Diffusion of Sulfur in Molten CaO-SiO_2-Al_2O_3 Slag

Diffusion of Sulfur in Molten CaO-SiO_2-Al_2O_3 Slag*

Tunezô SAITÔ and Yasuji KAWAI

The Research Institute of Mineral Dressing and Metallurgy

(Received August 8, 1953)

Synopsis

As the first step in the study on the kinetics of desulfurization of iron by slag, the rate of diffusion of sulfur in molten CaO-SiO_2-Al_2O_3 slag was determined by the use of radioactive sulfur S^{35}.

Iron sulfide powder made from barium sulfide containing S^{35} was mixed with powdered CaO-SiO_2-Al_2O_3 slag, and after melting, this radioactive sample was poured into a graphite tube, which was coupled with a graphite crucible containing a non-radioactive sample of nearly the same composition as the radioactive sample. Then, the couple was heated in a high frequency induction furnace in a nitrogen atmosphere for a definite time. After cooling in the furnace, thin slices were successively cut off from the top of the slag column, and the radioactive intensity of the polished surfaces of the remainder was measured by a Geiger-Müller counter.

From these measurements, the diffusion coefficient D of sulfur in a molten basic slag was determined as follows:

$$D = 1.4\, e^{-\frac{49,000}{RT}}.$$

The diffusion coefficient in an acid slag at 1,440°C was nearly the same as in the basic slag, but its values at higher temperatures could not be measured, owing to the evolution of gas by the reaction, $SiO_2 + 2C \rightarrow Si + 2CO$.

I. Introduction

Many studies have been published on the desulfurization of molten iron and steel, but most of them treat the problem from the viewpoint of chemical equilibrium, a few only taking up the subject from the side of chemical kinetics. According to recent studies[1], the speed of desulfurization by molten slag is reported as rather slow.

The mechanism of the desulfurization by slag may be analysed in the following three steps:

1) diffusion of sulfur in the iron melt,

2) transfer of sulfur at the interface between iron melt and molten slag, and

3) diffusion of sulfur in the molten slag.

The diffusion constant of sulfur in molten iron is of the order of 10^{-3} cm²/sec (Holbrook et al.[2]) and that in molten slag, of 10^{-5} cm²/sec (Derge et al.[3]). Thus, the speed of diffusion of sulfur in molten slag is comparatively slow, so that the diffusion in molten slag seems to be an important factor in determining the net rate of the reaction of desulfurizing the iron melt. To measure such low

(1) G. Hatch and J. Chipman, Tr. AIME, **185** (1949), 274.

(2) W. F. Holbrook, C. C. Furnas and L. Joseph, Ind. Eng. Chem., **24** (1932), 993.

(3) G. Derge, W.O. Philbrook and K. M. Goldman, Tr. AIME, **188** (1950), 1111.

speed of diffusion it is necessary either to perform a very long run or to make an accurate measurement of the concentration gradient of sulfur in the vicinity of the interface by means of some special method. Derge and his collaborators determined the diffusion coefficient by measuring the concentration gradient by cutting samples after diffusion run and analysing the successive slices chemically, but this method would give only the approximate value of the diffusion coefficient, and it was impossible to measure its change due to the variation in temperature and composition of slag. So, the authors have undertaken to measure accurately the diffusion coefficient of sulfur in molten slag, as the first step in the study of the velocity of desulfurization.

Preliminary to our experiments, we first measured the approximate concentration gradient of sulfur in samples after diffusion run by chemical analysis with the same method as used by Derge et al. and ascertained that the diffusion constant was of the order of 10^{-5} cm²/sec. Then, in the following experiment the diffusion constants were determined by measuring the concentration in the vicinity of the interface with precision, using radioactive sulfur S^{35}.

II. Preparation of Samples

A) Radioactive sulfur, S^{35}

3 mC of radioactive sulfur, produced in U.S.A. was used in our experiments, of which 1 mC was first provided and then 2 mC later on. It was provided in the form of BaS solution in 0.203 N Ba(OH)₂. The concentration was 4 mC/ml, so a solution of (NH₄)₂S was added as carrier. S^{35} emits β rays (the maximum energy is 0.17 MeV) and disintergrates into Cl^{35}. Its half-life is said to be 87.1 days but our measurement on the provided S^{35} indicated a little shorter half-life of 81 days.

