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Rate of Desulphurization of Molten Iron by Slag under Reducing Condition

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Synopsis

The rate of transfer of sulphur across a metal-slag interface under reducing condition was studied at the temperature range from 1,440° to 1,570°C. Radioactive sulphur, S³⁵, was used to improve the accuracy of the experiment.

The net rate of transfer of sulphur from metal to slag increases with increasing basicity of the slag and with temperature. This is ascribable to the fact that 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 with change in slag composition and temperature.

In the case of high viscosity slags, the rate of transfer of sulphur was interpreted on an assumption that the transfer is the reaction of the first order, but this assumption was inadequate for explaining the experimental results obtained with low viscosity slags. The rate of transfer of sulphur seems to be affected remarkably by side reaction.

I. Introduction

A study of the kinetics of desulphurization of iron by slag under reducing condition will contribute to a better understanding of desulphurization in the blast furnace process and in the electric furnace process. The process of desulphurization may be analysed in three steps, viz., diffusion of sulphur in molten iron, transfer of sulphur across a metal-slag interface and diffusion of sulphur in molten slag.

The diffusion coefficient of sulphur in molten CaO-SiO₂-Al₂O₃ slag was determined previously⁽¹⁾, which is of the order of 10⁻⁶ cm²/sec and seems to be much smaller than that in molten iron, and therefore, diffusion in molten slag is an important factor in determining the rate of desulphurization of iron by slag.

In this paper the result of the measurement of the rate of transfer of sulphur across a metal-slag interface under reducing condition will be described. Chang and Goldman⁽²⁾ had investigated the transfer reaction of sulphur and obtained fruitful results. But, it seems to require further examination of the results, so the present experiments were carried out.

II. Experimental procedure and results

The rate of transfer of sulphur was measured by determining sulphur content of slag samples taken from the melt in a graphite crucible at regular time intervals.

* The 68th Report of the Research Institute of Mineral Dressing and Metallurgy.

(1) T. Saitô and Y. Kawai, *Sci. Rep. RITU*, **A5** (1953), 460.

(2) L.C. Chang and K.M. Goldman, *Trans. Am. Inst. Mining Met. Engrs.*, **176** (1948), 309.

The experimental conditions were as follows :

- (1) A comparatively large amount of metal was used relative to slag so that the concentration of sulphur in metal would not change appreciably as a result of the transfer from metal to slag.
- (2) 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 a run.

For this purpose radioactive sulphur, S^{35} , was used, though not for the whole runs. The metal sample containing radioactive sulphur was made by melting a mixture of iron sulphide containing radioactive sulphur and iron powder, about 20 g in weight, using a graphite crucible in an air-tight induction furnace, and by casting into an iron mould. The method of preparing iron sulphide containing radioactive sulphur was reported previously and an air-tight induction furnace was the one used in the diffusion experiment⁽¹⁾. The radioactive metal was added to a non-radioactive metal melted in a graphite crucible and about 300 g of metal charge was used for an experimental run.

A graphite crucible used for melting the charge in the air-tight induction furnace was 4 cm in inner diameter and 10 cm in depth and covered with a graphite lid with a hole to improve the uniformity of temperature in the melt.

The temperature was measured with an optical pyrometer sighted on the surface of the bath through a sighting window at the top of the furnace. The optical pyrometer was calibrated against a Pt-Pt-Rh thermocouple dipped in molten metal and slag. The sighting window was made movable for charging and sampling of slag.

The molten metal was not rotated, even though the furnace was constructed to rotate the melt, because the area of metal-slag interface would be reduced by progressive sampling of slag during a run.

