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Rate of Desulphurization of Molten Iron by Slag under Reducing Condition. II
Influence of Silicon and Manganese

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Synopsis

The influence of silicon and manganese on the rate of transfer of sulphur across a slag-metal interface under reducing condition has been studied in temperature range from 1,490° to 1,560°C. The experimental method was the same as in the former experiment. The rate of transfer of sulphur from metal to slag increases with increasing content of silicon and manganese in iron, while that from slag to metal does not change appreciably; therefore, the rate of desulphurization of molten iron by slag increases with increasing silicon and manganese.

The consideration of sulphur activity does not account for the increase of the rate of desulphurization. The mechanism of desulphurization and the influence of silicon and manganese on the slag-metal sulphur reaction are discussed.

I. Introduction

In the former experiment(1) the effect of slag composition on the rate of transfer of sulphur from metal to slag under reducing condition had been measured by the use of radioactive sulphur, S\textsuperscript{35}, and the following conclusion had been derived from the experimental results.

The rate of transfer of sulphur from metal to slag increases rapidly with increasing basicity of slag and with temperature, while that from slag to metal does not change appreciably; consequently, the rate of desulphurization increases with increasing basicity of slag and with temperature.

The investigation had been continued to study the influence of silicon and manganese, the alloying elements normally present and of interest in commercial blast furnace operation, on the rate of transfer of sulphur. The result of the investigation will contribute to a better understanding of desulphurization in the blast furnace process. Radioactive sulphur was not used in the experiment because of the inconvenience of getting it.

II. Experimental method and results

The rate of transfer of sulphur was measured by determining the sulphur content of slag samples taken from the melt in a graphite crucible (4 cm in inner diameter and 10 cm in depth) at regular time intervals. The following experimental

conditions were selected to simplify the treatment of result.
(i) A large amount of metal (about 300 g) comparing with slag was used so that
the concentration of sulphur in metal would not change appreciably as a result of
the transfer from metal to slag.
(ii) The amount and number of slag samples taken during a run were reduced
as small as possible so that the amount of slag was assumed to be constant
throughout the run.
Metal charge was prepared by melting electrolytic iron in a graphite crucible in
a high frequency induction furnace and adding ferro-silicon or ferro-manganese
and iron sulphide. Synthetic slags used for this experiment were the same as in
the former experiment, composition of which are shown in Table 1.

<table>
<thead>
<tr>
<th>Slag</th>
<th>CaO (%)</th>
<th>SiO₂ (%)</th>
<th>Al₂O₃ (%)</th>
<th>S (%)</th>
<th>CaO/SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>44.0</td>
<td>45.5</td>
<td>10.4</td>
<td>0.08</td>
<td>0.97</td>
</tr>
<tr>
<td>B</td>
<td>53.0</td>
<td>36.2</td>
<td>10.7</td>
<td>0.08</td>
<td>1.46</td>
</tr>
</tbody>
</table>

The experimental procedure was the same as in the former experiment. The
influence of silicon in metal was studied up to about 1.8%. The transfer rate
curves at about 1500°C are shown for A slag in Fig. 1 and for B slag in Fig. 2,
which show the rate of transfer of sulphur from metal to slag increases with
increasing content of silicon in metal. The interesting feature of the role of

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Fig. 1. Effect of silicon on sulphur transfer with A slag at about 1,500°C.

Fig. 2. Effect of silicon on sulphur transfer with B slag at about 1,500°C.
alloyed silicon is that it is effective under both acid and basic slags. It was observed that silicon was always reduced from silica in the acid slag (A slag), but silicon was oxidized from the metal under the basic slag (B slag).

In Fig. 3 the effect of temperature on the rate of transfer is shown with metal containing about 1% silicon. As was expected, the rate of transfer increased with temperature.

