

T H E U N I V E R S I T Y O F M I C H I G A N

COLLEGE OF ENGINEERING

Department of Chemical and Metallurgical Engineering

Final Report

KINETICS OF LIME SOLUTION IN BASIC OXIDIZING SLAGS

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and

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Abstract

This report is a final summary of the National Lime Association research project, "Kinetics of Lime Solution in Basic Oxidizing Slags," carried out at the University of Michigan. The report covers the period July 1, 1963 - July 31, 1966.

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INTRODUCTION

The advent of the basic oxygen steelmaking process has opened an important new market for the lime industry: the new steelmaking technique requires burnt lime as a fluxing agent in amounts from 100-150 pounds of lime for each ton of steel produced. In the interest of developing fundamental relationships describing the behavior of lime as a fluxing agent in this steelmaking process, the National Lime Association undertook support of a research program at the University of Michigan in July, 1963. The purpose of this program was to study the behavior of lime as a flux, particularly with regard to the behavior of various types of lime and the mechanism by which they dissolve in slags encountered in oxygen steelmaking.

Before reporting the specific results of the research program, the following paragraphs present a brief discussion of the behavior of lime as a fluxing agent in oxygen steelmaking.

Steelmaking operations use the relatively impure product of the blast furnace, pig iron, which contains approximately 1% silicon, 1% manganese, 4% carbon, and up to 0.3% phosphorus, and 0.1% sulfur. In the conversion of pig iron into steel, these impurities are oxidized from the bath, and whereas the carbon, and perhaps some of the sulfur, are removed as gases, the oxides of silicon, manganese, and phosphorus, as well as part of the sulfur, must be absorbed into a slag. The ability of the slag to efficiently remove these impurities from the bath by dissolving them in a liquid oxide phase is very much enhanced if the slag is basic* in nature. The removal

* The term basicity relates to the fact that oxide compounds react with one another in a manner analogous to aqueous solutions of acids and bases, and also relates to the general nature of their reaction with water. On this basis, calcium oxide is classified as a strong base whereas silica is classified as a strong acid.

of sulfur and phosphorus in particular is strongly dependent upon the basicity of the slag in a steelmaking process.

The behavior of phosphorus and sulfur as influenced by slag basicity is shown in Figures 1 and 2. In Figure 1 the phosphorus content of liquid iron in contact with a given slag is shown as a function of basicity ratio and iron oxide content of the slag. When the calcium oxide in the slag is less than 2.5 times the silica in the slag, the phosphorus content of the metal is independent of iron oxide content and tends to be very much dependent upon the basicity ratio. However, at basicity ratios of 2.5 and higher, the phosphorus content of the metal is dependent only upon the iron oxide content of the slag. This behavior shows that increasing the basicity and the iron oxide content of the slag tend to promote good dephosphorization. However, from the standpoints of efficiency and vessel lining protection, it is best to keep the iron oxide at as low a level as possible. Furthermore, the use of lime is kept at a minimum both for economic reasons and for obtaining a fluid slag. Consequently, the basicity ratio is maintained between 2.5 and 3 in steelmaking operations; in this range the dephosphorization has been maximized by as high a basicity ratio as necessary, and is then directly dependent upon the oxidizing condition of the slag.

In Figure 2 the behavior of sulfur is shown. It can be noted that as the fraction of excess base (excess beyond oxide compound formation) in the slag increases, the relative amount of sulfur absorbed by the slag is increased. Thus, a basic slag also favors desulfurization.

BASIC OXYGEN STEELMAKING PROCESS

During the past decade the world steel industry has rapidly adopted the basic oxygen steelmaking process. The growth in this period has been from a production of about one million ingot tons to about one hundred million ingot tons per year. Basic oxygen steelmaking is carried out in a refractory-lined converter into which gaseous oxygen is jetted, penetrating into the pig iron bath and oxidizing the impurities carbon, silicon, and manganese from the metal. To promote fusion of a slag that is capable of refining the metal, burnt lime is added to the process in an amount to provide a CaO to SiO_2 ratio of approximately 3. As mentioned above, addition of burnt lime, in providing a basic slag, assists in the removal of phosphorus and sulfur from the metal phase: the phosphorus is oxidized to P_2O_5 and combines with lime to form calcium tetraphosphate, while the sulfur dissolves in the slag, most probably in the form of calcium sulfide. The addition of burnt lime as a flux is consequently an important and integral part of the steelmaking process. In addition to the oxidation reactions mentioned above, a considerable amount of iron is oxidized with the impurities. This manifests itself both as iron oxide in the slag and as a dense red fume which must be separated from the waste gases.

The production of steels with relatively low phosphorus and sulfur specifications therefore can be successfully accomplished in the basic oxygen process provided the slag practice is satisfactory. With a relatively short blowing time (usually less than thirty minutes), the development of an early basic oxidizing slag, and its maintenance throughout the course of the blow, has been shown to be a requisite for successful operation of the process. Burned dolomite is often substituted in part for the high calcium lime, and

in addition, fluxing agents which promote the generation of an early fluid slag, such as iron oxide or fluorspar, are often added.

Burnt lime is used almost exclusively today as the primary slag-making material in the basic oxygen process. The demand for shorter heat times and the necessity for processing pig iron of relatively high phosphorus content have led to the need for rapid solution of lime in the slag. The demand for rapid lime solution and the availability of several types of lime have raised questions regarding the factors influencing the rate of lime solution in basic oxidizing slags.

The mechanism by which lime dissolves in oxidizing slags is not very well understood. In particular, the solution rate of lime has not been studied, although the kinetics of mass transfer in slag-metal systems has received considerable research attention. The lack of understanding and specific data in this area led to the NLA supported research program at the University of Michigan.

RESEARCH PROGRAM ON LIME SOLUTION IN BASIC OXIDIZING SLAGS

A project was initiated in the Department of Chemical and Metallurgical Engineering at the University of Michigan in July 1963 by the National Lime Association. This research has been directed toward evaluating the mechanism which controls the rate of lime solution in basic oxidizing slags.

Since a study of this type involves the preparation of burnt lime specimens for dissolution experiments, it was necessary to develop a laboratory technique for calcining samples of limestone in which properties of the limestone could be varied and measured in a controlled manner by calcining at various temperatures and for given lengths of time. In an effort to

describe the nature of the lime being used in the dissolution experiments, calcining rate studies were carried out on the limestones used in this program. To characterize the properties of the lime, the ASTM standard water reactivity test for lime was used.¹ Shrinkage, in the case of over-burning, also was measured for samples calcined at higher temperatures and for longer times.

CALCINATION PROCESS EQUIPMENT

The kinetics of calcination of various limestones can be determined by measuring the volume of carbon dioxide evolved from a limestone sample as a function of time. The equipment necessary for accomplishing this involves a closed high temperature system in which the limestone sample can be placed and a method for measuring the volume of CO₂ evolved as a function of time. In the present research, a resistance-heated furnace with a closed reaction tube was chosen for carrying out the calcination. The analytical equipment consisted of a series of absorption cells for collecting the carbon dioxide and determining its weight gravimetrically. This equipment is shown schematically in Figure 3, and a photograph of the laboratory arrangement is presented in Figure 4. The reaction chamber was a closed-end mullite reaction tube 1-1/2" in diameter by 24" long. One end was closed with a pyrex glass ground joint, equipped with gas inlet and outlet tubes, and a thermocouple protection tube. Dry argon gas was used as a carrier to flush the evolved carbon dioxide from the reaction tube and carry it to the analytical system. The resistance-heated furnace, built by Hevi-Duty, was capable of going to

1. ASTM Standards 1965, part 9, pp. 77-88 (C-110-58).

2200°F (1200°C), and was controlled on a signal from a platinum/platinum-10% rhodium thermocouple.

The equipment for measuring the evolved carbon dioxide consisted of glass absorption bulbs containing a bed of 120 cc of ascarite with top and bottom layers of anhydrous. The absorbers were equipped with ground glass joints at the inlet and outlet to permit removal and intermediate weighing, with the bulbs connected in parallel so that one bulb could be removed for weighing while the other was absorbing gas. The system was sealed from the atmosphere with vacuum pump-oil bubblers and adjoining traps. This equipment is shown in the lower portion of Figure 3.

Experimental studies were carried out on a fine-grained limestone and a coarse-grained limestone, both of which were nearly pure calcium carbonate. The rate of calcination at various times was measured, and the results for the fine-grained stone calcined at two temperatures are shown in Figure 5. The calcination behavior was essentially the same for the two limestones.

In addition to determining the calcination characteristics of the limestones, their reactivity with water was measured by using the standard ASTM test. In Figure 6, the increase in slurry temperature is plotted against time for the fine-grained and coarse-grained limestones calcined to completion at 980 and 1150°C. The water reactivity of the two stones is essentially the same for a calcination temperature of 1150°, but the reactivity of the fine-grained stone is significantly higher for the lower calcination temperature.

In carrying out the solution experiments in which lime was dissolved in a liquid slag, several experimental procedures were attempted (see the following section of this report). One of those procedures involved preheating the lime by placing a one-half inch diameter cylinder of lime in the hot zone of the

furnace and allowing it to preheat for 25 minutes, such that the lime reached the slag temperature prior to initiating the solution reaction. This procedure was found to alter the characteristics of the "as-calcined" lime. This modification of the nature of the lime is reflected by a change in the ASTM water reactivity test, as shown in Figure 7, using as an example the fine-grained stone. In view of this result, the preheating technique was abandoned.

EXPERIMENTAL PROCEDURE FOR LIME SOLUTION STUDIES

The furnace used initially in this study was a circular-shaped resistance furnace, employing four helix-type silicon-carbide heating elements. The furnace contained an impervious mullite tube that was sealed at the bottom, with provision for an argon gas inlet. The top was closed with a water-cooled brass head containing an outlet for the furnace atmosphere. The temperature was controlled by an Electromax off-on controller, which operated on a signal from a platinum-platinum-10% rhodium thermocouple inserted through the side of the furnace with the couple bead in contact with the reaction tube. The controller was connected through a relay to a 220-volt Variac, which was used to regulate the power input to the heating elements. The actual temperature inside the furnace tube was calibrated with another platinum/platinum-10% rhodium thermocouple.

The original proposal for carrying out the solution experiments involved the immersion of a rotating "carrot" of lime in a slag. Several months of experimenting with this method failed to produce a satisfactory means for holding the sample; failure occurred either at the point of gripping, or at the liquid slag surface. A schematic diagram of the equipment used initially

in this program is shown in Figure 8 and a photograph of the laboratory arrangement is presented in Figure 9.

The furnace described above proved to be inadequately insulated, so a new furnace was constructed in the form of a two-foot cube with the capability of reaching temperatures in excess of 1550°C. The same controller, power supply, and furnace tube were employed.

Other early experimentation was meanwhile conducted; a number of techniques were explored in an effort to obtain a suitable means for reacting the lime with the slag. Initially, a cylinder of lime or limestone was suspended in a slag and rotated with a variable-speed electric motor. This worked reasonably well for the limestone, but when the stone cylinder was calcined prior to immersion in the slag, the lime did not have adequate physical stability and inevitably fell from its suspension point and was lost in the slag. This technique was consequently abandoned in favor of a straightforward procedure not employing stirring. A synthetic slag prepared from premixed powdered reagent grade materials* was charged to an iron crucible as shown in Figure 8. The crucible was placed in the furnace after the reaction tube had been purged with argon to provide an inert atmosphere, and then approximately 30 minutes was allowed for the slag to melt down. A piece of lime, preheated by placing it on the lid of the crucible, was placed in the slag mixture and allowed to react for a given period of time. The crucible was then removed from the furnace and the slag was quenched in an argon blast. As suggested earlier, the preheating of the lime was shown to modify its "as-calcined" character, and since this could alter, as well, its solution rate in slags, the technique was modified.

