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DISSOLUTION OF LIME IN BASIC OXIDIZING SLAGS

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Abstract

This report summarizes progress on the National Lime Association research project, "Dissolution of Lime in Basic Oxidizing Slags," being carried out at the University of Michigan. The report covers the period July 1, 1964 - June 30, 1965.

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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 per 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 June 1963. The purpose of this program is 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 during the past year, a brief discussion of the behavior of lime as a fluxing agent in oxygen steelmaking is given in the following paragraphs.

Used in steelmaking operations is the relatively impure product of the blast furnace, pig iron, which contains silicon and manganese in concentrations on the order of 1% and carbon on the order of 4%, as well as some phosphorus and sulfur which vary depending upon the blast furnace practice but may range 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 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 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. A basic slag is quite important in the control of sulfur and phosphorus. The removal of these elements is strongly dependent upon the nature 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 increasing the iron oxide content of the slag tend to promote good dephosphorization. From the standpoint of efficiency in the steelmaking process and protection of the lining, 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. Consequently, a basic slag favors desulfurization.

BASIC OXYGEN STEELMAKING PROCESS

During the past ten years the steel industry throughout the world 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 almost fifty million ingot tons per year. This process is carried out in a refractory lined converter into which gaseous oxygen is jetted such that it penetrates into the pig iron bath and oxidizes the impurities, carbon, silicon, and manganese from the metal. To promote fusion of a slag which 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. Addition of burnt lime, in providing a basic slag, assists in the removal of phosphorus and sulfur from the metal phase as described above. 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. Burned dolomite is often substituted in part for the high calcium lime, and in addition, other fluxing agents which promote the generation of an early fluid slag, such as iron oxide or fluorspar, are often added to the 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 amount of oxygen required to carry out the steelmaking operation is on the order of one cubic foot per pound of steel. At the flow rates encountered in practice, blowing times for a heat are usually less than 30 minutes. The production of steels with relatively low phosphorus and sulfur specifications can be successfully accomplished in the basic oxygen process provided the slag practice is satisfactory. With a relatively short blowing time, 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.

Burnt lime is used almost exclusively today as the primary slag-making material in the basic oxygen process. The demand for shorter heat time 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 formed by oxidation of silicon, manganese, and iron from the molten metal bath in the top-blown oxygen vessel. The demand for rapid lime solution and the availability of several types of lime have resulted in questions regarding the factors influencing the rate of lime solution in basic oxidizing slags.

The mechanism by which lime dissolves in oxidizing slags which are developed in this steelmaking process 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 has led to the NLA supported research program at the University of Michigan.

RESEARCH PROGRAM ON LIME SOLUTION IN BASIC OXIDIZING SLAGS

A project on the kinetics of lime solution in basic oxidizing slags was initiated in the Department of Chemical and Metallurgical Engineering at the University of Michigan in July 1963 by the National Lime Association.

The proposed research is directed toward evaluating the mechanism which controls the rate of lime solution in basic oxidizing slags. This rate of solution is probably influenced by lime structure and composition; the method of calcining; temperature, slag composition, and, in a qualitative manner, stirring rate.

Since a study of this type involves the preparation of burnt lime specimens for dissolution experiments, it has been necessary to develop a laboratory technique for calcining samples of limestone in which properties of the limestone can 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 have been carried out on the limestone used in this program. To evaluate the properties of the lime in terms of water reactivity tests, the ASTM standard reactivity test for lime has been used. Shrinkage, in the case of over-burning, has also been 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 CO_2 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 consists 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 is a closed-end mullite reaction tube 1-1/2" in diameter by 24" long. One end is closed with a pyrex glass ground joint, equipped with gas inlet and outlet tubes, and a thermocouple protection tube. The resistance heated furnace is capable of going to 2000°F (1100°C). The furnace, built by Hevi-Duty, is controlled on a signal from a platinum/platinum-10% rhodium thermocouple. Dry argon gas is used as a carrier to flush the evolved carbon dioxide from the reaction tube and carry it to the analytical system.

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

The experimental studies to date have been carried out on a fine grained limestone which is nearly pure calcium carbonate. The rate of calcination at various times has been measured and these results are shown for two temperatures in Figure 5. In addition to determining the calcination characteristics of this limestone, the reactivity with water has been measured using the standard ASTM test. The results for samples calcined to various extents at 1150°C ranging up to complete calcination are shown in Figure 6. The increased temperature rise in the reactivity test with increasing calcination time is indicative of the fact that these samples were not fully calcined. Figure 7 shows a cross-plot of the results of Figure 6 showing that the temperature rise in 30 seconds and the total temperature rise in the reactivity test both increased with increasing calcination time. Additional studies on fully calcined samples, and samples calcined at higher temperatures where shrinkage has occurred, have also been evaluated in this same manner.

These studies have been carried out since it is necessary to fingerprint the lime used in the dissolution studies with the hope that the results of these experimental studies can be carried over into steelmaking practice. The characteristics of lime used in these studies will be specified in terms of lime structure or source, its chemical composition, its calcination behavior, and its reactivity after calcining.

DISSOLUTION EXPERIMENTS

The original proposal for carrying out the dissolution 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, as the samples failed either at the point of gripping, or at the liquid slag interface. Consequently, the technique at present is simply to immerse the calcined material in the molten slag and permit it to react for a given period of time. A schematic diagram of this equipment is shown in Figure 8, and a photograph of the laboratory arrangement is presented in Figure 9. The slag used to date has been of two compositions, one involving a 30% CaO-30% SiO_2-40% FeO slag, and the second, the same slag without silica, which would be approximately 43% CaO and 57% FeO. The slags are prepared by mixing pure CaO, pure SiO_2, and a stoichiometric mixture of Fe_2O_3 and Fe powders. This synthetic slag is charged to a low carbon steel crucible and placed in the furnace under an argon atmosphere. A half-lid of steel partially covers the crucible. A small piece of 1/2" diameter lime is placed on the lid and permitted to come to the furnace temperature. The lime is then rolled over the lip of the half-lid and immersed in the slag for the desired reaction time. The crucible is then removed from the furnace, quenched in an argon blast, and subsequently mounted in plastic, sectioned, and polished for examination.

MECHANISM OF SOLUTION - PROGRESS REPORT

A diffusion model for the dissolution of lime in the slag was originally proposed. This model is shown schematically in Figure 10. The solid particle of Figure 10 would be the undissolved lime, and extending out into the bulk liquid slag is a concentration gradient for calcium or calcium oxide. Corresponding to this gradient would be gradients which decreased with distance from the bulk liquid slag toward the solid particle for both iron oxide and silica. Since the slag contains a lower calcium oxide content than the solid particle, the gradients for the calcium ion decrease to the right in Figure 10, whereas the slag would be higher in silica and iron oxide than the lime particle, and the gradients for silicon and iron would decrease toward the left in Figure 10. Microscopic examination of samples showed general agreement with this mechanism.

In an effort to ascertain quantitatively what diffusion processes were extant when lime dissolves in a slag, electron microprobe analyses were carried out on several sample sections. Two specific samples are discussed in the following paragraphs.

The electron microprobe analyses were obtained through the courtesy of the Ford Motor Company Scientific Laboratory in Dearborn, Michigan. The electron microprobe is an instrument which is able to focus a beam of electrons on the sample at a spot less than one micron in diameter. By measuring the intensity of various fluorescent radiation given off 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. 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 interface. However, despite the fact that the readings on a structure of this type tend to show large fluctuations, several quantitative conclusions can be drawn from the results of examinations on two specific samples. The two samples were immersed at 1400°C in a 30% CaO-30% SiO_2-40% FeO slag. The first sample had been immersed for one minute and thirty seconds and was partially reacted, i.e., showed a central core of unreacted calcium oxide. The second sample, which had been immersed for two minutes and forty-five seconds, had fully reacted, i.e., showed no core of unreactd CaO. Neither sample showed any evidence of a diameter change during this short immersion time at these relatively low slag temperatures.

