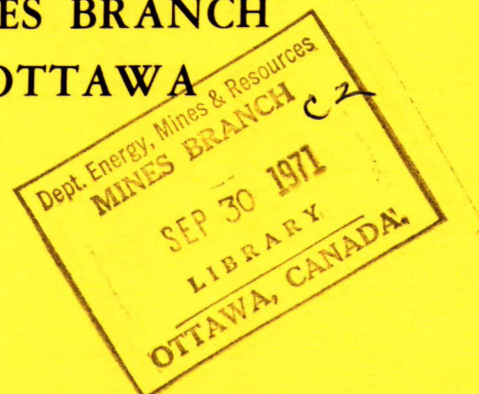


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*THE DISSOLUTION OF FUSED QUARTZ
IN FERROUS SILICATE SLAGS*

D. A. REEVE

METALS REDUCTION AND ENERGY CENTRE

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The Dissolution of Fused Quartz in Ferrous Silicate Slags

by

D.A. Reeve*

ABSTRACT

The dissolution of fused quartz in ferrous silicate slags was studied at 1250 and 1350°C by measuring the decrease in diameter of lengths of fused quartz rod rotated in the slags. The dissolution rate was thought to be controlled by mass transfer of the dissolving species through a liquid boundary layer on the surface of the rotating specimen. Devitrification occurred on the outer surface of the specimen and the amount of devitrification was probably governed by the degree of penetration of the slag into the crystallizing layer. The dissolution rate of fused quartz in ferrous silicate slags, with silica contents varying from close to wüstite saturation to close to silica saturation, decreased with increasing silica content of the slag.

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La dissolution du quartz fondu dans des scories de silicate de fer

par

D.A. Reeve *

RESUME

On a étudié la dissolution du quartz fondu dans des scories de silicate de fer à 1250 et 1350°C en mesurant la diminution en diamètre de diverse longueurs de barres de quartz fondu, subissant une rotation dans les laitiers. On a pensé que le taux de dissolution était contrôlé par un transfert massif des éléments dissolvants à travers une couche limitrophe liquide sur la surface du spécimen en rotation. La dévitrification se produisit sur la surface extérieure du spécimen et son importance fut probablement régie par le degré de pénétration du laitier dans la couche en cristallisation. Le taux de dissolution du quartz fondu dans les scories de silicate de fer, avec des teneurs en silice allant de saturations approchant la wüstite à celles approchant silice, a diminué pour des teneurs croissantes en silice dans les scories.

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INTRODUCTION

A study has been made of the rate of dissolution of silica in ferrous silicate slags which were unsaturated with respect to silica. The erosion of silica-containing refractory bricks is of considerable interest to iron- and steelmaking, and the dissolution rate of silica in ferrous-oxide-containing liquids is important in copper smelting and converting.

During recent years, several workers (1-4) have studied high-temperature solid-liquid kinetics using the rotating-disc method, in which the solid, in the form of a disc, is rotated at various speeds in the solvent and dissolution rate from the bottom surface of the disc is measured as a function of the rotational speed. In particular, Ershov and Popova (1) used this method to study the kinetics of dissolution of silica in synthetic oxide melts of interest in the electro-slag method of steel production. All these investigators concluded that dissolution rate was controlled by mass transfer of the dissolving species through a liquid boundary layer on the surface of the rotating specimen.

The theory of the rotating-disc method, based on Levich's analytical solution for the hydrodynamic conditions near the uniformly accessible reaction surface of a rotating disc (5), has been discussed in the references already cited. In general, however, for a two-phase solid-liquid dissolution process, the rate may be controlled either by mass transport of reactants or products through a liquid boundary layer between the solid surface and the bulk liquid, or by a chemical reaction at the phase boundary. If mass transport is the controlling factor, the rate of dissolution will be a function of the disc rotational speed because the stirring effect produced by the rotation reduces resistance to mass transport. For non-turbulent flow conditions, Levich's theory predicts that the boundary layer thickness is constant across the surface of the rotating disc and is given by:

$$\delta = 1.61 D^{1/3} \nu^{1/6} \omega^{-1/2} \quad (1)$$

for:

$$\frac{\nu}{D} \gg 1 \text{ and } 10 < \frac{\gamma^2 \omega}{\nu} < 10^4,$$

where δ = boundary layer thickness, cm
 D = diffusion coefficient, cm^2/sec .
 ν = kinematic viscosity, cm^2/sec .
 ω = angular velocity, radians/sec.