* Pure powdered components were used, except in the case of FeO where Fe and Fe₃O₄ powders were stoichiometrically mixed.

The technique that was finally adopted employed high-alumina refractory crucibles (as used in a Leco Carbon Analyzer). The ceramic crucibles were charged with a prefused and crushed slag along with a short section of a lime cylinder. Approximately 3 minutes were required for the slag to fuse and initiate a reaction with the lime cylinder, after which the crucible was removed from the furnace and permitted to cool.

For microscopic examination and microprobe analysis, the samples were sectioned to provide a cross-section of the reacted lime cylinder and the adjoining solidified slag. These cross-sections were metallographically polished, and selected specimens of both types of limestone and of the employed slags were prepared for analysis with an electron-beam microprobe.

The slags employed are summarized in the key to Appendix A. The compositions included iron oxide-silica, iron oxide-lime, iron oxide-lime-silica, and iron oxide-lime-silica slags modified by the addition of manganese oxide. Several ratios of these components were used, as well as modifications with fluorspar additions. Two limestones were studied, a fine-grained and a coarse-grained stone, both nearly pure calcium carbonate with the solution experiments carried out in the temperature range 1400 - 1470°C. The test conditions for the experiments are also summarized in Appendix A.

RESULTS OF SOLUTION EXPERIMENTS

The samples were examined on a macro- and microscopic basis, and electron-probe analyses were carried out across the lime-slag interface on several specimens.

The photomicrographs shown in Figures 10 and 11 illustrate the types of samples which were obtained under various experimental conditions. In

Figure 10, a fine-grained lime was partially dissolved in a lime-silica-iron oxide-manganese oxide slag. This sample shows the lime-slag interface at the same position as at the start of the experiment, and is typical of a slag containing SiO_2 . In Figure 11, the effect of removing the silica from the slag is illustrated by a specimen that was reacted with a 47% CaO-53% FeO slag. Here the reaction was observed to be much more rapid, and there is no distinct boundary between the lime particle and the slag. Based on this observation, and on the microprobe results which are discussed below, it can be concluded that calcium silicate forms in the silica-bearing slags and the silica does not penetrate into the lime particle; the result is a distinct boundary at the original lime-slag interface.

Figures 12-14 permit a more detailed examination of the interface between the fine-grained lime samples and the slag. Figure 12 illustrates a phase boundary that mechanically separated during cooling, with a slag that contained 30% CaO - 30% SiO_2 - 40% FeO and includes regions of unreacted lime, reacted lime, a phase boundary between the lime particle and slag, and the slag. Figure 13 shows the lime-slag interface for a sample which was reacted with a slag containing 40% silica and 60% iron oxide. Although the slag reacted very rapidly with the lime, a distinct phase boundary exists between the slag and the lime. Figure 14 shows the boundary between the reacted and unreacted portion of a fine-grained sample immersed in an 80% FeO-20% SiO_2 slag. The bright area with at least two identifiable phases is the reacted lime zone. In the dark area adjacent to this, the iron content shows a gradient from its relatively constant concentration in the reacted lime zone to the, as yet, unreacted lime phase, which appears gray in the photomicrograph. On a microscopic basis, this sample shows that the iron, which appears as a bright phase, penetrates into the lime particle.

Microprobe analyses* were carried out at the Ford Scientific Laboratory to provide a measurement of the chemical composition of the lime-slag reaction zone. This technique is extremely powerful, and in fact might be said to be too powerful for the segregated and finely precipitated structure of the lime-slag reaction zone. However, despite the fact that the readings on a structure of this type tend to show large fluctuation, several conclusions can be drawn from the results of microprobe examinations on the samples prepared throughout the course of this study.

The microprobe results presented in Figures 15 to 18 must be considered to be qualitative with respect to the absolute levels of concentration, in view of the difficulties in standardizing the instrument and evaluating the interference factors unique to each sample. The results are presented as measured, and no attempt has been made to standardize the results to the initial slag charge analyses. In evaluating these concentration gradients across the lime-slag interface, the important aspect is where the concentration gradients exist and not the absolute concentration levels.

A photomicrograph of sample 1-MC is shown in Figure 12, and the microprobe analyses across the lime-slag interface are shown in Figure 15. The slag zone of the sample shows the content of calcium, iron, and silicon corresponding to the bulk slag analysis. As the microprobe trace for each element enters the zone between the slag and the lime, an increase in calcium concentration and a decrease in iron concentration is observed. There is an indication of an abrupt decrease in silicon content, with a precipitous

* The electron microprobe is an instrument which is able to focus a beam of electrons on a sample at a spot less than one micron in diameter. By measuring the intensity of fluorescent radiation of a given wave-length emitted from the surface of the sample, and standardizing these intensity measurements, one is able to determine the chemical composition of the material at that point. It is possible, then, in a linear distance of about one inch to make 25,000 individual measurements of chemical composition.

drop to nearly zero, which shows that the silica does not penetrate beyond the interfacial zone between the slag and the lime. Within the lime particle, the calcium content remains relatively constant, and the iron content levels out until near the end of the reacted zone, where it decreases to zero. This relatively constant iron content within the reacted zone of the lime particle may indicate that iron diffuses into the lime particle as a second phase, possibly calcium ferrite. The particularly interesting aspect of this analysis, as observed in previous metallographic examinations, is that the silica does not penetrate the lime particle.

Figure 16 shows a microprobe analysis for iron, silicon, and calcium on sample 12-MA, a sample reacted with a 40% silica-60% FeO slag. The photomicrograph of this sample is shown in Figure 13. Again, the calcium increases and iron decreases as one moves into the lime particle. The silicon shows a very slight penetration of the sample but markedly drops to zero near the interface, indicating that silicon does not penetrate the lime particle. Again, the iron analysis levels off to a constant value, indicating that a specific compound is forming within the lime. In Figure 17, lime prepared from a coarse-grained limestone was reacted with a 40% silica-60% FeO slag. Similar concentration profiles were obtained.

In slags containing manganese oxide, the manganese showed approximately the same penetration as did the iron. This is shown in Figure 18, where the concentration profiles are shown for sample 1-HD, which was calcined from the coarse-grained stone and reacted with a 27% CaO-27% SiO₂-36% FeO-10% MnO slag at 1450°C for 4 minutes. Thus, manganese oxide in the slag at moderately low concentrations behaves in a manner similar to iron oxide.

In the samples reacted with CaO-FeO slags, a considerable amount of scatter was observed, undoubtedly caused by the precipitation of fine ferrite particles observed in these specimens. The absence of silica in these experiments had a pronounced effect on the solution of the lime in that no distinct phase boundary existed between the slag and the lime.

The addition of 5 weight percent fluorspar (CaF_2) to the 30% CaO-30% SiO_2 -40% FeO slag markedly increased the rate of solution (see Appendix A, Experiments 26-28). The presence of a solid phase in the slag was observed at this temperature with the addition of spar. The phase was not fully identified, although chemical analyses indicated that it was slightly higher in iron oxide content than the bulk liquid slag.

In comparing the coarse-grained and fine-grained limestones for reactivity with the slag, the results are quite similar. Visual observations of samples prepared from each type of stone at comparable reaction times and temperatures and with the same slags did not indicate any appreciable difference in the extent of reaction, or the change in diameter of the sample.

The mechanism of solution is related to the diffusion of iron into the lime and of calcium from the lime into the slag. A model for this process was originally proposed² and is shown schematically in Figure 19. The solid particle in Figure 19 is the lime, and extending out into the bulk liquid slag is a concentration gradient for calcium or calcium oxide. Corresponding to the calcium oxide gradient are concentration gradients from the bulk liquid slag toward the solid lime particle for iron oxide and silica. Since the slag contains a lower calcium oxide content than the solid particle, the concentration

2. "Some Considerations on the Kinetics of Lime Solution in Basic Oxidizing Slags," presented at the AIME National Open Hearth and Basic Oxygen Steel Conference, Pittsburgh, April, 1964, AIME Open Hearth Proceedings, 1964, Vol. 47, p. 77.

of calcium decreases to the right in Figure 19, whereas the slag, which is higher in silica and iron oxide than the lime particle, would show analyses for silicon and iron, which decrease toward the left. Microscopic examination of the samples showed general agreement with this mechanism. The microprobe analyses showed agreement with this model with the exception that the silica did not penetrate the lime.

In examining the samples microscopically, the process of dissolving the lime appeared as a penetration of iron oxide throughout the sample, and then a disintegration into much smaller particles, possibly along grain boundaries, although no specific proof of this result was obtained, and the solution times for the coarse- and fine-grained stones were observed to be essentially the same. The effect of temperature was studied for the fine-grained stone in the 30% CaO-30% SiO₂-40% FeO slag, as shown in Appendix A, for Experiments 1-14 carried out at 1400°C and Experiments 18-30 carried out at 1450°C. In the initial stage of the reaction, the samples reacted at 1400°C did not become fully penetrated by the iron until the reaction time had reached 2.75 minutes, whereas this stage of the process was achieved within 1.25 minutes at 1450°C. An activation energy for this process can be estimated from this result but appears to be quite low when compared with the activation energy one would expect for a diffusion process in these systems.

DISCUSSION

The experiments in this study were carried out at temperatures on the order of 100 to 150°C below normal steelmaking temperatures. The phenomena observed cannot be related quantitatively to the reactions occurring in the steelmaking vessel, but the mechanism and nature of the attack of a lime

particle by liquid slag observed experimentally should be maintained at higher temperatures, although the diffusion processes would be much faster. Difficulties in attempting to interpret the behavior of lime in a steelmaking operation in the light of these experimental results include the problems of preheating time of the lime, usually charged cold into the steelmaking vessel, and the indeterminate stirring and physical actions occurring in the steel-making vessel.

It should be noted, however, due to the fact that the rate-limiting process has been shown to be a diffusion process, that the particle size of the lime is significant and, correspondingly, its physical structure is important. In other words, a lime that will break up under strong thermal gradients would be expected to expose a larger surface area to the slag and hence result in a more rapid dissolution in the steelmaking operation. Additional basic work should be carried out on these systems at higher temperatures, and the study of the concentration gradients as obtained might gainfully be utilized in evaluating diffusion coefficients in these systems.

CONCLUSIONS

As a result of this investigation, some general conclusions can be drawn in regard to the solution of lime in basic oxidizing slags:

1. The solution of lime in basic oxidizing slags is controlled by diffusion of iron into the lime particle, and, to some extent, by the diffusion of calcium out of the lime particle. In slags without lime as a constituent (specifically FeO-SiO₂ slags) the lime dissolves more rapidly than in a slag containing lime with a similar iron-to-silicon ratio.

2. The rate of solution increases with increasing temperature.
3. The silica does not diffuse into the lime particle, and its presence appears to retard the solution process. Silica-free slags form no definite interface between the lime particle and the slag, whereas slags containing silica show a distinct interface.
4. Manganese in the form of small amounts of MnO in the slag does not appear to influence markedly the solution of lime in the slags investigated. Manganese is similar to iron in diffusing into the lime particle.
5. Fluorspar increases the rate of solution of lime in slag when present in amounts up to 5%.
6. No significant differences in the rates of solution of lime prepared from fine-grained and coarse-grained limestones were observed.