Previous microscopic examinations of several samples indicated that iron oxide had penetrated into the lime, but that in general silica did not penetrate the lime. The microprobe results verified these observations.

A photomicrograph of the first sample is shown in Figure 11. The microstructure can be identified as slag at the lower portion of the photograph. The island of material is the interface between the slag and the lime particle and shows cracking on either side of this area. The light central zone is the reacted zone within the lime particle, and the dark upper zone is the unreacted core of calcium oxide. It is possible to see very light vertical lines on the photomicrograph. The sample is coated with an extremely thin layer of carbon to promote electrical conductivity of the surface during the microprobe analysis, and the white lines are tracks of microprobe traces.

The equipment is arranged with crosshairs such that one can directly follow the trace and identify its location as it passes across the surface of the sample. Figure 12 is a summary of the microprobe analysis of the sample shown in Figure 11. The slag zone at the left of Figure 12 shows the content of calcium, iron, and silicon in the slag. As the trace entered the interface zone, an increase in calcium concentration and a decrease in iron concentration was observed. At first an abrupt increase in silicon content and then a precipitous drop to nearly zero indicates that the silica does not penetrate beyond the interfacial zone between the slag and the lime. Within the lime particle, the calcium content increases with distance and the iron content remains relatively constant until one reaches the end of the reacted zone, where the iron content drops off. This relatively constant iron content within the reacted zone of the lime particle indicates that iron diffuses into the lime particle as a second phase, probably calcium ferrite. The interesting aspect is, as indicated in previous metallographic examinations, that the silica does not penetrate the lime particle.

Figure 13 is a photomicrograph of the second sample. The lower portion of the photomicrograph shows slag up to the center of the photomicrograph where there is a crack, and above the crack the reacted lime particle. A microprobe trace of this sample showed a behavior similar to that of the first sample. These results are presented in Figure 14. At the interface zone between slag and reacted lime particle there is a precipitous drop in the silicon content, a decrease in the iron content, and an increase in the calcium content. Within the lime particle the reacted zone is essentially the same as that shown in Figure 12 for the reacted area of the lime particle. The iron content is relatively constant within the lime particle. Again, the silica does not penetrate into the lime particle during this initial state of the dissolution process.

AREAS FOR FURTHER STUDY

These results have shown some interesting phenomena with respect to the mechanism of the dissolution process. Of additional interest is the influence of the presence of manganese oxide in the slag, the influence of fluorspar additions, the influence of temperature (particularly on the dissolution rate as well as the mechanism), the behavior of other limestones, including dolomitic stone. At the present stage of this research program, general conclusions regarding the fluxing behavior of lime are not possible. However, the investigation to this point has indicated that there are a number of critical experiments which can be performed to provide additional information regarding the dissolution process and, hopefully, a basis for improvement in fluxing practices in the basic oxygen steelmaking process.

LIST OF FIGURES

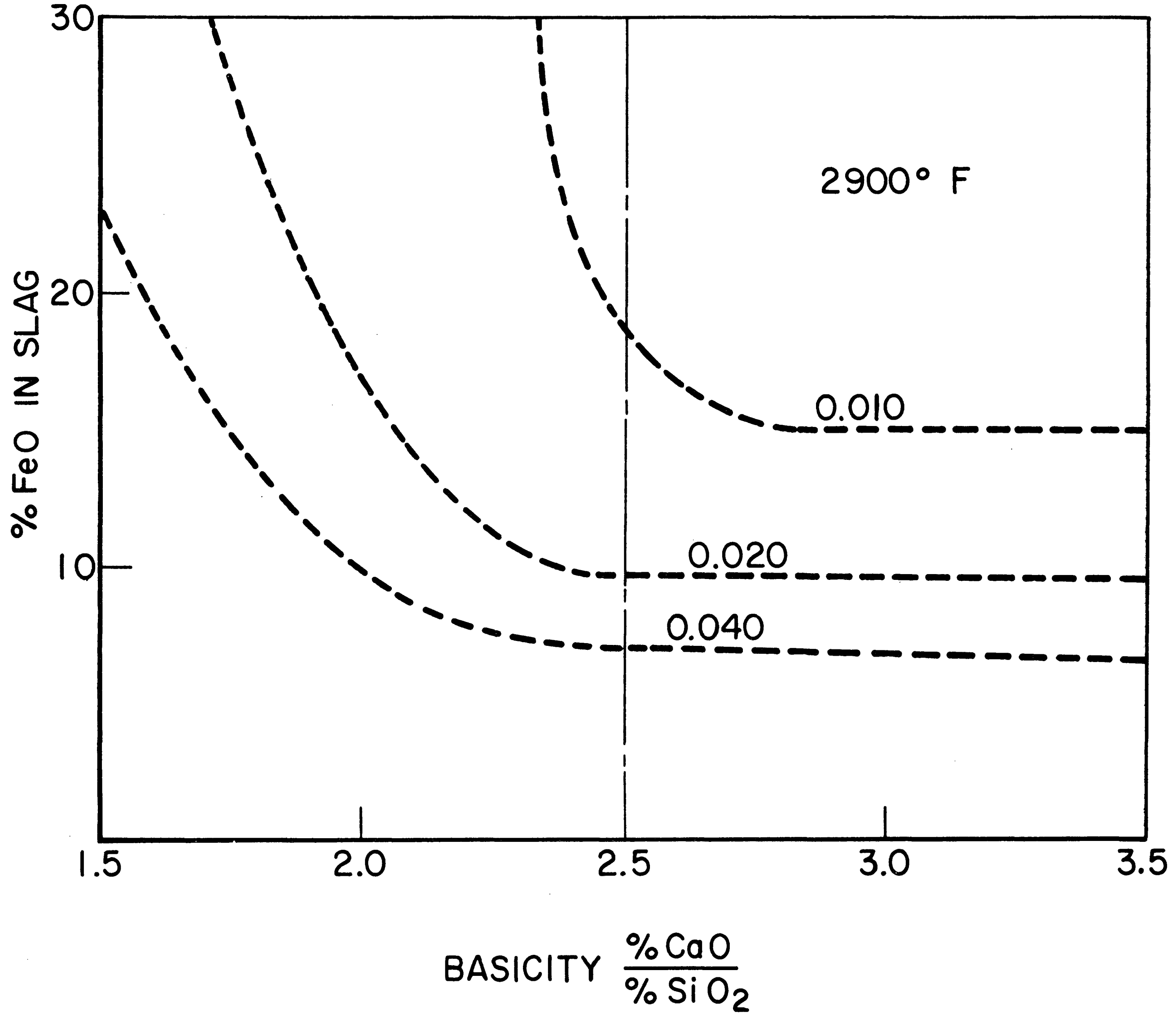

Figure 1: Residual Phosphorus in Steel as Influenced by Slag Basicity and Iron Oxide

