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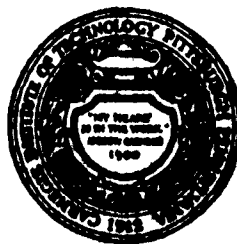
METALS RESEARCH LABORATORY
Pittsburgh 13, Pennsylvania

**EFFECT OF ALLOYING ELEMENTS ON THE MECHANISM
OF SULFUR TRANSFER ACROSS A SLAG-METAL INTERFACE**

SILICON-MANGANESE-PHOSPHORUS-ALUMINUM-CARBON-NICKEL-COPPER

By

K. M. Goldman, G. Derge, W. O. Philbrook



TECHNICAL REPORT

OFFICE OF NAVAL RESEARCH

Contract N6ori-47/IV - Project NR 031-014

October 16, 1953

EFFECT OF ALLOYING ELEMENTS ON THE MECHANISM OF SULFUR TRANSFER

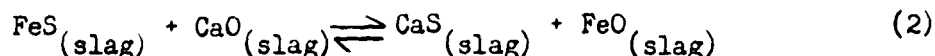
ACROSS A SLAG-METAL INTERFACE--

SILICON, MANGANESE, PHOSPHORUS, ALUMINUM, CARBON, NICKEL, COPPER

by

K. M. Goldman*, G. Derge**, W. O. Philbrook***

This is the third in a series of papers from the Metals Research Laboratory dealing with the transfer of sulfur across the iron-slag interface in a carbon-saturated system. The first paper¹ showed that the transfer obeyed first order kinetics. The second² presented detailed evidence in support of the three stage mechanism:



This emphasized the role of an iron-sulfur complex as the transfer agent across the interface and as an essential intermediate in the over-all process.

The present paper shows the influence on the process of the individual elements C, Si, Mn, P, the alloying elements normally present and of interest in commercial blast furnace operations, Al, which has a pronounced accelerating influence, and Ni and Cu, which are common minor impurities in the raw materials.

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The experimental methods and procedures for interpretation of data are the same as described in the earlier papers^{1,2}. Induction heated, graphite crucibles were used, and sulfur-free slag was added to the molten iron containing sulfur and the selected alloy. Slag samples were then taken at regular time intervals and analyzed for sulfur and other components of interest.

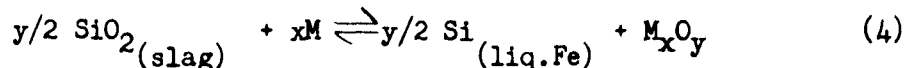
A rigorous evaluation of the accuracy of rate studies is difficult. Recognized sources of error include sampling and analysis of both slag and metal, temperature measurement and control, selection of zero time, composition of the gaseous atmosphere over the reaction system, and extraneous sources of sulfur from the graphite crucible and reagent materials. In this study carefully standardized procedures were followed consistently in order to minimize the errors. It is believed that the reproducibility of duplicate runs indicates that errors have been rendered negligible relative to the observed effects from intentional variables. For example, original experimental points for duplicate runs are shown in Figs. 1,2, 7, etc. In most cases in this paper the drawn curves represent an average of at least two heats. The spread in sulfur values at a given time ranges from 0.02 to 0.08 pct., which is a small fraction of the total values ranging up to 2 pct. S in slag.

In the systematic study of the influence of alloy additions, each element was added over a range of concentrations. The two slags used in this study were designated as "acid" or 1530 and "basic" or 1545. They had the following nominal composition:

<u>Slag Designation</u>	<u>Nominal composition, per cent</u>		
	<u>Al₂O₃</u>	<u>CaO</u>	<u>SiO₂</u>
Basic or 1545	15	45	40
Acid or 1530	15	30	55

Rates were measured in the temperature range 1500 - 1650^o C. Data will now be presented to illustrate the various features of the study.

SILICON: The first alloying element examined was silicon, because its presence is unavoidable in any silicate slag system through the reaction:



where M is any reducing agent such as iron or carbon. It is known that the attainment of equilibrium by this reaction is extremely slow and probably not reached in the blast furnace³. The influence of silicon on the final stages of the sulfur reaction has also been studied⁴. It has been shown⁵ that silicon increases the activity of sulfur in iron. For such reasons silicon may also be expected to influence the kinetics of the reaction. The observed effects will now be described.

The general procedure was to melt 530 grams of ingot iron in a graphite crucible, 3 in. O.D., 2 1/4 in. I.D., 5 in. deep. When the melt was saturated with carbon, ferrosilicon was added, the temperature adjusted, and granulated ferrous sulfide added to achieve a nominal bath composition of 0.8 pct. sulfur. A preliminary metal sample was taken and the prepared slag added. Slag samples were dipped at determined time intervals and a final metal sample was taken at the end of the run. Initial compositions ranged from 0.43 to 1.30 pct. silicon, and the temperature range studied was from 1500° to 1620°C.

The original data at 1500°C for pct. sulfur in the slag vs time are shown for the acid slag in Fig. 1 and for the basic slag in Fig. 2. The procedure of Chang and Goldman¹ was applied to these data to obtain the specific rate constants* K_m^{Si} and K_s^{Si} . The graphical determination of the rate constants involved a plot

* In writing rate constants, the convention will be followed of indicating the alloying element in the iron by a superscript, Si in this example, and the direction of sulfur transfer by a subscript, m for transfer from metal to slag and s for slag to metal.

of values of dC_s/dt , the slopes of the rate curve taken at selected concentration levels, against C_s , the corresponding concentration of sulfur in the slag. In all cases this plot was linear, indicating that the presence of silicon had not altered the first-order kinetics of the process. This statement is equally true for each of the other alloying elements reported in this paper and will not be repeated for each individual case.

The values of K_m^{Si} and K_s^{Si} calculated from the data by the method just outlined are plotted as a function of initial silicon content of the metal for the acid slag at 1500°C in Fig. 3 and for the basic slag in Fig. 4. (Initial silicon was used as the basis of plotting because the silicon content of the metal changed during the run, increasing under acid slags and decreasing under basic slags, as will be noted later.) Similar data were obtained for the extremes of silicon content at two other temperatures, and the effect of temperature on K_m^{Si} is shown for the basic slag as a plot of $\log K_m^{Si}$ vs $1/T$ in Fig. 5. The values of K_s^{Si} are not shown, since they show no additional features of interest. This also applies to the other alloys considered in this paper. The observed influence of silicon as an alloying element is to increase the rate of desulfurization under all conditions investigated.

The effect of silicon on the amount of iron found in the slag during sulfur transfer was also studied. The maximum in the curve of combined iron in the slag vs time, which is characteristic of the unalloyed system², is also evident in the presence of silicon; it is most pronounced at higher temperatures and with more basic slags. As was pointed out in the earlier paper², this behavior is to be expected of an intermediate component in a sequence of reactions such as postulated for the desulfurization mechanism. The chief difference caused by silicon is that the molar ratio of iron to sulfur in the slag is much lower than for the unalloyed system. Silicon may serve in step 1 to supplement iron as a

sulfur carrier similar to manganese (see later discussion), but the data are inadequate to confirm this. Another interpretation is that silicon contributes to lowering the iron oxide content of the slag and speeding the desulfurization reaction by acting along with carbon in step 3 to remove oxygen from the slag-metal interface.

The interesting feature of the role of alloyed silicon in desulfurization 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 -- at an essentially constant rate regardless of silicon level -- but silicon was oxidized from the metal under basic slags; see Table I. In desulfurization the silicon must therefore serve to deoxidize the slag (step 3) more rapidly than can be done by carbon alone, even when the silicon content is not high enough to create a lower oxygen potential than would be equivalent to equilibrium with carbon.

Further evidence that the simultaneous reduction of silica, or the presence of silica as a source of oxygen, is not deleterious to desulfurization is offered by an alloy-free experiment on the rate of desulfurization by a slag composed of 50 pct. CaO and 50 pct. Al_2O_3 , without any silica content except for incidental impurity in the raw materials. This can be compared with a heat by Chang and Goldman for a slag of comparable basicity composed of 50 pct. CaO, 15 pct. Al_2O_3 , 35 pct SiO_2 at the same temperature, where an initial silica reduction should have occurred. The curves showing the rate of sulfur pickup by these two slags are given in Fig. 6 and are identical within experimental accuracy. Thus, the slag where no silica reduction was possible had no advantage in desulfurizing power. Furthermore, the usual high iron content of the slag at intermediate times was noted under the calcium aluminate slag, indicating that the iron enters the slags in association with sulfur and not as iron oxide formed as the result of silica reduction. From these observations it is concluded that the desulfurization reaction and the reduction of silica, even though occurring concurrently, are not phenomenologically related.

MANGANESE: The influence of manganese on the desulfurization reaction was studied because this metal is normally present in blast furnace iron and operators have frequently associated it favorably with desulfurization^{6, 7, 8, 9, 10, 11.} It has also been the subject of laboratory studies,^{12, 13, 14, 15,} which have assigned this action to the strong interaction of manganese and sulfur in iron solutions, resulting in a decrease in sulfur activity. The original rate curves for increasing amounts of manganese in iron up to 0.73 pct. Mn are shown for acid slags at 1500°C in Fig. 7, and up to 0.53 pct. Mn in iron for basic slags at 1500°C in Fig. 8. The rate constants calculated from these data are listed in Table II.. The increase in rate of the reaction with increase in temperature with 0.4/^{pct.} Mn is shown for both acid and basic slags in Fig. 9, which plots log K_m vs $1/T$. The expected Arrhenius relation is obeyed.

The accompanying phenomena peculiar to desulfurization in the presence of manganese are also of interest. Unlike silicon, alloyed manganese decreases the activity of sulfur in iron, but nevertheless it increases the rate of sulfur transfer to slag. Apparently manganese acts even more effectively than iron in reaction/¹ of the mechanism and promotes the over-all process in this way. An auxiliary reaction is required:



This is seen from Fig. 10, which compares the molar quantities of iron and manganese in the acid slags as a function of moles of sulfur in the slag for the entire series of manganese rate determinations at 1500°C. Comparing this with similar data in the alloy free system:² the slope of the iron vs sulfur curve in the absence of manganese is 1.7; with manganese it drops to 0.25, but now manganese has assumed the predominant role and the slope of the manganese vs sulfur curve is 0.85. In order to provide suitable control data for these experiments it is necessary to determine the rate of manganese transfer to the slags in the

absence of sulfur. These data will be presented in suitable detail in a separate paper. Manganese may also function in reaction 3 but no clear evidence of this has been obtained.

CARBON: It is of course imperative to understand the role of carbon in the desulfurization process since blast furnace iron is nominally saturated with this element while in the hearth, and because of the general importance of carbon in all iron and steelmaking operations. The broad significance of the function of carbon in desulfurization has long been recognized through the realization that sulfur removal is most effective under reducing conditions and that the carbon-oxygen reaction plays a dominant role in the oxygen control of the refining system. It is also known that carbon increases the activity of sulfur in iron¹⁵.

