In this paper, the effect of MgO, BaO, Na_2O and SrO addition to a pre-melted $CaO-Al_2O_3-Si_2O$ synthetic slag on sulfur removal from plain carbon steel was studied under the same experimental conditions. The slags were pre-melted at 1400°C in an electric resistant furnace and desulfurization experiments were carried out in a high frequency induction furnace. The results showed that the optimum reaction time for desulfurization was 15 min. It was found that while SrO addition to the ternary slag enhances the sulfur removal capability, MgO, Na_2O and BaO additions reduce desulfurization efficiency of the ternary slag. Moreover, it was observed that restricting access to oxygen from the atmosphere by using a covered crucible, could increase desulfurization efficiency of the slag by more than two fold.*

Keywords: *Synthetic slag, Calcium aluminate, Desulfurization, Steelmaking.*

1. INTRODUCTION

Ultra clean steels are manufactured with some special processes such as synthetic slag, VIM (Vacuum Induction Melting) and ESR (Electro Slag Refining) [1]. Synthetic slag process is a ladle metallurgy operation aiming for improving quality of steels used for special applications such as gas pipe lines, construction of nuclear power plants and instruments that need higher mechanical properties [2]. The process has been regarded as one of the most convenient and cheapest methods for steel refining in ladle metallurgy operations. It not only could improve inclusion removal [2-6] but also decrease sulfur and phosphorus content of steel [3] and also extent refractories life time [7].

The desulfurization reaction at molten steel-slag interface can be expressed by Eq. (1):

$$[S] + (O^{2-}) = (S^{2-}) + [O] \quad (1)$$

where [ ] and ( ) denotes species in the metal and slag phase, respectively. Based on this equation, sulfur removal from molten steel and formation of sulfide phases in slag would improve by increasing basic components to the slag [8]. In desulfurization reaction by synthetic slags, physical and chemical properties of slags such as melting point, viscosity, basicity and sulfide capacity are important. Although, CaF_2–containing slags used to be mostly applied due to its positive effect on slag properties [9], because of harmful effects of fluoride components on environment and refractories life time, fluoride-free slags have become attractive to researchers.

Synthetic slags based on calcium aluminate showed good results in desulfurization process [10,11]. However, investigations are still ongoing to improve desulfurization and increase the rate of sulfur removal from molten steel via adding fourth and fifth component to the slags. Chol et al. [12] have reported that Na_2O addition to $CaO-Al_2O_3-SiO_2$ ternary slag under neutral atmosphere would increase both desulfurization efficiency and the rate of sulfur removal from molten steel by, while Al_2O_3 addition could have a reverse effect.

Solid-state synthesis is the conventional rout to produce the $MgAl_2O_4$ spinel from reaction between MgO and Al_2O_3 as primary materials [13]. Taniguchi et al. [14] showed that while sulfide capacity of slag increased by adding 2 wt% MgO at 1400°C, there is no noticeable changes in desulfurization capability of slag with 2-6 wt% MgO addition.

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Gao et al. [15] mentioned that BaO is thermodynamically a more powerful desulfurizer than CaO and sulfide capacity of slag increases by adding BaO. Also, they showed that sulfur removal from steel improves by BaO addition to slag for constant Al_2O_3:CaO ratio and desulfurization would be negligible when increasing BaO to more than 8 wt%.

Hernandez et al. [16] showed that increasing FeO content in $CaO-SiO_2-CaF_2-FeO-Na_2O$ slag lead to an increase in oxygen potential and a decrease in desulfurization capability of slag. Results reported by Park et al. [17] indicated that desulfurization process improved by adding MnO, as a basic oxide, to CaO-based slag which containing more than 40 wt% SiO_2 while in low SiO_2 containing slag, no significant effect on sulfur removal observed by increasing MnO content.

In spite of the above-mentioned studies on the effect of basic component addition to the slag on desulfurization process, no accurate comparison among different basic oxide effects on desulfurization process is possible due to the different experimental conditions.