The boundary layer thickness, δ , is defined by:

$$N = \frac{D \cdot \Delta c}{\delta}, \quad (2)$$

where N = rate of mass transfer

Δc = concentration difference between the bulk liquid and the disc surface

Thus, from equation (2), for a diffusion controlled process, the amount of dissolution should be linearly related to $\omega^{1/2}$.

In the present study, short lengths of fused-quartz rod were rotated at various speeds in ferrous silicate slags contained in iron crucibles at 1250 and 1350°C. However, it was inconvenient to measure the rates of dissolution from the bottom surface of the rotating specimens, but more convenient to measure the decrease in diameter. Thus, in this case, Levich's theory may not be applied and, if conditions of diffusion control obtain, then a mass transfer correlation applicable to rotating cylinders must be obeyed. Such a correlation has been given by Eisenberg, Tobias and Wilke (6) and expressed in terms of dimensionless groups according to the following equation:

$$\frac{\kappa}{V} Sc^{0.644} = \text{const. } f(R_d) \quad (3)$$

where κ = mass transfer coefficient, cm/sec .

V = peripheral velocity, cm/sec .

Sc = Schmidt number (ν/D)

$f(R_d)$ = a function of Reynolds number, based on the cylinder diameter.

The functional dependence of the mass transfer coefficient on the rotational speed is given by:

$$\kappa = \text{const. } V^{0.644}, \quad (4)$$

and thus, for conditions of forced-convection mass transfer at a circular cylinder, the dissolution rate of the lengths of fused-quartz rod should be directly proportional to the peripheral velocity raised to the power of 0.644.

Also in this study the effect of the silica content of the slag on the dissolution rate at 1300°C of the fused-quartz specimens was examined.

EXPERIMENTAL

Materials

A stock slag with the stoichiometric composition of fayalite ($2\text{FeO}\cdot\text{SiO}_2$) was prepared by melting in an electric-arc furnace the calculated quantities of electrolytic iron, mill scale, and high-purity quartz sand (containing a minimum of 99.8 percent SiO_2). After coarse crushing, any of the cooled slag which appeared to be contaminated by the refractory lining of the electric furnace was discarded before fine crushing. X-ray powder diffraction analysis of a sample from the final product showed that fayalite was the only phase present. Conventional wet chemical analysis of the final product reported 30.4 percent by weight SiO_2 , which is close to the value of 29.4 percent for stoichiometric fayalite.

Slags with silica contents between 15 and 35 weight percent were prepared by intimately grinding together a wüstite slag (also made in the electric furnace) and silica sand. Complete homogenization was achieved by melting prior to the silica dissolution experiments.

The quartz specimens were prepared by cutting $1\frac{1}{2}$ -inch lengths from General Electric, Type 201, clear, fused-quartz rod ($\frac{1}{2}$ -inch diameter). The bottom surfaces of the specimens were made smooth on a diamond-impregnated polishing wheel.

Apparatus and Procedure

50-g samples of slag were melted in an Armco-iron crucible (25 ml) supported on a pedestal in a vertical, water-cooled, graphite resistance furnace (Figure 1). An inert atmosphere of purified argon was maintained in the furnace. The temperature of the slag was measured with a Pt/Pt-10% Rh thermocouple located so that the thermocouple sheath was in contact with the bottom of the crucible. The temperature reading given by this thermocouple had been previously correlated with the reading given by another thermocouple in an iron sheath immersed in the melt.

The fused-quartz specimens were held above the melt in a stainless-steel chuck connected to a 5/16-inch-diameter stainless-steel shaft. The shaft passed through a boron-nitride furnace plug, which acted both to control the thermal gradient within the furnace and also to provide a bearing surface for the rotating shaft. A Teflon bearing above the furnace provided additional

guidance for the shaft which was connected directly to a variable-speed DC motor. The speed of rotation of the shaft was measured by visual counting at speeds below 150 rpm and stroboscopically at higher rotational speeds.

While the furnace was heating up, the quartz specimen was held in the cool zone of the furnace just beneath the boron-nitride plug. When the slag had reached the required temperature, the specimen was lowered into the melt so that half an inch was immersed and, at the same time, rotation was started. In most cases, dissolution of the rotating specimen was allowed to proceed for one minute, after which time there was no significant change in the silica concentration of the melt. The amount of dissolution of the quartz specimen was calculated from measurements of the diameter, taken in several places (at least ten) with a micrometer screw gauge before and after the experiment.