In the other parts of this study the slag-metal system was contained in a graphite crucible and both phases were in equilibrium with carbon. The modified crucible assembly required to study variations in carbon content of the iron is shown in Fig. 11. The silica crucible (D) permitted the melting of iron of any desired carbon content while the graphite ring (E) kept the slag in equilibrium with carbon (i.e. the same oxygen activity as in the graphite crucible), and the graphite sleeve (F) maintained the same atmosphere as in the remainder of the study. The original data for the acid slags are shown in Fig. 12 and for the basic slags in Fig. 13. The rate constants calculated from these data are listed in Table III. It was assumed that the temperature coefficient determined by Chang and Goldman¹ for the carbon-saturated system could be applied over the entire range of carbon composition. Changes in the iron content of the slag were observed in association with the sulfur reaction. They were consistent with the proposed mechanism and the data will not be presented in detail. Thus, in addition to its normal function in relation to oxygen, alloy carbon has a direct influence in favor of desulfurization.

PHOSPHORUS, COPPER, NICKEL: Since varying amounts of phosphorus are normally present in the blast furnace, its influence on the desulfurization reaction was examined for both acid and basic slags by making nominal alloy additions of 0.1 and 1% P. No significant variations from the alloy-free runs were observed and the data will not be reported.

Copper and nickel were also included in the study because they frequently enter the system as minor raw material impurities and because it has been suggested that copper may play an effective role in desulfurization¹⁴. Nickel might influence the mechanism due to its chemical similarity to iron. Runs were made in both acid and basic slags with up to 1% of copper and nickel in the iron but no significant departures from the behavior of alloy-free heats were observed.

ALUMINUM: Unlike the other elements studied, aluminum is not a normal component of blast furnace irons. It was included in the study as a means of testing the reaction mechanism, with the expectation that it should function like silicon, but more effectively, in favoring step 3 and maintaining a low oxygen activity at the slag-metal interface. The alumina formed by this reaction would dissolve in the slag. The original data are shown in Fig. 14 for acid slags at 1550°C and for basic slags at 1500°C. It is apparent that Al additions are unusually effective in increasing the rate of desulfurization, and this will be considered in more detail in another section.

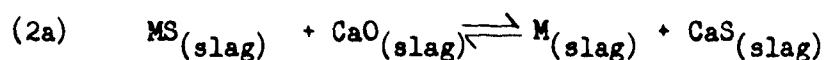
Other features associated with the addition of aluminum were observed. The increased rate of sulfur transfer is accompanied by a high iron content of the slags, as shown in Fig. 15 for basic slags. Here the iron content of the slag during sulfur transfer is compared with that when no sulfur is present. In both cases nominal additions of 1% Al were made at the beginning of the run. Thus the iron in the slag is associated definitely with the sulfur transfer. In these runs

the aluminum was effective in lowering the oxygen activity, as indicated by the reduction of silicon from the basic slag shown in Table IV. Comparison with Table I will show that this reduction does not occur in the absence of aluminum.

The data for iron in slag in the aluminum runs were more erratic than normal. This is attributed to sampling difficulties. It was observed that the iron beads in the slag which are commonly associated with the sulfur reaction^{2,16} were much more profuse in the aluminum runs. The separation of metallic iron in the slag was thus more difficult and uncertain. These same beads, however, provided metallographic confirmation of step 3 of the reaction mechanism. Fig. 16 shows the beads adhering to a carbon monoxide gas bubble which was trapped in the slag during freezing at the end of a run. Fig. 17 shows a micrograph of one of these trapped beads. The dendrites can be identified as pro-eutectoid austenite, proving that the beads were not mechanically entrained portions of the iron bath, which was carbon-saturated and could not exhibit this structure. Thus, the beads were formed in the slag by reaction 3.

GENERAL CONCLUSIONS:

The relative effectiveness of the various alloy elements on the rate of sulfur transfer is observed by the comparison of the rate constants in Fig. 18 for acid slags and Fig. 19 for basic slags. Cu, Ni, and P have not been included as they have no observable influence on the rate. Of the other elements studied, C, Si, Mn, and Al all increase the rate of sulfur transfer from iron to carbon-saturated slag with increasing effectiveness in the order named. The supplementary data allow interpretation of reasons for the influence of the individual elements in terms of the three stage mechanism:





R = C, Si, Al, Mn (?)

M = Fe, Mn, Si (?)

On the basis of the observed relations between S, Fe, and Mn in the slag during the reaction, it seems clear that in the unalloyed system iron is the principal carrier of sulfur across the slag-metal interface in step 1. When manganese is present as an alloying element it not only replaces iron as indicated in reaction 1a, but causes the over-all process to proceed more rapidly. Although the data approach the stoichiometric relations of Fe_2S and MnS in the slag, the evidence does not establish the identity of these molecular entities and the reactions as written are only intended to indicate the type of metal-sulfur complex involved in the process. On the basis of chemical similarity, copper and nickel might have been expected to participate in the reaction in the same manner as manganese, but no evidence for this was obtained.

The elements silicon and aluminum appear to act through reaction 3 by supplanting carbon in removing oxygen from the system. Since the oxides of these elements are already present in the slag in large amounts, it would not be observed directly if they acted as sulfur carriers in step 1. In the case of aluminum, large amounts of iron are still observed in the slag, both chemically combined and as droplets. The participation of these elements in reaction 3 can be studied quantitatively through their influence on carbon monoxide evolution. This is in progress and will be the subject of a separate publication.

The influence of the various alloying elements on the activity of sulfur in iron is known¹⁵ and has been carefully considered in interpretation of the data. The use of activities instead of concentrations does not alter the percentage variation of rate constants for a given alloy with composition. Neither does the consideration of sulfur activity account even qualitatively for the influence of the different alloy elements on the rate of sulfur transfer. For example,

manganese decreases the sulfur activity but increases the rate of transfer. Other factors such as interfacial energies, viscosity, and diffusion must therefore be rate determining and additional study will be required to understand these processes.

ACKNOWLEDGMENT

The Office of Naval Research provided a Fellowship to one of the authors and additional support for this research under Contract N6ori-47/IV, Project NR 031-014.

The analytical services of Elizabeth Duncan, Audrey Kraus, and Virginia Johnson and the experimental assistance of Jack Shegog and Robert Miller are gratefully acknowledged.

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4. Effect of alloyed silicon on rate constants for sulfur transfer with basic slags, 1500°C.
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6. Comparison of sulfur transfer curves for slags of same basicity with and without silica.

	<u>%Al₂O₃</u>	<u>%CaO</u>	<u>%SiO₂</u>
Silica free	50	50	0
With silica	15	50	35

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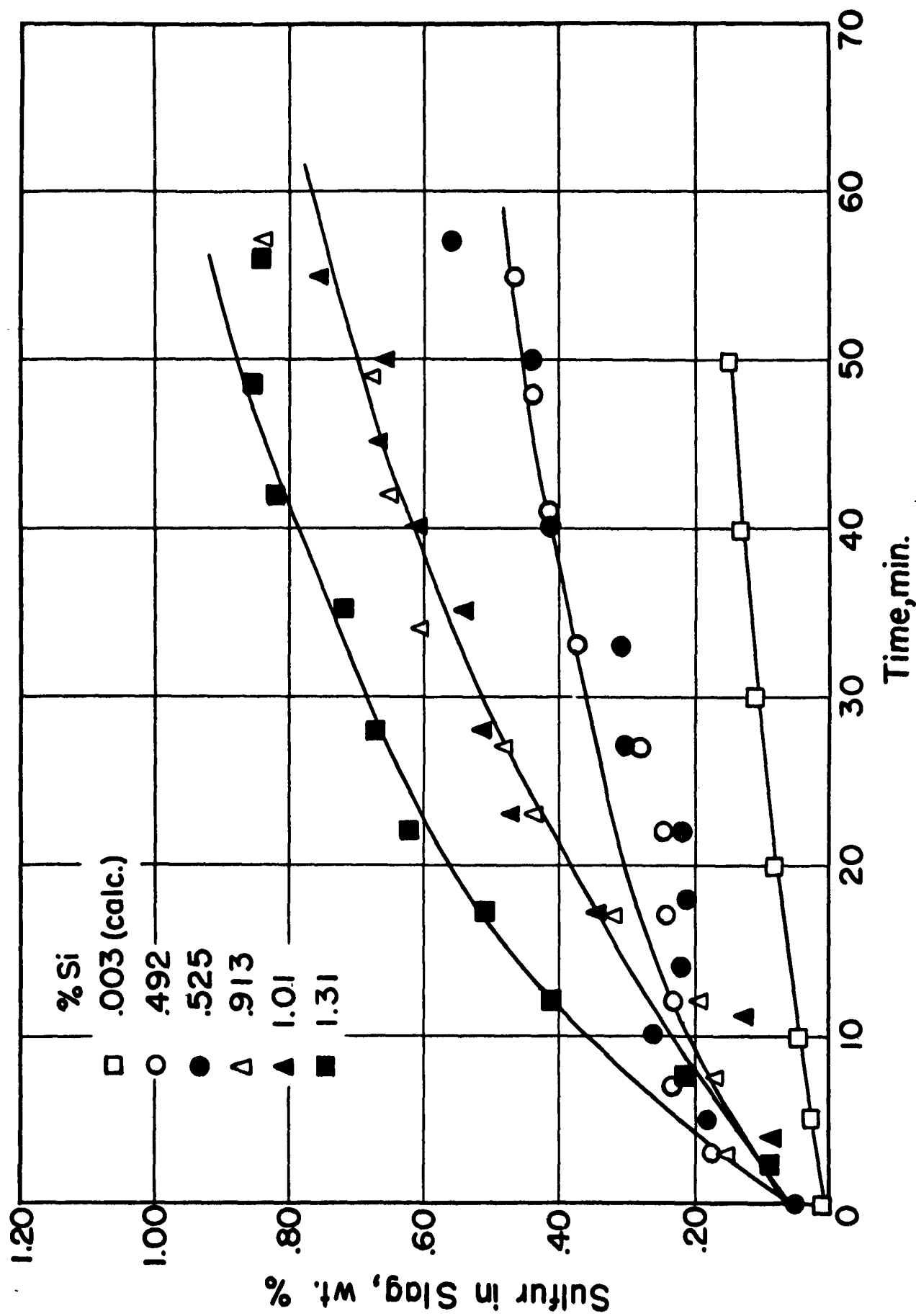


Fig. 1. Effect of alloyed silicon on sulfur transfer with acid slags, 1500°C.