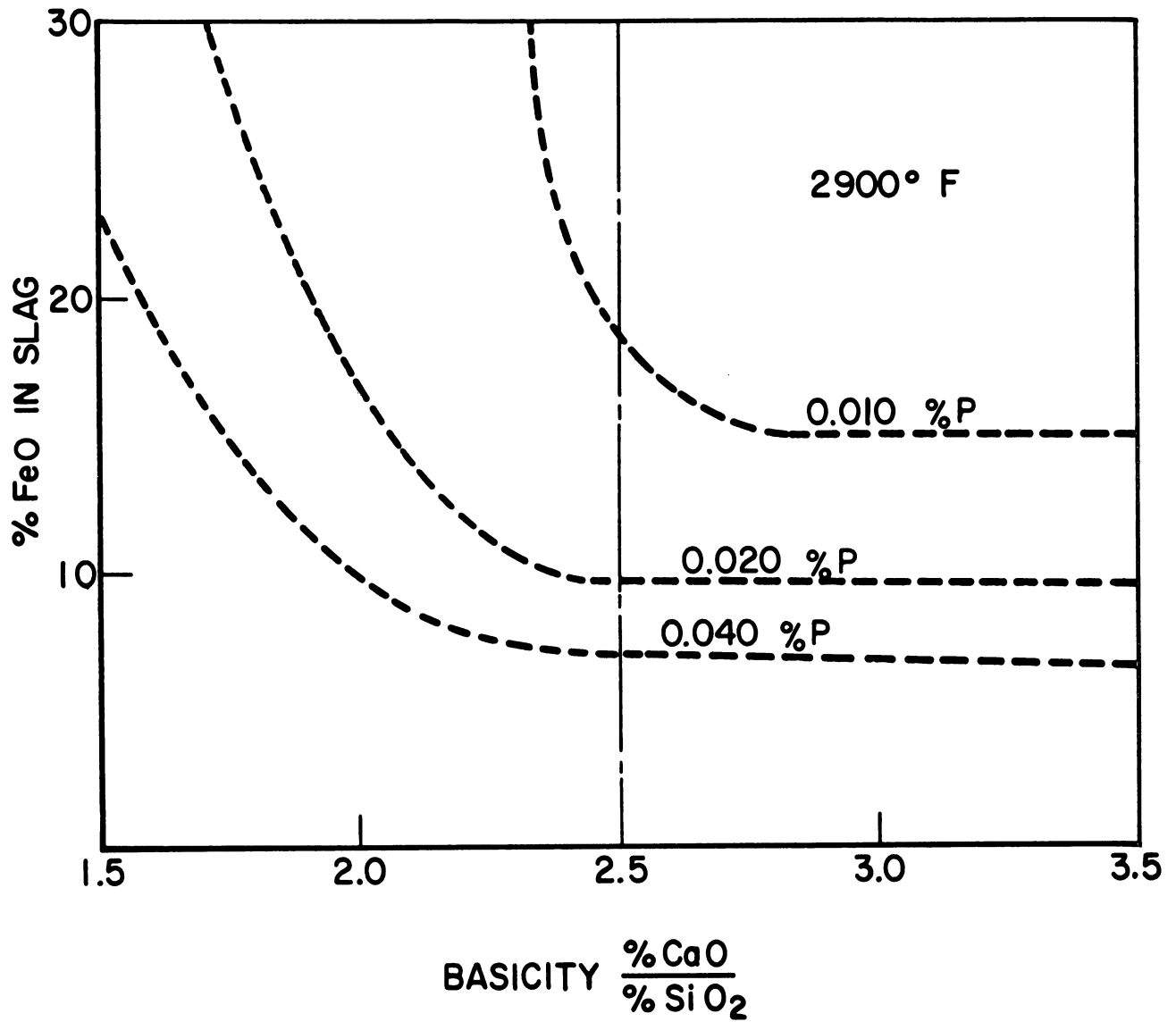


Figure 1: Residual Phosphorus in Steel as Influenced by Slag Basicity and Iron Oxide

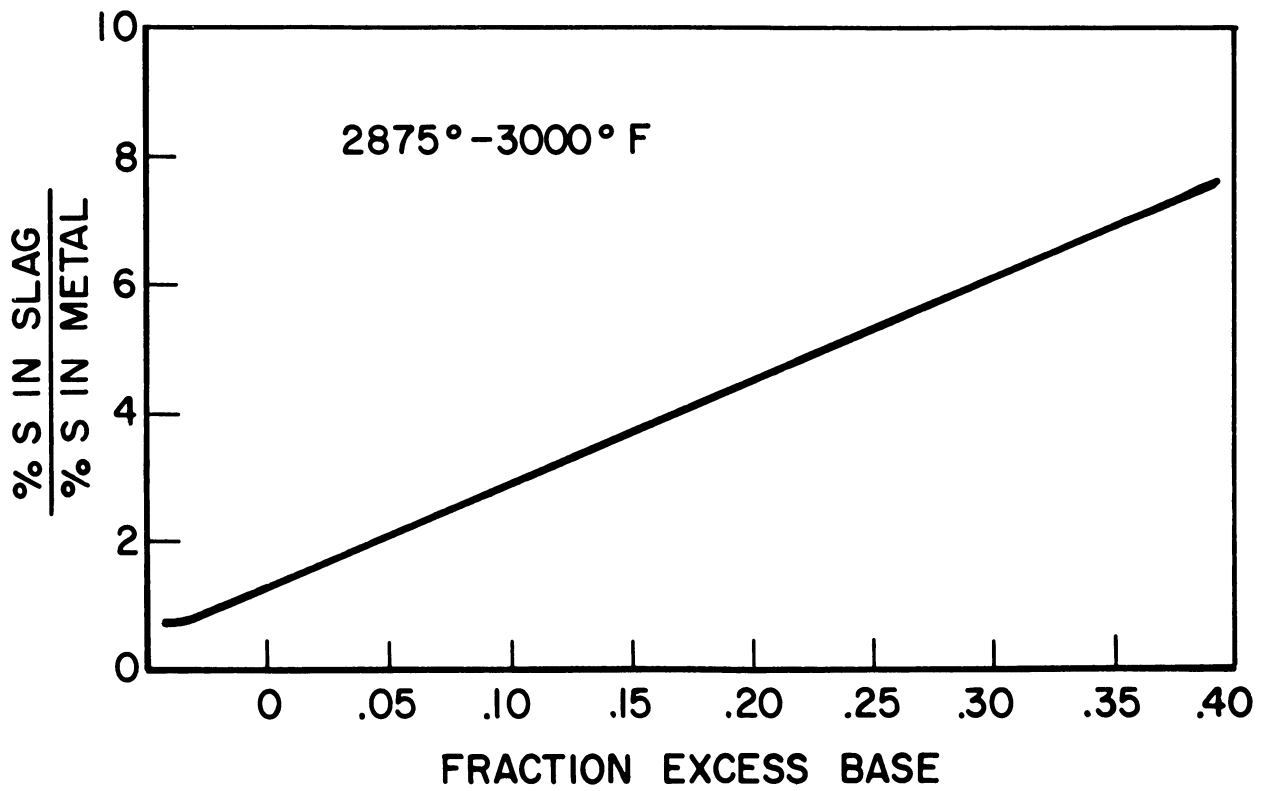


Figure 2: Influence of Available Base on Sulfur Distribution Between Slag and Metal