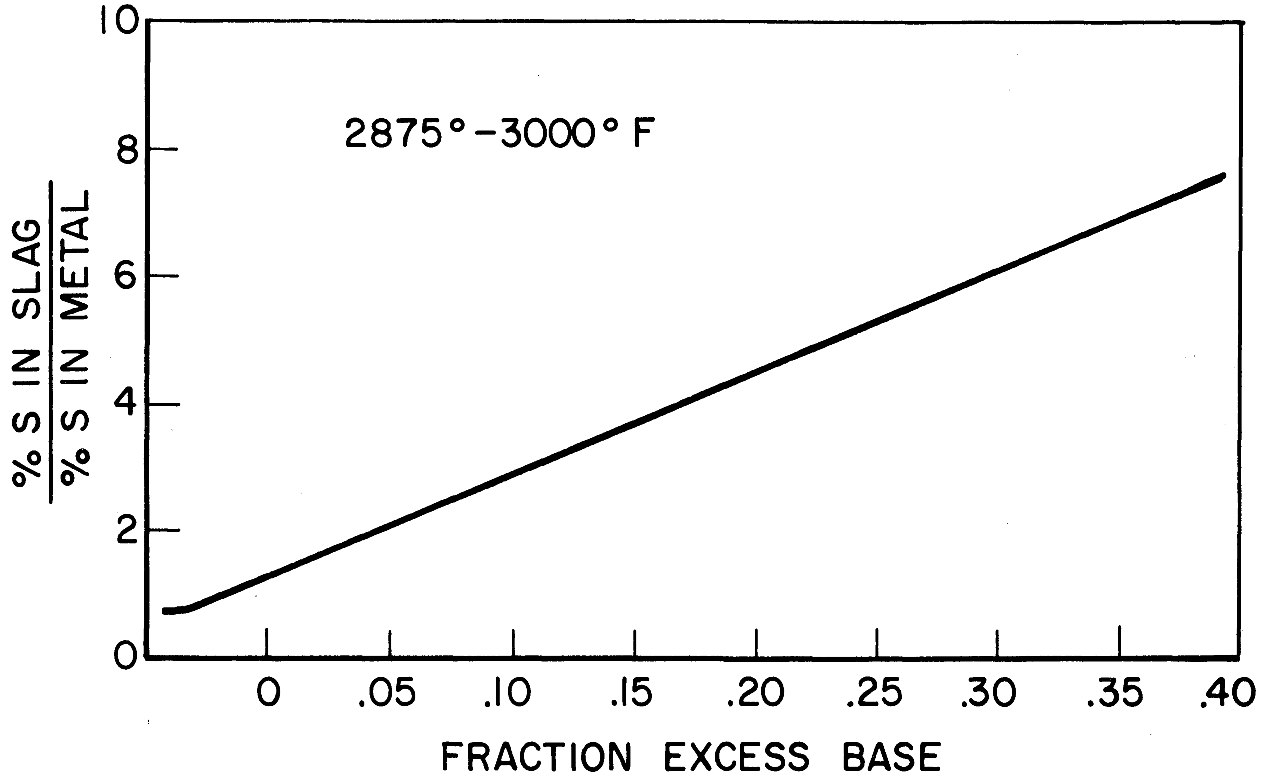

Figure 2: Influence of Available Base on Sulfur Distribution Between Slag and Metal