In this paper, the effect of Na_2O, MgO, BaO and SrO addition to $CaO-Al_2O_3-SiO_2$ ternary slag on the efficiency of desulfurization from plain carbon steel is studied under the same experimental condition to make it possible a reliable comparison between different basic oxides (oxide of alkali and alkaline earth metals) affecting sulfur removal. Moreover, because no sufficient information about SrO behavior in desulfurization process could be found in previous studies, experiments are conducted around the effect of SrO addition to the ternary slag on desulfurization efficiency.

Table 1. Chemical composition of steel sample(wt%).

C	Si	Mn	P	S	Cr	Ni
0.177	0.427	1.44	0.0313	0.0182	0.0095	0.0099
Al	Co	Cu	Nb	Ti	V	W
0.00056	0.0058	0.0261	0.0011	0.0011	0.0037	0.0074

2. EXPERIMENTAL PROCEDURE

2. 1. Materials

Desulfurization experiments were performed on a plain carbon steel with chemical composition as in Table 1. Commercial $CaCO_3$, $BaCO_3$, $SrCO_3$, $MgCO_3$, Na_2CO_3, $Al(OH)_3$ and SiO_2 were used for the preparation of synthetic

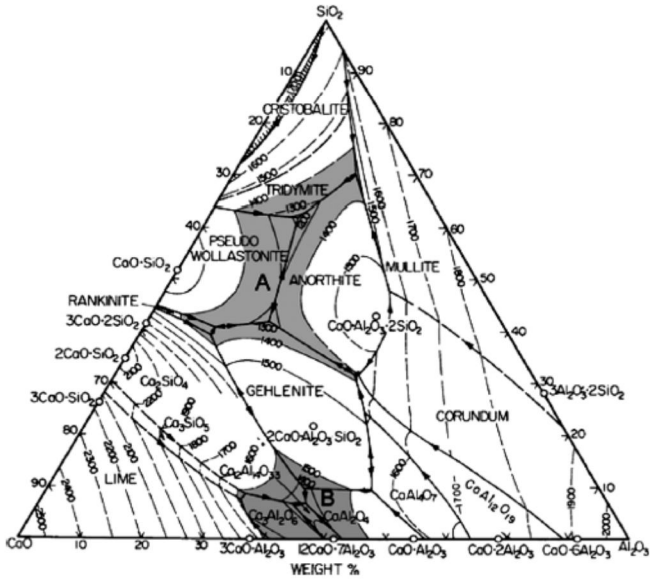

Fig. 1. Low melting temperature region A and B in $CaO-Al_2O_3-SiO_2$ system [4].

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Table 2. Chemical compositions of the ternary and quaternary slags (wt%).

Sample No	CaO	Al_2O_3	SiO_2	MgO	BaO	Na_2O	SrO
CAS	50	43	7				
CAS-5MgO	47.64	40.95	6.66	4.75			
CAS-5BaO	47.64	40.95	6.66		4.75		
CAS-5Na_2O	47.64	40.95	6.66			4.75	
CAS-5SrO	47.64	40.95	6.66				4.75

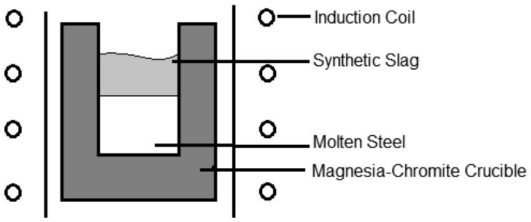

Fig. 2. Schematic diagram of experimental apparatus.

slags.