B) Iron sulfide

Sulfur is believed to be present in molten slag in the form of CaS, so it was deemed appropriate to turn the BaS*(* indicates presence of radioactive sulphur) into CaS* before mixing with the molten slag, but considering the complexity of the process for manufacturing CaS and the consequent loss of S* in the process, we proceeded to make FeS* by the following process:

A solution of FeSO₄ was taken in the flask B in Fig. 1, into which NH₄OH was added in drops from flask A, to precipitate Fe(OH)₂. Next, the mixed solution of BaS* and its carrier (NH₄)₂S was added from the same flask, also in drops. Care was taken to keep the quantity of FeSO₄ solution in excess of the equivalent quantity of the BaS*+(NH₄)₂S solution, to assure
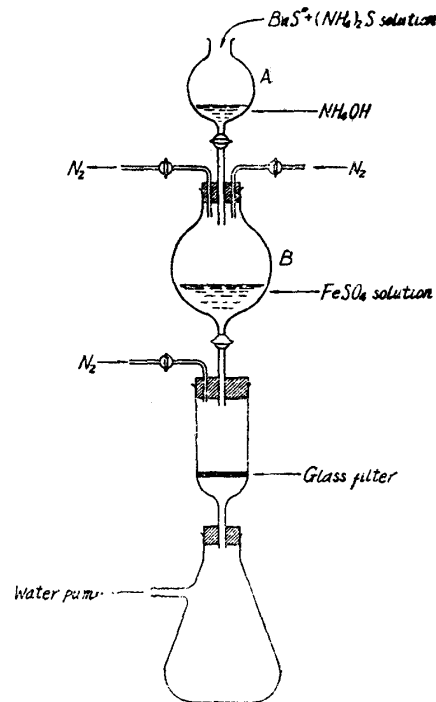

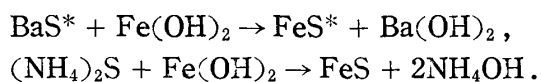Fig. 1. Apparatus for preparing FeS*.

complete transformation of BaS* into FeS*. By a good shake of the flask, the following reactions were completed:

$$BaS^* + Fe(OH)_2 \rightarrow FeS^* + Ba(OH)_2,$$

$$(NH_4)_2S + Fe(OH)_2 \rightarrow FeS + 2NH_4OH.$$

Then, the solution and the precipitate were poured through the cock at the bottom of the flask into a glass-filter and filtered under suction of a water pump. The precipitating and filtering processes were done under nitrogen atmosphere to prevent oxidation of the precipitate as far as possible. The produced precipitate, which contains also some $Fe(OH)_2$ and $Fe(OH)_3$ produced by the $FeSO_4$ in excess, was dried at 50°C under vacuum, ground in a porcelain mortar and kept in a dessicator.

As the BaS* solution was provided twice at different times, 1 and 2 mC respectively, we had to repeat the above process twice. The quantity of the produced FeS* powder amounted to about 4 g at the first operation when 1 mC was used and to about 3.2 g on the next occasion when 2 mC of BaS* was used. The sulphur content was about 28 per cent in both of the samples.

C) Sample slag

Powders of CaO (99 per cent), SiO_2 (99.5 per cent) and Al_2O_3 (98.5 per cent) were used for preparation of sample slag.

Required quantities of these materials were mixed and melted in a graphite crucible by a high frequency induction furnace at about 1,600°C under incessant stirring. The melt was cooled and solidified, then the mass was ground to powder and remelted, to assure a thorough homogeneity. The resultant lump was again ground down, one half of it into fine powder and the other half into granules. One set of the samples was basic and two sets acid in composition, as shown in Table 1. For preparation of S*-containing slag, FeS* and CaS was added to the powdered slag, so that the sulphur content amounted to about 1.5 per cent, and melted in a graphite crucible (inner diameter 30 mm × depth 90 mm) placed in a

Table 1. Composition of slags.

	CaO (%)	SiO₂(%)	Al₂O₃(%)	CaO/SiO₂
Basic Slag	50.3	39.3	10.4	1.28
Acid Slag (I)	37.5	53.9	8.6	0.69
,, (II)	42.5	47.9	9.6	0.89

hermetically sealed high frequency induction furnace (Fig. 3) to prevent leakage of S* into the atmosphere, which may cause danger. The crucible was frequently turned to expedite the mixture of the sample materials to homogeneity and upon cooling, the sample was taken out and tested for the homogenous distribution of S* before using in the experiment. During the process, the iron separated out as granules.