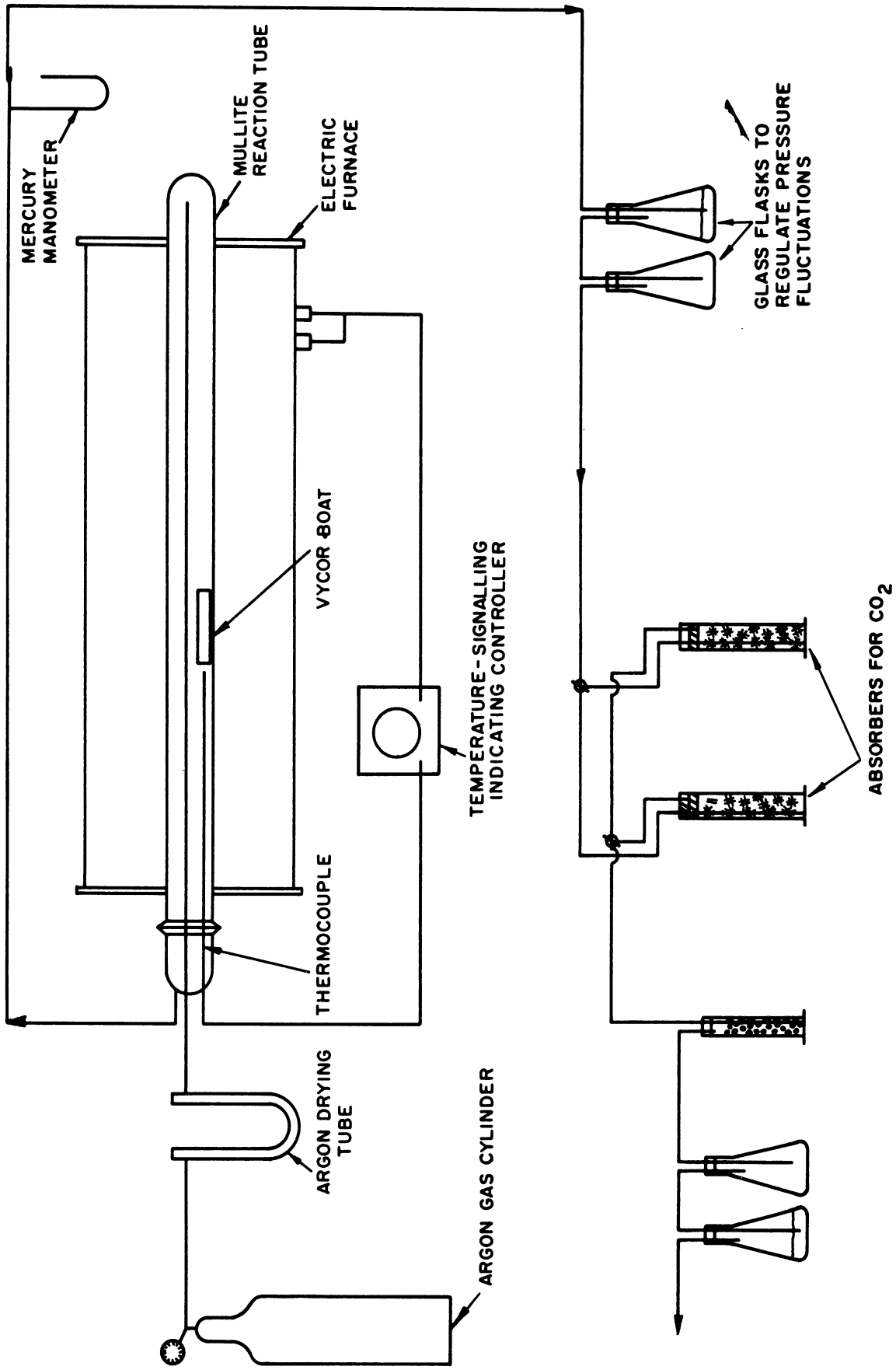


Figure 3: Laboratory System for Calcination Studies

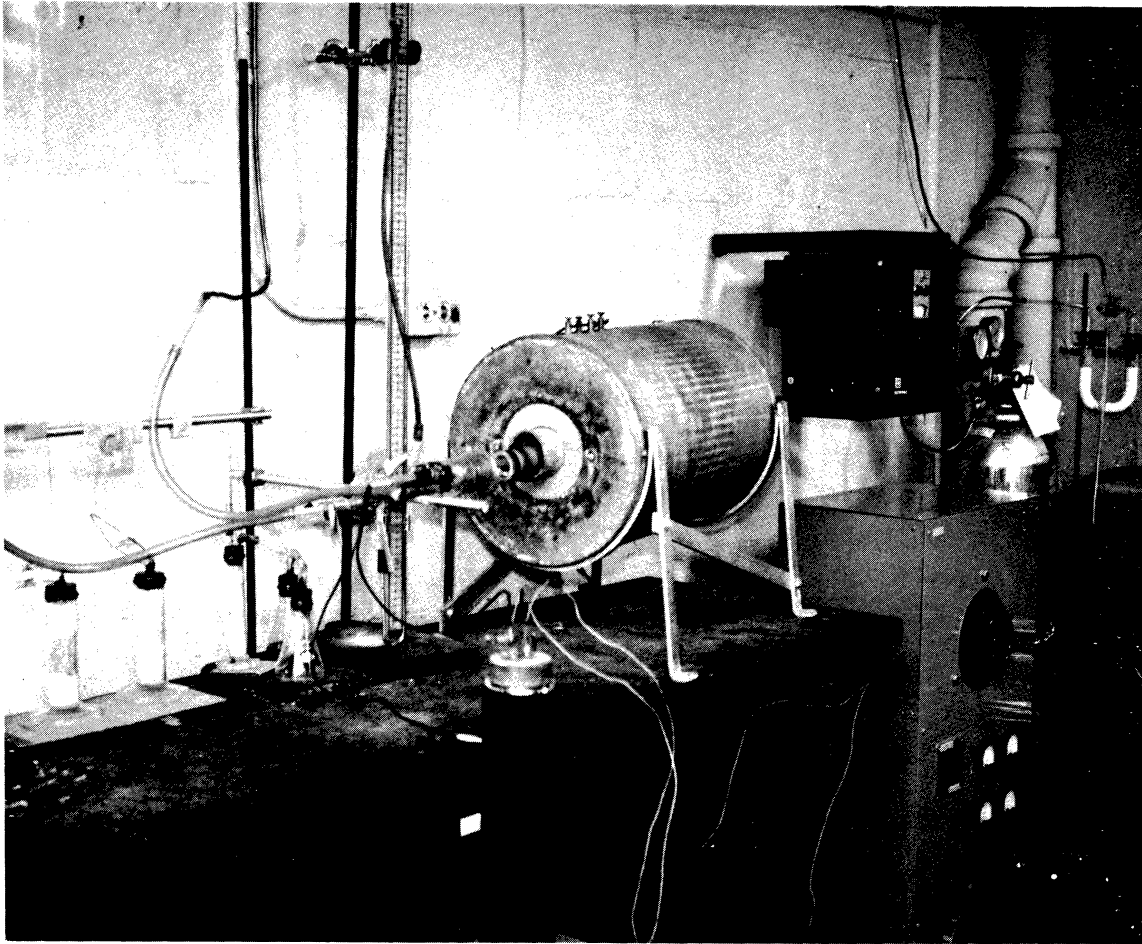
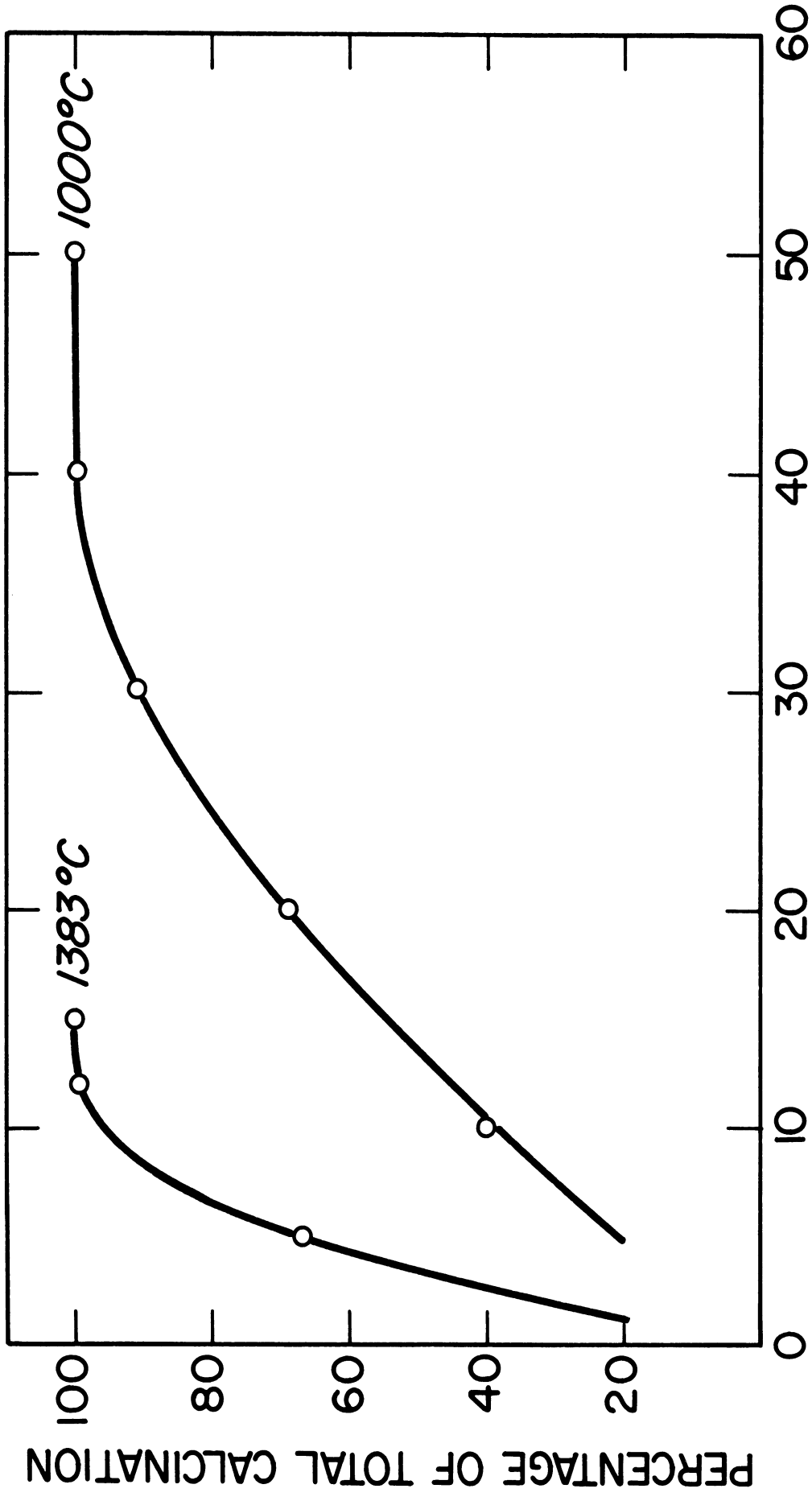


Figure 4: Photograph of Laboratory Arrangement for Calcination Studies



CALCINATION TIME, Min.

Figure 5: Calcination Behavior of Fine-Grained Limestone at Temperatures of 1000 and 1383°C

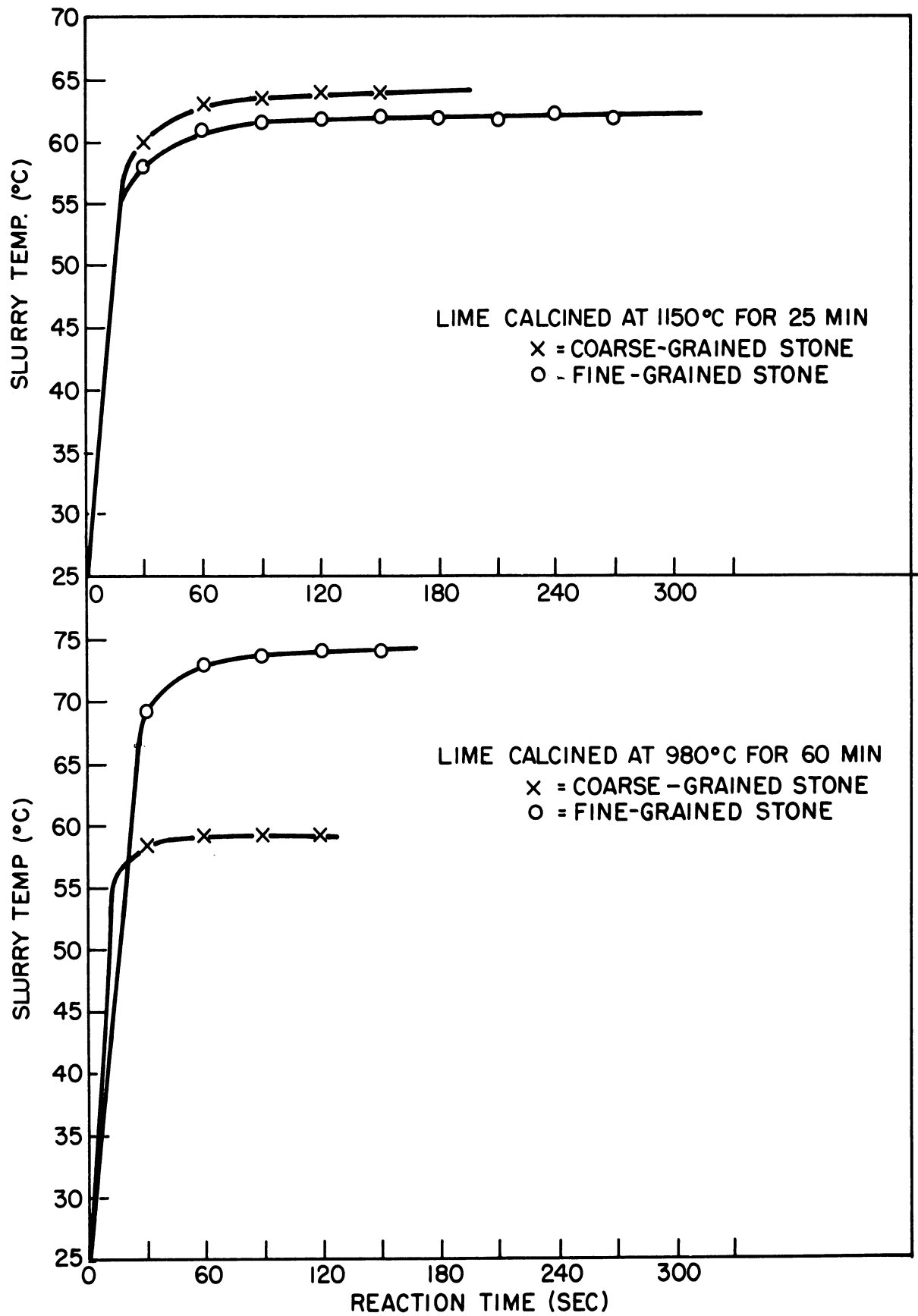


Figure 6: Influence of Calcination Temperature on Water Reactivity of Coarse- and Fine-Grained Limestones