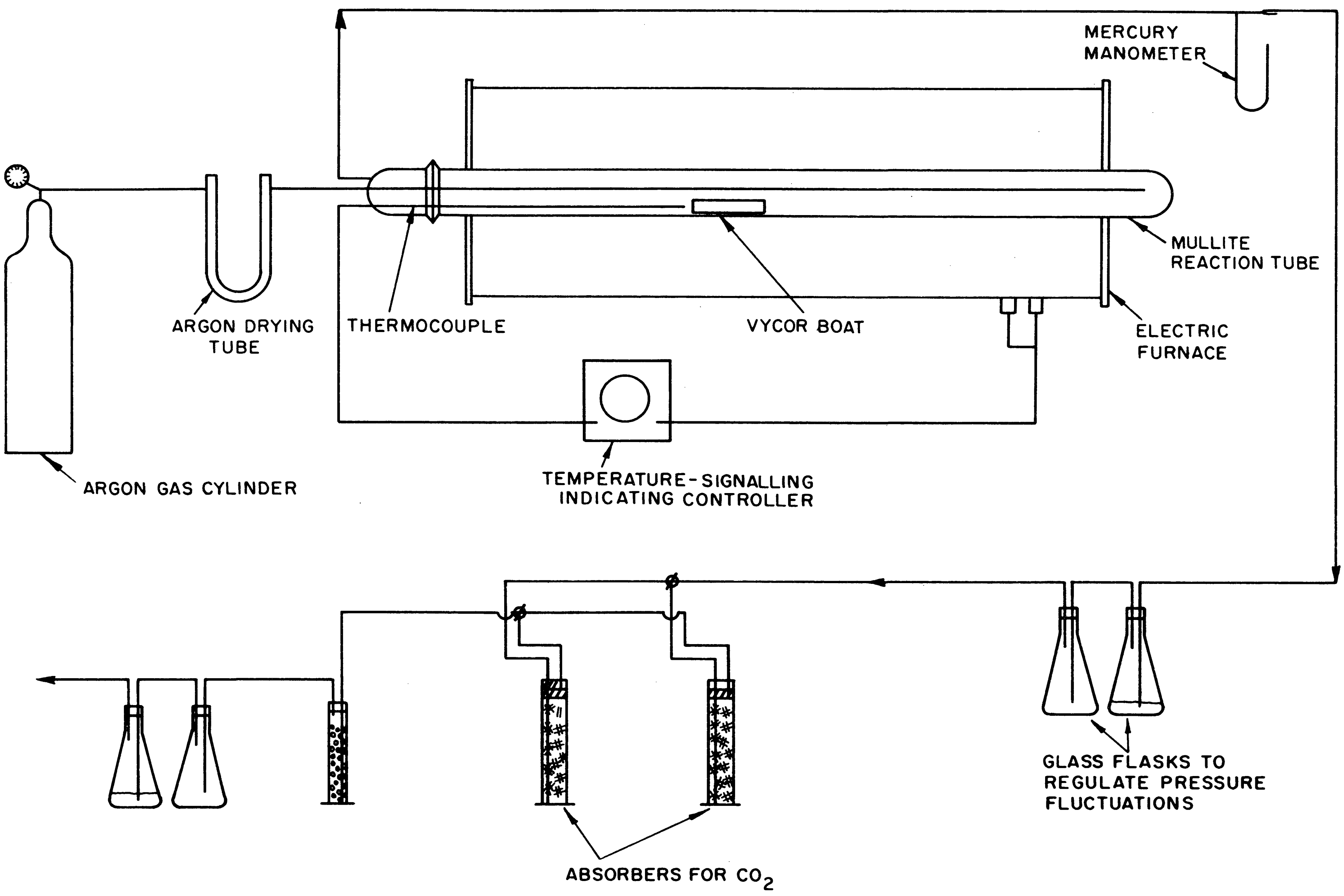

Figure 3: Laboratory System for Calcination Studies

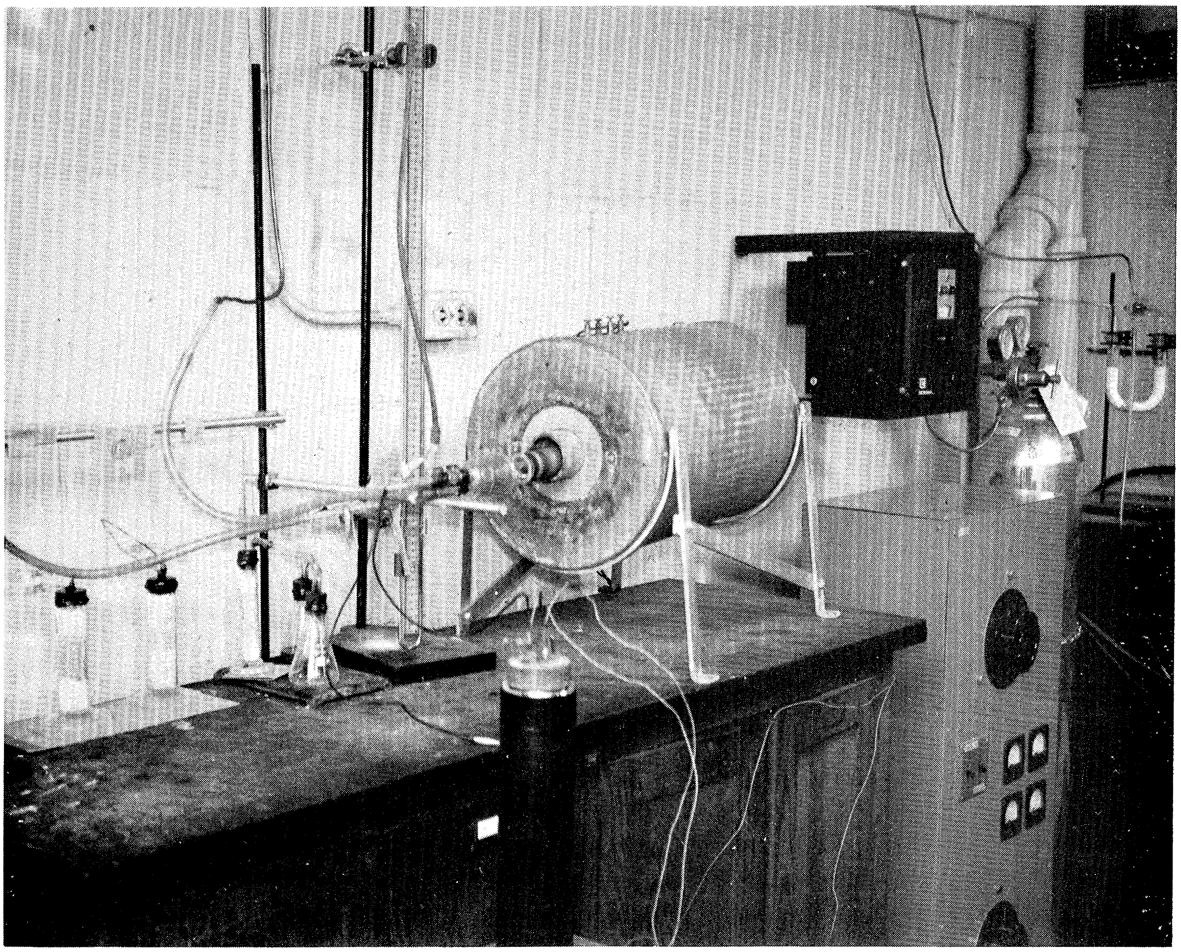

Figure 4: Photograph of Laboratory Arrangement for Calcination Studies

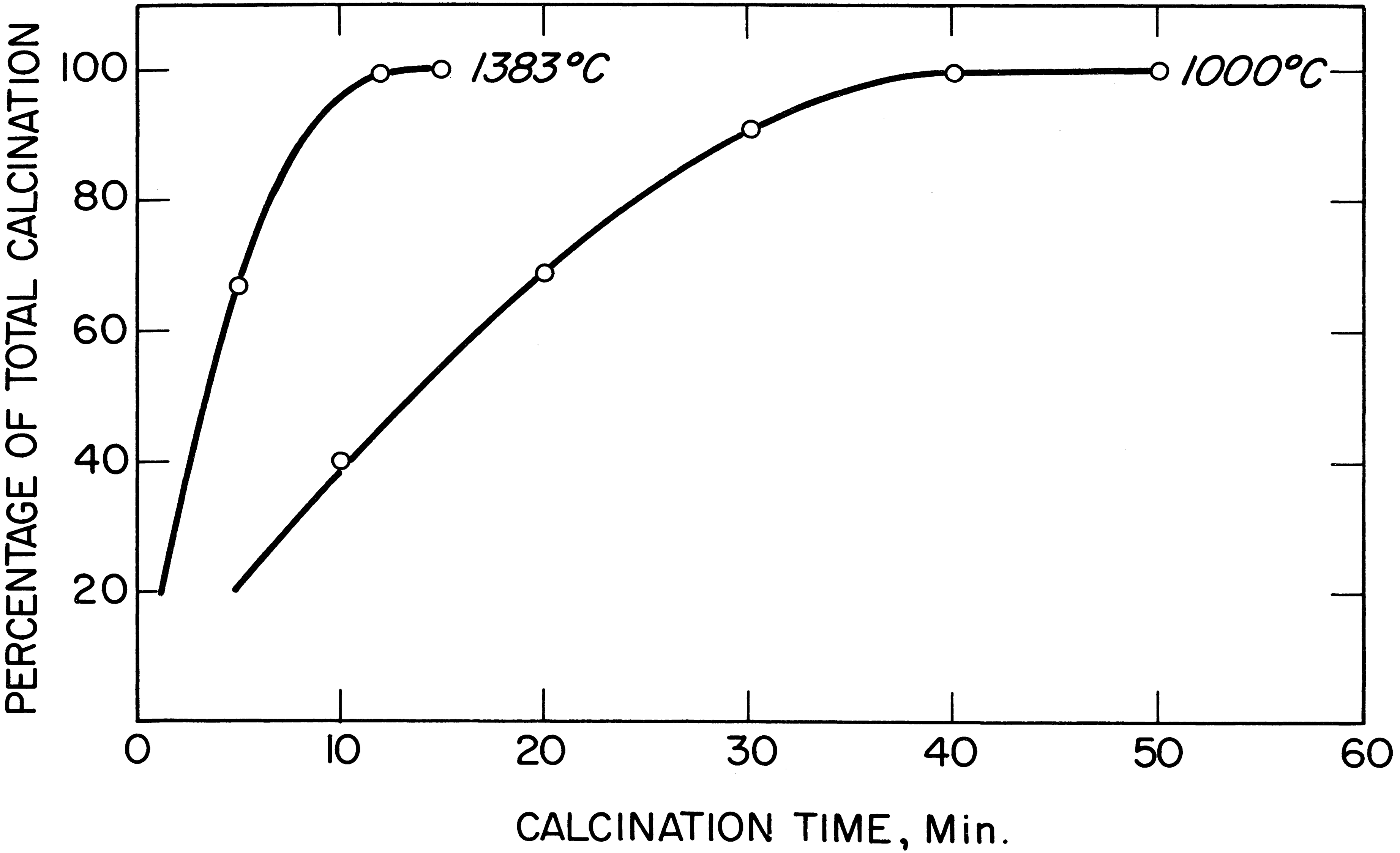

Figure 5: Calcination Behavior of Fine Grained Limestone at Temperatures of 1000 and 1383°C

