Influence of Solid CaO and Liquid Slag on Hot Metal Desulfurization

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Mechanical stirring is widely used for hot metal desulfurization in Japan. In this process, solid lime is added as flux and emulsified into molten iron using a vortex formed by the stirrer. However, in addition to the added solid lime, the liquid top slag on the ladle is emulsified and forms granules. To clarify the roles of the solid lime and liquid slag in hot metal desulfurization, the reaction rates of slag, solid lime, and slag with solid lime are determined and the interfacial layers are observed.

The results are summarized as follows:

(1) The desulfurization rate is very slow when a solid lime rod is immersed into hot metal without slag. The reason for the slow desulfurization is the formation of an interfacial layer, which inhibits the mass transfer of sulfur.

(2) Because sulfur is not detected inside the solid CaO, the mass transfer of sulfur from the liquid slag to the solid CaO does not occur. Therefore, it is believed that solid CaO does not play a direct role in the desulfurization reaction, and thus, the reaction is solely due to the liquid slag. A good relationship between the desulfurization rates and the sulfide capacity of the liquid slag is found.

(3) When tricalcium aluminate forms at the interface, the desulfurization rate is increased by the immersion of a CaO rod. This is due to the supply of CaO to the slag because this interfacial layer does not inhibit the mass transfer.

KEY WORDS: desulfurization; solid lime; interfacial layer; sulfide capacity.

1. Introduction

The process of mechanical stirring is widely used for hot metal desulfurization in Japan. In this process, solid lime is added as flux and emulsified into molten iron using a vortex formed by the stirrer. The desulfurization mechanism of solid lime has already been investigated by various researchers. Kawai et al.1) performed fundamental experiments on hot metal desulfurization using a CaO crucible heated in an electric resistance furnace, whereas Ueda et al.2) also achieved hot metal desulfurization using lime powder stirred using an impeller. Although desulfurization occurred in both of these cases, the reaction rate was slow. Kawai et al. found that the rate-controlling step of the reaction was the mass transfer of sulfur in the solid sulfide phase formed on the CaO surface. In addition, they showed that the desulfurization rate decreased when the hot metal contained Si, owing to the formation of a calcium silicate phase on the CaO surface. Ueda et al. observed that the desulfurization rate was influenced by the geometrical characteristics of the lime and concluded that the relatively large pores, which were approximately 20 μm or more in diameter, played an important role in the reaction kinetics. Further to these findings, Shoji et al.3) clarified that the addition of Al to the Si-containing hot metal improved the reaction rate. According to their investigation, the enhanced rate was due to the formation of a slag layer of the CaO–Al2O3–FeO system on the lime surface. Recently, Tanaka et al.4) proposed the novel concept of desulfurization by solid lime. They immersed porous lime in the slag layer on the hot metal, such that the slag penetrated into the pores, thus achieving efficient desulfurization. This process gives a high desulfurization rate; however, the roles of the solid lime and liquid slag were not separately evaluated.

Most of the previous research indicates that desulfurization by solid lime is slow, owing to the fact that the mass transfer in the solid phase is the rate-controlling step; therefore, an adequate liquid phase is necessary to improve the reaction rate. In the case of the mechanical stirring process, the lime and the top slag on the ladle are both emulsified and form granules. Nakai et al.5) estimated the diameter of the granules to be 1.55 mm, which implies that approximately 3700 lime powder particles were granulated. Although they did not find slag between the lime particles, it is understood
that liquid slag would be necessary for granulation.

In the present experiment, hot metal desulfurization experiments were performed using slag, solid lime, and slag with solid lime to clarify the roles of solid lime and liquid slag in the reaction.

2. Experimental Methods

2.1. Desulfurization by Slag, Solid Lime, and Slag with Solid Lime

The experiments are performed using a high-frequency induction furnace. The experimental setup is shown in Fig. 1. A fired MgO crucible (59 mm inner diameter, 150 mm height) is placed inside a transparent quartz tube (120 mm inner diameter) in order to protect the inner crucible, which is also made of fired MgO (32 mm inner diameter, 100 mm height). A graphite tube (31 mm outer diameter, 24 mm inner diameter, 101 mm height) is placed inside the inner crucible, such that it is immersed into the hot metal bath to a depth of 3–5 mm. The purpose of this graphite tube is to heat the slag and to provide protection against a reaction between the MgO crucible and the slag.

The following three types of experiments are performed, as shown in Fig. 2:

(1) Reaction between metal and solid lime: In this experiment, a solid lime rod is immersed into molten metal (Fig. 2(A)).