III. Apparatus and Procedure of Diffusion Experiment

In this diffusion experiments, the graphite container shown in Fig. 2 was used.

When the graphite crucible shown in the lower part of Fig. 2 was heated to the desired temperature in a high frequency induction furnace, some granules of the sample slag containing no S* was slowly melted, taking care to prevent blowhole formation, and then cooled down to solidification. The top of this column was polished to a smooth level. Next, the S*-containing slag was cast into the graphite tube appearing in the upper part of Fig. 2.

The two samples of slag were then joined into a couple and melted in a high frequency induction furnace, and the diffusion was kept going on for a definite time at the desired temperature under an atmosphere of nitrogen. For keeping all the parts of the samples at a uniform temperature, the graphite couple was placed in a graphite vessel and covered with a graphite lid, as shown in Fig. 3. The temperature was measured with an optical pyrometer previously corrected by means of a Pt-Pt·Rh thermo-couple.

After the diffusion run at the desired temperature for a definite time (5 hrs for the basic and less hours for acid samples), the samples were furnace-cooled and the cooled

Fig. 2. Graphite crucible for diffusion run.

samples, without extracting them from the graphite crucible, were pared at the top by successive thin slices. After polishing by a polishing machine in a draft chamber, each new surface was measured for the intensity of radioactivity by a Geiger-Müller counter manufactured by Kôbe Kôgyo K.K. This G-M counter had a mica window of 1.58 mg/cm² thickness and a 100 scaling circuit.

To equalize the geometrical condition of each test, a brass plate with a hole 7 mm in diameter was placed in contact with the surface of the sample and the relative position of the hole was kept constant against the mica window of the G-M counter.

In consideration of the great importance of the change of radioactivity especially in the vicinity of the interface, small quantity of the samples was polished off at each polishing, and the thickness of the polished-

Fig. 3. Furnace for diffusion run.

off surface was measured with a micrometer to the precision of 1/100 mm.

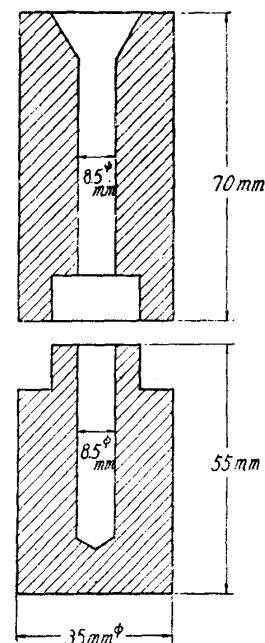The diffusion constant of the samples was calculated from the measurement of
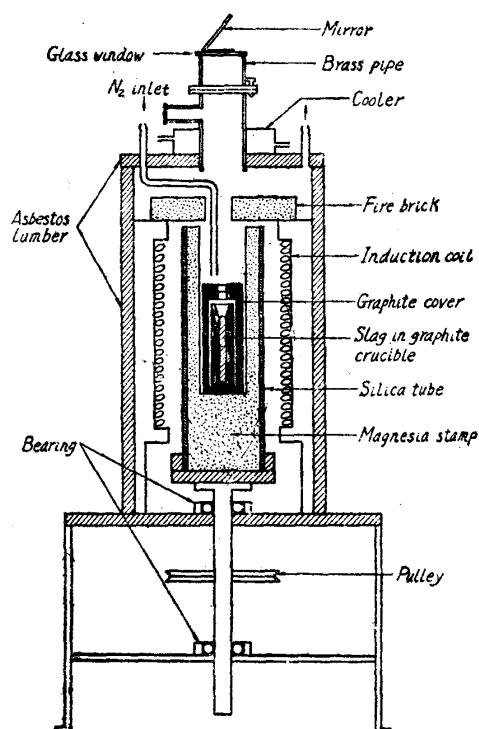
the change in surface activities at the succesive layers, by the method described in the following.

IV. Method of Calculating the Diffusion Constant

If the diffusion constant of sulfur is presumed to be unaffected by its concentration, the concentration gradient after the lapse of time t may be represented as follows:

$$C_x = C_0\left(1 - \frac{2}{\sqrt{\pi}}\int_0^{\frac{x}{2\sqrt{Dt}}} e^{-y^2} dy\right),\qquad(1)$$

in which C_x stands for the concentration at a distance x from the interface, C_0 for the half of the difference between original concentrations and D for the diffusion constant.