After holding the metal at desired temperature for about 5 minutes, non-radioactive iron sulphide was added to molten iron in order that the concentration of sulphur in metal might be about 1 per cent, and after holding it for another 5 minutes, metal sample was taken by suction into a silica tube. Immediately after the metal sample was taken, 20 g of the prefused and crushed synthetic slag was introduced to the metal bath. The slag reached the temperature of the furnace in 1.5 to 2 minutes. Slag samples were taken at regular time intervals with a copper sampler shown in Fig. 1. Among various kinds of sampler used in the experiment, this was the best to take a small and definite amount of slag sample. After the last slag sample had been taken, the metal sample was taken again through the slag. The number of slag sample

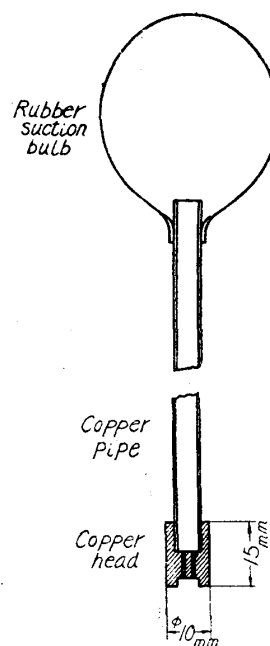


Fig. 1. Slag sampler.

was 5 to 8 and the amount of a sample was 0.2 to 0.4 g.

Synthetic slags were prepared from chemically pure oxide components by melting the mixture in a graphite crucible and melting was repeated twice to secure a thorough homogeneity. The chemical compositions and the value of basicity are shown in Table 1.

Table 1. Composition of slags.

Slag	CaO (%)	SiO ₂ (%)	Al ₂ O ₃ (%)	MgO (%)	S (%)	(CaO+MgO)/SiO ₂
A slag	44.0	45.5	10.4	—	0.08	0.97
B "	53.0	36.2	10.7	—	0.08	1.46
M "	45.1	35.6	11.3	7.9	0.11	1.49

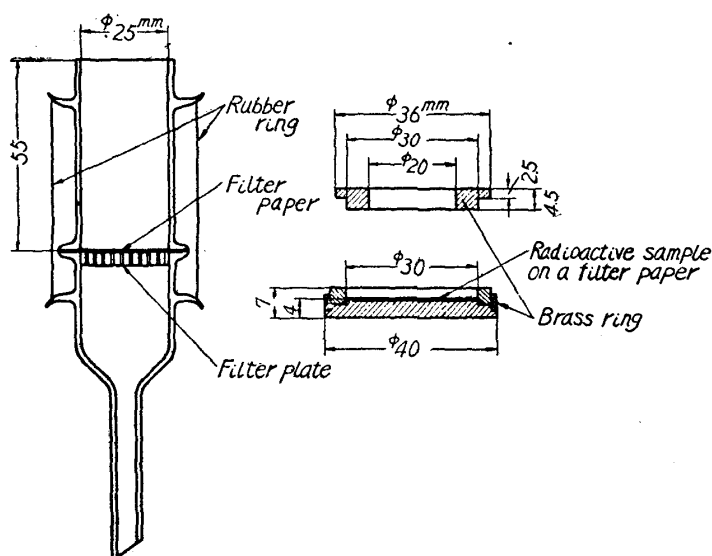


Fig. 2. Glass filter and brass holder for radioactive sample.

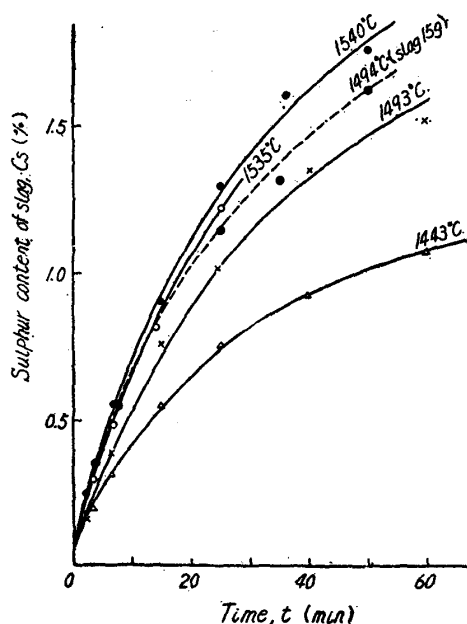


Fig. 3. Transfer rate curves for A slag (acid slag).

Metal and slag samples taken during a run were pulverized to powders under 100 mesh screen and magnetic materials in slag samples were separated. In the case of radioactive sample, about 0.2 g of each powders was introduced into a glass filter shown in Fig. 2 and suspended in a small amount of alcoholic solution. By carefully filtering this suspension, a thin layer of powders uniformly distributed on a filter paper was obtained⁽³⁾. After drying, the radioactive intensity of the powder layer was measured by a Geiger-Müller counter of end-window type under a definite geometrical condition.