(2) Reaction between metal, slag, and solid lime: In this experiment, a solid lime rod is immersed into molten slag and hot metal (Fig. 2(B)).

(3) Reaction between metal and slag: In this experiment, slag and metal are melted without the immersion of a solid lime rod (Fig. 2(C)).

To produce the slag, reagent-grade SiO₂, CaCO₃, Al₂O₃, and MgO are used. First, CaCO₃ is heated to 1273 K for 60 min under air. The heating takes place in an Al₂O₃ crucible to produce CaO. The reagents are then mixed in various ratios and melted in a Pt crucible at 1773 K for 3 h or more, before the melted slag is quenched on a Cu plate and crushed. Table 1 lists the initial composition of the slag. Slags S and A are liquids at the experimental temperature in the CaO–SiO₂–Al₂O₃ system and are close to the dicalcium-silicate- and tricalcium-aluminate-saturated compositions, respectively. Slag C is also a liquid at the experimental temperature in the CaO–SiO₂–MgO–Al₂O₃ system and is close to the CaO-saturated composition. The experiments are performed at 1673 K for slag S and at 1723 K for slags A and C.

Sintered CaO and metallurgical lime are used for the solid lime rods. To prepare the sintered CaO rod, CaO produced by the above method is first pressed to form a rod of approximately 13 mm in diameter and 40 mm in length, before being heated at 1873 K for 48 h. After cooling, the rod is mounted on an alumina tube. Metallurgical lime (Yoshizawa Lime Industry Co. Ltd.) is heated in air at 1273 K for 20 h to eliminate gaseous materials and then formed into a rectangular parallelepiped with a square section having 9-mm sides and a length of 25 mm. This rod is also mounted on an alumina tube. The bulk density of the sintered CaO is 2.92 g/cm³, and that of metallurgical lime is 1.79 g/cm³, as measured by the Archimedean method using ethanol. For the experimental setup shown in Fig. 2(A), the immersion depth of sintered CaO and metallurgical lime was approximately 15 mm and 18 mm, respectively. The interfacial area between the solid lime rod and the metal was almost the same in each experiment. For the experimental setup shown in Fig. 2(B), the slag thickness was approximately 10 mm. In the case of sintered CaO, the immersion depth in slag was 10 mm and that in metal was 5 mm. In the case of metallurgical lime, the immersion depth in slag was also 10 mm, but that in metal was changed to 8 mm. Therefore, the interfacial area of sintered CaO with slag was approximately 1.6 times larger than that of metallurgical lime with slag.

Table 1. Initial composition of slag for the desulfurization experiment.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CaO (mass%)</th>
<th>SiO₂ (mass%)</th>
<th>Al₂O₃ (mass%)</th>
<th>MgO (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slag S</td>
<td>47</td>
<td>41.1</td>
<td>11.9</td>
<td>0</td>
</tr>
<tr>
<td>Slag A</td>
<td>47.9</td>
<td>7.2</td>
<td>44.9</td>
<td>0</td>
</tr>
<tr>
<td>Slag C</td>
<td>53</td>
<td>7.4</td>
<td>35</td>
<td>4.6</td>
</tr>
</tbody>
</table>
that of metallurgical lime with slag, even though the interfacial area of solid lime with metal was almost the same. The experimental conditions are summarized in Table 2.

The experiment is performed according to the following procedure. Fragments of solid iron (~130 g), which are made in a laboratory furnace at the JFE Steel Corporation, are first melted in the inner crucible. The solid iron contains only carbon (4.5% by mass) and sulfur (0.03% by mass). After the temperature reaches the aimed value, a metal sample is extracted via the quartz tube, and 8 g of the crushed slag is placed on the surface of the molten metal. For the experiments involving immersion of the solid lime rod, the alumina tube with the lime rod is inserted into the furnace, and after heating for 3 min at a position just above the slag or metal, the rod is immersed for an appropriate length of time. The rod is then withdrawn and quenched by He gas. The interface of the rod and adhered slag is observed using an electron probe microanalyzer (EPMA: JEOL JXA-8200). After an appropriate length of time, a metal sample is taken and the slag is sampled by using a Mo wire. The sulfur content in the metal and slag samples is analyzed by an infrared absorption method after combustion in a high-frequency induction furnace (LECO CS-444LS).