RESULTS AND DISCUSSION

The rates of dissolution of half-inch-diameter fused-quartz specimens in slags having the stoichiometric composition of fayalite ($2\text{FeO}\cdot\text{SiO}_2$) were measured at 1250 and 1350°C and at specimen rotation speeds in the range 50 to 1020 rpm. After dissolution for one minute, the specimens still had a circular surface after the reaction; longer dissolution times led to less reliable results because of the difficulty of exactly centering the specimens in the crucibles. However, some experiments were done at 1350°C and 500 rpm for times up to 15 minutes, and a linear relationship was found for the decrease in specimen diameter with time (Figure 2).

The results of the dissolution experiments at 1250 and 1350°C are given in Table 1. In Figure 3, the amount of dissolution, expressed in $\text{mg}/\text{cm}^2/\text{sec}$, is plotted against the peripheral velocity, raised to the power 0.644, of the rotating specimen. The linear relationships would appear to indicate that the dissolution process may be controlled by diffusion, the mechanism probably being one of mass transfer of the dissolving species through a liquid boundary layer on the surface of the rotating specimen.

It should be pointed out that a reasonable correlation is also obtained by plotting the amount of dissolution against the square root of the angular velocity of rotation (Levich's postulation (5)) and, indeed, by plotting the amount of dissolution against the first power of the angular velocity (especially

TABLE 1 Experimental Results

Run	rpm	Diameter of Specimen (inches)	(Peripheral Velocity) ^{0.644}	Dissolution Rate (mg/cm ² /sec) x 10 ⁻²
(i) <u>1250°C</u>				
<u>1st Series</u>				
8	50.6	0.5218	0.68	1.24
9	103.5	0.5227	1.07	1.47
11	200	0.5226	1.64	1.77
12	270	0.5143	1.97	2.05
13	352	0.5259	2.37	2.07
16	700	0.5226	3.67	2.75
15	880	0.5219	4.25	3.02
17	1020	0.5196	4.66	3.31
<u>2nd Series</u>				
59	104	0.4850	1.02	1.59
54	430	0.4870	2.56	2.32
56	552	0.4807	2.99	2.42
55	710	0.4857	3.54	2.71
(ii) <u>1350°C</u>				
<u>1st Series</u>				
18	85.3	0.5233	0.95	2.99
19	166	0.5247	1.46	4.17
20	280	0.5200	2.03	5.42
21	589	0.5194	3.27	7.85
23	715	0.5167	3.70	8.65
22	930	0.5216	4.40	9.87
<u>2nd Series</u>				
51	114	0.5079	1.12	3.46
52	690	0.5070	3.57	8.50
46	880	0.5065	4.17	9.60
47	905	0.5048	4.24	9.74

for the 1350°C first series results). However, wall effects of the non-cylindrical crucible may be enough to cause a significant deviation from the mass transfer correlation for circular cylinders given by Eisenberg, Tobias and Wilke (6). It is perhaps sufficient to note that a correlation was found between the amount of dissolution and some function of the velocity of rotation of the specimens; no such correlation would be expected if the dissolution reaction were controlled by some chemical process.

The reaction rate at 1350°C was less than at 1250°C, which is the reverse of the expected result. Because of the very small decrease in specimen diameter with dissolution, this apparent reversal of expected reaction rate for the two temperatures was, at first, ascribed to experimental error; however a second series of experiments, repeating the first series, confirmed that the difference in reaction rates for the two temperatures was significant. The two series of experiments are shown in Figure 3.

Inspection of sectioned rods after dissolution revealed a dark-coloured crust surrounding the clear fused-quartz core. This crust was thicker for reactions at 1250°C than at 1350°C. For instance, using a rotational speed of 500 rpm, the crust thickness was approximately 2 mm for 1250°C and 1/2 to 3/4 mm for 1350°C, as shown in Figure 4. Experiments done at 500 rpm over the temperature range 1225 to 1400°C in 25°C intervals showed a trend of decreasing specimen crust thickness with increasing temperature.

X-ray powder diffraction analysis of the crust showed that the main constituent was crystalline quartz with minor amounts of α -cristobalite (low temperature form) and fayalite. Electron microprobe analysis indicated that the iron-bearing phase (fayalite) occurred as thin veins (approximately two microns across) in a quartz matrix. Figure 5 is a photomicrograph (magnification x800) of a typical specimen crust. This pattern of thin veins of fayalite in a quartz matrix could be considered to be typical of an ex-solution phenomenon, in which the secondary phase is fayalite. From theoretical considerations, for a diffusion-controlled reaction, the solid-liquid interface is at equilibrium and the liquid at the interface has the liquidus composition. In the present case, reference to the FeO-SiO₂ binary system (7) indicates that a liquid saturated with silica, on cooling, would yield fayalite as the secondary and tridymite as the primary crystalline phase. However, no metastable tridymite was reported in any of the X-ray analyses of the crustal material and the above explanation of the composition of the crust was rejected in favour of

one based on the devitrification of the fused quartz. It would also seem unlikely that a reproducibly uniform layer of liquid would have solidified on the outer surface of the quartz specimens after they had been raised out of the slag after the completion of the reaction.