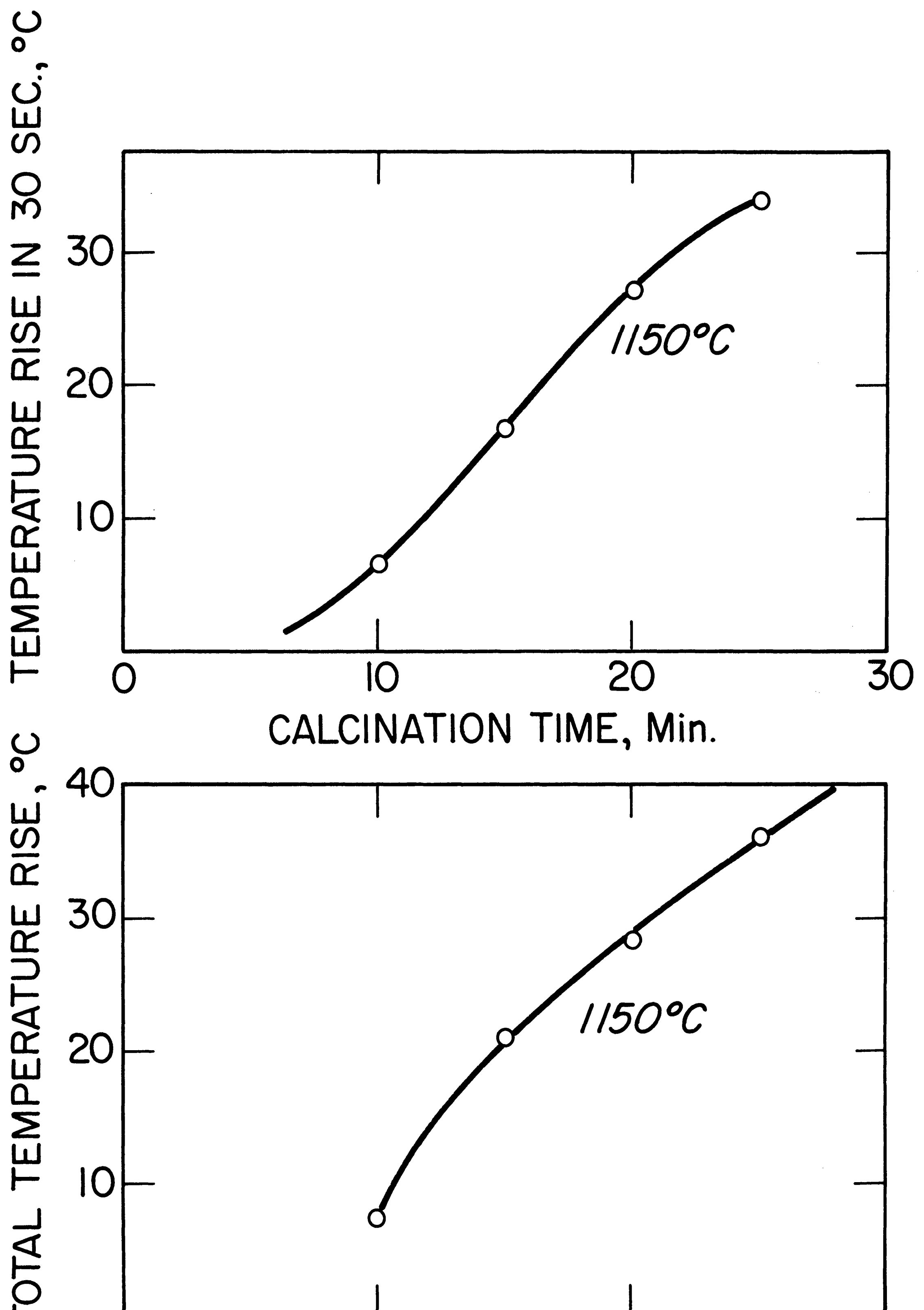

Figure 6: Results of ASTM Reactivity Tests on Samples Calcined at 1150°C

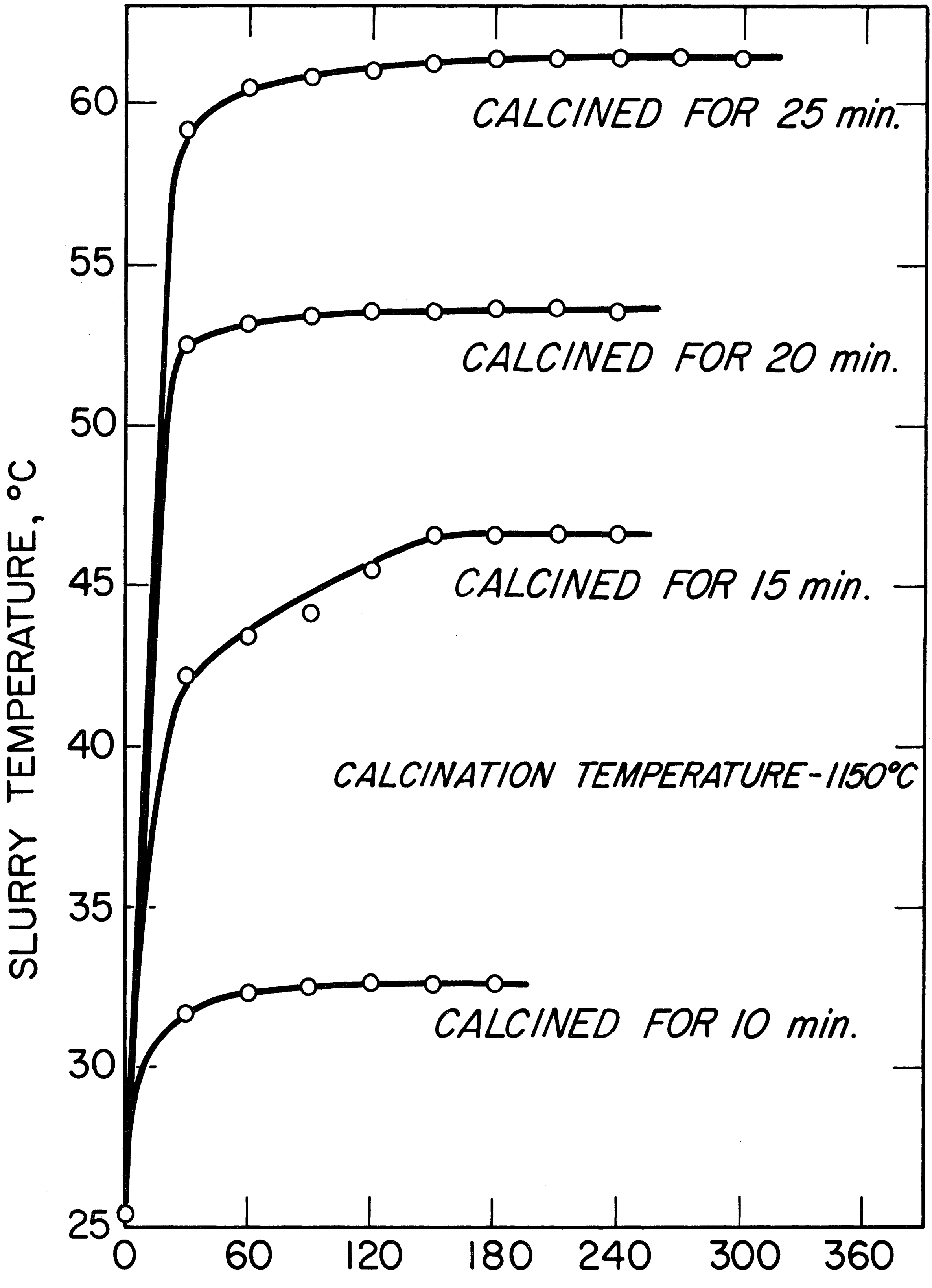

Figure 7: Reactivity Test Temperature versus Calcination Time at 1150°C

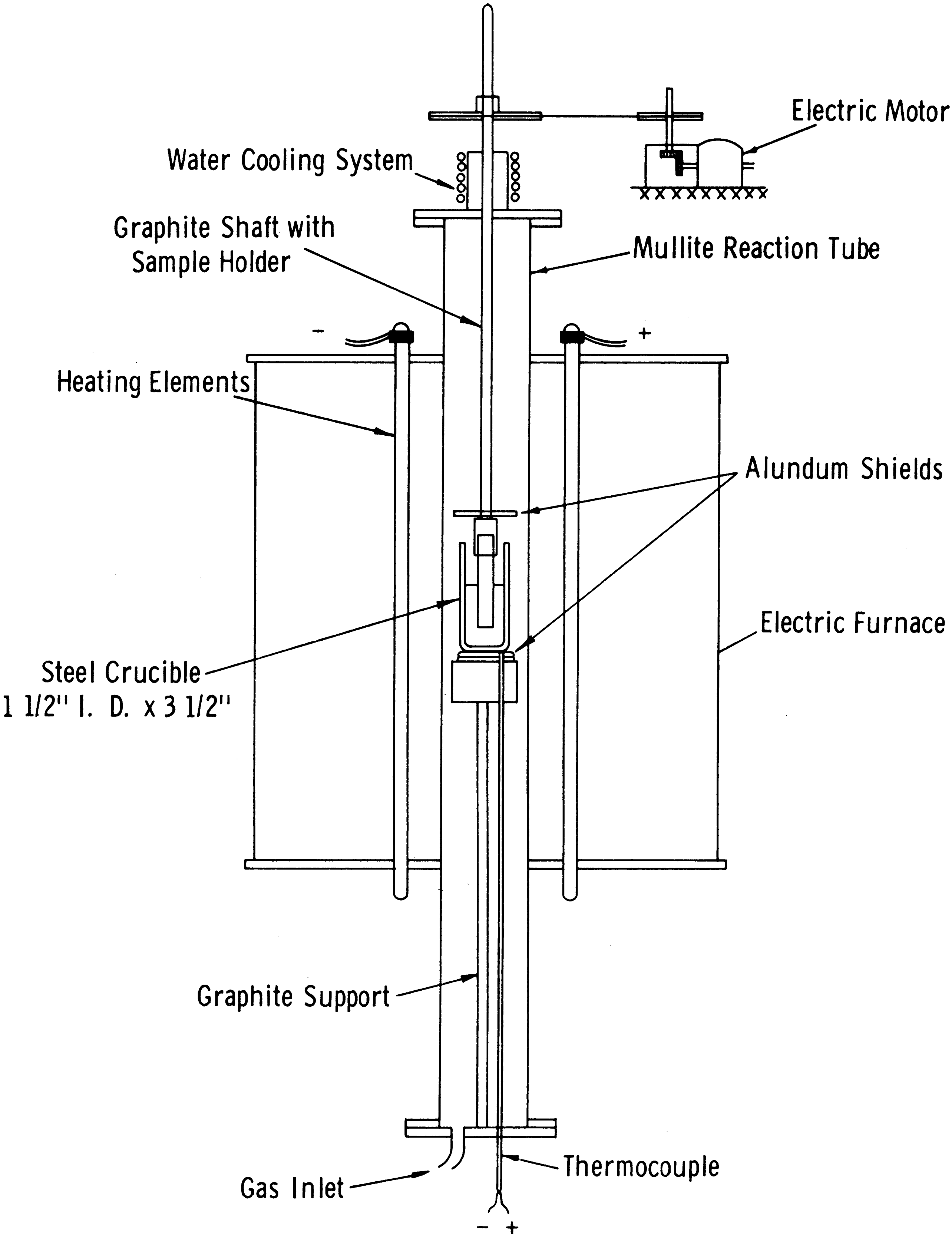