A thermocouple and radiation thermometer are used to control the temperature during the experiments. After the metal is melted, the thermocouple is immersed into the hot metal to adjust the temperature. Simultaneously, the temperature of the outside surface of the MgO crucible is measured by the radiation thermometer. Because the temperatures measured by these two devices are not equivalent, the temperature measured by the thermocouple represented the actual value. After the temperature measured by the thermocouple reached the aimed value, the thermocouple was removed and a PID controller was connected to the signal from the radiation thermometer to maintain the target value. The positions of these two devices are clearly shown in Fig. 1(b). To measure the surface temperature of the MgO crucible, a hole with approximately 15-mm diameter was created in the insulation material.

2.2. Mass Transfer of Sulfur from Liquid Slag to Solid Lime

During the desulfurization experiments, the sulfur content in the slag is not very high. To confirm the transfer of sulfur from the liquid slag to the solid lime, an experiment is performed in which solid CaO is immersed in slag containing a high percentage of sulfur. The experiment is performed using an electric residence furnace. Approximately 10 g of slag is melted in the Pt crucible (30 mm diameter, 30 mm height), and the CaO rod is immersed for an appropriate length of time. The method used to make the slag is the same as that in the previous experiments. The CaO rod (6 mm wide, 2.5 mm thick, 30 mm long) is cut from the CaO crucible, and to identify the original surface, Pt powder is partially pasted onto the surface. The immersion method is the same as that in the previous experiments. The initial composition of the slag is summarized in Table 3.

3. Experimental Results

3.1. Desulfurization by Slag, Solid Lime, and Slag with Solid Lime

Figure 3 shows the results of desulfurization obtained by using slag A with a sintered CaO rod, compared with those obtained by using only a sintered CaO rod or only slag A. In each experiment, the metal is sampled before and after immersion; the immersion times are set at 300, 600, and 1200 s. Because the initial sulfur contents differ, even though the same solid iron is used, the sulfur content following immersion is divided by the initial content ([S]o). From Fig. 3, it is clear that the desulfurization rate obtained using slag A with the solid CaO rod is relatively fast and that the rate obtained using only the solid CaO rod is quite slow. In addition, the desulfurization rate using slag A without CaO immersion is slower than that with immersion. Figures 4(a) and 4(b) show the surface of the CaO rod after immersion for 1200 s into hot metal without and with slag.

![Fig. 3. Desulfurization behavior obtained using slag A with the sintered CaO rod compared with the behavior obtained using only sintered CaO and only slag A.](image-url)
In Fig. 4(a), a sulfur-rich phase is observed on the CaO rod; however, sulfur is not detected inside the CaO rod. This result is in agreement with the observations of Kawai et al. In Fig. 4(b), the formation of a dendritic tricalcium aluminate phase on the interface is observed. However, the sulfur content in the liquid slag among the dendrites is not high compared with the sulfur content in the bulk slag. In addition, sulfur is not detected inside the CaO rod. Figure 5 shows a comparison of the results of desulfurization using each slag with and without the sintered CaO rods. For slags A and C, the desulfurization rates increase when the CaO rods are immersed; however, in the case of slag S, the desulfurization rate decreases. In addition, the desulfurization rates are in the order slag C > slag A > slag S, regardless of whether CaO is immersed or not. In this result, not only the influence of slag composition but also the difference in temperature is included. Figures 6(a) and 6(b) show the surface

![Figure 4](image1.png)

![Figure 5](image2.png)

![Figure 6](image3.png)
of the CaO rod after immersion into hot metal using slag S and slag C, respectively. In Fig. 6(a), the formation of a dense dicalcium silicate phase at the interface is observed. Sulfur is not detected in the interfacial layer, liquid slag, or CaO rod. In Fig. 6(b), an interfacial layer is not observed and liquid slag has penetrated into the sintered CaO. The sulfur content in the liquid slag that penetrated into the solid CaO is the same as that in the bulk slag, and sulfur is not detected inside the CaO rod. Figure 7 shows the differences in desulfurization behavior due to immersion of a sintered CaO rod and a metallurgical lime rod. Without slag, the desulfurization rate is slow even when porous metallurgical lime is used. The desulfurization rate using slag A does not change much in either case. Figures 8(a) and 8(b) show the surface of the metallurgical lime rod after immersion into the hot metal without and with slag A, respectively. In Fig. 8(a), a sulfur-rich dense phase is observed on the lime rod, but sulfur is not detected inside the lime rod. In Fig. 8(b), a tricalcium aluminate phase in dendritic form is observed, and penetration of liquid slag into the solid metallurgical lime is found. However, the sulfur content in the liquid slag among the dendrites is not high compared with the sulfur content in the bulk slag. In addition, sulfur is not detected in the solid and liquid phases of the metallurgical lime rod.