Transfer rate curves for increasing amounts of manganese in iron up to 0.6% are shown for A slag at about 1,500°C in Fig. 4 and up to 0.4% for B slag in Fig. 5. The rate of transfer of sulphur from metal to slag increases more rapidly with increasing amount of manganese than in the case of silicon. Transfer rate curves for B slag (Fig. 5) were different from others, that is, the rate of transfer at the initial period was very rapid which will be discussed later. Manganese in iron decreased considerably during a run as a result of the transfer from metal to slag.

Fig. 3. Effect of temperature on sulphur transfer with A slag.

Fig. 4. Effect of manganese on sulphur transfer with A slag at about 1,500°C.

Fig. 5. Effect of manganese on sulphur transfer with B slag at about 1,500°C.
III. Discussion of results

The results of the present experiment coincides with the observation of previous investigators\(^{(2)\text{,}} (3)\), that is, silicon and manganese promote the rate of desulphurization of carbon-saturated iron by slag and silicon is not so effective as manganese.

The following two reasons may be considered for the effect of alloying elements on the rate of desulphurization:

(i) The change of activity of sulphur in iron and slag.

(ii) The change of the rate of slag-metal sulphur reaction.

Silicon increases the activity coefficient of sulphur in iron, but manganese decreases\(^{(4)\text{,}} (5)\). The solubility of carbon in iron is decreased by silicon, while increased by manganese\(^{(6)\text{.}}\). Carbon is the element which increases the activity coefficient of sulphur\(^{(7)}\). Therefore, the activity coefficient of sulphur in carbon-saturated iron will be nearly constant, when silicon or manganese is added to iron. The values of the activity coefficient of sulphur calculated by the method described by Sherman and Chipman\(^{(8)}\) showed that the change of the activity coefficient was so small that it did not account for the increase of the rate of desulphurization.

The activity coefficient of sulphur in slag has not yet been studied, but it may be thought that the change of activity coefficient by the change in slag composition at the initial period of desulphurization is very small.

Thus, the increase of the rate of desulphurization of iron containing silicon or manganese cannot be accounted for by the consideration of activity coefficient of sulphur.

1. On the mechanism of slag-metal sulphur reaction and the influence of silicon and manganese.

Goldman, Derge and Philbrook\(^{(2)\text{.}}\) proposed the following three-stage mechanism of desulphurization by slag:

\[
\text{[FeS]} = \text{(FeS)} \tag{1}
\]

\[
\text{(FeS)} + \text{(CaO)} = \text{(CaS)} + \text{(FeO)} \tag{2}
\]

\[
\text{(FeO)} + \text{C} = \text{[Fe]} + \text{CO} \tag{3}
\]

According to their explanation, in the unalloyed system iron is the principal carrier of sulphur across the slag-metal interface as shown in reaction (1), but when manganese is present as an alloying element, it replaces iron in reaction (1).


\(^{(6)}\) J. Chipman and et. al., Trans. Am. Soc. Metals, 44 (1952), 1215.


and causes the overall process to proceed more rapidly. Silicon acts through reaction (3) by supplanting carbon in removing oxygen from the system and promotes desulphurization.

Turkdogan, Hancock and Pearson (3) discussed the effect of silicon, manganese and aluminum on the rate of desulphurization by slag under reducing condition as follows:

The slag-metal sulphur reaction can be represented by the following equation:

\[ [S] + (O) = (S) + [O] \]  \hspace{1cm} (4)

As desulphurization proceeds, oxygen in iron increases, but will be removed by carbon in iron as follows:

\[ [O] + [C] = CO \]  \hspace{1cm} (5)

Because of the sluggishness of carbon-oxygen reaction, carbon dissolved in iron does not improve the rate of desulphurization as much as might be expected from thermodynamic consideration and deoxidizing elements such as silicon, manganese and aluminum increase the rate of desulphurization by lowering the activity of oxygen in iron.