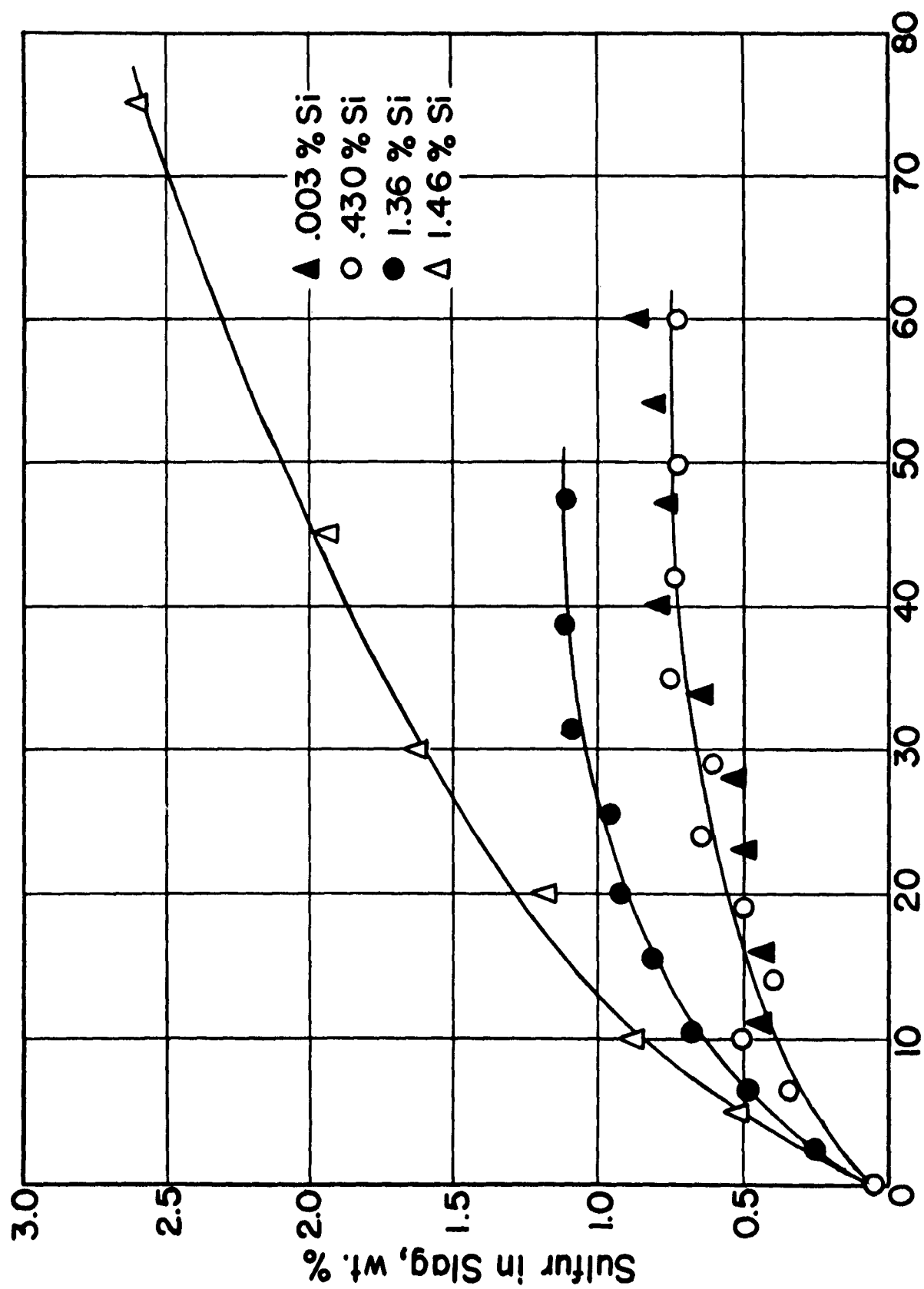


Fig. 2. Effect of alloyed silicon on sulfur transfer with basic slags, 1500°C.

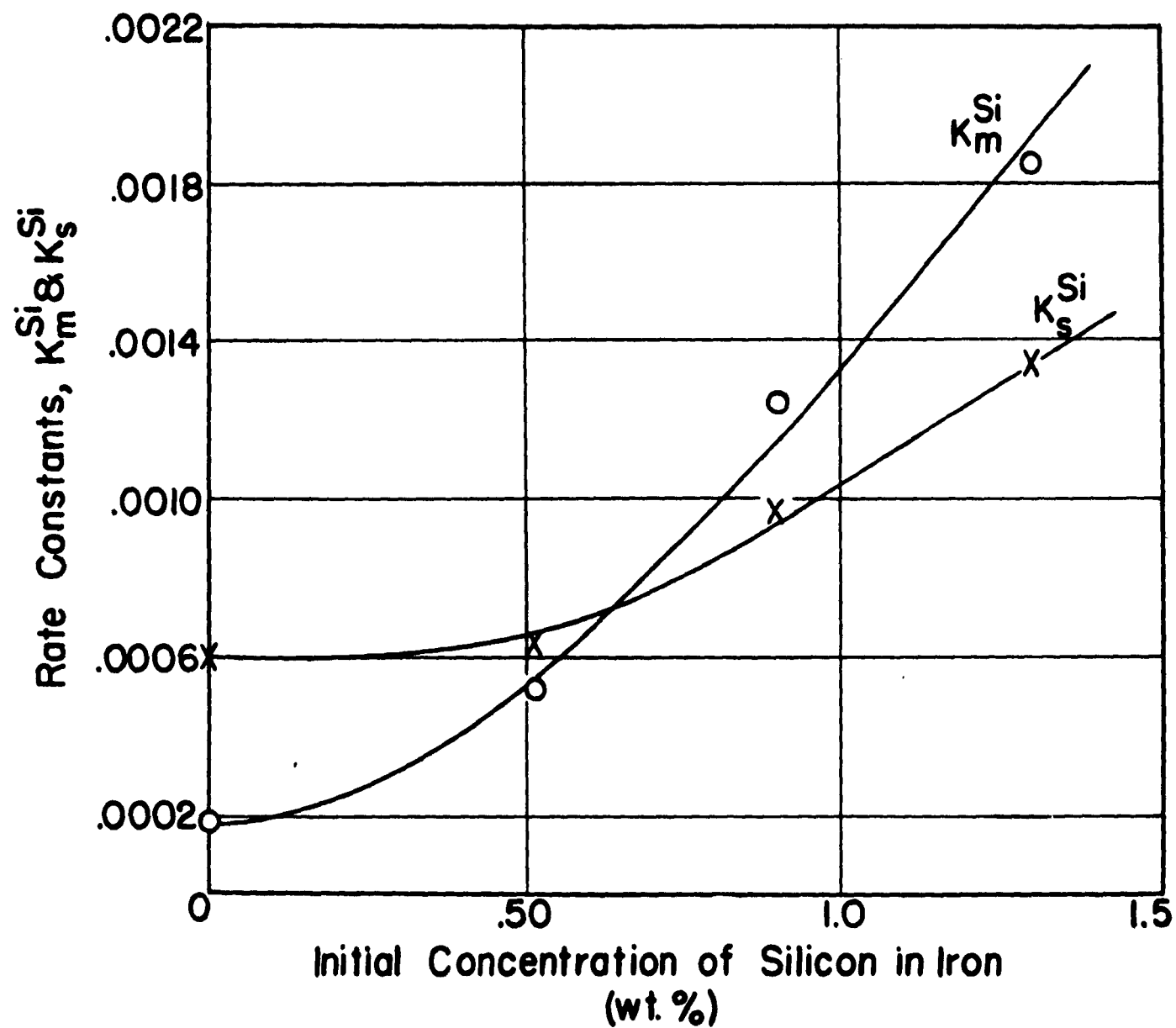


Fig. 3. Effect of alloyed silicon on rate constants for sulfur transfer with acid slags, 1500°C.

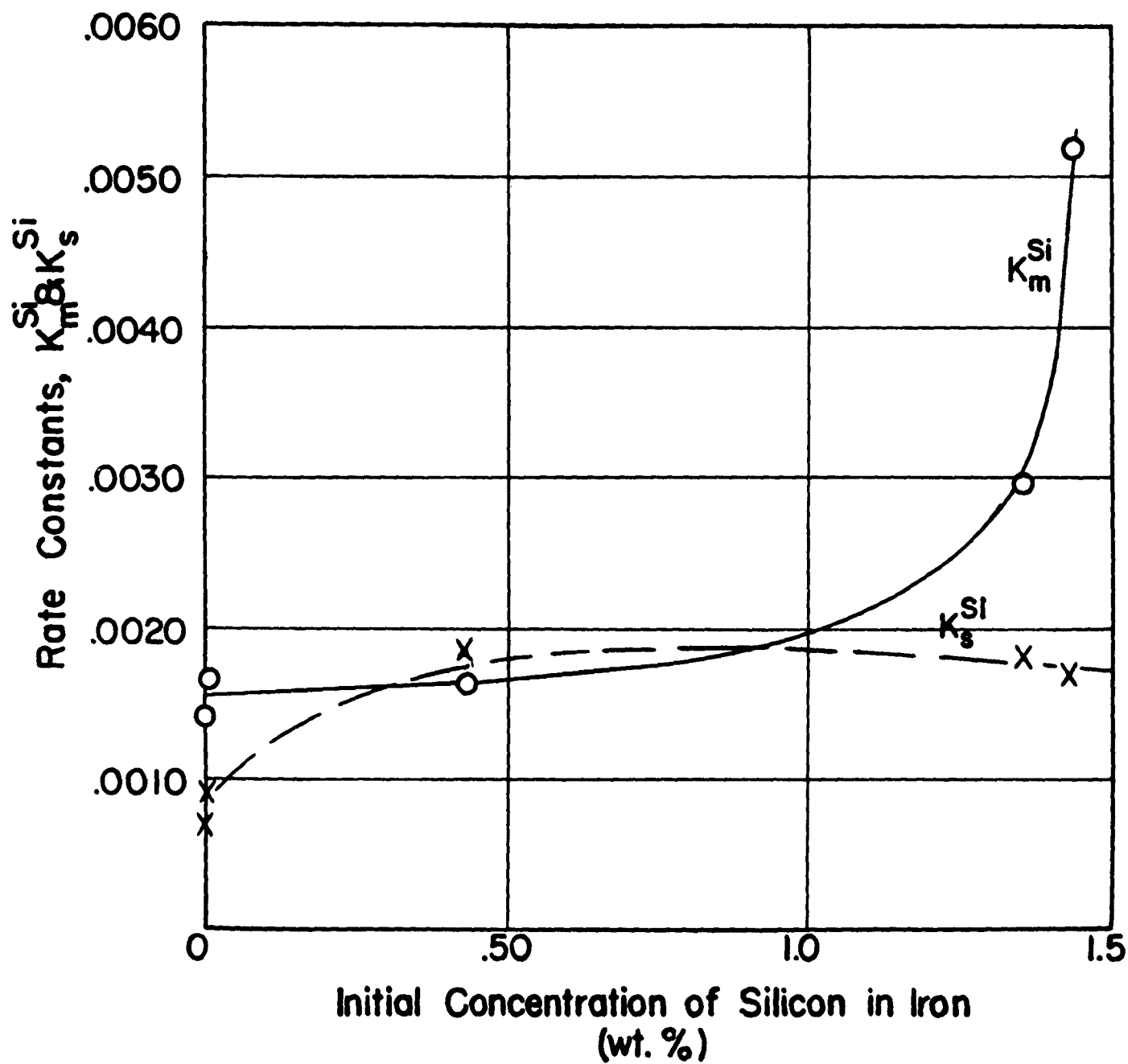


Fig. 4. Effect of alloyed silicon on rate constants for sulfur transfer with basic slags, 1500°C.