3.2. Mass Transfer of Sulfur from the Liquid Slag to Solid Lime

Figures 9(a), 9(b), and 9(c) show the interface between solid CaO and liquid slag after immersion for 300 s with slag A', slag S', and slag C', respectively. Figure 9(a) is very similar to Fig. 4(b), and 9(b) is very similar to Fig. 6(b). In Fig. 9(a), a dendritic structure of tricalcium aluminate is observed in the solid CaO and the Pt marker. In Fig. 9(b), granular-shaped dicalcium silicate is observed between the solid CaO and the Pt marker. These results indicate that the CaO dissolves into the liquid slag first, after which the tricalcium aluminate or dicalcium silicate phase is formed because of the increase in the CaO content of the slag near the solid CaO interface. In Fig. 9(c), an interfacial layer is not observed; this result is similar to that shown in Fig. 6(a). In addition, sulfur is not detected in any of the solid CaO rods even though the sulfur content in the bulk slag is high. Therefore, it can be concluded that the mass transfer of sulfur from the liquid slag to solid CaO hardly occurs under any liquid slag conditions.

4. Discussion

The experimental results are summarized in Fig. 10. In this figure, the desulfurization rate constant (K) and the distribution ratio at 20 min (LS) are used to describe the experimental results. K and LS are calculated as

\[ K = \ln \left( \frac{1}{[S]/[S_0]} \right)/t \]........................ (1)

\[ LS = \frac{[S]_{t=20}}{[S]_{t=20}} \]........................ (2)

In these equations, t is time (min); [S], and [S₀] are the sulfur contents of the metal at t and before the start of the experiment, respectively; and [S]_{t=20} and [S]_{t=20} are the sulfur contents of the slag and the metal, respectively, 20 min after the start of the experiment. The results are summarized...
as follows. First, the desulfurization rate is very slow when the solid lime rod is immersed into hot metal without slag. In this case, the immersion of metallurgical lime does not significantly change the reaction rate. Second, the desulfurization rate decreases in the order slag C > slag A > slag S, regardless of whether CaO is immersed or not. Third, when slags A and C are used, the desulfurization rates increase after the immersion of solid lime. In contrast, when slag S is used, the desulfurization rate decreases after the immersion of solid lime. Finally, in the case of slag A, the difference in desulfurization rates between the immersion of metallurgical lime and sintered CaO is not clear.

4.1. Effect of Slag Composition on the Desulfurization Rate

According to the observations by EPMA, sulfur is not detected in the solid CaO even though the sulfur content in the bulk slag is high. This result indicates that the mass transfer of sulfur from liquid slag to solid CaO hardly occurs. Therefore, it can be said that solid CaO does not play a direct role in the desulfurization reaction and that the reaction is solely due to the liquid slag. The sulfide capacity (CS) is commonly used to describe the slag characteristics for desulfurization. Sosinsky et al. [6] reported the correlation between optical basicity and sulfide capacity and proposed the following equation:

$$\log C_S = \frac{22690 - 54640\Lambda}{T} + 43.6\Lambda - 25.2 \ldots (3)$$

where $\Lambda$ is the optical basicity and $T$ is the temperature.
Recently, Hayakawa et al.\(^7\) applied this equation to the CaO–SiO\(_2–\)Al\(_2\)O\(_3–\)MgO system and found a good correlation. In our experiment, the slag compositions were not analyzed, with the exception of sulfur. To calculate the sulfide capacity, the slag composition when the CaO rod was not immersed was assumed to be the same as the initial composition listed in Table 1. In contrast, when the CaO rod is immersed, the average value of the slag composition obtained by EPMA at positions that are not close to the interface of the CaO is used. The slag composition and the sulfide capacity of each slag are summarized in Table 4, and the relation between \(C_S\) and \(L_S\) is shown in Fig. 11. Although this experiment does not reach equilibrium after 20 min, the influence of the sulfide capacity on the distribution ratio is clearly evident. In this figure, the results of the systems with slag S are included although the experimental temperature is different. This indicates that the influence of slag composition and temperature on the desulfurization behavior can be analyzed by the sulfide capacity. According to this result, it can be concluded that the desulfurization rate is mainly controlled by the liquid slag composition and that the role of the solid lime is to supply CaO to the slag. The increase in the CaO content causes an increase in the sulfide capacity, and therefore, the desulfurization rate is increased by the immersion of solid lime.