Figure 1 shows low melting temperature regions in CaO-Al_2O_3-SiO_2 ternary system. Regarding to the effect of slag basicity on desulfurization, region B as the appropriate slag composition is much more preferable than region A. So, a ternary eutectic point from CaO-Al_2O_3-SiO_2 system in region B was considered as the basic slag chemical composition to prepare a ternary slag (hereinafter referred to CAS). Effect of fourth components on sulfur removal from molten steel is studied by adding about 5 wt% MgO, BaO, Na_2O and SrO to CAS to obtain quaternary slags CAS-5MgO, CAS-5BaO, CAS-5Na_2O and CAS-5SrO, respectively. Chemical composition of the slags are summarized in Table 2.

2. 2. Preparation and Pre-Melting of Slags

First, slag ingredients were separately calcined for 2 hours at 1000 °C and then collectively milled for 5 hours to mix and homogenize. 5 wt% polyvinyl alcohol was added to the mixture as plasticizer. Pellets (30 mm diameter) were formed from the mixture by cold press (40 bar pressure) and dried for 16 hours at 50 °C. To pre-melt the pellets, temperature was increased to 1000 °C during 3 hours and from 1000 °C to 1400 °C during 1 hour and holding the samples for 20 min at 1400 °C in an electric resistance furnace with SiC heating elements. The synthetic slag was finally cooled in the air.

2. 3. Desulfurization

Desulfurization experiments were carried out in an open high frequency induction furnace using magnesia-chromite crucibles. Temperature was indirectly controlled via output power of the furnace fixed at 8 kW. Schematic diagram of experimental apparatus is shown in Figure 2. A two-stage process was designed for experiments. In the first stage, optimum reaction time (topt) for desulfurization by ternary slag, CAS, was found out. In the second stage, desulfurization by quaternary slags was carried out for topt.

Sulfur content of steel before and after desulfurization process was analyzed by Spark Emission Spectroscopy method according to ASTM 415-08:2010. In addition, Accuracy of result was checked out by LECO combustion-infrared spectrometer according to ASTM E1019-08:2010. Desulfurization efficiency (η_S) was calculated based on Eq. (2) to evaluate desulfurization capability of the slags.

$$\eta_S\ (\%) = 100 \times ([S]_i - [S]_f) / [S]_i \qquad (2)$$

where [S]i and [S]f are initial and final sulfur content of the metal, respectively.

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3. RESULTS AND DISCUSSION

Figure 3 shows X-Ray diffraction (XRD) pattern of the pre-melted CAS slag. $12CaO.7Al_2O_3$ (Mayenite), $2CaO.SiO_2$ (Larenite) and $CaO.Al_2O_3$ phases are indicated in the pattern as the main constituents of ternary slag. According to the $CaO\text{-}Al_2O_3\text{-}SiO_2$ phase diagram, composition of CAS synthetic slag after cooling is a ternary eutectic with melting temperature of about 1370 °C in the composition region of above-mentioned phases.

3. 1. Reaction Time

Figure 4 shows the effect of reaction time on sulfur content of steel and desulfurization efficiency by CAS ternary slag. For the first 15 min, sulfur content decreased to 0.0104 wt% and desulfurization efficiency increased to 43%, while slight changes of sulfur content and desulfurization efficiency were observed for longer reaction time. Therefore, it would be reasonable to assume that equilibrium state has

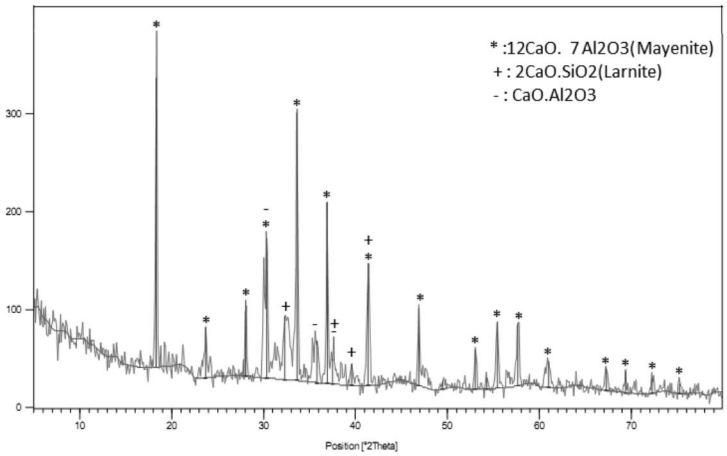

Fig. 3. X-Ray diffraction pattern of pre-melted ternary slag at 1400°C.