Figure 8: Laboratory System for Dissolution Studies

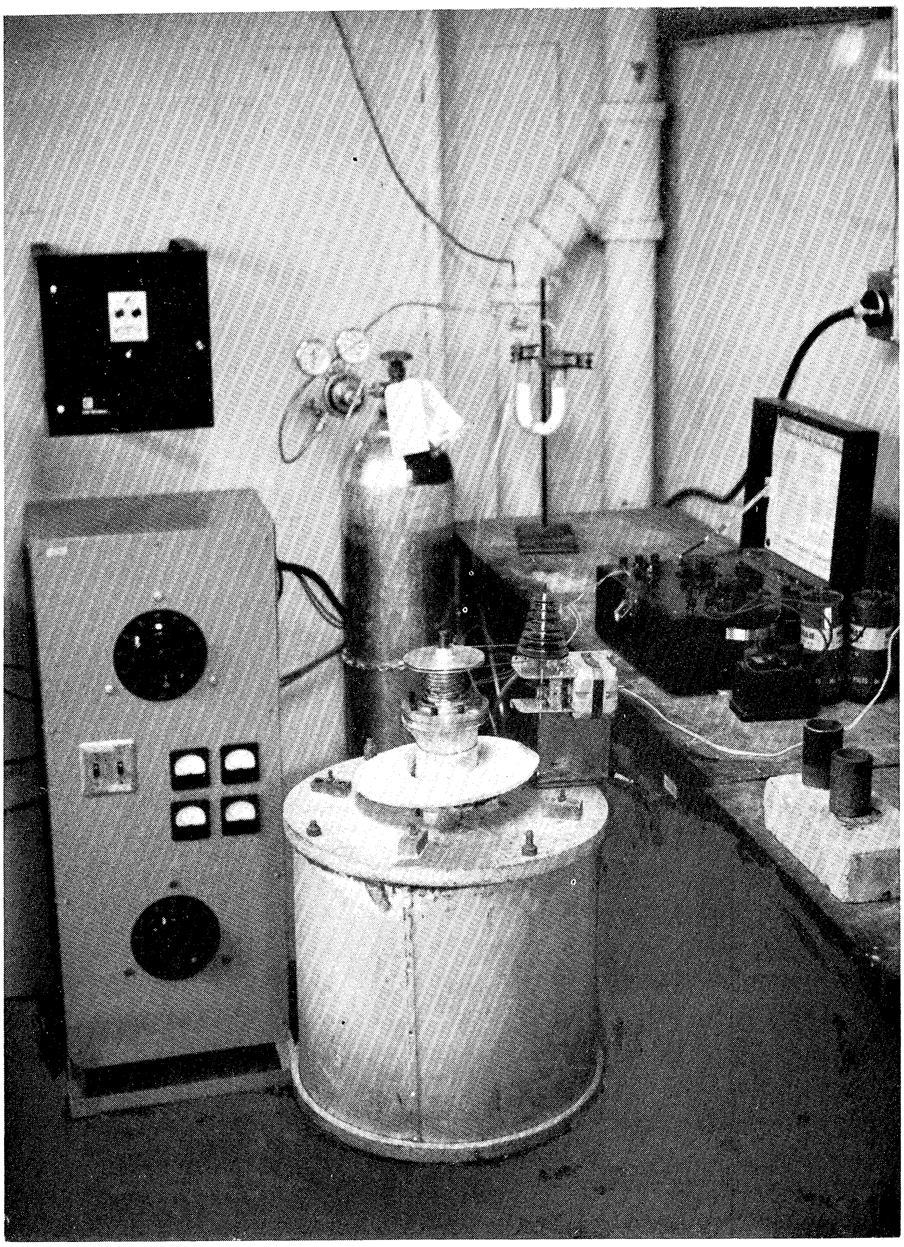

Figure 9: Photograph of Laboratory Arrangement for Dissolution Studies

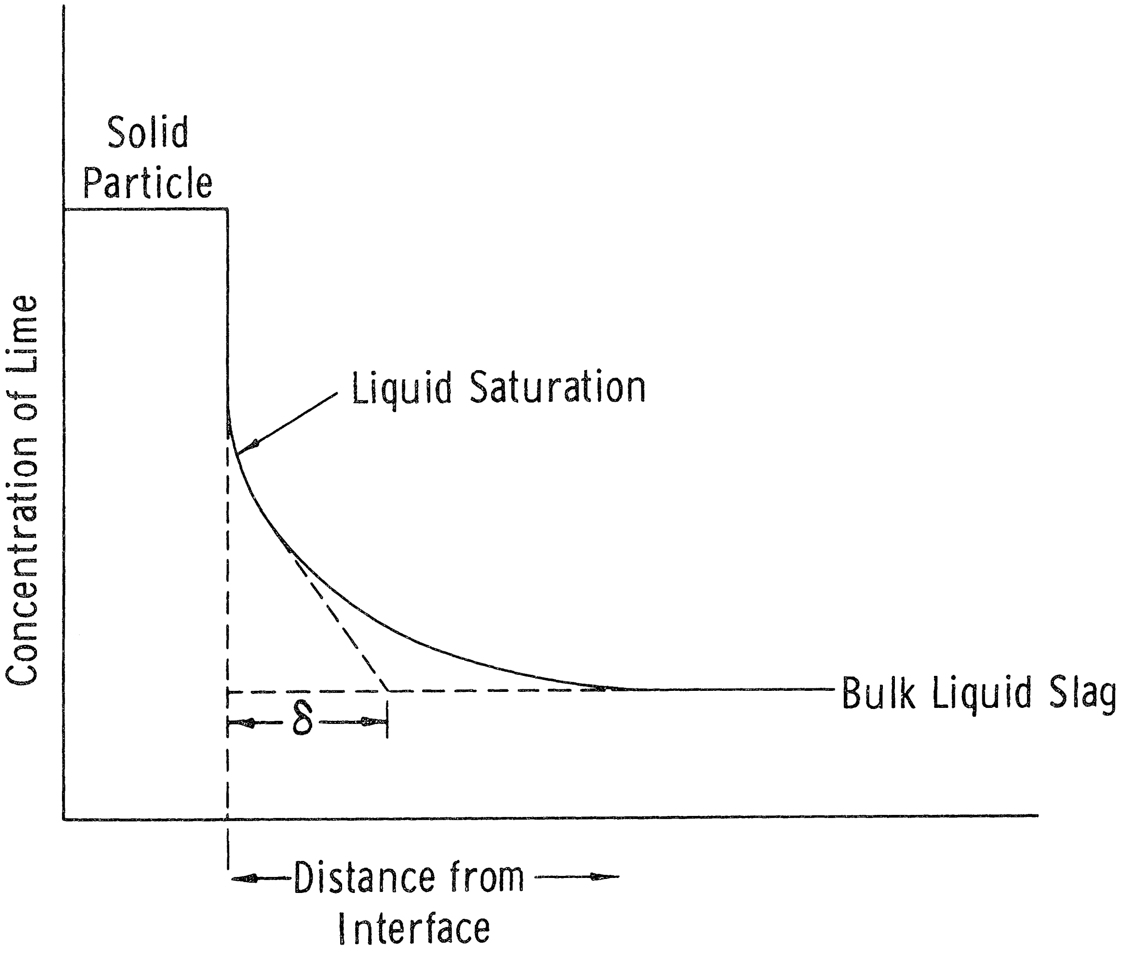

Figure 10: Schematic Diagram of Concentration