The ratio of the radioactive intensity to the concentration of sulphur was determined by the chemical analysis of arbitrary one or two samples. Using this value of the ratio, sulphur content of whole metal and slag samples were determined.

(3) Y. Kawai, Bulletin Research Inst. Mineral Dress. Metall., (in Japanese), 9 (1953), 103.

When radioactive sulphur was not used, all samples were chemically analysed.

Experimental results now obtained are shown in Figs. 3, 4, 5. It is seen from these results that the rate of transfer of sulphur from metal to slag increases with increasing basicity of the slag and with temperature.

In the case of the slag containing magnesia, the shape of transfer rate curves (Fig. 5) was different from others and this will be discussed later.

III. Coefficients of transfer of sulphur

Assuming that the rate of transfer of sulphur from metal to slag is proportional to the concentration of sulphur in the metal and that from slag to metal is proportional to the concentration of sulphur in the slag, the following equation may be obtained for the net transfer of sulphur from metal to slag at a constant temperature:

$$\frac{dW}{dt} = \frac{dC_s \cdot M/100}{dt} = A(K_m C_m - K_s C_s), \quad (1)$$

where dW/dt is the net rate of transfer of sulphur from metal to slag in g/min, M , the weight of slag (20 g), A , the interfacial area between metal and slag (12.6 cm²), C_m , C_s , the concentration of sulphur in metal and slag respectively (%), and K_m , K_s , the coefficient of transfer of sulphur from metal to slag and from slag to metal respectively.

In this equation, activities of sulphur in metal and slag should be considered instead of concentrations, but concentrations were used for the reason that activity coefficients in slag were unknown, though activity coefficients in metal could be estimated from the composition of metals.

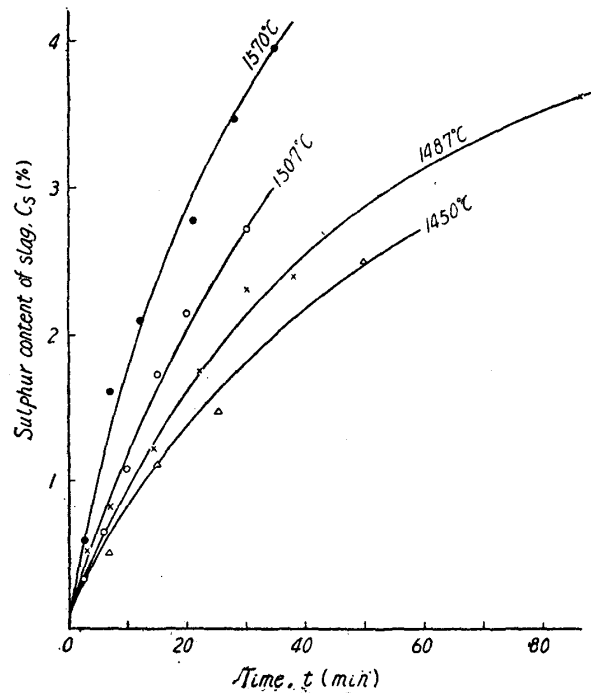


Fig. 4. Transfer rate curves for B slag (basic slag).

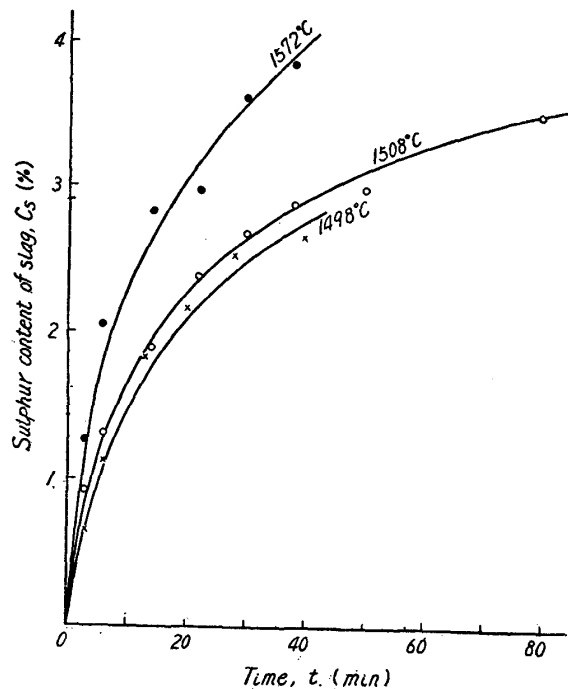


Fig. 5. Transfer rate curves for M slag (slag containing MgO).