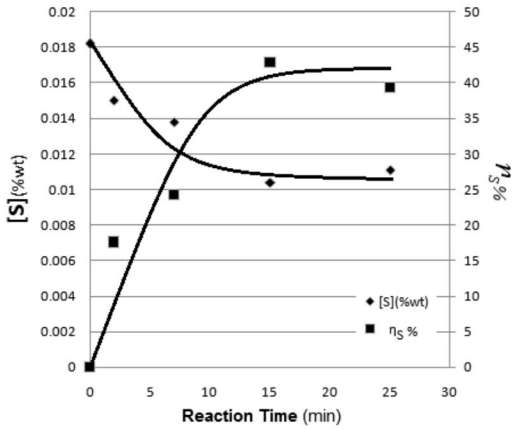

Fig. 4. Effect of reaction time on sulfur content of steel and desulfurization efficiency.

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been achieved after 15 min reaction time.

Previous studies [9,12] have shown that sulfur removal from steel via synthetic slag process is controlled by mass transfer phenomena. So, desulfurization rate is dependent on concentration gradient in the boundary layer. Initially, the concentration gradient is large and the rate of sulfur removal is high. By passing the time and transferring more sulfur from molten steel to the slag, the difference between sulfur content of steel and equilibrium content of sulfur at the slag-metal interface, which is the driving force for desulfurization reaction, is decreased and as a result, sulfur transfer is slowed down. Therefore under experimental condition of the present work, reaction times longer than 15 min is not profitable.

3. 3. Quaternary Slags

As mentioned earlier, quaternary slags were made by addition of the same amount (5 wt%) of MgO, Na_2O, BaO and SrO to the CAS ternary slag in order to compare the effect of the fourth component on sulfur removal efficiency.

Figure 5 shows sulfur content of steel and desulfurization efficiency after 15 min desulfurization by the ternary and quaternary synthetic slags. It can be observed that sulfur content of steel decreases to 0.0122, 0.0127, 0.0148, 0.0169 and 0.0120 weight percent and desulfurization efficiency increases to 33, 30, 19, 7 and 34 percent for CAS, CAS-5MgO, CAS-5BaO, CAS-5Na_2O and CAS-5SrO, respectively.

The results indicated that the desulfurization efficiency for CAS-5Na_2O is comparatively very low. Stephen [10] has reported an increase of desulfurization rate and efficiency by increasing Na_2O content of slag in the neutral atmosphere. However, Hernandez et al. [16] reported sodium phosphate formation in slag after simultaneous desulfurization and dephosphorization by Na_2O-containing slag in an oxidizing atmosphere. It seems under oxidizing atmosphere and in the presence of phosphorus, sodium phosphate will be formed instead of sodium sulfide and the reaction between Na_2O and phosphorus is more preferable than Na_2O and sulfur. In fact, thermodynamic condition is not favored for Na_2O to react with phosphorus in the neutral atmosphere. Conversely, in an oxidizing atmosphere, sodium phosphate is much more stable than sodium sulfide. Low phosphorus content of the refined steel and dephosphorization efficiency of 87% obtained after CAS-5Na_2O synthetic slag usage in the present investigation, proves Na_2O preference for reaction with phosphorus than sulfur. Therefore, it seems minimum desulfurization efficiency that was obtained by CAS-5Na_2O slag could be related to the presence of phosphorus and turbulent liquid steel and slag condition in an