These considerations on the slag-metal sulphur reaction explain well the increase of the rate of desulphurization by the presence of the deoxidizing element in iron, but a further consideration seems to be necessary for the effect of silicon, because the rate of desulphurization increases in both cases when silicon in iron increases (silica reduction from slag) and when it decreases (oxidation of silicon). Before considering the effect of alloying element, desulphurization mechanism in the case where the alloying element is absent will be discussed briefly.

Sulphur in iron transfers to slag in combination with iron conserving the electrical neutrality as follows:

\[ [\text{Fe}] + [S] = (\text{Fe}^{++}) + (S^{-}) \]  \hspace{1cm} (6)

In slags containing suspended graphite the following reaction may take place:

\[ (\text{Fe}^{++}) + (O^{-}) + C = [\text{Fe}] + CO \]  \hspace{1cm} (7)

Reaction (7) proceeds at a rate lower than the rate of dissolution of iron in slag at the initial stage of desulphurization, so iron in slag returns to iron in combination with oxygen as follows:

\[ (\text{Fe}^{++}) + (O^{-}) = [\text{Fe}] + [O] \]  \hspace{1cm} (8)

In the absence of carbon suspended in the slag, reaction (7) will not occur and oxygen will be transferred from slag to metal for each ion of sulphur which moves in the opposite direction. Oxygen dissolved in iron may be removed by reaction (5), but the rate of reaction is sluggish.

When iron contains manganese, the following reaction may proceed simultaneously with reaction (6):

\[ [\text{Mn}] + [S] = (\text{Mn}^{++}) + (S^{-}) \]  \hspace{1cm} (9)
Moreover, manganese removes oxygen from the metal acting as a deoxidizer:

\[ [\text{Mn}] + [\text{O}] = \text{(Mn}^{\text{II}}\text{)} + \text{(O}^{\text{2-}}\text{)} \]

(10)

Therefore, manganese in iron increases the rate of desulphurization remarkably. On the contrary, by the addition of manganese oxide to slag, metal will be oxidized temporarily and desulphurization will be disturbed as observed by Grant, Kalling and Chipman\(^{(9)}\).

When silicon is not present in initial metal, silica reduction from slag will continue until it reaches the equilibrium state of the following reaction:

\[ (\text{SiO}_2) + 2\text{C} = [\text{Si}] + 2\text{CO} \]

(11)

The reaction of reducing silica from slag accompanying the evolution of carbon monoxide gas suppresses the proceeding of reaction(5) and the rate of desulphurization is decreased as compared with the case where silica reduction dose not occur. So, an addition of silicon to iron improves the rate of desulphurization, but the contribution is not so great when the addition is less than the equilibrium concentration of reaction(11).

When silicon is added to iron above the equilibrium concentration, it removes the oxygen increasing with the proceeding of desulphurization in iron and improves the rate of desulphurization remarkably.

\[ [\text{Si}] + 2[\text{O}] = (\text{SiO}_2) \]

(12)

\[ (\text{SiO}_2) + 2(\text{O}^{\text{2-}}) = (\text{SiO}_4^{\text{2-}}) \]

(13)

Thus, the presence of silicon in iron contributes to the desulphurization, but the effect is less than that of manganese, because silicon does not act as a carrier of sulphur.

2. On the coefficient of transfer of sulphur

Transfer rate curves were treated as in the former report on an assumption that the transfer of sulphur is of the first order reaction, and the coefficient of transfer of sulphur were calculated. The following equation was derived under the experimental condition that the concentration of sulphur in iron and the amount of slag were constant during a run was applied to curves in Figs. 1, 2, 3, 4, and 5.

\[ C_s = \frac{K_mC_m}{K_s} \left( 1 - e^{-\frac{160AK_s}{M}t} \right) \]

(14)

where \( C_m \) and \( C_s \) are the concentration of sulphur in metal and slag respectively (\%), \( M \) is the weight of slag (20 g), \( A \) is the interfacial area (12.6 cm\(^2\)), \( t \) is the time (min), and \( K_m \) and \( K_s \) are the coefficient of transfer of sulphur from metal to slag and from slag to metal respectively.