When fused quartz devitrifies, the primary product at the temperatures used in this investigation is β -cristobalite (high-temperature form), in spite of tridymite being the stable crystalline form of silica in this temperature range. On cooling, the β -cristobalite inverts to the α -form at about 250°C. It is known that the rate-controlling factor in the isothermal transformation of amorphous silica into cristobalite is a heterogeneous nucleation process (8); this nucleation occurs at the surface of the silica or at an interface between the silica and some other material.

In the present case, it may be speculated that the transformation of amorphous silica into a crystalline form may be nucleated by the formation of fayalite in the silica matrix because of diffusion of iron or merely by the contact of the rotating specimen with the liquid slag. Fayalite would be expected to penetrate the devitrifying layer but the decreasing thickness of the crust, with increasing temperature for a given speed of rotation of the specimen, may be attributed to less penetration of the more fluid fayalite, because of centrifugal force, causing less crystallization.

The occurrence of crystalline quartz as the major phase in the crust with α -cristobalite as a minor constituent is unexpected but in the same way that a contaminant will act as a flux to alter the devitrification product β -cristobalite to tridymite so the presence of the fayalite may promote the rapid inversion of high-temperature cristobalite to crystalline quartz on cooling.

Finally, the apparently paradoxical situation shown in Figure 3 that the reaction rate for the dissolution process is less at 1350°C than at 1250°C very likely reflects the fact that the crystallographic transformations which occur during the cooling of the specimen are accompanied by drastic decreases in volume. Specimens with thick crusts will have undergone a greater decrease in volume than those with thin crusts, hence it would be difficult to compare dissolution reaction rates at different temperatures by measuring decreases in specimen diameters.

The dissolution rate of fused quartz as a function of the percentage by weight of silica in the slag is shown in Figure 6. Dissolution experiments

were done at 500 rpm and 1300°C in slags with a range in silica content from 15 (close to wüstite saturation) to 35 weight percent (close to silica saturation). The rate of dissolution decreased with increasing silica saturation of the slag.

In conclusion, the dissolution of fused quartz in ferrous silicate slags is thought to be a diffusion controlled reaction. Devitrification occurs on the outer surface of the specimen and the amount of devitrification is probably governed by the degree of penetration of the slag into the crystallizing layer. This devitrified outer layer undergoes a large volume change on cooling, which may account for the rate of dissolution appearing to decrease with increasing temperature.