The weight of the slag decreased by about 10 per cent during the experiment and the concentrations of sulphur in the metal also varied up to 20 per cent. These variation should be very small at the beginning of the run and become progressively larger during the run.

By integrating the equation (1), the following equation can be obtained:

$$C_s = \frac{K_m C_m}{K_s} \left(1 - e^{-\frac{100AK_s}{M}t} \right) \quad (2)$$

From this equation it is seen that the plotting of $\log \Delta C_s$, logarithms of the increment of sulphur content of slag during a definite time interval, versus t , the time, should form a straight line. Values of K_m and K_s can be calculated from the slope and the intercept on the ordinate.

Chang and Goldman⁽²⁾ calculated K_m and K_s by equation (1) which shows the straight line relationship between dC_s/dt and C_s . But the estimation of the value

of dC_s/dt from the transfer rate curve seems to be inaccurate at the beginning of the transfer, and therefore, the calculation based on equation (2) is preferable.

It must be mentioned here that equation (1) or (2) is applicable only to the reaction which accompanies no side reaction. Looking at the slag surface during a run, bubble formation was observed, and this showed that the transfer reaction of sulphur under reducing condition accompanied a side reaction, presumably $(\text{FeO}) + \text{C} \rightarrow [\text{Fe}] + \text{CO}$. Consequently, the application of the equation to the transfer rate curves should have some limitations.

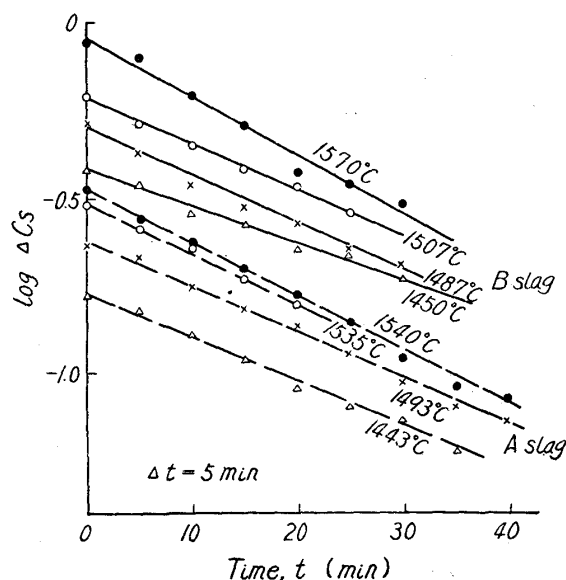


Fig. 6. Relation between $\log \Delta C_s$ and t (A and B slag).

Table 2. Values of the coefficient of transfer, K_m and K_s .

Slag	Temp. (°C)	C_m (%)	K_m	K_s	K_m/K_s
A slag	1,540	0.94*	0.0013	0.00059	2.2
	1,535	0.99*	0.0011	0.00053	2.1
	1,494	1.03	0.00084	0.00050	1.7
	1,493	0.93*	0.00097	0.00051	1.9
	1,443	1.00*	0.00062	0.00046	1.3
B slag	1,570	1.02*	0.0032	0.00061	5.2
	1,507	0.90*	0.0024	0.00047	5.1
	1,487	0.97	0.0017	0.00045	3.8
	1,450	1.00*	0.0013	0.00037	3.5
M slag	1,572	1.00	0.0109→0.0030	0.0051→0.00066	2.1→4.5
	1,508	0.97	0.0067→0.0021	0.0041→0.00057	1.6→3.7

(1) Silicon contents of metals were below 0.1% and manganese below 0.05%.

(2) Asterisk shows that radioactive sulphur was used.