From this equation it is seen that the relation between logarithms of the increment of sulphur content of slag during a definite time interval, log \( \Delta C_m \) and time, \( t \), will be linear and values of \( K_m \) and \( K_s \) can be obtained from this linear

\( \text{(9)} \) N. J. Grant, U. Kalling and J. Chipman, J. Metals, 3 (1951), 666.
relationship. As mentioned in the former report, the application of the equation to transfer rate curves should have some limitations, because the overall process of desulphurization under reducing condition can not be interpreted as the reaction of the first order.

The equation (14) held for the transfer rate curves obtained with iron containing silicon. Calculated values of $K_m$ and $K_s$ are given in Table 2 and changes of $K_m$ and $K_s$ with silicon content are shown in Figs. 6 and 7. (Initial silicon content of iron was used.) With increasing silicon content $K_m$ increases, while $K_s$ is nearly constant (with A slag decreases slightly and with B slag increases slightly). This implies that the rate of transfer of sulphur from metal to slag increases with increasing silicon, but that from slag to metal does not change, therefore, the net rate of transfer of sulphur from metal to slag increases. The increase of $K_m$ with silicon was greater with B slag than with A slag.

The effect of temperature on $K_m$ and $K_s$ is shown for A slag as plots of $\log K_m$.

**Table 2. Effect of silicon on the coefficient of transfer of sulphur.**

<table>
<thead>
<tr>
<th>Slag</th>
<th>Temp. (°C)</th>
<th>Metal</th>
<th>$K_m$</th>
<th>$K_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A slag</td>
<td>1,493</td>
<td>0.02</td>
<td>0.93</td>
<td>0.00093</td>
</tr>
<tr>
<td></td>
<td>1,503</td>
<td>0.32</td>
<td>0.96</td>
<td>0.0011</td>
</tr>
<tr>
<td></td>
<td>1,493</td>
<td>0.83</td>
<td>0.84</td>
<td>0.0015</td>
</tr>
<tr>
<td></td>
<td>1,500</td>
<td>0.98</td>
<td>1.00</td>
<td>0.0015</td>
</tr>
<tr>
<td></td>
<td>1,500</td>
<td>1.76</td>
<td>0.83</td>
<td>0.0022</td>
</tr>
<tr>
<td></td>
<td>1,512</td>
<td>1.00</td>
<td>0.91</td>
<td>0.0019</td>
</tr>
<tr>
<td></td>
<td>1,558</td>
<td>0.92</td>
<td>0.90</td>
<td>0.0023</td>
</tr>
<tr>
<td>B slag</td>
<td>1,507</td>
<td>0.03</td>
<td>0.90</td>
<td>0.0023</td>
</tr>
<tr>
<td></td>
<td>1,508</td>
<td>0.39</td>
<td>0.89</td>
<td>0.0028</td>
</tr>
<tr>
<td></td>
<td>1,505</td>
<td>0.87</td>
<td>0.97</td>
<td>0.0032</td>
</tr>
</tbody>
</table>

![Fig. 6. Effect of silicon on coefficients of transfer of sulphur with A slag at about 1,500°C.](image)

![Fig. 7. Effect of silicon on coefficients of transfer of sulphur with B slag at about 1,500°C.](image)
and \( \log K_m \) vs. \( 1/T \) in Fig. 8. The temperature dependency of \( K_m \) and \( K_s \) are nearly the same with silicon free iron and activation energy are 45000 and 13000 cal/mol for \( K_m \) and \( K_s \) respectively.