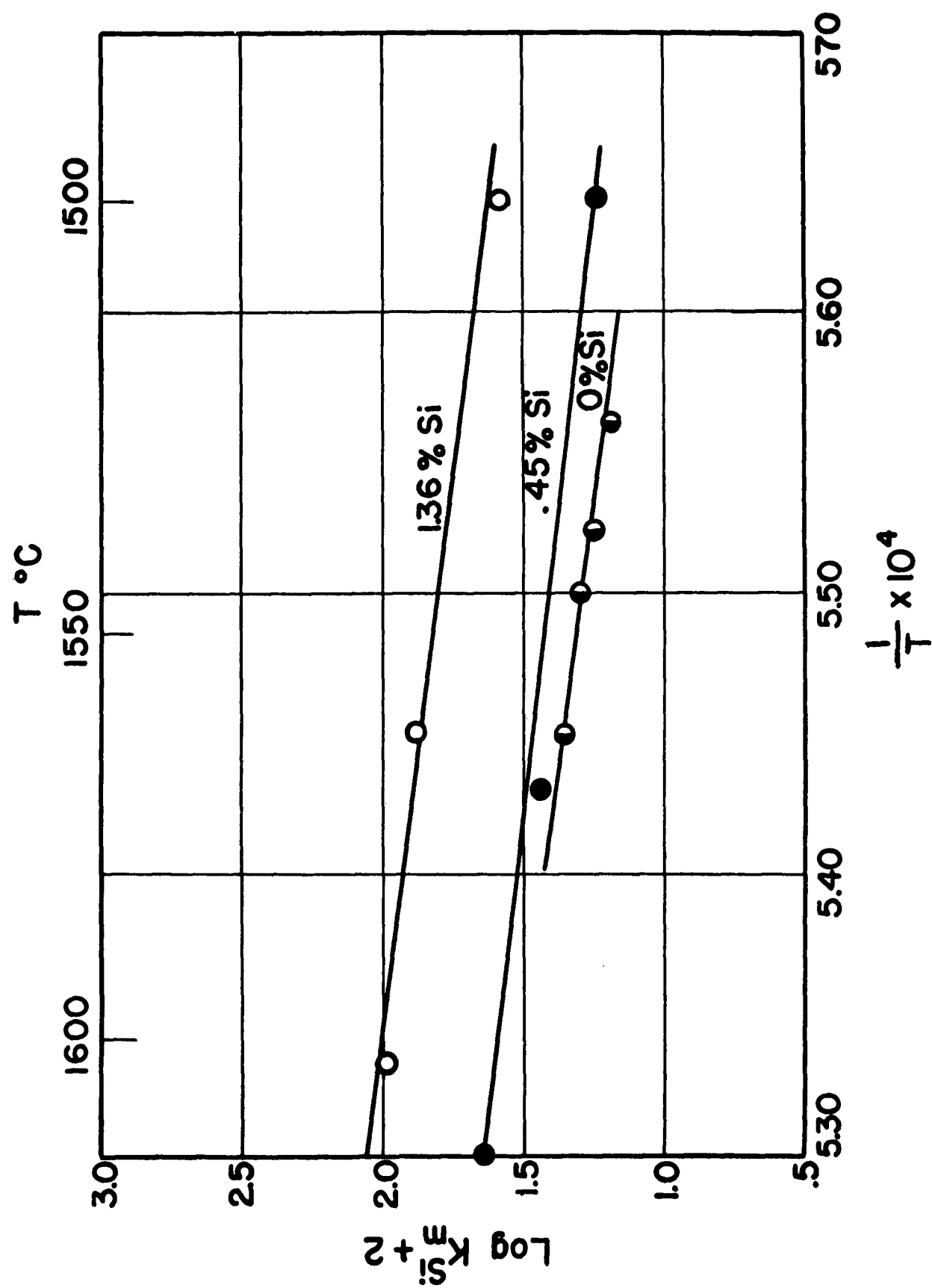


Fig. 5. Temperature dependence of rate constants for sulfur transfer with alloyed silicon and basic slags.

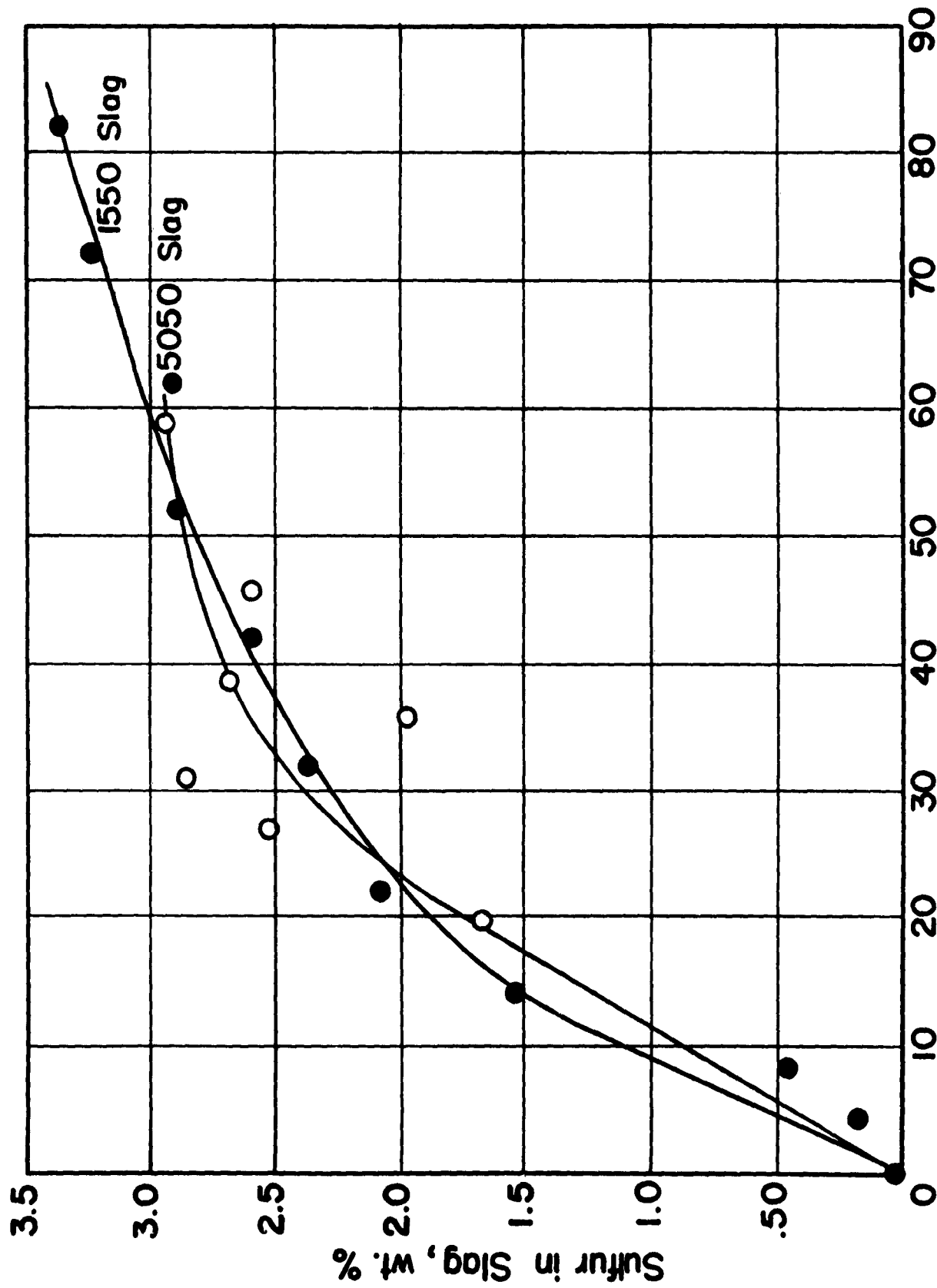


Fig. 6. Comparison of sulfur transfer curves for slags of same basicity with and without silica.

Silica free With silica	%Al ₂ O ₃	%CaO	%SiO ₂
	50 15	50 50	0 35

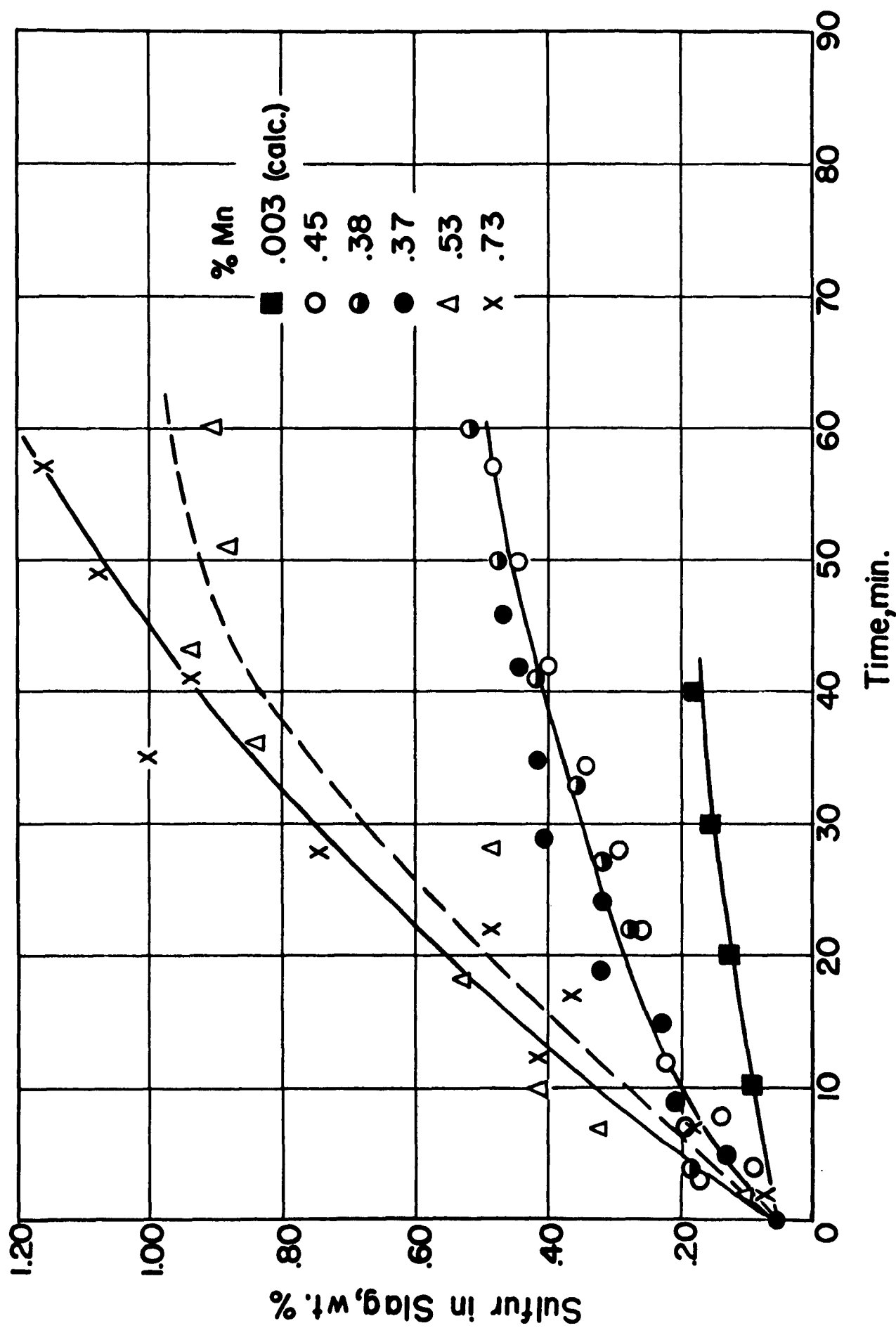


Fig. 7. Effect of alloyed manganese on sulfur transfer with acid slags, 1500°C.