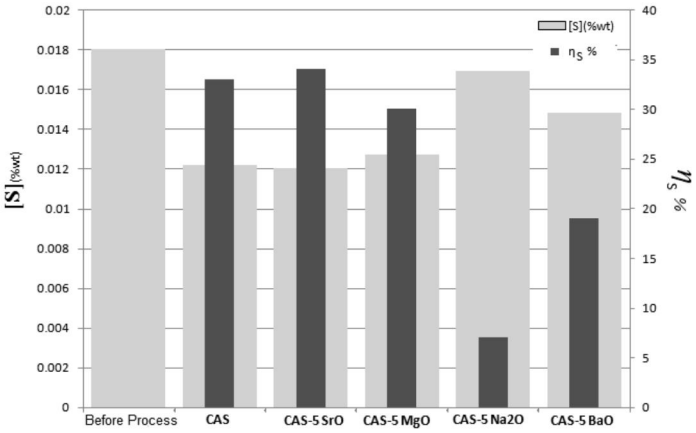

Fig. 5. Sulfur content of steel and desulfurization efficiency after 15min desulfurization by CAS, CAS-5MgO, CAS-5BaO, CAS-5Na_2O and CAS-5SrO synthetic slags.

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open induction furnace that would create an oxidizing atmosphere.

MgO has a lower molecular weight compared with CaO. Therefore, increasing of MgO content in the CAS slag may lead to increase of the molar fraction of the basic components in the slag and as a result, desulfurization reaction would be improved. Besides, MgO addition to slags with low Al_2O_3/CaO ratio, improves sulfur removal because of low-melting temperature phases that would be formed by MgO, Al_2O_3 and SiO_2. However, for the higher Al_2O_3/CaO ratio (>0.7), MgO provides a converse effect on desulfurization due to an increase of

Melting point and viscosity of the slags [15]. On the other hand, effect of MgO will be similar to CaO in systems containing CaO and SiO_2, although MgO has no significant effect on desulfurization in low SiO_2 slags [14]. By attention to the Al_2O_3/CaO ratio (= 0.86) and low SiO_2-containing slags in the present work, a negligible decrease of the desulfurization efficiency by MgO addition to CAS slag is in good agreement with previous reports [14,15].

Based on the thermodynamic data [18], BaS free energy of formation is more negative than CaS. Beside, BaO is a more powerful desulfurizer than CaO [15] and has higher ability for providing oxygen ion, O^{2-}. Therefore, improving desulfurization by adding BaO to CaO-based slags is expected. On the other hand, BaS is not so stable and tends to decompose with increase of this sulfide as the desulfurization product. In addition, melting temperature of slag may increase by BaO addition as a basic oxide. From this point of view, desulfurization efficiency could be decreased by increasing BaO content of the synthetic slag.

Thermodynamic data reveals that SrS Gibbs Free Energy of formation is more negative than CaS, which means SrO is a more powerful desulfurizer than CaO. However, results of experiments showed a 1 percent increase in desulfurization efficiency by adding 5 wt% SrO to CAS slag. It would be because of an increase in basicity of slag by adding SrO, as a basic oxide, to the ternary CAS slag.

3. 4. Desulfurization by Covered Crucible

Figure 6 shows X-Ray diffraction patterns of CAS-5SrO slag after 15 min desulfurization in both open and covered crucibles. Comparison of patterns indicated that no FeO is recognizable in