As we have measured the intensity of the radioactivity at each successive surface created by repeated slicing off of the sample columns, the β rays emanating from the inside of the radioactive sample are not excluded in our measurements. The β rays are absorbed by matter so that the following equation expresses the relation between the thicknness x of the absorbent matter and the intensity I:

$$I = I_0 e^{-\mu x},\qquad(2)$$

in which I_0 stands for the intensity of radioactivity where there is no matter to absorb the β rays and μ for the absorption coefficient, which is about $0.2\sim0.3$ cm^2/mg for S^{35}.

Thus, when a column of radioactive substance is cut and polished at the distance of a from the interface, the intensity of the radioactivity I_a measured at this surface will be given as follows:

$$I_a = k\int_a^\infty C_x e^{-\mu(x-a)} dx,\qquad x \geq a,\qquad(3)$$

where k is a constant related to the condition of measurement.

Combining equation (1) and (3), the following equation may be obtained:

$$I_a = \frac{kC_0}{\mu}\left(1 - \frac{2}{\sqrt{\pi}}\int_0^{\frac{a}{2\sqrt{Dt}}} e^{-y^2} dy\right) - \frac{kC_0}{\mu} e^{\mu(a+\mu Dt)}\left(1 - \frac{2}{\sqrt{\pi}}\int_0^{\frac{a}{2\sqrt{Dt}}+\mu\sqrt{Dt}} e^{-y^2} dy\right).\quad(4)$$

Taking the values of 0.3 cm^2/mg for μ and calculating the first and second terms on the right side of the above equation, corresponding to various values of $\sqrt{Dt}$ and a, it becomes clear that the second term is negligibly small in comparison with the first term. So that, within the accuracy obtainable in our experiments, the following approximation is justified:

$$I_a \fallingdotseq \frac{kC_0}{\mu}\left(1 - \frac{2}{\sqrt{\pi}}\int_0^{\frac{a}{2\sqrt{Dt}}} e^{-y^2} dy\right) = \frac{k}{\mu}C_a.\qquad(5)$$

However, the error due to disregarding the second term as negligible becomes larger when $\sqrt{Dt}$ becomes smaller and a larger.

Equation (5) shows that the surface activity at a given section may be taken to stand in a direct ratio with the concentration of the radioactive substance at

the surface. Consequently, it is possible to calculate the diffusion constant by measuring the surface activity which gives the concentration at the section.

The fact that the surface activity at the section stands in a direct ratio with the concentration may otherwise be concluded from the considerable absorption of β rays from S* by slag. The value of 0.2~0.3 cm²/mg for μ will give 600~900 cm⁻¹ upon taking the specific gravity of slag at 3 g/cm³. Thus, when the thickness of the absorber increases, the intensity of the radioactivity decreases rapidly, for example in the case of 0.01 cm thickness, the radioactivity drops to 1/400~1/8,000 in intensity. Consequently, a measurement at the surface will give the sum of radioactivity emanating from an extremely thin layer beneath the surface, and if the concentration in such a thin layer is uniform, the equation (5) will stand without further dispute.

V. Experimental Results

A) Basic slag

The composition of the tested slag is given in Table 1, the ratio of FeS* and CaS added for making S*-containing slag and the conditions for the diffusion runs in Table 2. The result of the measurements of the surface activities in the successive layers in the sample columns after diffusion is summarized in Fig. 4.

Table 2. Data on diffusion runs (basic slag).

Experiment No.	Mixing ratio for radioactive slag			S (%) analysed	Diffusion run
13	Slag 9.2 g,	FeS* 0.2 g,	CaS 0.6 g	1.78	1518±8°C, 5 hrs
14	"	"	"	1.80	1580±10°C, 5 hrs
15	"	"	"	1.75	1500°C, 5 min (blank run)
16	"	FeS* 0.3 g,	CaS 0.5 g	1.62	1445±10°C, 5 hrs
17	"	"	"	1.61	1580±10°C, 5 hrs