Profile in Diffusion Controlled Solution Process

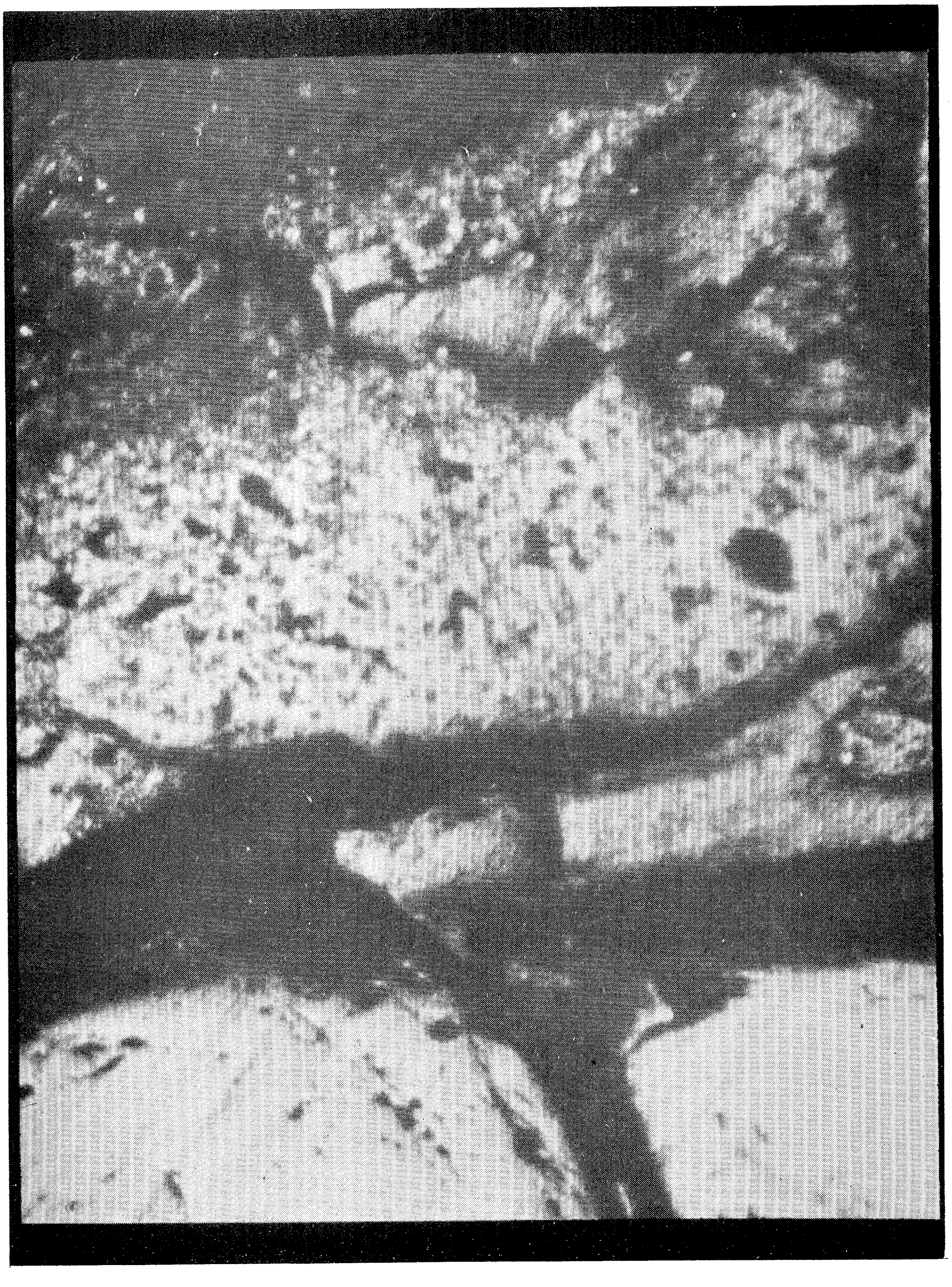

Figure 11: Photomicrograph at 50X of Lime Sample Partially Reacted in 30 CaO-30 SiO_2-40 FeO Slag for One Minute-Thirty Seconds at 1400°C (enlarged 4 times for reproduction)