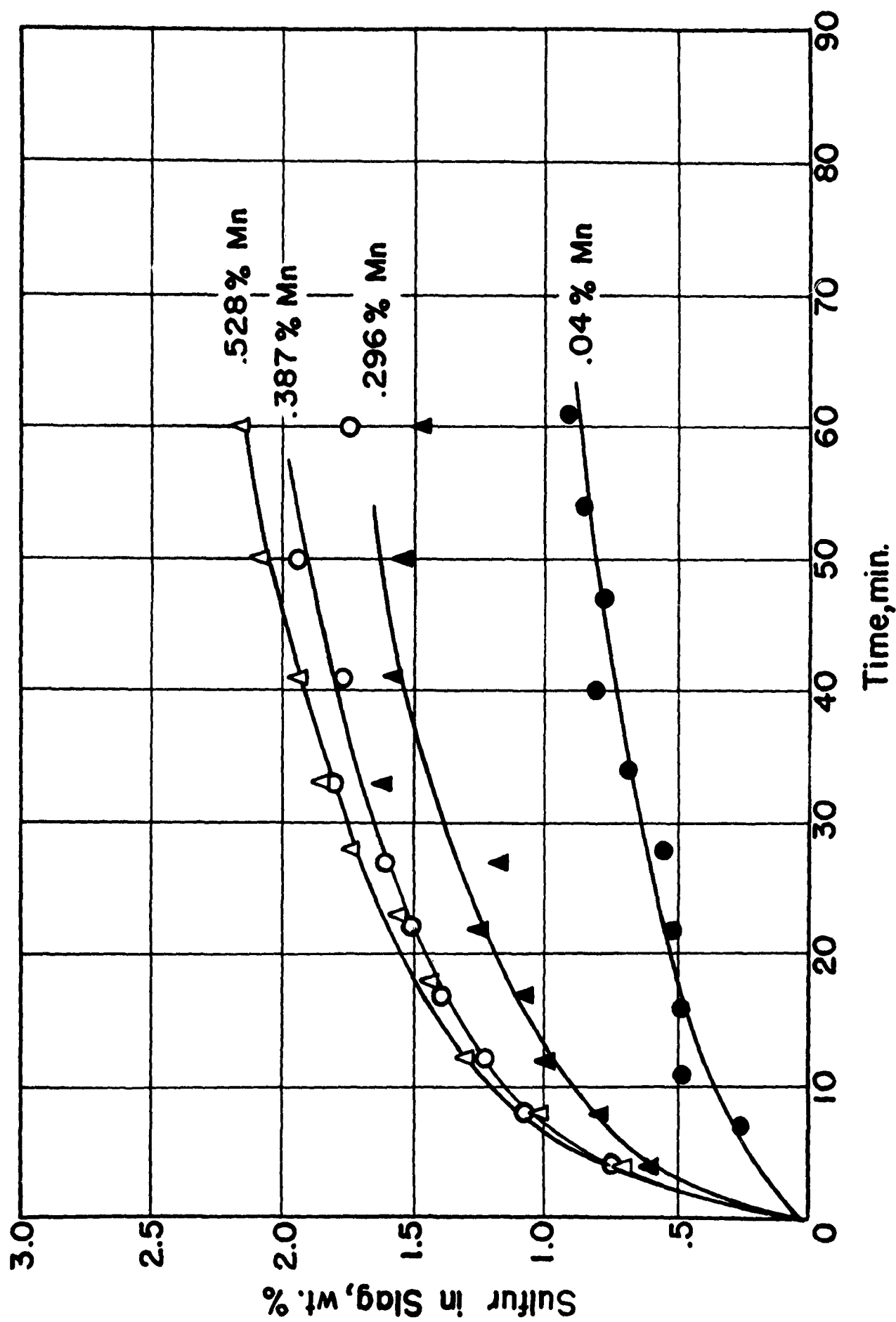


Fig. 8. Effect of alloyed manganese on sulfur transfer with basic slags, 1500 C.

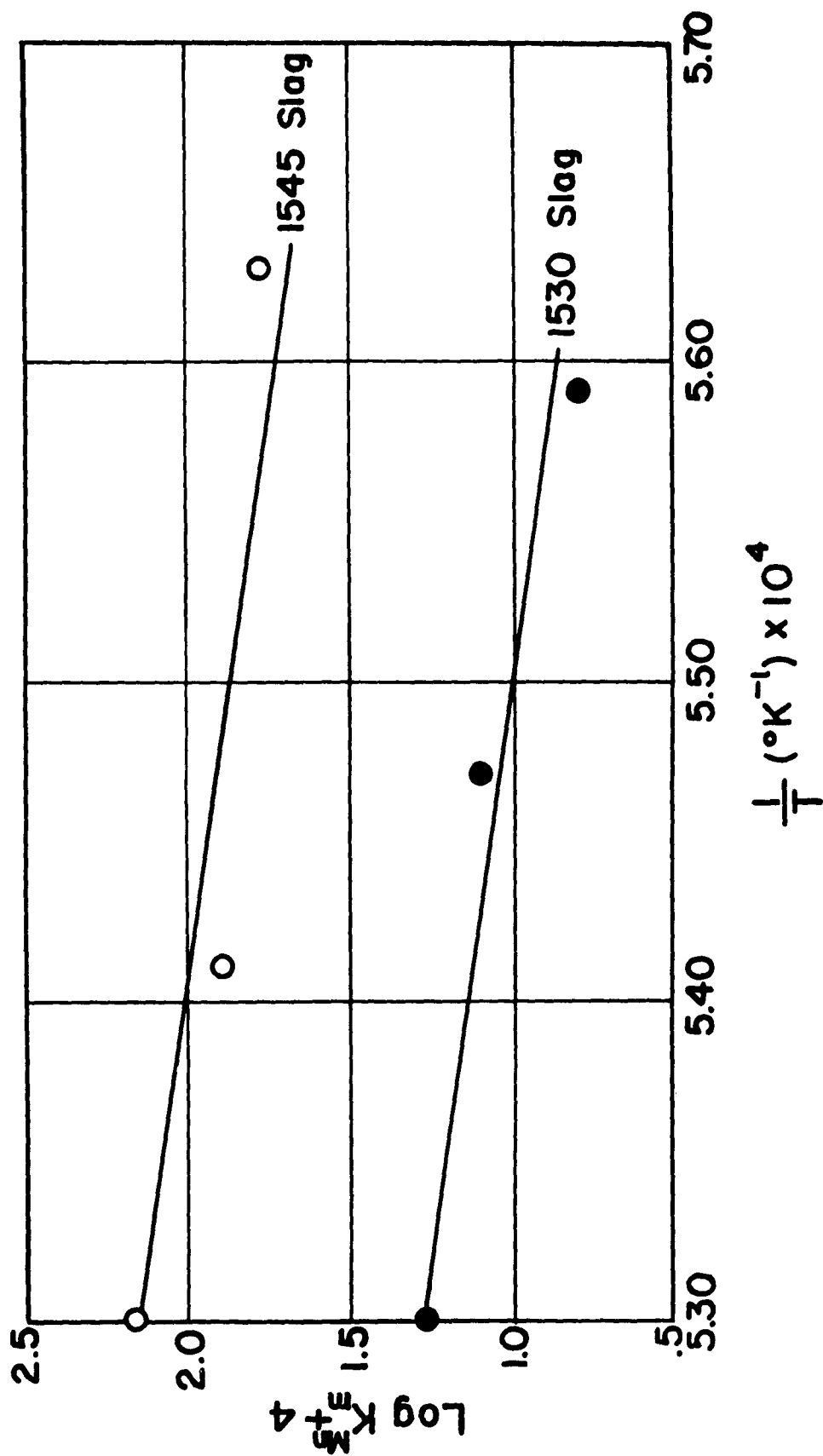


Fig. 9. Temperature dependence of rate constants for sulfur transfer with alloyed manganese, acid and basic slags.