The experiments by Derge and his collaborators failed to discern the difference between a blank and a diffusion run. In our experiments utilizing radioactive sulfur, as shown in the figure, not only the difference between a blank and a diffusion run, but also the difference caused by variation of temperature were clearly brought to light.
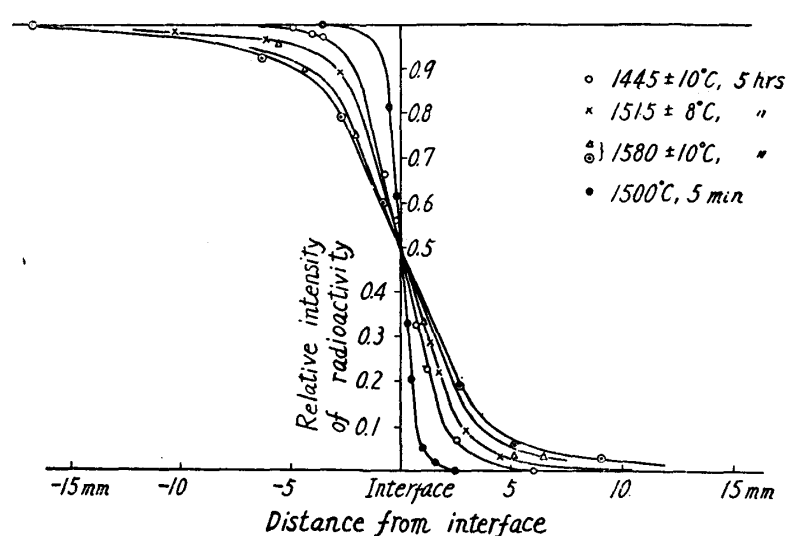

Fig. 4. Distribution of radioactivities in a basic slag after diffusion.

Considering the slow rate of diffusion of sulfur in molten slag, we presumed it unnecessary to make tests on blank run at variuos temperatures, so that we calculated the diffusion constants after subtracting the value of blank run for 5 min at 1,500°C from the values at various temperatures. The results are shown in Table 3. With a rise of 100°C in temperature, the value of D nearly doubled.

Table 3.　Diffusion constants of sulfur in molten basic slag.

Temperature (°C)	1445	1515	1580
Diffusion Constant (cm²/sec)	0.89×10^{-6}	1.5×10^{-6}	2.6×10^{-6}

Between the diffusion constant and the temperature holds the following relation :

$$D = Ae^{-\frac{Q}{RT}},$$

where Q is the activation energy and A a constant.

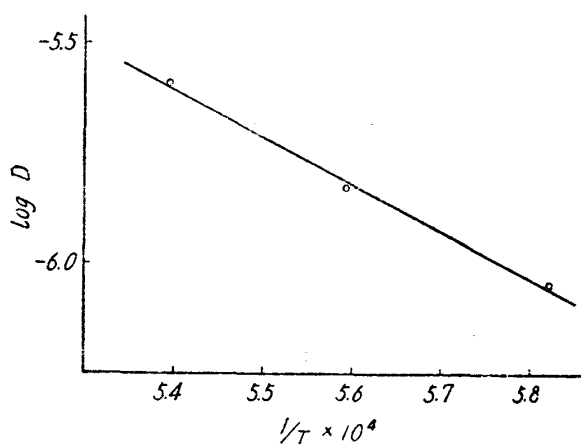When logarithms of D are plotted against the reciprocals of the absolute temperatures, as illustrated in Fig. 5, it may be seen that the locus approximately represents a straight line, though it would seem rather indiscrete to conclude from only three points of data. Upon calculating the approximate values of A and Q from this line, the above equation may be evolved as follows :

$$D = 1.4 \times e^{-\frac{49,000}{RT}}.$$

Fig. 5.　Relation between log D and $1/T$.

B)　Acid slag

When a strongly acid slag with $CaO/SiO_2 = 0.69$ in its composition, as shown in Table 1, was tested for diffusion, the distribution of radioactive sulfur in the sample after diffusion was found to be very irregular. The irregularity, moreover, increased further with higher temperature and longer diffusion time. When SiO_2 content in the slag was high, it seems the CO gas generated by the reaction, $SiO_2 + 2C \rightarrow Si + 2CO$, stirs up the slag, with the result that the distribution of the radioactive sulfur becomes irregular.