### 4.2. Influence of the Interfacial Layer on the Desulfurization Rate

Figure 12 shows the change in average thickness of the interfacial layer with time in the case of sintered CaO rod immersion. When the rod is immersed without slag and with slag S, the interfacial layers are thin and do not increase in thickness with increased immersion time. This result indicates that the mass transfers in these interfacial layers are slow. On the other hand, when the CaO rod is immersed into hot metal with slag A, the interfacial layer thickens over time, indicating that the mass transfer is not hindered by the formation of the interfacial layer in this case. Figure 13 compares the change in the thickness of the interfacial layer formed on the sintered CaO with that formed on the metallurgical lime. No obvious difference between the interfacial layers on the two rod types is found.

The reason for the slow desulfurization when the CaO rod is immersed without slag is the formation of a dense interfacial layer, which hinders the mass transfer of sulfur. Because the formation of this interfacial layer does not change between the sintered CaO and the metallurgical lime, the porosity of the lime does not affect the desulfurization rate.

When the CaO rod is immersed with slag S, the desulfurization rate decreases. This is due to the formation of the interfacial layer, which inhibits the mass transfer of sulfur. In this case, the influence on the CaO supply of the solid lime immersion is small compared with the influence of the interfacial layer formation.

In contrast, in the case of slag A, the interfacial layer does

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**Table 4.** Sulfide capacity of each slag.

<table>
<thead>
<tr>
<th>Slag</th>
<th>CaO</th>
<th>SiO(_2)</th>
<th>Al(_2)O(_3)</th>
<th>MgO</th>
<th>(A)</th>
<th>log(CS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slag A</td>
<td>47.9</td>
<td>7.2</td>
<td>44.9</td>
<td>0</td>
<td>0.835</td>
<td>-2.109</td>
</tr>
<tr>
<td>Slag A + CaO</td>
<td>53.0</td>
<td>6.3</td>
<td>40.7</td>
<td>0</td>
<td>0.855</td>
<td>-1.867</td>
</tr>
<tr>
<td>Slag S</td>
<td>47.0</td>
<td>41.1</td>
<td>11.9</td>
<td>0</td>
<td>0.755</td>
<td>-3.375</td>
</tr>
<tr>
<td>Slag S + CaO</td>
<td>47.9</td>
<td>40.0</td>
<td>12.1</td>
<td>0</td>
<td>0.760</td>
<td>-3.320</td>
</tr>
<tr>
<td>Slag C</td>
<td>53.0</td>
<td>7.4</td>
<td>35</td>
<td>4.6</td>
<td>0.854</td>
<td>-1.880</td>
</tr>
<tr>
<td>Slag C + CaO</td>
<td>56.6</td>
<td>6.4</td>
<td>32.8</td>
<td>4.3</td>
<td>0.868</td>
<td>-1.713</td>
</tr>
</tbody>
</table>

**Fig. 11.** Relationship between the sulfide capacity (\(C_S\)) and the distribution ratio of sulfur at 20 min (\(L_S\)).

**Fig. 12.** Change in the average thickness of the interfacial layer with time in the case of sintered CaO rod immersion.

**Fig. 13.** Comparison of the interfacial layer thickness for sintered CaO with that for metallurgical lime.
not impede the mass transfer; therefore, when the CaO rod is immersed with the slag, the desulfurization rate increases owing to the increased supply of CaO to the slag. The same result is obtained in the case of slag C because an interfacial layer does not form.

5. Conclusions

To clarify the roles of solid lime and liquid slag in hot metal desulfurization, the reaction rate using slag, solid lime, and slag with solid lime was investigated and the interfacial layers were observed. The results are summarized as follows:

(1) The desulfurization rate is quite slow when the solid lime rod is immersed into hot metal without slag. This is because the formation of an interfacial layer inhibits the mass transfer of sulfur.

(2) Because sulfur is not detected in the solid CaO, the mass transfer of sulfur from the liquid slag to the solid CaO does not occur. Therefore, it can be said that the solid CaO does not play a direct role in the desulfurization reaction and that the reaction is solely due to the liquid slag.

(3) A good correlation between the desulfurization rates and the sulfide capacity of the liquid slag was found. Based on this result, it can be concluded that the supply of CaO from the solid lime to the slag causes an increase in sulfide capacity and consequent increase in the desulfurization rate via immersion of the lime rod.

(4) When dicalcium silicate forms at the interface, the desulfurization rate is decreased by the immersion of the CaO rod because this layer hinders the mass transfer of sulfur. On the other hand, when tricalcium aluminate forms at the interface, the desulfurization rate is increased by the immersion of the CaO rod owing to the increased supply of CaO to the slag; this is because the interfacial tricalcium aluminate layer does not hinder the mass transfer.

REFERENCES