In experimental results from A and B slags, straight line relationships were observed, as shown in Fig. 6. Values of K_m and K_s are given in Table 2.

Assuming that the specific gravity of molten slag is about 3 g/cm^3 , the thickness of molten slag layer of 20g in weight is about 5.3 mm. In order to clarify whether the thickness have any influences on the value of transfer coefficients, an experiment on A slag was carried out, the amount of which was reduced to 15g. 15g was the minimum amount which could cover the whole surface of molten metal. The transfer rate curve, values of K_m and K_s , and $\log K_m$ and $\log K_s$, are shown in Fig. 3, Table 2 and Fig. 8, respectively. This result was consistent with results from the slag of 20g in weight within the experimental error.

The transfer rate curves for slag containing magnesia were different from others. The relation between $\log \Delta C_s$ and t was not linear at the initial period of transfer, as shown in Fig. 7, but became linear in about 10 minutes, showing that the values of K_m and K_s decreased with time. In Table 2, the values of K_m and K_s at the initial period calculated from the tangent of the curves at $t = 0$ and values from the straight line relationship about 10 minutes after are given.

IV. Discussion of results

1. Effect of temperature and basicity of slag on the rate of transfer

In the case of A and B slag, transfer rate curves could be analysed on the assumption that transfer is the reaction of the first order.

The following equation of Arrhenius should hold between the coefficients of transfer and temperatures :

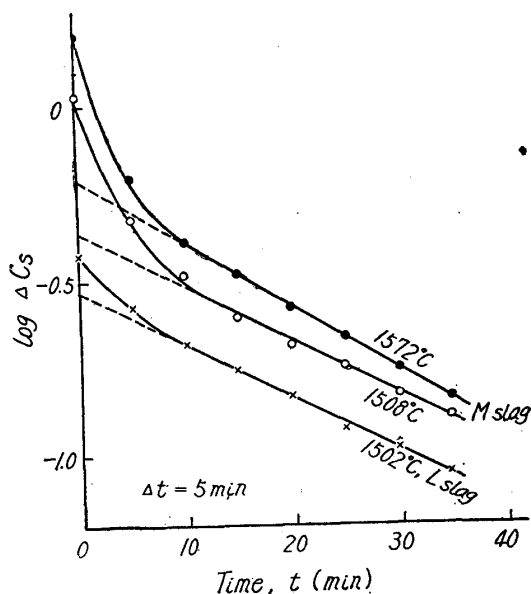


Fig. 7. Relation between $\log \Delta C_s$ and t for low viscosity slag (M and L slag).

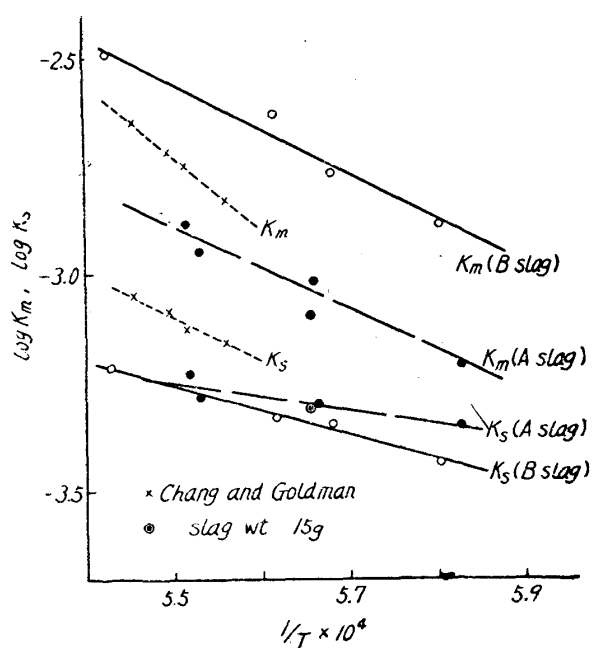


Fig. 8. Relation between $1/T$ and $\log K_m$ or $\log K_s$.

$$K_m = A_m e^{-\frac{Q_m}{RT}}, \quad K_s = A_s e^{-\frac{Q_s}{RT}} \quad (3)$$

where A_m and A_s are constants independent of temperature, Q_m and Q_s , activation energies for the transfer of sulphur from metal to slag and from slag to metal respectively, R , the gas constant, and T , absolute temperature.