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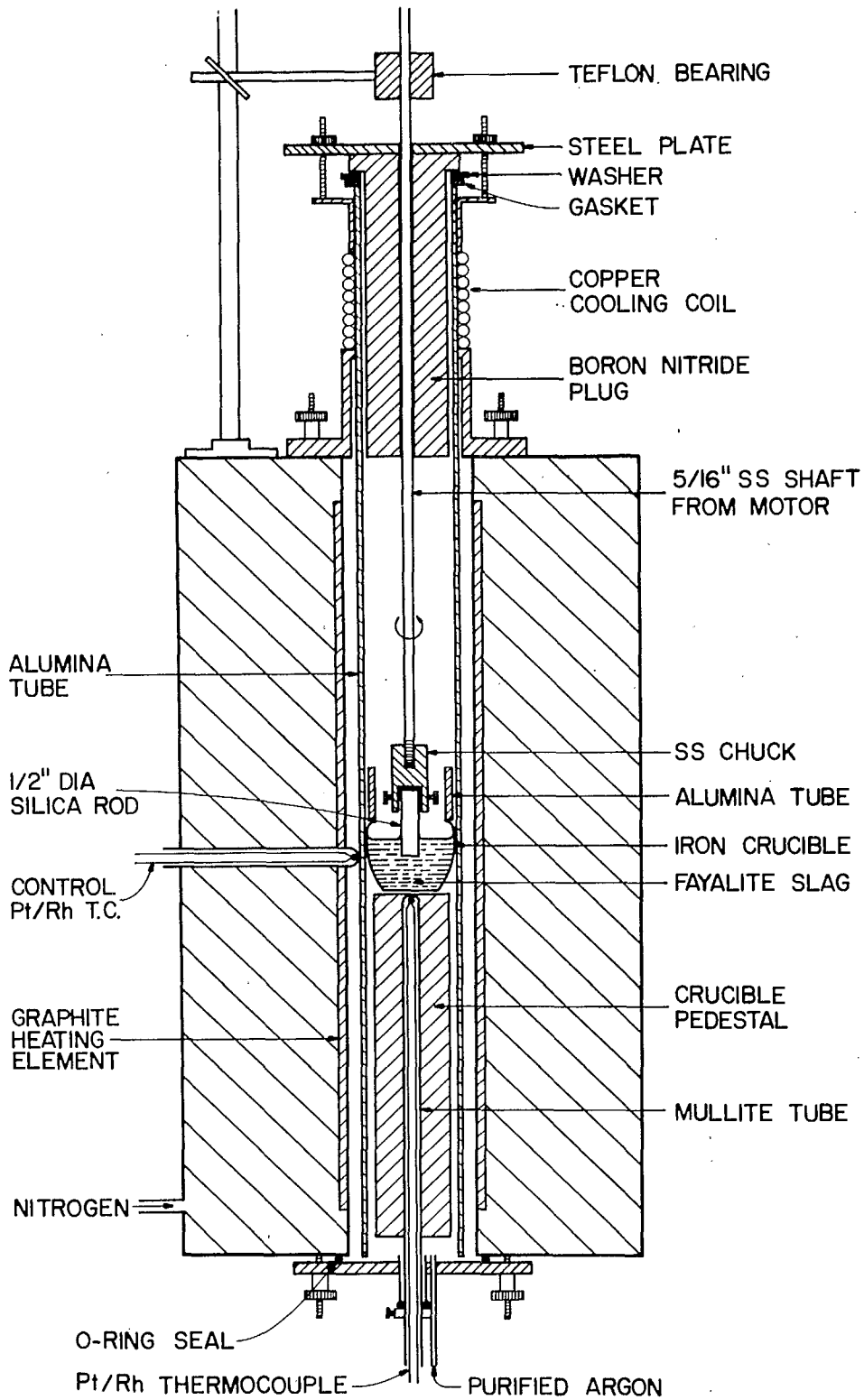