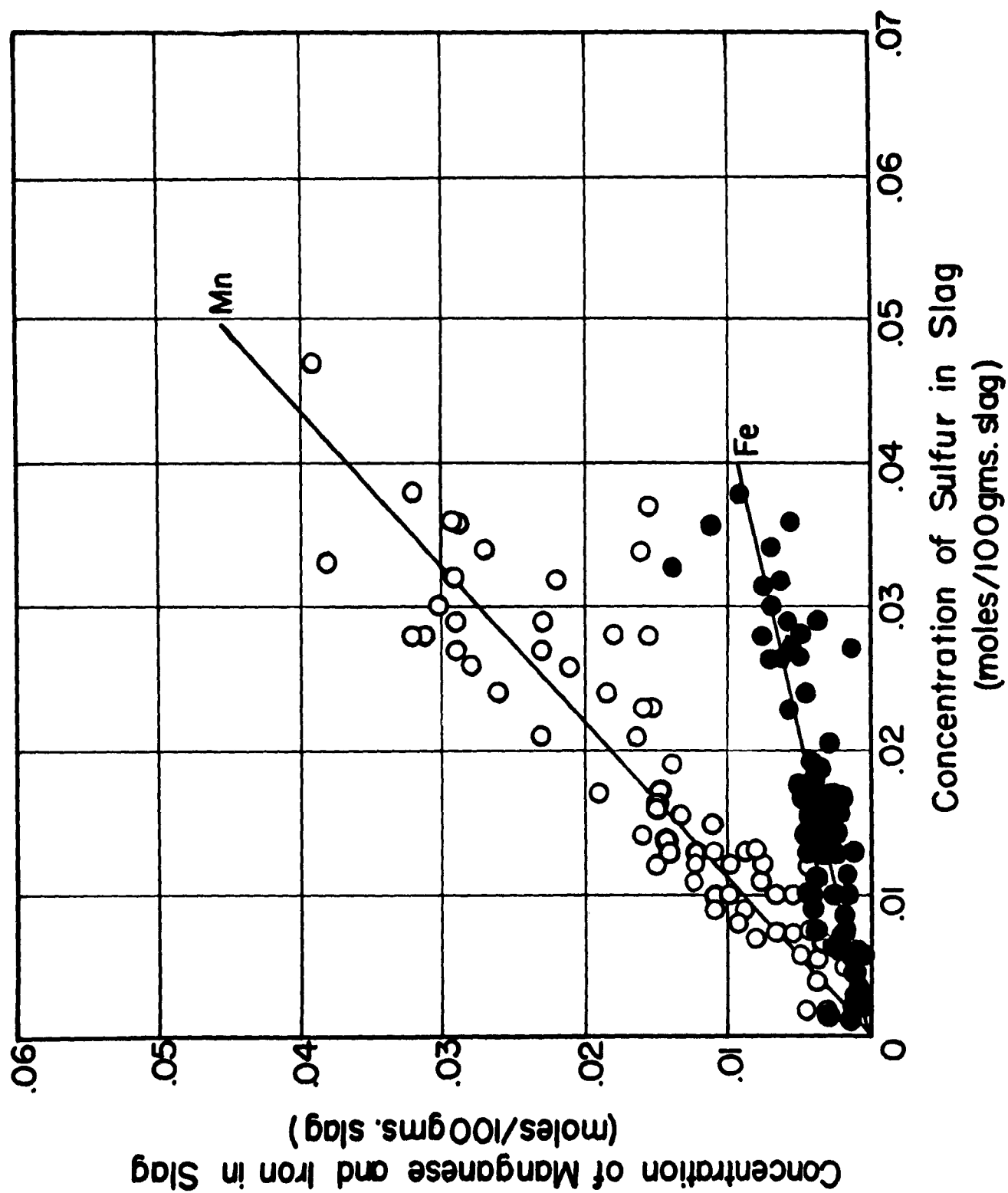
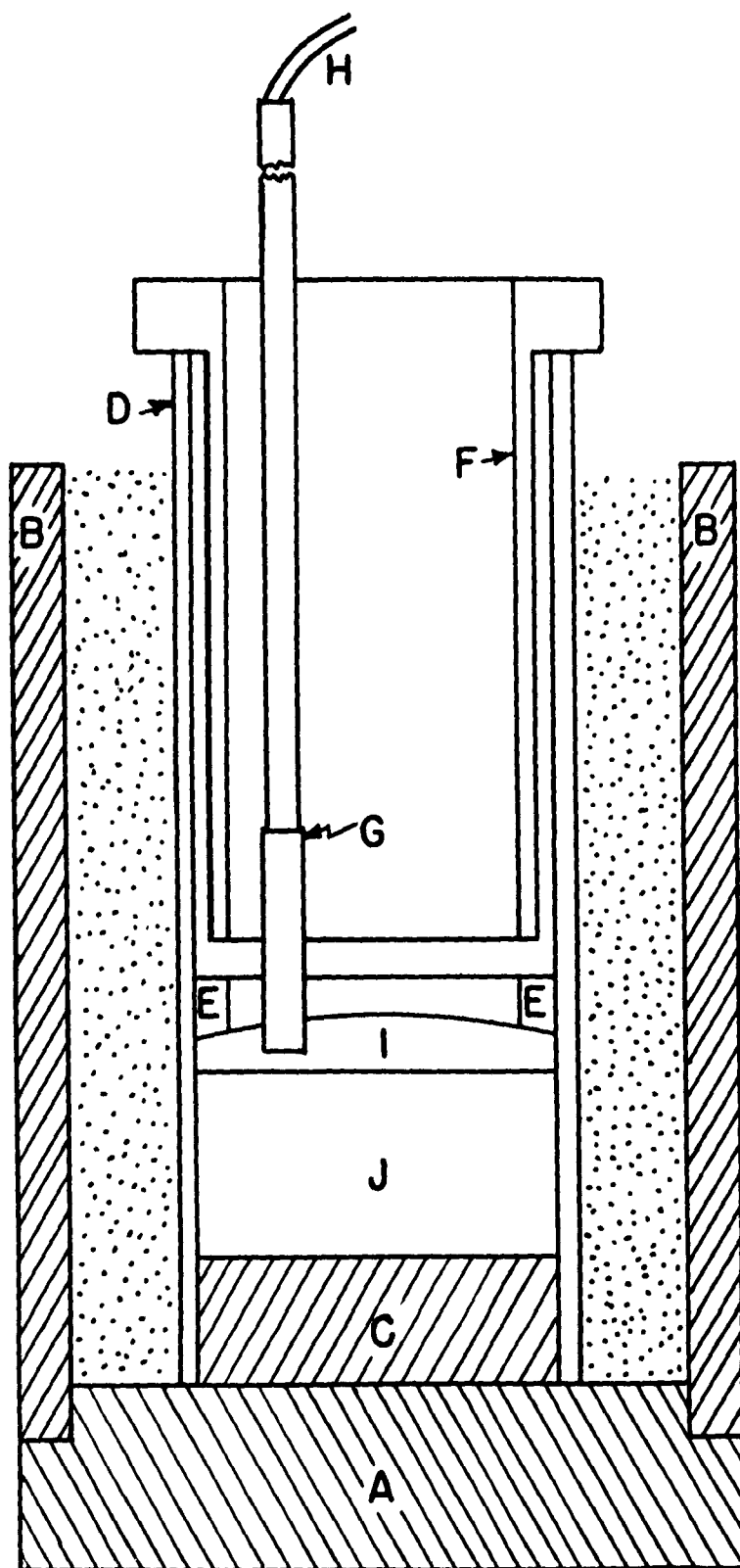


Fig. 10. Molar reactions between iron, manganese and sulfur in acid slags, 1500°C.



- A Silica Brick
- B Alundum Sleeve
- C Tamped Silica Bottom
- D Fused Silica Tube
- E Graphite Ring
- F Graphite Sleeve
- G Thermocouple Protection Tube
- H W-Mo Thermocouple
- I Slag
- J Iron

Fig. 11. Schematic section of crucible assembly for low carbon heats.

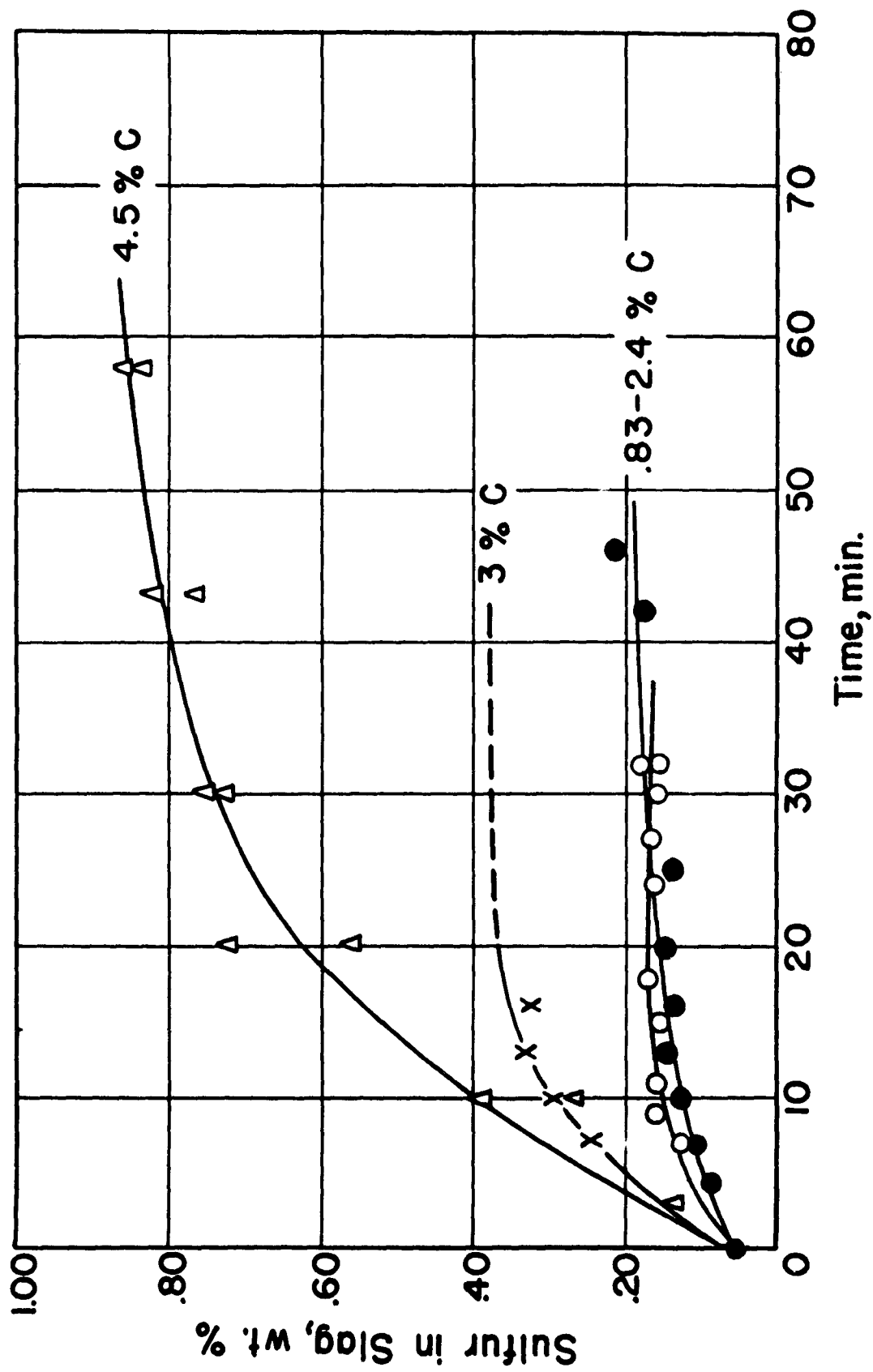


Fig. 12. Effect of alloyed carbon on sulfur transfer with acid slags, 1635°C.