In the case of iron containing manganese, transfer rate curves for A slag were interpreted by the equation (14). Values of \( K_m \) and \( K_s \) are given in Table 3 and the effect of manganese on \( K_m \) and \( K_s \) are shown in Fig. 9. But transfer rate curves for B slag were different from others. The relation between \( \log A \) and \( t \) was not linear at the initial period of desulphurization and became linear about 10 minutes after as shown in Fig. 10, showing that the values of \( K_m \) and \( K_s \) decreased with time. This phenomena is the same as those observed in low viscosity slags in the former experiment. With the progress of desulphurization, manganese transfers from metal to slag according to the reactions (9) and (10) and lowers the viscosity of slag remarkably; therefore, the mixing of the slag by the evolution of carbon monoxide gas seems to be complete. In this case slag samples taken at the initial period from the upper part of molten slag layer may represent the true sulphur content differing that in the case of high viscosity slag. This seems to be the reason why transfer rate curves with B slag and iron containing manganese are different from others and suggests that the treatment of the transfer of sulphur as the first order reaction is inadequate. But the values of \( K_m \) and \( K_s \) obtained from the linear relationship about 10 minutes after as shown in Fig. 10 will be of use in comparing the rate of desulphurization with one another.

The values of \( K_m \) and \( K_s \) at the initial period calculated from the tangent of the curves at \( t = 0 \) and from the linear relationship are given in Table 3.

### Table 3. Effect of manganese on the coefficient of transfer of sulphur.

<table>
<thead>
<tr>
<th>Slag</th>
<th>Temp. (°C)</th>
<th>Metal</th>
<th>( K_m )</th>
<th>( K_s )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mn (%)</td>
<td>S (%)</td>
<td></td>
</tr>
<tr>
<td>A slag</td>
<td>1,493</td>
<td>tr.</td>
<td>0.93</td>
<td>0.00093</td>
</tr>
<tr>
<td></td>
<td>1,506</td>
<td>0.13</td>
<td>0.66</td>
<td>0.0018</td>
</tr>
<tr>
<td></td>
<td>1,502</td>
<td>0.18</td>
<td>0.69</td>
<td>0.0020</td>
</tr>
<tr>
<td></td>
<td>1,508</td>
<td>0.40</td>
<td>0.56</td>
<td>0.0042</td>
</tr>
<tr>
<td></td>
<td>1,510</td>
<td>0.62</td>
<td>0.47</td>
<td>0.0065</td>
</tr>
<tr>
<td>B slag</td>
<td>1,507</td>
<td>tr.</td>
<td>0.90</td>
<td>0.0023</td>
</tr>
<tr>
<td></td>
<td>1,505</td>
<td>0.23</td>
<td>0.84</td>
<td>0.0059\rightarrow 0.0043</td>
</tr>
<tr>
<td></td>
<td>1,498</td>
<td>0.40</td>
<td>0.99</td>
<td>0.0198\rightarrow 0.0091</td>
</tr>
</tbody>
</table>
increases more rapidly with manganese in iron than $K_s$; consequently, the net rate of transfer of sulphur from metal to slag increases.

The increase of $K_m$ with manganese in iron is greater than that with silicon for the reason mentioned before.

**Summary**

The influence of silicon and manganese on the rate of desulphurization of carbon saturated iron by CaO-SiO$_2$-Al$_2$O$_3$ slag was investigated. Two synthetic slags (CaO/SiO$_2$ = 0.97, 1.46) were used in this study. Silicon was added to iron up to 1.76% and manganese up to 0.62%.

Silicon and manganese increase the rate of transfer of sulphur from metal to slag. Consideration of sulphur activity does not account for the influence of these elements on the rate of transfer. The influence of these elements was explained on the basis of reaction mechanism of desulfurization.

The relative effectiveness of silicon and manganese on the rate of sulphur transfer is shown by the coefficients of transfer of sulphur in Figs. 6, 7 and 9.

The rate of transfer of sulphur from metal to slag increases rapidly with increasing silicon and manganese, while that from slag to metal does not change appreciably; consequently, the net rate of transfer from metal to slag increases rapidly.

In conclusion the author expresses his hearty thanks to Prof. T. Saito for his valuable suggestions and encouragement in the course of this work.