Figure 1. Reaction Furnace

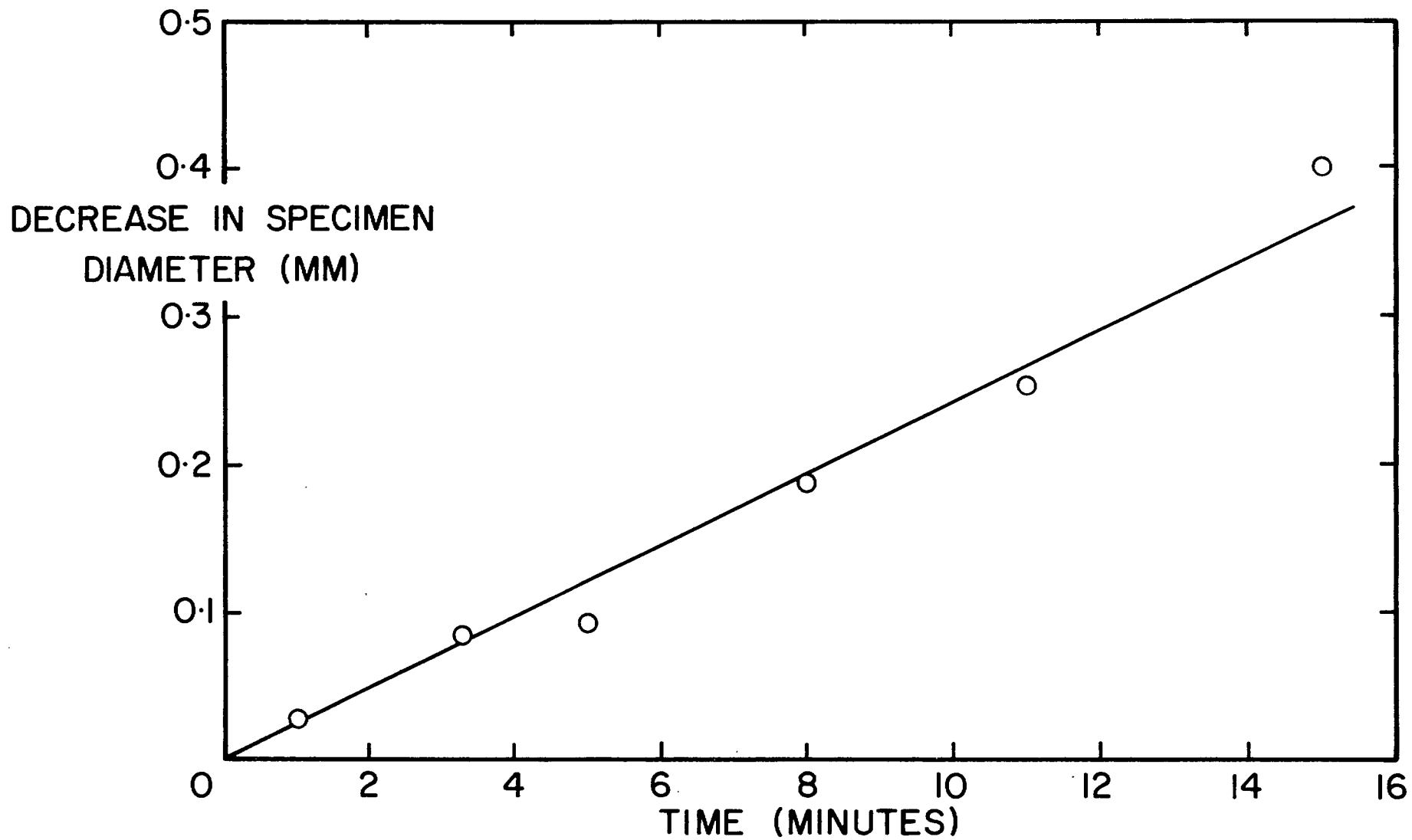


Figure 2. Decrease in specimen diameter with time at 1350°C and 500 rpm.

