Kinetics of the Desulfurization of Molten Iron.

Progress Report
for the Period March 1, 1980 - October 1, 1980

D. R. Gaskell
University of Pennsylvania
Philadelphia, Pennsylvania 19104

October 1980

Prepared for
The U. S. Department of Energy
Under Contract Number EM-78-S-02-4725

There is no objection from the patent
point of view to the publication or
dissemination of the document(s)
listed in this letter.

BROOKHAVEN PATENT GROUP
10/25 1980
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
Abstract

The rate of desulfurization of liquid iron by liquid CaO-saturated CaO-FeO has been measured at 1600°C. The initial oxygen content of the iron is that which is in equilibrium with the slag at 1600°C and the experimental observation that the oxygen content of the metal does not vary with time indicates that the coupled reactions occurring are

\[
[S]_{\text{metal}} + 2e^- \rightarrow (S^{2-})_{\text{slag}}
\]

and

\[
[Fe]_{\text{metal}} \rightarrow (Fe^{2+})_{\text{slag}} + 2e^-
\]

The rate of desulfurization is controlled by diffusion of sulfur in the metal. The observed initial stage of rapid desulfurization is due to interfacial tension-induced local turbulence at the interface. Work is continuing on study of the rate of desulfurization of liquid iron by CaO-saturated FeO-CaO containing CaF₂.
The results of the experimental study of the rate of desulfurization of liquid iron by CaO-saturated liquid FeO-CaO are shown in Fig. 1. Each datum point was obtained from a single experimental run and slight variations, from one run to another, in the inner diameter of the CaO crucible containing the slag-metal couple and the weight of metal being desulfurized, are accounted for by plotting the time variable as $At^{1/2}/W$, where $A$ is the measured area of the slag-metal interface, $W$ is the weight of the metal and $t$ is the reaction time.

Fig. 2 shows the variation of the oxygen content of the metal with reaction time. The initial oxygen content of 720 ppm is virtually equal to the value calculated for equilibrium with the experimental slag at 1600°C, namely 760 ppm. The absence of a discernable variation in the oxygen content of the metal indicates that the coupled reactions occurring at the slag-metal interface are

$$[S]_{\text{metal}} + 2e^- + (S^{2-})_{\text{slag}}$$

and $$[\text{Fe}]_{\text{metal}} + (\text{Fe}^{2+})_{\text{slag}} + 2e^-$$

Fig. 1 shows, as the broken line, the expected variation of the average sulfur content of the metal with time if the desulfurization rate were controlled by linear diffusion of sulfur in stagnant metal to the interface. This calculation was made using the value of $D_S$ obtained from measurement of the rate of desulfurization of the metal by the solid CaO crucible and assuming a constant zero concentration of sulfur
at the interface. Within the experimental reaction time identical results are obtained assuming finite and semi-infinite diffusion. The assumption of $C_S = 0$ at the interface is an approximation which is made until the results of current equilibration experiments are available. It is expected, however, that recalculation using the measured small value of $C_S$ at $x = 0$ will not significantly alter the slope of the broken line.

In Fig. 1 it can be seen that, after an initial period of desulfurization, the experimental line becomes parallel with the calculated broken line. The tentative explanation of the observed behavior is as follows. The initial, relatively rapid, rate of transfer of iron and sulfur across the slag-metal interface decreases the interfacial tension to an extent sufficient to cause local turbulence at and adjacent to the interface. Thus, in the initial slag, transport of sulfur to the interface is aided by local convection. As the rate of transfer decreases, the interfacial tension increases and local convection ceases, after which time the rate of desulfurization is controlled by diffusion of sulfur in the stagnant iron.

At the present time kinetics experiments are being conducted with a CaO-saturated FeO-CaO slag containing ~ 4.5 wt % CaF$_2$. 
Calculated with $D_g = 7 \times 10^{-5}$ cm$^2$s$^{-1}$ assuming linear diffusion and $C_g = 0$ at $x = 0$

**FIG 1.**

**FIG 2.**