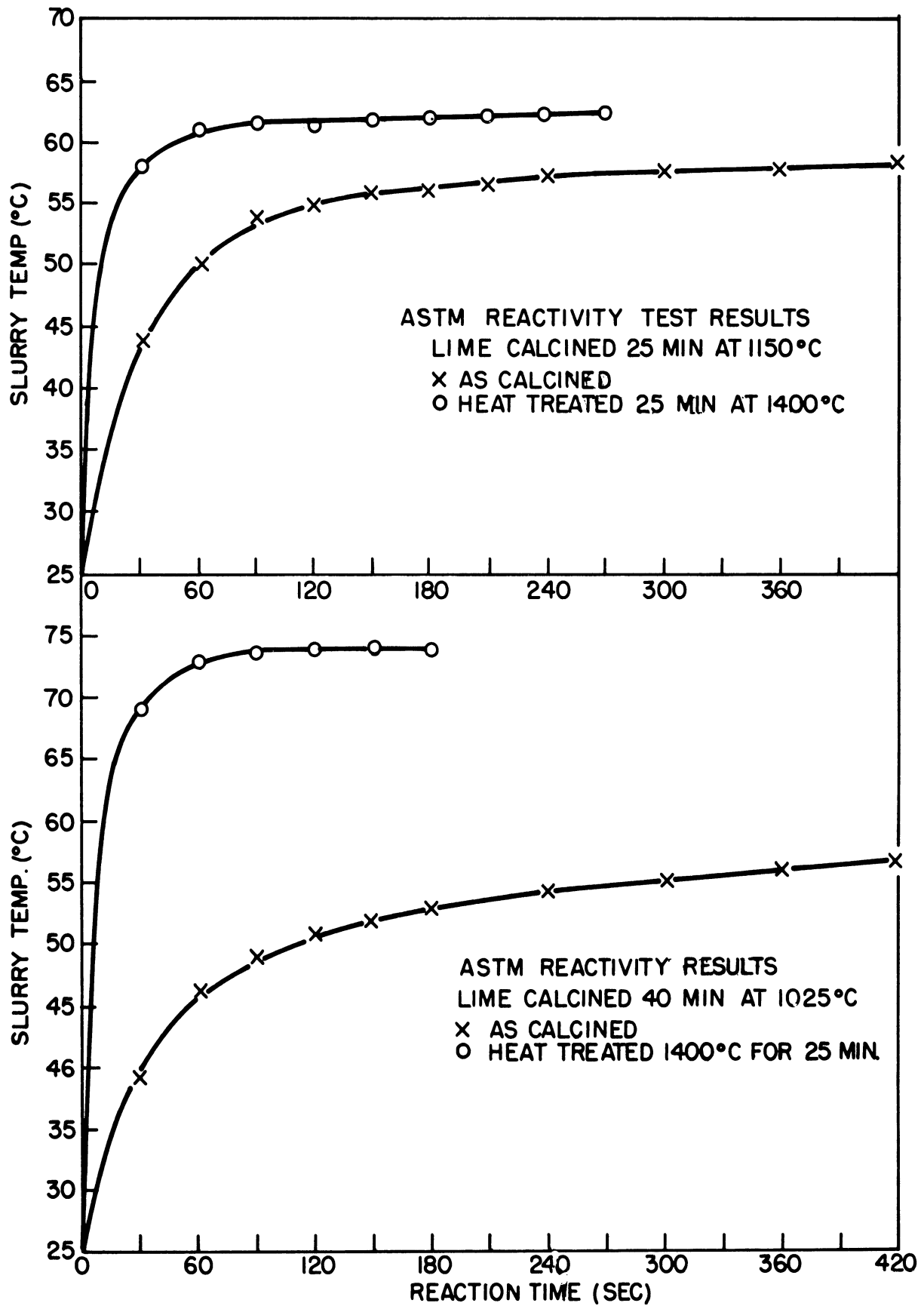


Figure 7: Influence of Preheating at 1400°C for 25 Minutes on Water Reactivity of Lime from Fine-Grained Stone