To avoid such a disturbance, a sample of slag weakly acid ($CaO/SiO_2 = 0.89$) was used and the experiment completed in a short time at a comparatively low tem-

Table 4.　Data on diffusion runs (acid slag).

Experiment No.	Mixing ratio for radioactive slag	S (%) analysed	Diffusion run
27	Slag 11.5 g, FeS* 0.15 g, CaS 0.6 g	1.29	1440°C, 　　5 min
28	″　　　　　″　　　　　″	″	1440 ± 7°C, 65 min
29	″　　　　　″　　　　　″	1.33	1460°C, 　　5 min
30	″　　　　　″　　　　　″	″	1435 ± 8°C, 205 min

perature. The ratio of FeS* and CaS added to the slag and the conditions
of the experiment are as shown in Table 4. The distribution of the intensity of
the radioactivity in the
sample after the diffusion
is shown in Fig. 6.
Though the short time
allowed for the experi-
ments makes it immature
to deduce exact results
therefrom, the diffusion
constant is calculated as
around 0.8×10^{-6}cm²/sec at
1,440°C in approximation.

At higher temperatures,
the distribution of the
radioactive sulfur falls
into irregularity, due to

Fig. 6. Distribution of radioactivities in an acid slag
after diffusion.

the generation of CO gas, so that it was impossible to calculate the change of the
diffusion constant with temperature. However, it may be presumed that the
diffusion constant is about the same order in acid slags as in basic slags, judging
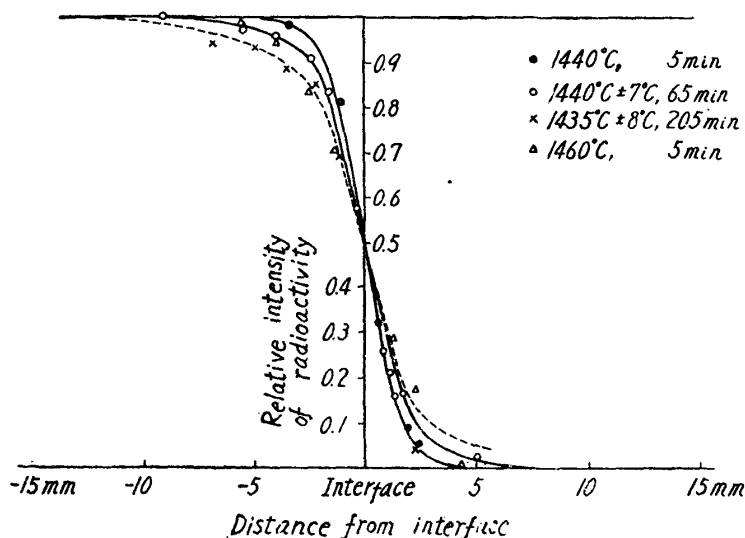from the result obtained in the tests at 1,440°C cited above.

Summary

The velocity of diffusion of sulfur in molten slags was measured with utilization
of radioactive sulfur S³⁵. The results showed that the diffusion of sulfur in
molten slags is considerably slower than in molten iron. The diffusion constants
in a basic slag were 0.90×10^{-6} cm²/sec at 1,445°C, 1.5×10^{-6} cm²/sec at 1,515°C and
2.6×10^{-6} cm²/sec at 1,580°C, and its change with temperatures was expressed as
follows:

$$D = 1.4 \times e^{-\frac{49,000}{RT}} .$$

A rise in temperature by 100°C will approximately double the value of D.

In an acid slag, the value of D was 0.8×10^{-6} cm²/sec at 1,440°C, but owing to
the generation of CO gas at higher temperatures, the slag became agitated and
the concentration gradient was thrown out of normal order, so that the diffusion
constant could not be measured at higher temperatures.

The above values are indeed rather small, if we recollect that the diffusion
constant of sulfur in molten iron is of the order of 10^{-3} cm²/sec. This makes it
likely that the net velocity of the desulfurizing reaction is mainly controlled by
the speed of diffusion of sulfur in the molten slag. It follows that it is of high
importance to provide as large as possible interface between the molten iron and
slag, that is, to take care that the melt is well stirred for assuring good de-
sulfurization of the product.

In conclusion, we express herewith our deep appreciation due to Prof. Oka of this Institue for his valuable suggestions in the preparation of FeS*. Thanks are also due to Messrs. R. Shimanuki, N. Ito and H. Sato for their assistance in our experiments.