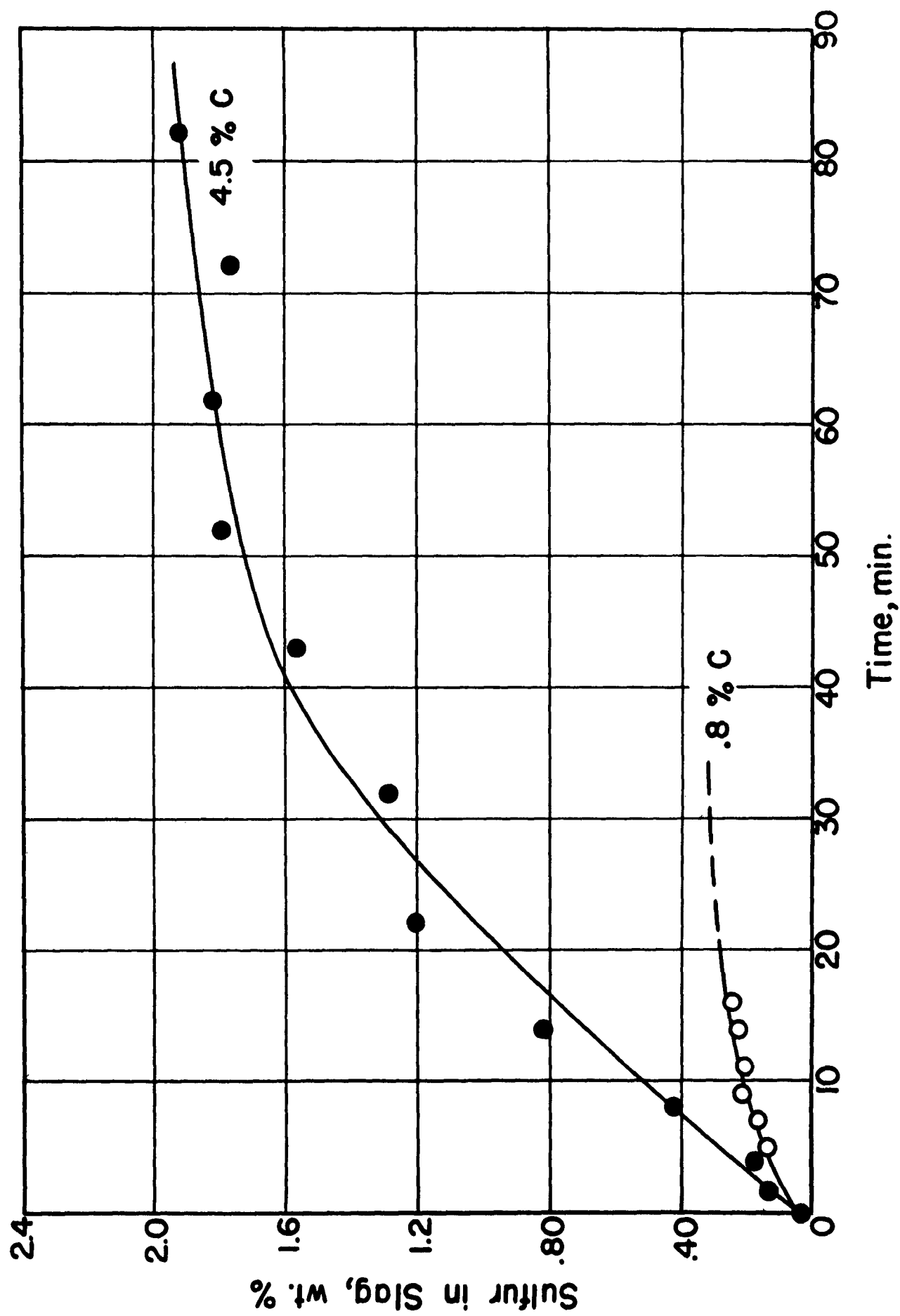


Fig. 13. Effect of alloyed carbon on sulfur transfer with basic slags, 1635°C.

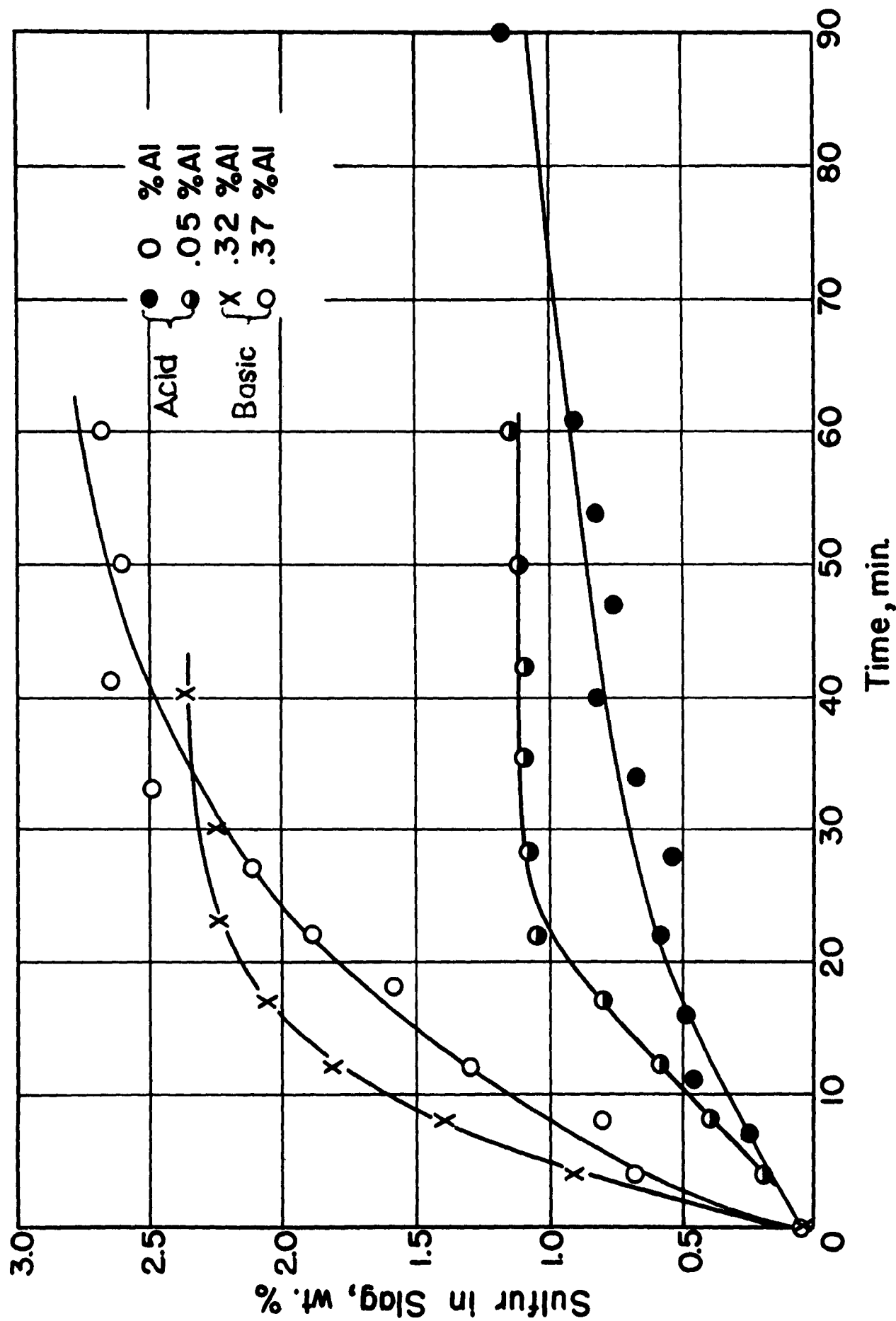


Fig. 14. Effect of alloyed aluminum on sulfur transfer with acid slags at 1550°C, and basic slags at 1500°C.

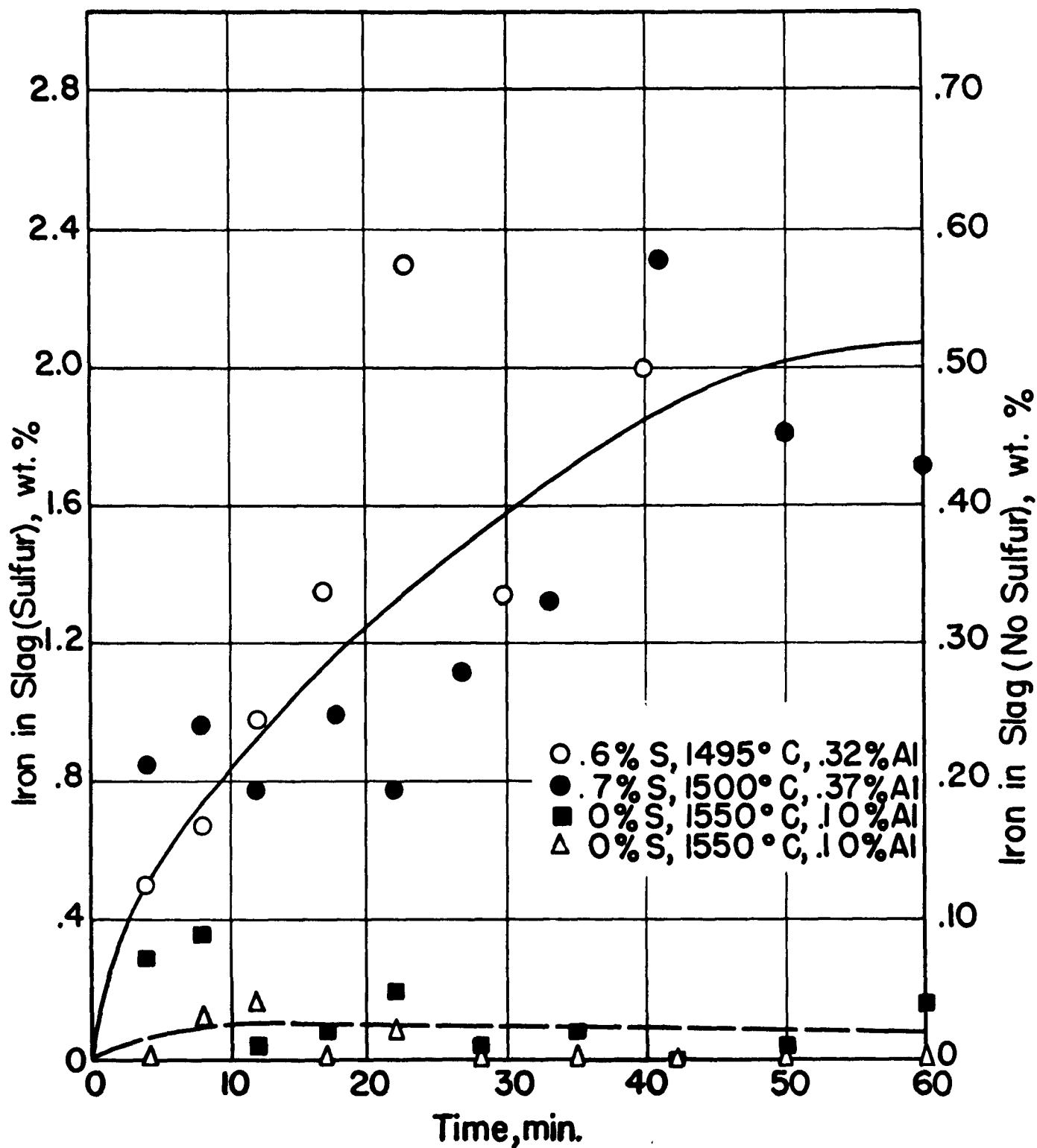


Fig. 15. Iron in basic slag associated with sulfur transfer with alloyed aluminum, 1500°C.



Fig. 16. Section of trapped gas bubble in acid slag, showing iron beads associated with sulfur reaction, 5.5X.