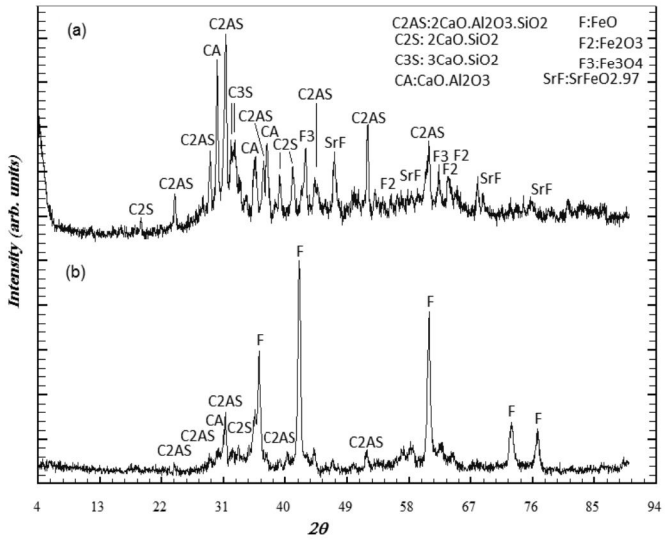

Fig. 6. X-Ray diffraction patterns of CaO-Al_2O3-SiO_2-5SrO synthetic slag after 15min desulfurization in (a) covered crucible, (b) open crucible.

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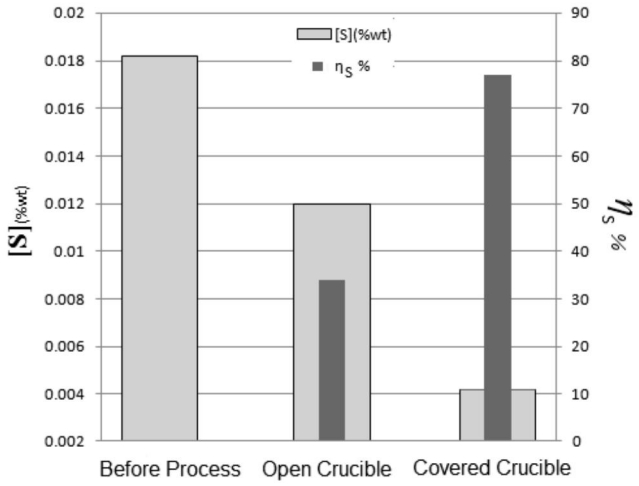

Fig. 7. Desulfurization efficiency and sulfur content of steel after 15min desulfurization by CaO-Al_2O_3-SiO_2-5SrO synthetic slag in open and covered crucibles.

covered crucible slag and small amounts of Fe_2O_3 and Fe_3O_4 would be existed, while in open crucible slag, FeO is the main phase. According to these observations and by attention to equilibrium between dissolved oxygen of steel and FeO in slag, a noticeable increase in desulfurization efficiency is expected by using covered crucible. In fact, decreasing the oxygen content of steel improves sulfur removal, as expressed in Eq. (1).

Desulfurization efficiency and sulfur content of steel after 15 min desulfurization by CAS-5SrO synthetic slag in open and covered crucibles are illustrated in Figure 7. It can be seen that, sulfur content of steel is decreased from 0.012 wt% for open crucible to 0.0042 wt% for covered crucible (a correspondingly desulfurization efficiency of 34 and 77%). This means that sulfur removal efficiency could be more than doubled by covering the crucible. As mentioned above, oxygen contact with steel and slag melts is restricted by using covered crucible and sulfur removal from steel is improved according to Eq. (1).

4. CONCLUSIONS

Based on the experimental results of the present investigation, the main conclusions are as follows:

1. Optimum reaction time for desulfurization by CaO-Al_2O_3-SiO_2 ternary slag was found to be 15 min with a desulfurization efficiency of 34%.
2. Na_2O addition to CaO-Al_2O_3-SiO_2 ternary slag was shown to encourage removal of phosphorus than sulfur in oxidizing atmosphere. It was related to the fact that sodium phosphate is much more stable than sodium sulfide.
3. Under the same experimental condition, desulfurization efficiency was improved by SrO addition to the ternary slag, while MgO, BaO and Na_2O additions lead to a decrease of the sulfur removal efficiency.
4. Desulfurization efficiency could be more than doubled (from 34 to 77%) by restricting oxygen availability by using a covered crucible.

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