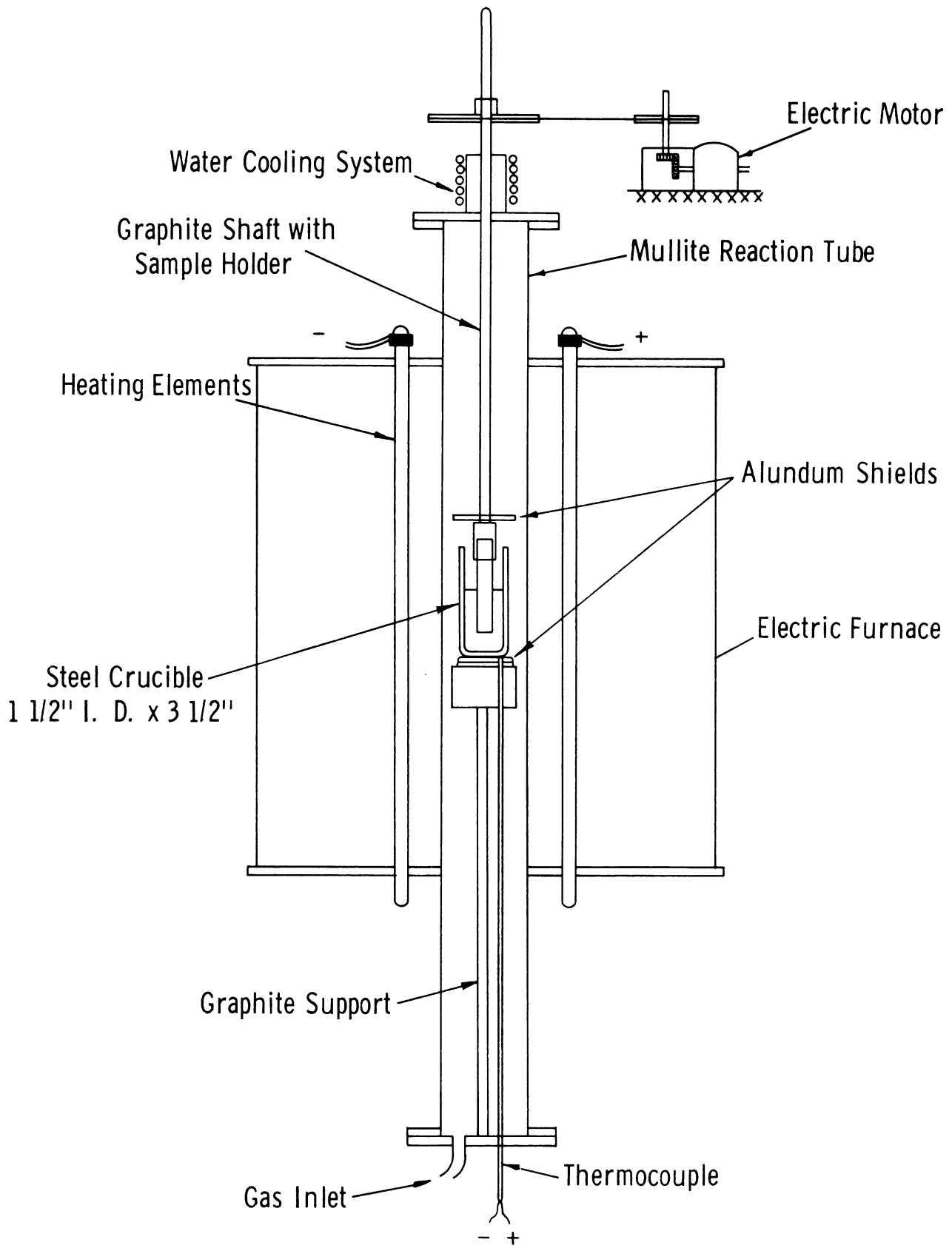


Figure 8: Laboratory System for Dissolution Studies

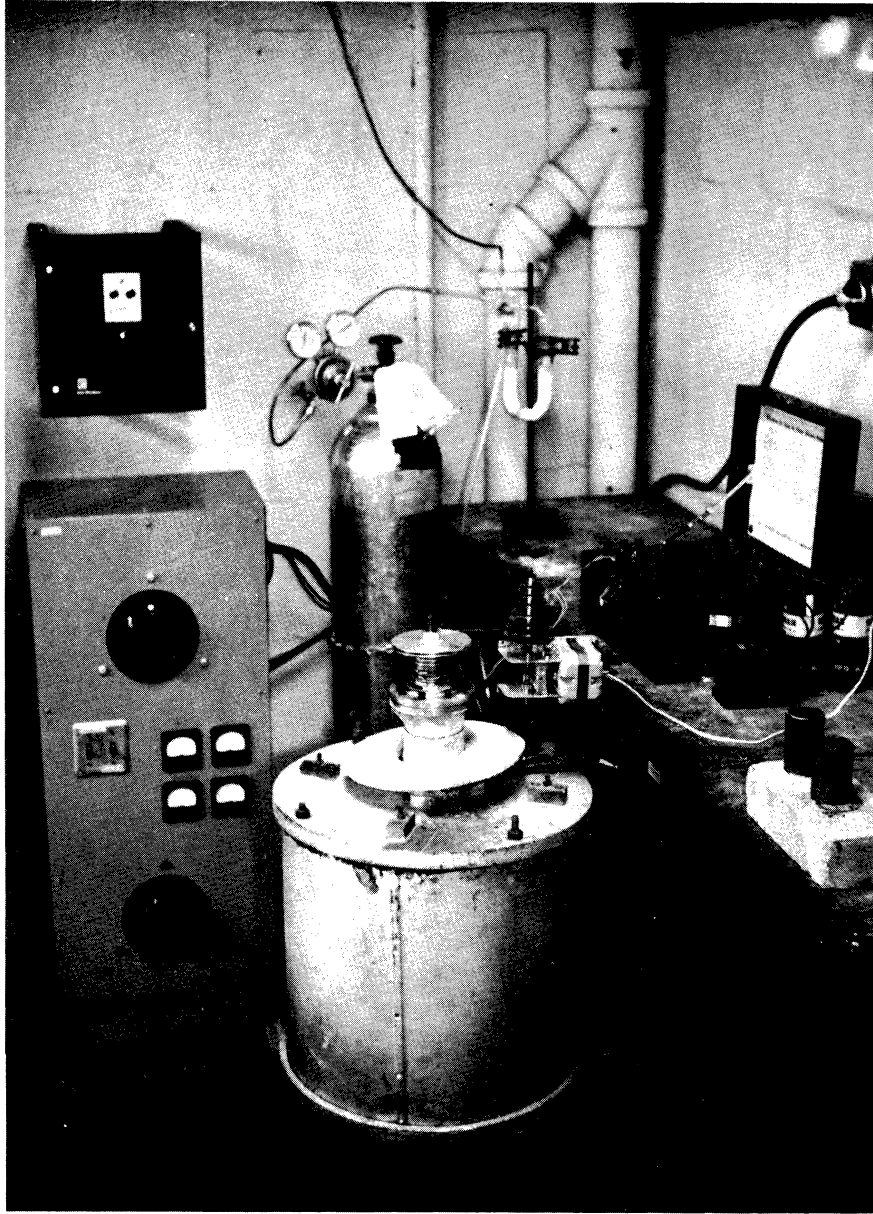


Figure 9: Photograph of Laboratory Arrangement for Dissolution Studies

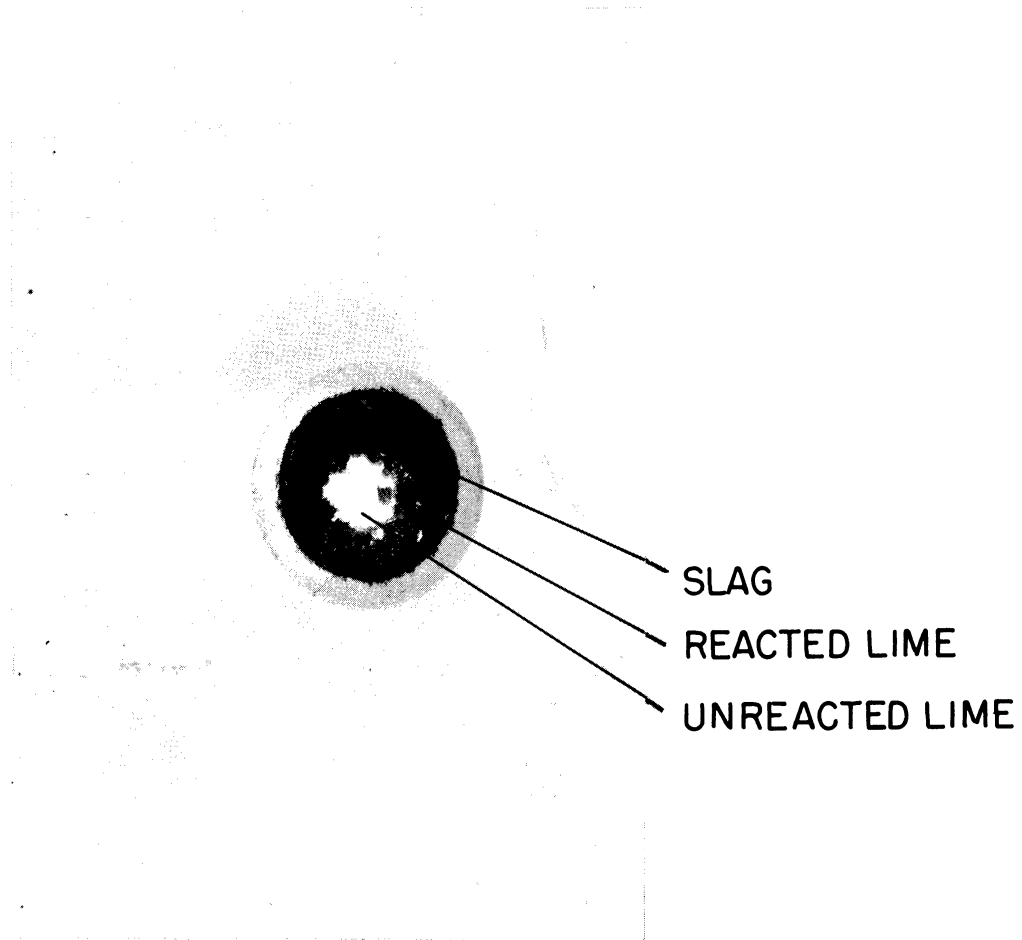


Figure 10: Cross Section of Sample 2-MD after Reaction with $27\text{CaO}-27\text{SiO}_2-$
 $36\text{FeO}-10\text{MnO}$ Slag at 1450°C (Actual Size)

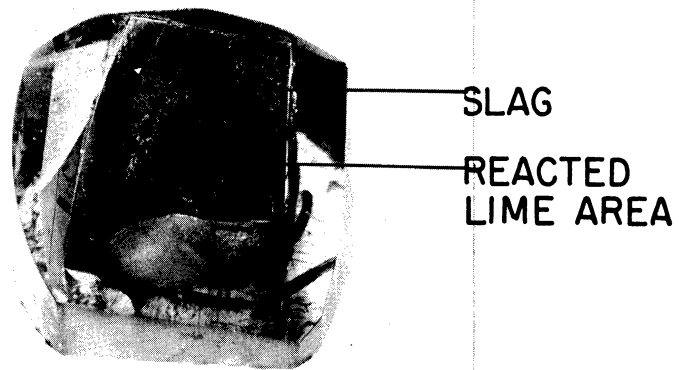


Figure 11: Cross Section of Sample 2-MB after Reaction with ^{47}CaO - ^{53}FeO Slag at 1400°C (Actual Size)



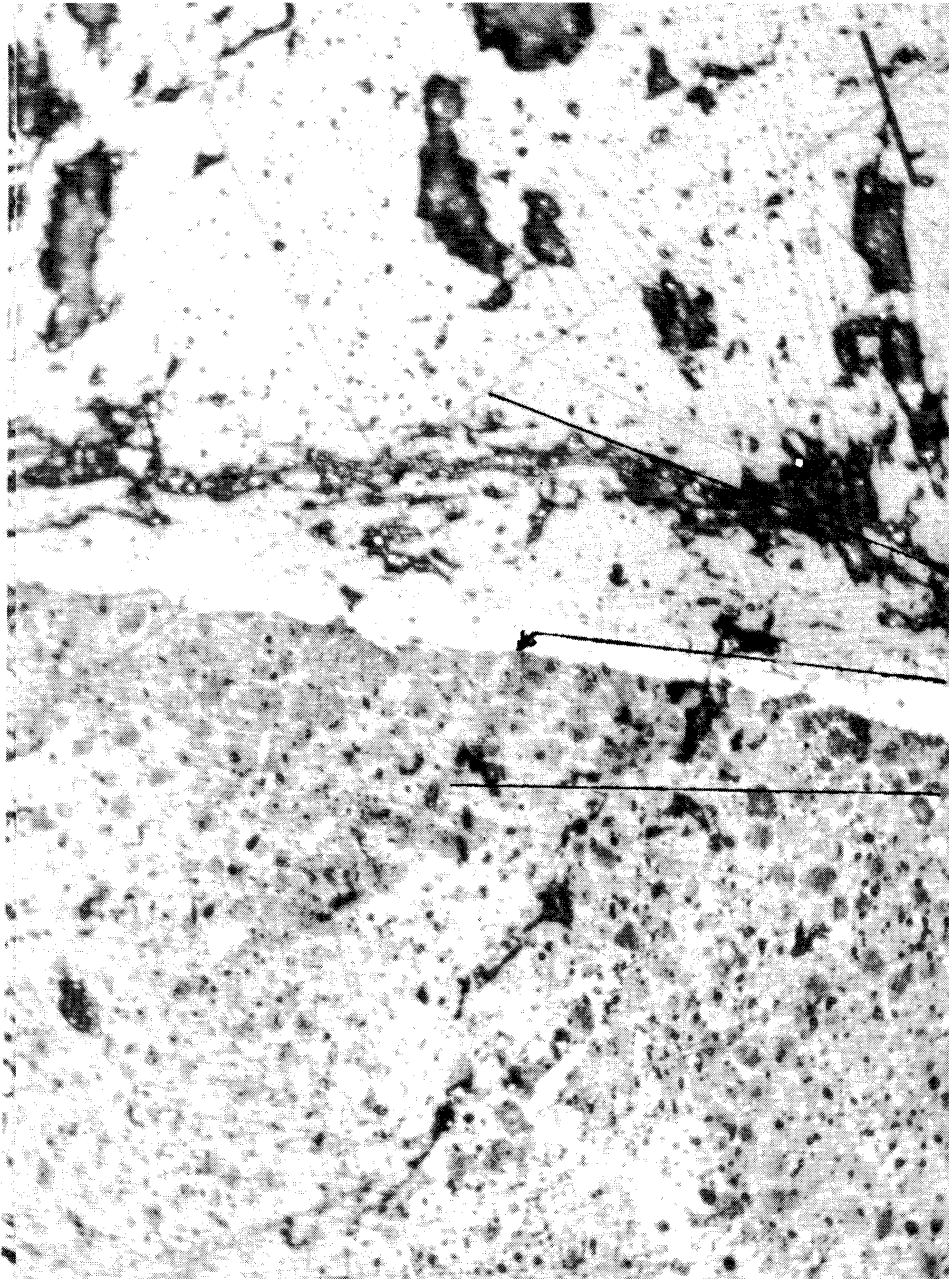
SLAG

PHASE BOUNDARY

REACTED LIME

UNREACTED LIME

Figure 12: Photomicrograph at 50X of Lime Sample from Fine-Grained Stone Reacted with $30\text{CaO}-30\text{SiO}_2-40\text{FeO}$ Slag at 1400°C
(Enlarged 2 times for reproduction)



SLAG
PHASE BOUNDARY
REACTED LIME

Figure 13: Photomicrograph at 150X of Lime Sample from Fine-Grained Stone Reacted with $40\text{SiO}_2-60\text{FeO}$ Slag at 1470°C (Enlarged 2 times for reproduction)



REACTED LIME
REACTION ZONE
UNREACTED LIME

Figure 14: Photomicrograph at 50X of Lime Sample from Fine-Grained Stone Reacted with 20SiO_2 - 80FeO Slag at 1470°C (Enlarged 2 times for reproduction)