Log K_m and log K_s are plotted against $1/T$ in Fig. 8, in which straight lines are drawn by the method of least squares.

Activation energies were obtained as follows :

$$\begin{aligned} Q_m &= 45,000, & Q_s &= 13,000 & \text{cal/mol for A slag,} \\ Q_m &= 49,000, & Q_s &= 27,000 & \text{cal/mol for B slag.} \end{aligned}$$

In Fig. 8, the result of the experiment for the slag containing 46.66 % CaO, 37.24 % SiO₂ and 16.29 % Al₂O₃ by Chang and Goldman⁽²⁾ is also shown for comparison. Activation energies obtained by them were $Q_m = 79,000$ and $Q_s = 39,000$ cal/mol. These values are much greater than those now obtained.

It is a well-known fact that the temperature of the furnace and basicity of slag must be maintained as high as possible in order to get good desulphurization.

Though this had been explained hitherto from the measurement of chemical equilibrium of sulphur between metal and slag, the results of present investigation gives a better explanation.

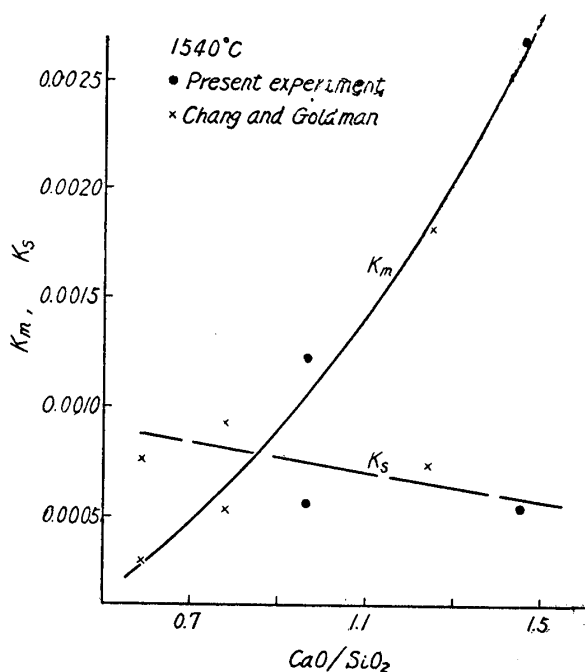


Fig. 9. Variation of K_m and K_s with CaO/SiO₂ ratio at 1,540°C.

From Fig. 8 it is clearly seen that K_m is more temperature-sensitive than K_s , and that the value of K_m of basic slag is much greater than that of acid slag, while the values of K_s are nearly the same in both slags. The effect of the composition of slag on K_m and K_s is more clearly shown in Fig. 9, which shows the plotting of K_m and K_s at 1,540°C against CaO/SiO₂ ratio. At this temperature K_s tends to decrease with increasing CaO/SiO₂ ratio.

From these results it is concluded that good desulphurization by basic slag at high temperature may be ascribable to the fact that the rate of transfer from metal to slag increases rapidly with increasing basicity of slag and with temperature.

2. On the interpretation of transfer rate curves

As mentioned in the preceding section, transfer rate curves for the slag containing magnesia could not be interpreted on the assumption that the transfer is the reaction of the first order. This suggests that the treatment of the transfer

of sulphur as the first order reaction was inadequate, so the results were examined from various points of view.

The slag containing magnesia has lower viscosity than others, as shown in Table 3⁽⁴⁾. Experiments were carried out with a slag of low viscosity which contained no magnesia (L slag in Table 3, 48.1% CaO, 41.1% SiO₂, 10.8% Al₂O₃), to see whether similar transfer rate curve would appear. The result which is shown in Fig. 7 indicates the rapid transfer of sulphur at the initial period, though not

Table 3. Viscosity of slags used in the present experiments.