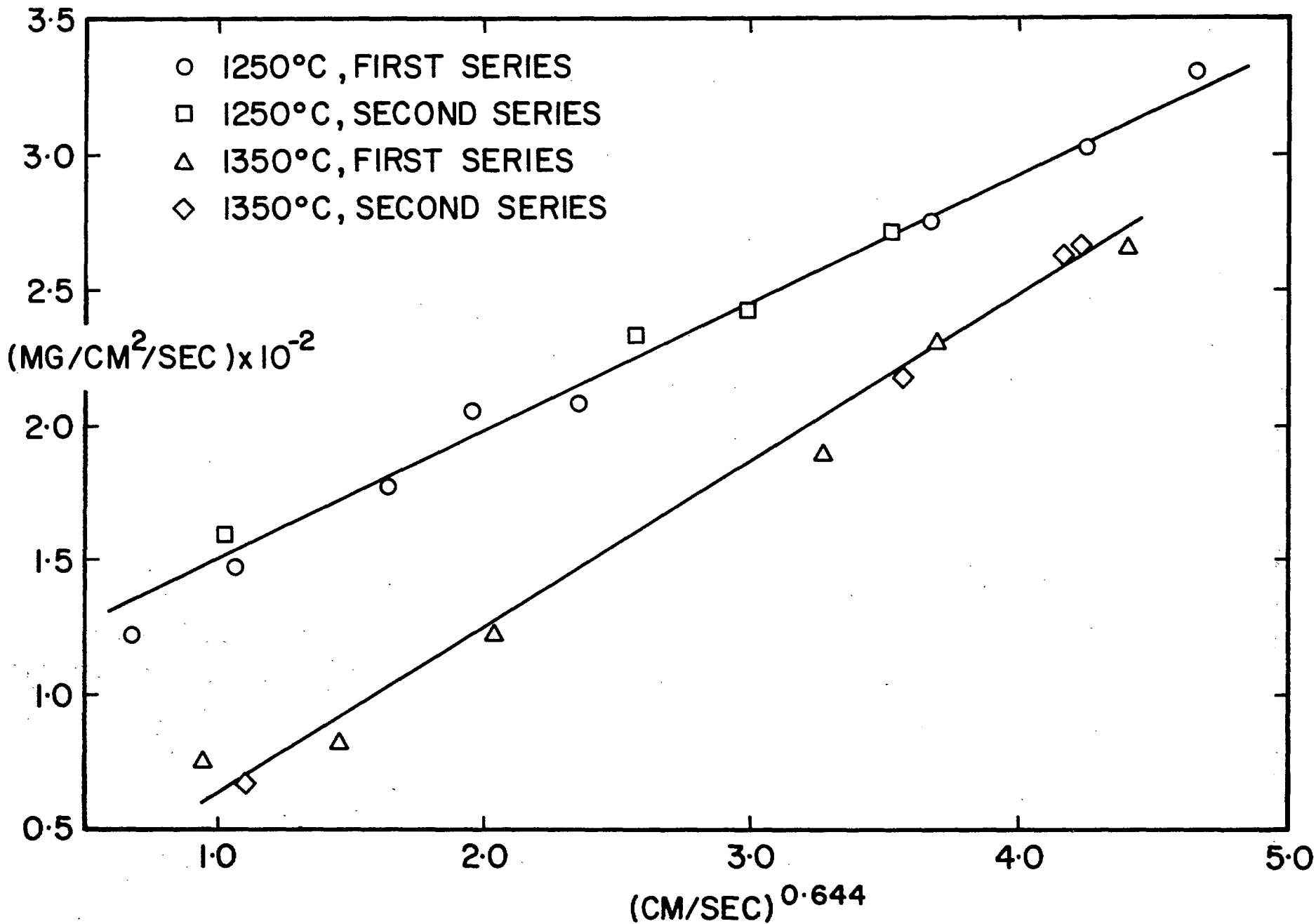


Figure 3. Plot of rate of dissolution of fused quartz against (peripheral velocity)^{0.644}

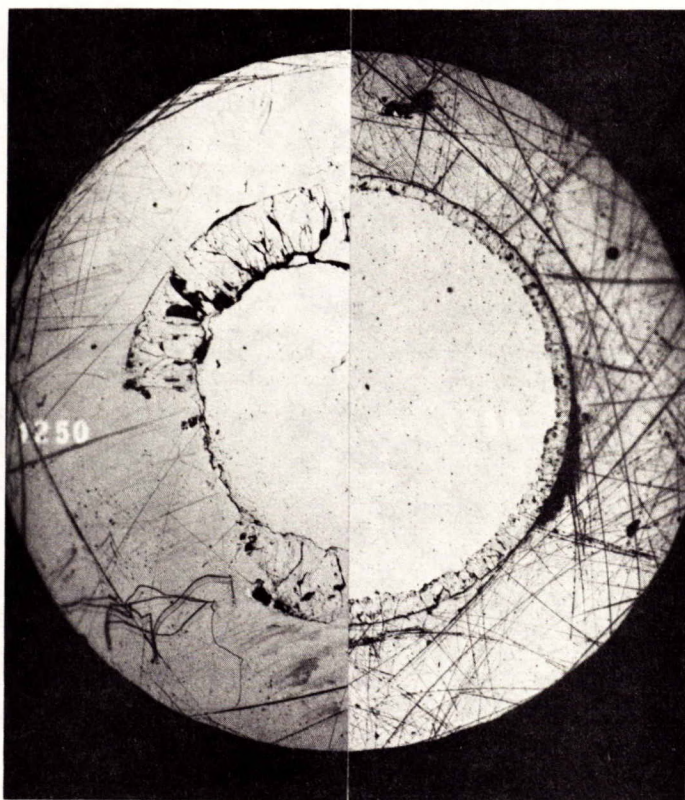


Figure 4. Photomicrograph of cross-section of specimens rotated at 500 rpm and 1250 and 1350°C, respectively. Magnification: x5