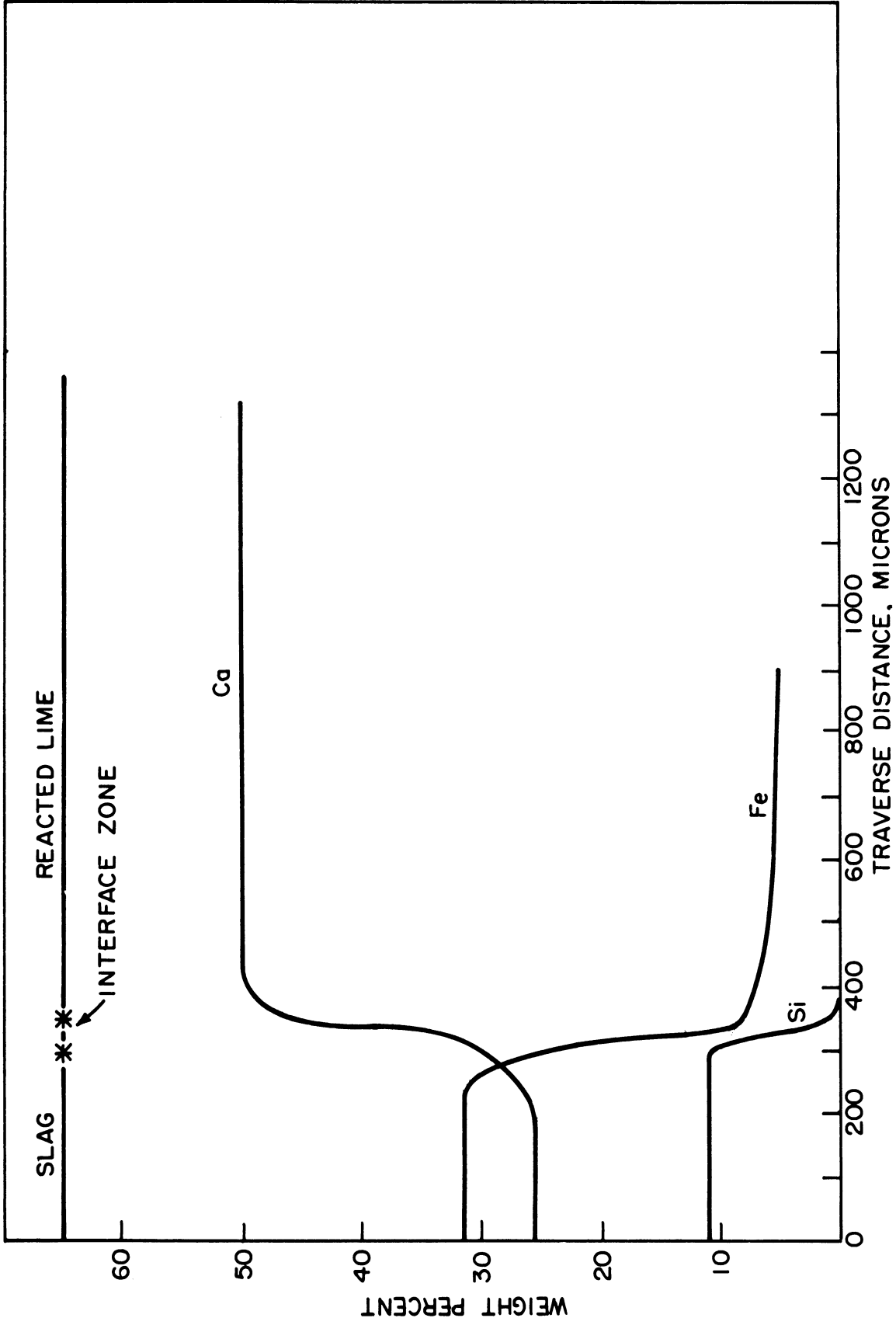


Figure 15: Microprobe Analysis of Sample Shown in Figure 12

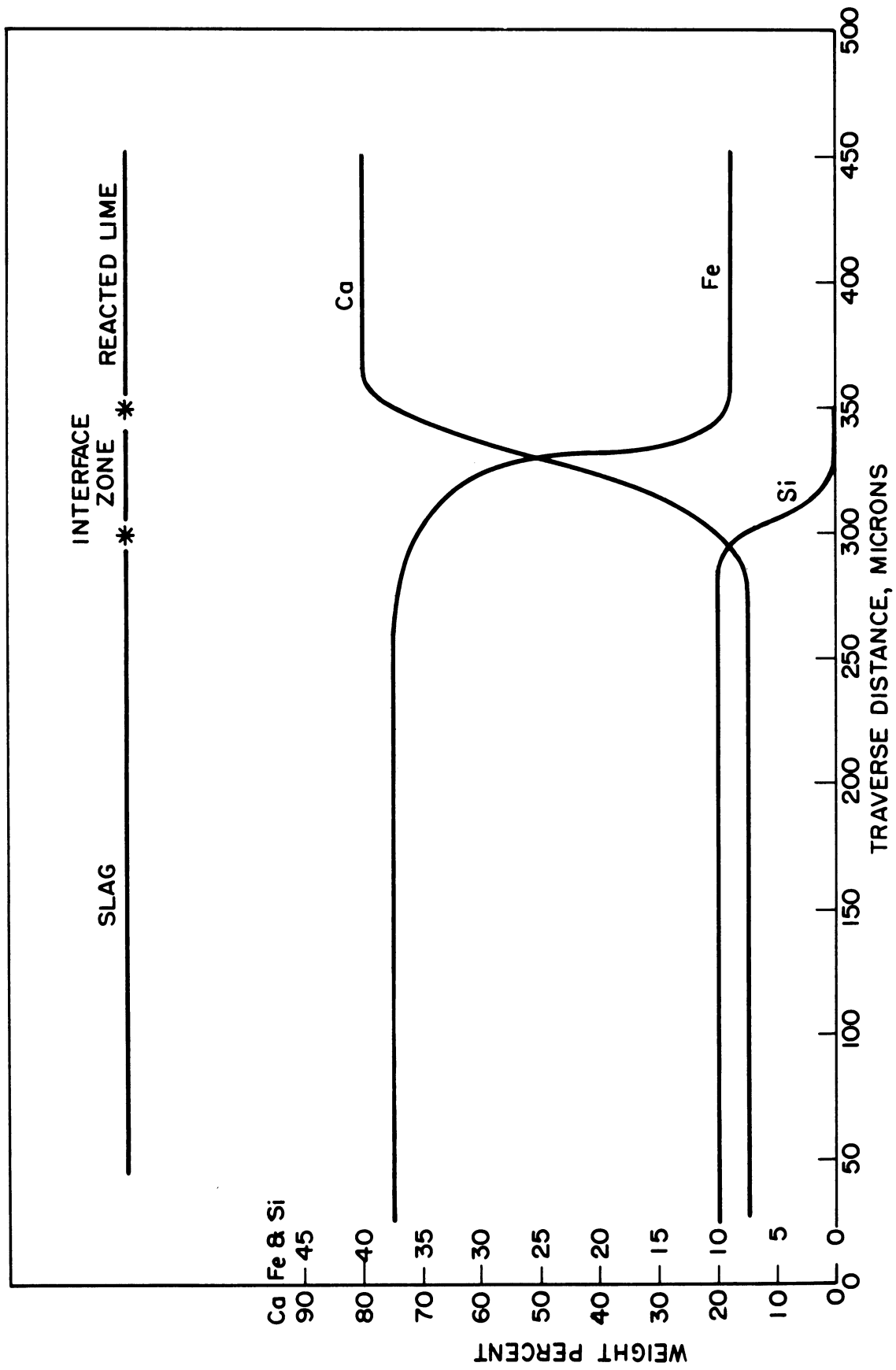


Figure 16: Microprobe Analysis of Sample Shown in Figure 13

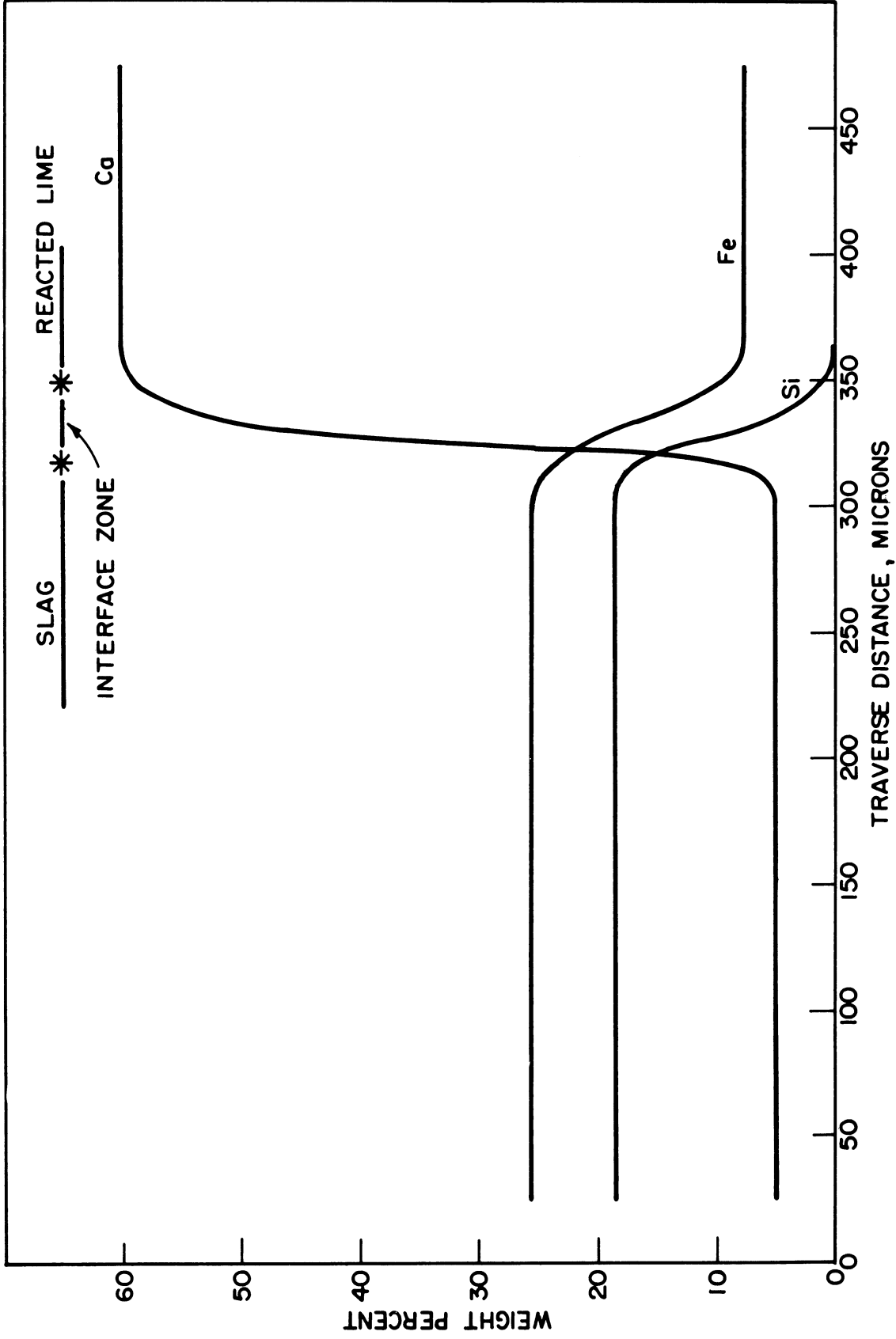


Figure 17: Microprobe Analysis of Lime Sample from Coarse-Grained Stone Reacted with $4\text{OSiO}_2\text{-60FeO}$ Slag at 1450°C