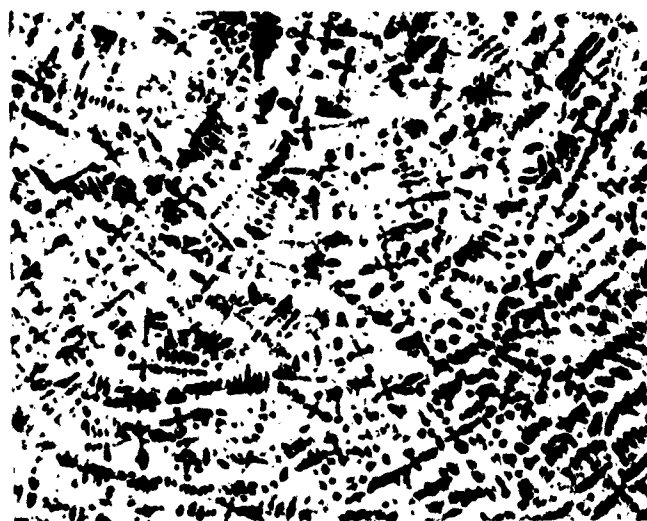


Fig. 17. Micrograph of iron bead of type shown in Fig. 16, showing dendrites of primary austenite, nital etch, 250X.

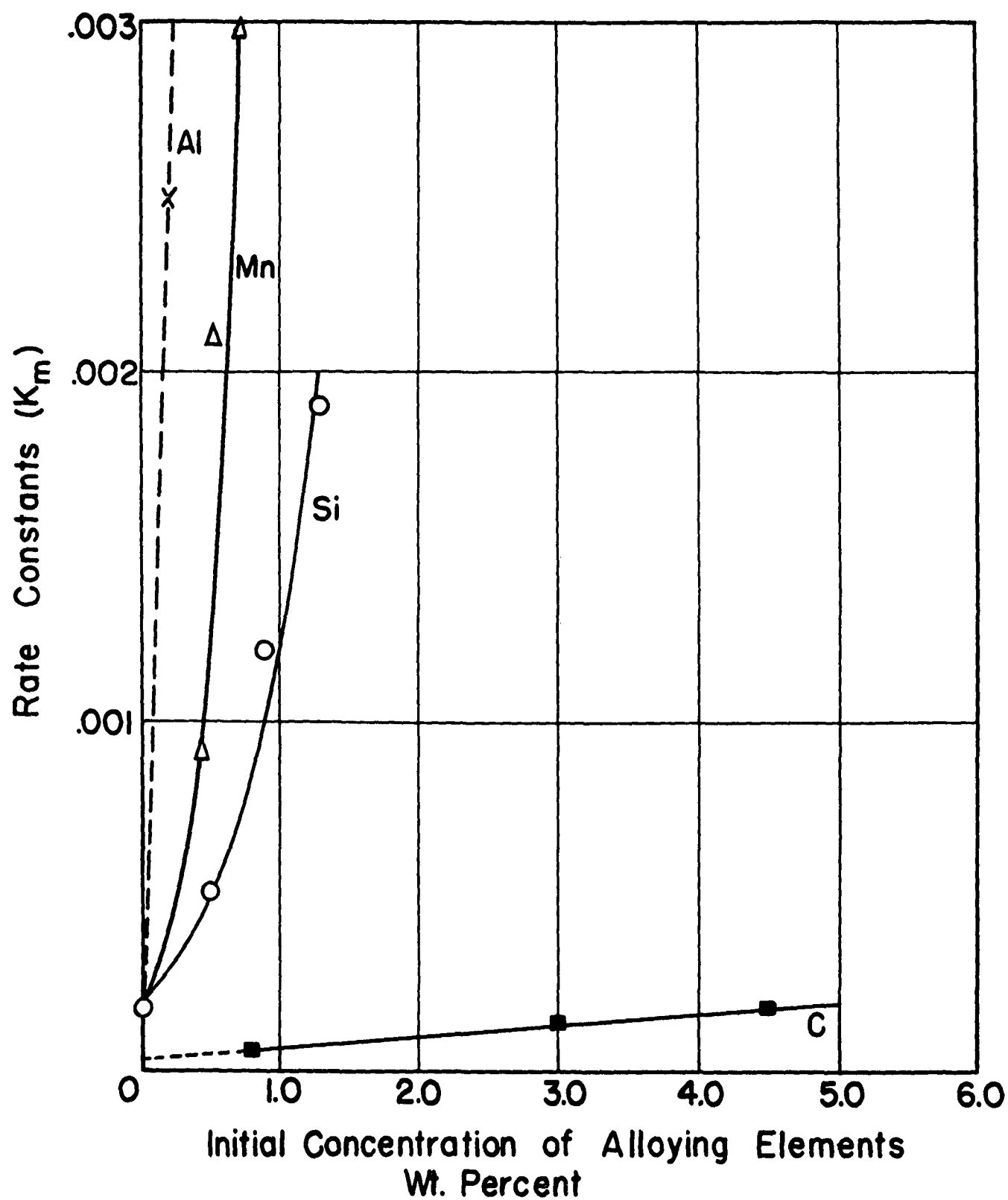


Fig. 18. Comparison of the effect of alloying elements on rate constants for sulfur transfer with acid slags.

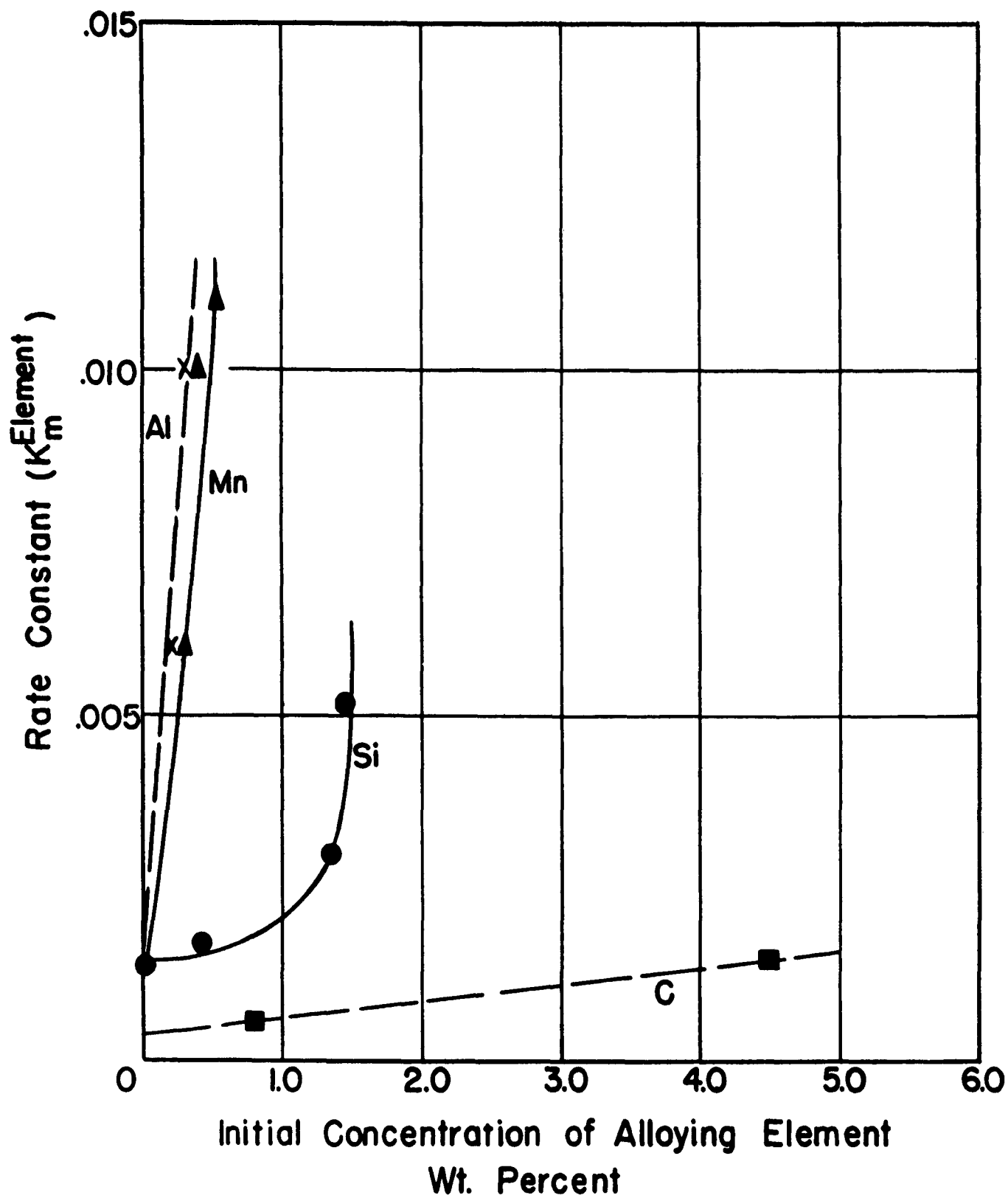


Fig. 19. Comparison of the effect of alloying elements on rate constants for sulfur transfer with basic slags.

Table I. The Change of Silicon in Iron
Under Acid and Basic Slags.

<u>Slag Designation</u>	<u>°C</u>	<u>%Si in Iron</u>	
		<u>Initial</u>	<u>Final</u>
1530 <u>acid</u>	1490	1.01	1.30
	1490	1.31	1.36
	1490	.49	.56
	1500	.53	.63
	1510	.91	1.28
	1560	1.50	1.62
	1570	.45	.56
	1610	1.43	1.65
	1630	.15	1.27
1545 <u>basic</u>	1490	1.45	1.36
	1500	.43	.34
	1500	.78	.52
	1520	.003	.003
	1560	1.37	1.14
	1570	.44	.26
	1600	1.35	1.17
	1615	.46	.39

Table II. Rate Constants for Desulfurization as
a Function of Manganese Concentrations.

<u>%Mn</u>	<u>k_m^{Mn}</u>	<u>Conditions</u>
0	0.00018	Acid slag, 1500°C
0.45	0.00090	
0.53	0.0021	
0.73	0.0029	
0	0.0016	Basic slag, 1500°C
0.30	0.0066	
0.39	0.010	
0.53	0.012	

Table III. Rate Constants for Desulfurization as a
Function of Carbon Concentration.

<u>% C</u>	<u>K_m^C</u>	<u>Conditions</u>
0.8-	0.00071	Acid slag, 1640°C
2.4	0.00071	
3.0	0.0016	
4.5	0.0022	
0.8	0.00068	Basic slag, 1520°C
4.5	0.0015	

Table IV. Reduction of Silica from Basic Slags
in the Presence of Alloyed Aluminum.

<u>Heat No.</u>	<u>%Al in Iron</u>		<u>%Si in Iron</u>	
	<u>Initial</u>	<u>Final</u>	<u>Initial</u>	<u>Final</u>
G41	0.37	0.07	.02*	0.15
G62	0.32	0.12	.02*	0.25
59	—	0.74	.02	0.15
50	—	0.78	.02	0.16

* Nominal