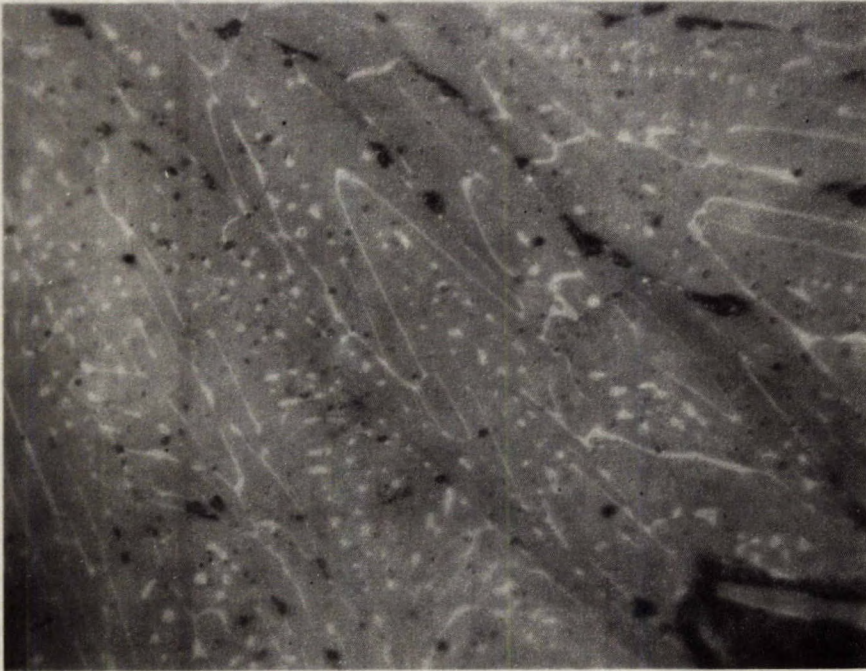


Figure 5. Photomicrograph of specimen crust.
Magnification: x800

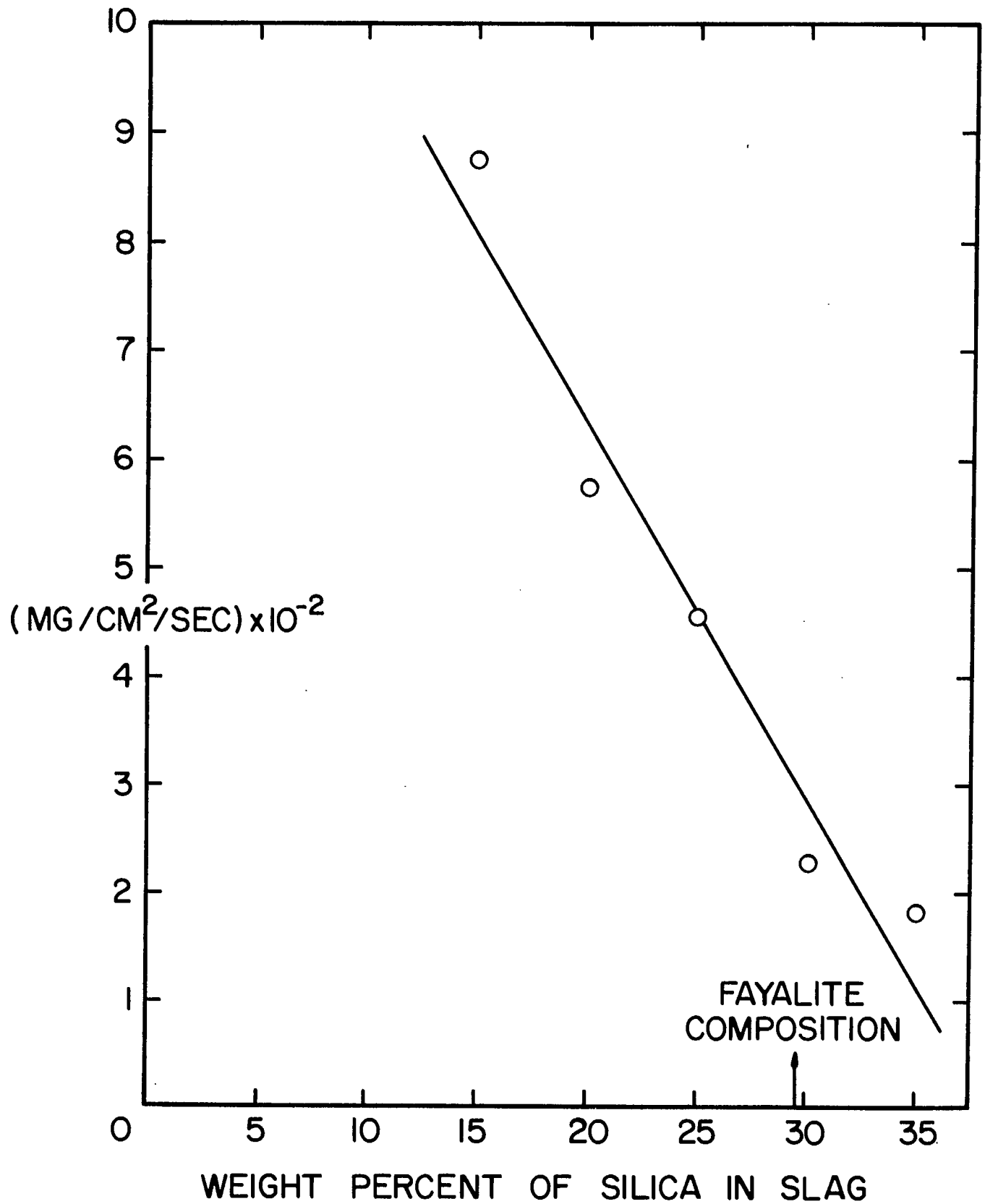


Figure 6. Plot of rate of dissolution of fused quartz against the weight percent of silica in the slag at 1300°C .