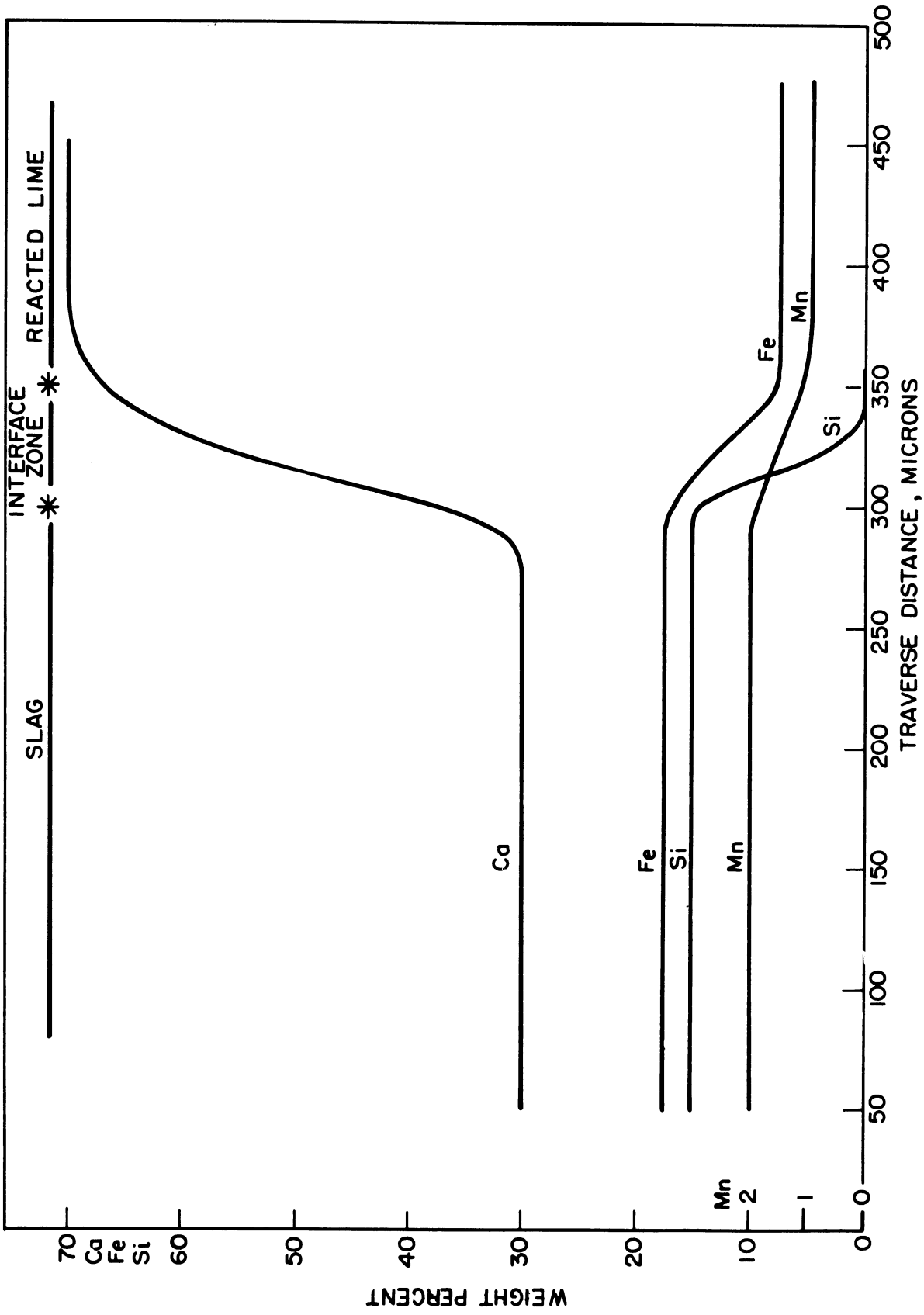


Figure 18: Microprobe Analysis of Lime Sample from Coarse-Grained Stone Reacted with 27CaO-27SiO₂-36FeO-10MnO Slag at 1450°C

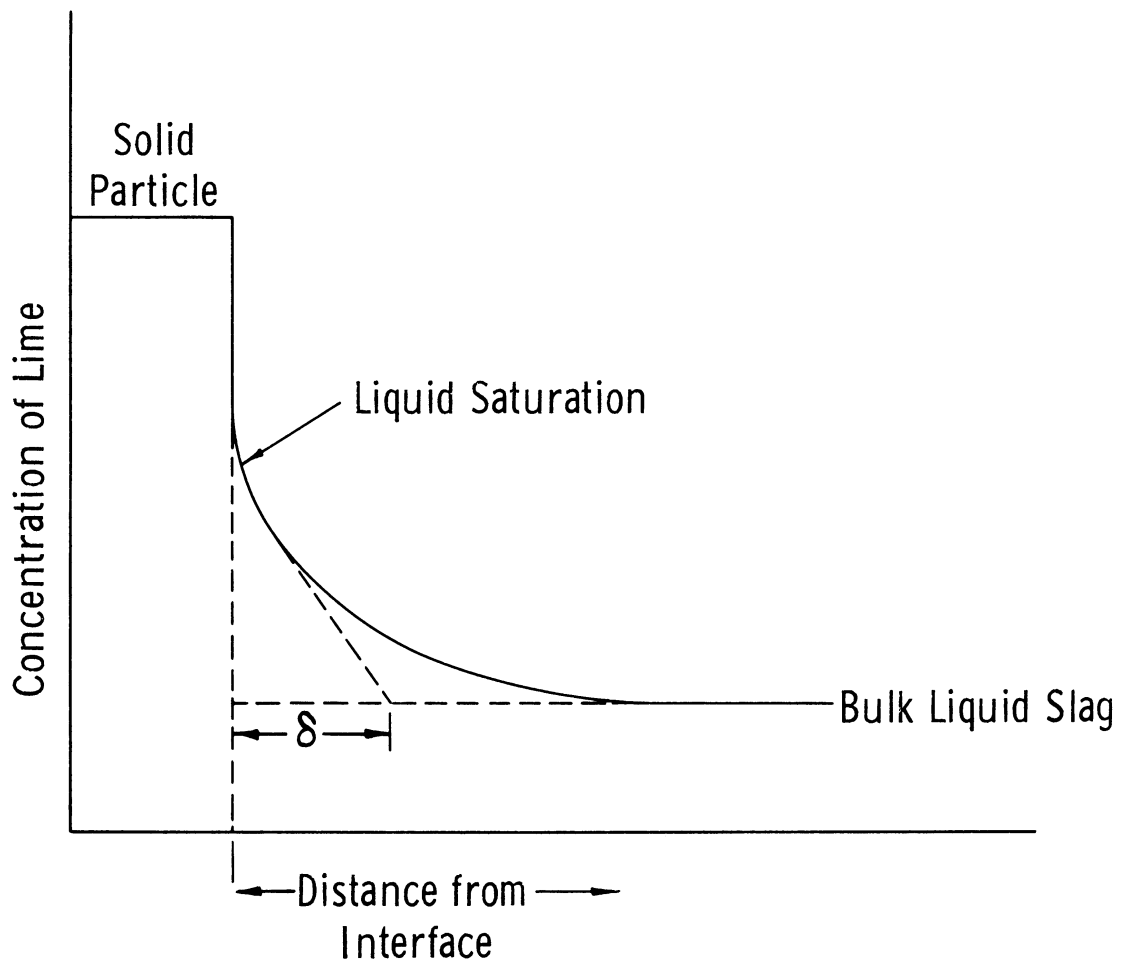


Figure 19: Schematic Diagram of Concentration Profile in Diffusion Controlled Solution Process

Appendix A
Summary of Experiments

Key

H - Coarse-grained Limestone

M - Fine-grained Limestone

Nominal Slag Compositions

Slag A: 40% SiO₂
60% FeO

Slag C: 40% FeO
30% CaO
30% SiO₂

Slag B: 47% CaO
53% FeO

Slag D: 36% FeO
27% CaO
27% SiO₂
10% MnO

Note: All lime was calcined
30 min. at 1050°C
(except where noted)

Experiment Number	Sample Designation	Reaction Temp. °C	Slag	Limestone	Reaction Time, Min:Sec	Remarks
1	1-MC	1400	C	M	1:30	Slag reacted with 20% of lime cross section
2	2-MC	1400	C	M	3:00	
3	3-MC	1400	C	M		
4	4-MC	1400	C	M	2:00	Slag reacted with 80% of lime cross section
5	5-MC	1400	C	M	2:30	Slag penetrated, fragmented, and dissolved 90% of lime
6	6-MC	1400	C	M	2:45	Slag reaction fully penetrated cross section of lime sample
7	7-MC	1400	C	M	4:30	Same as 6
8	8-MC	1400	C	M		Same as 6
9	9-MC	1400	C	M		Same as 6
10	10-MC	1400	C	M		Same as 6
11	11-MC	1400	C	M	6:00	Same as 6
12	12-MC	1400	C	M	8:30	Lime fragmented into a greater number of smaller pieces
13	13-MC	1400	C	M	12:00	Same as 12; also 10% diameter decrease

14	14-MC	1400	C	M		
15	1-MB	1400	B	M	4:30	Slight, but irregular slag penetration
16	2-MB	1400	B	M	1:00	Same as 15
17	3-MB	1400	B	M	8:00	Slag fully penetrated the lime cross section
18	15-MC	1450	C	M	1:15	Same as 17
19	16-MC	1450	C	M	2:00	Slag fully penetrated the lime cross section with lime starting to fragment
20	17-MC	1450	C	M	2:45	Same as 19
21	18-MC	1450	C	M		Same as 19
22	19-MC	1450	C	M	4:30	Same as 19
23	20-MC	1450	C	M	6:09	Greater fragmentation of lime, but sample diameter unchanged
24	21-MC	1450	C	M	10:00	Lime sample diameter 10% smaller
25	22-MC	1450	C	M	12:30	Very irregular cross section; much fragmentation
26	23-MC	1450	C+5%CaF ₂	M	6:00	Second phase appears to be present in liquid phase. Lime all dissolved.
27	24-MC	1450	C+5%CaF ₂	M	1:00	Cross section completely penetrated by slag. CaF ₂ greatly increases slag reaction and penetration

28	25-MC	1450	C+5%CaF ₂	M	2:00	Same as 27
29	26-MC	1450	C	M(calcained at 1100°C for 30 min.)	1:00	
30	27-MC	1450	C	"	2:00	
31	1-MA	1470	10%SiO ₂ 90%FeO ₂	M	2:00	Rapid slag reaction; complete dissolution of lime.
32	2-MA	1470	"	M		Lime broke before immersion, no sample
33	3-MA	1470	"	M		
34	4-MA	1470	"	M	1:00	Complete lime dissolution
35	5-MA	1470	"	M	0:10	Same as 34
36	6-MA	1470	"	M	0:15	Same as 34
37	7-MA	1470	"	M	0:10	Same as 34
38	8-MA	1470	30%SiO ₂ 70%FeO ₂	M	0:12	15% of lime cross section remains unreacted
39	9-MA	1470	"	M	1:30	Complete lime dissolution by slag
40	10-MA	1470	20%SiO ₂ 80%FeO ₂	M	1:00	Same as 39
41	11-MA	1470	"	M	1:15	
42	12-MA	1470	40%SiO ₂ 60%FeO ₂	M	0:07	Reaction slower in the higher SiO ₂ slags
43	1-MD	1450	D	M	3:00	Slag only slightly sintered

2-MD	1450	D	M	5:00	Slag completely melted
3-MD	1450	D	M	7:00	Dissolution of 50% of lime cross section
4-MD	1450	D	M	8:00	Slag reaction complete
5-MD	1450	D	M	11:00	Same as 4-MD
6-MD	1450	D	M	13:00	Same as 4-MD
7-MD	1450	D	M	15:00	Same as 4-MD
1-HC	1450	C	H	3:00	Slag completely sintered
2-HC	1450	C	H	5:00	Lime reaction initiated; slag molten
3-HC	1450	C	H	7:00	Same as 2-HC
4-HC	1450	C	H	9:00	Complete penetration and dissolution of lime by slag
5-HC	1450	C	H	11:00	Same as 4-HC
6-HC	1450	C	H	13:00	Same as 4-HC
7-HC	1450	C	H	15:00	Same as 4-HC
8-HC	1450	C	H	4:00	Same as 4-HC
1-AH	1450	A	H	2:00	Slag completely melted
2-AH	1450	A	H	3:00	Slag penetration begun
3-AH	1450	A	H	4:00	Complete slag penetration
4-AH	1450	A	H	5:00	Same as 3-AH
5-AH	1450	A	H	10:00	Same as 3-AH

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6-AH	1450	A	H	7:00	Same as 3-AH
7-AH	1450	A	H	6:00	Same as 3-AH
1-HD	1450	D	H	4:00	Slag reaction 60% complete
2-HD	1450	D	H	7:00	Slag reaction 100% complete
3-HD	1450	D	H	10:00	Same as 2-HD
4-HD	1450	D	H	15:00	Same as 2-HD
5-HD	1450	D	H	8:30	Same as 2-HD