Slag	Viscosity (poise)		Remarks
	1,500°C	1,600°C	
A slag	10	5	} values estimated from iso-viscosity diagram ⁽⁴⁾
B "	15	10	
M "	3.5	1	} values by measurement ⁽⁴⁾
L "	5.5	1.5	

so remarkable as that for the slag containing magnesia. This fact seems to be an evidence that the viscosity of slag has some influences upon the transfer rate of sulphur. In the case of high viscosity slags, slag samples taken at the initial period from the upper part of molten slag layer might not show their true sulphur content because of the inhomogeneity of sulphur owing to the weakness of agitation by gas evolution. True sulphur content would be higher than values observed. Therefore, it seems to be impossible to measure the actual transfer rate curves of these slags at the initial period.

If the assumption of the first order reaction holds for the transfer of sulphur throughout the run, the distribution ratio of sulphur between slag and metal, C_s/C_m , should be equal to K_m/K_s , when the rate of transfer reaches equilibrium.

Table 4. Distribution ratio of sulphur at 1,500°C.

Slag	K_m/K_s	$\frac{(S)}{[S]}$ (Hatch and Chipman ⁽⁵⁾)
A slag	1.9	100
B "	4.3	200

In Table 4 the values of K_m/K_s at 1,500°C for A and B slags were compared with values of distribution ratio at equilibrium measured by Hatch and Chipman⁽⁵⁾. The values of K_m/K_s were much smaller and this indicates that the plotting of $\log \Delta C_s$ vs. t should deviate from a straight line relationship with time. In this respect it is noteworthy that in the case of the slag containing magnesia the values of K_m/K_s increased with time, though K_m and K_s decreased with time, as shown in Table 2.

These facts also suggest that the transfer of sulphur from metal to slag is not a simple reaction of the first order, but a complex one.

(4) T. Saitô and Y. Kawai, Sci. Rep. RITU, A3 (1951), 491; A4 (1952), 615.

(5) G.G. Hatch and J. Chipman, Trans. Am. Inst. Mining Metall. Engrs., 185 (1949), 274.

According to the studies of Derge, Philbrook and Goldman⁽⁶⁾ and of Rocca, Grant and Chipman⁽⁷⁾, desulphurization of iron by slag under reducing condition may be expressed by the following reactions based on the molecular theory:



Sulphur originally present in the iron is transferred across the interface into the slag in combination with iron, and then the sulphur is stabilized in the slag by combination with calcium. The iron oxide resulting from the slag phase reaction is, in turn, reduced to iron by carbon as follows:



If the reaction (6) is suppressed or proceeds very slowly compared with the reaction (4), the rate of transfer of sulphur at the initial period may be analysed as the reaction of the first order. Nevertheless, the results of the present investigation indicates that the transfer of sulphur should not generally be interpreted as the first order reaction. The transfer of sulphur under reducing condition must be a complex reaction which is affected by the reaction (6), therefore, further experiments must be carried out in order to determine the order of reaction.

Summary

The rate of transfer of sulphur from metal to slag under reducing condition was measured at the temperature range from 1,440 to 1,570°C by the determination of sulphur content of slag samples taken from the melt in a graphite crucible. The experimental condition was planned so that the concentration of sulphur in metal and the amount of slag could be constant throughout a heat run.

Radioactive sulphur was used, though not for the whole runs, to improve the accuracy of the experiment.

The results obtained may be summarized as follows:

- (1) The rate of transfer of sulphur from metal to slag increases very rapidly with increasing basicity of slag, while that from slag to metal does not change appreciably. Also, the former is more sensitive to temperature than the latter. These contribute to good desulphurization of iron by basic slag at high temperature.
- (2) It is inadequate to express the rate of transfer of sulphur under reducing condition as the first order reaction, though the equation of the first order reaction holds for slags of high viscosity. It seems that the side reaction remarkably influences the proceeding of the transfer of sulphur.

In conclusion, the authors express their thanks to Messrs. K. Maruya and H. Satô for their assistance. The present investigation was supported by a Grant in Aid for Fundamental Scientific Research of the Ministry of Education.

(6) G. Derge, W.O. Philbrook and K.M. Goldman, *Trans. Am. Inst. Mining Metall. Engrs.*, 188 (1950), 1111.

(7) R. Rocca, N.J. Grant and J. Chipman, *Ibid.*, 191 (1951), 319.