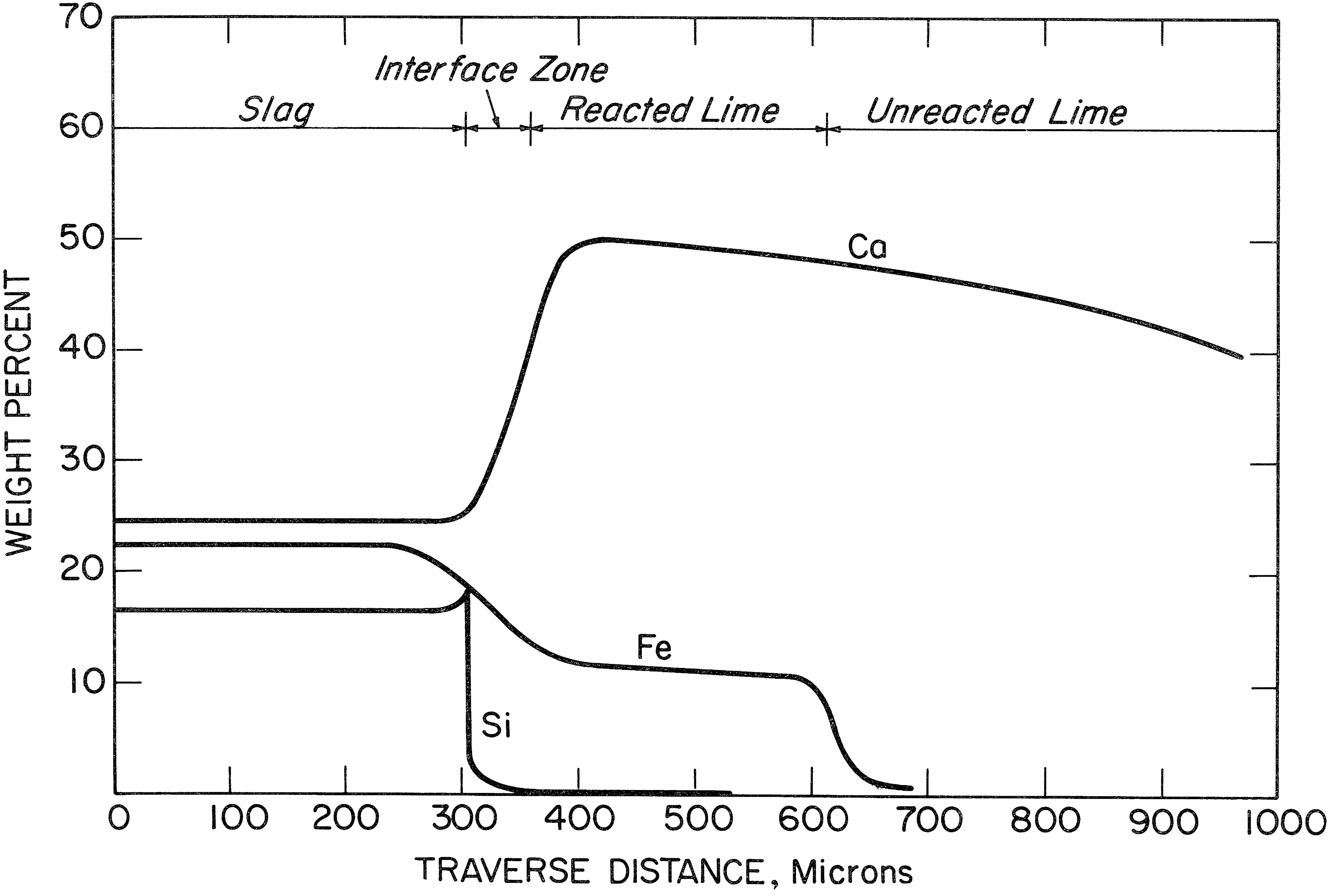

Figure 12: Microprobe Analysis of Sample Shown in Figure 11

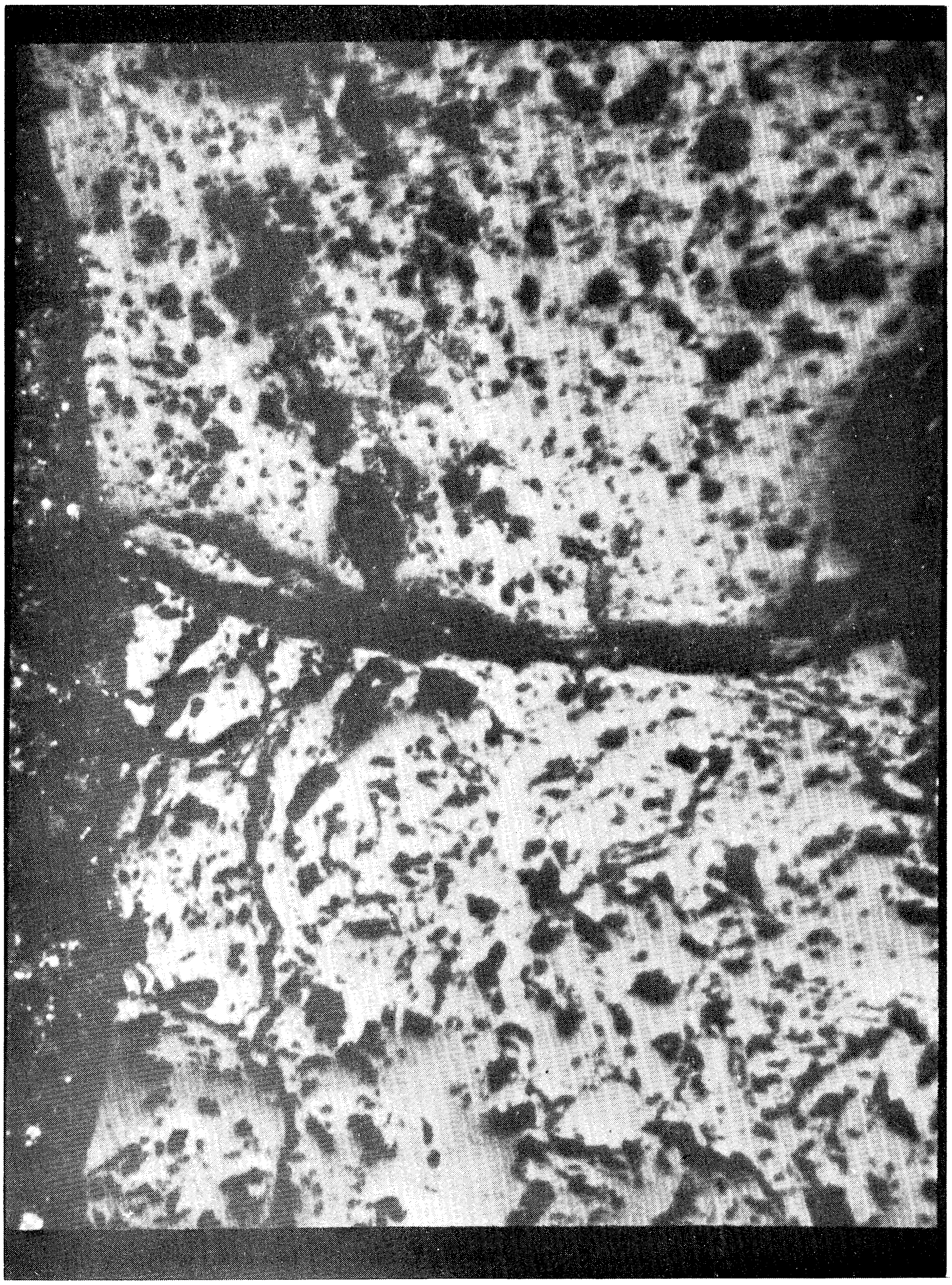

Figure 13: Photomicrograph at 50X of Lime Sample Fully Reacted in 30 CaO-30 SiO_2-40 FeO Slag for Two Minutes-Forty-five Seconds at 1400°C (enlarged 4 times for reproduction)

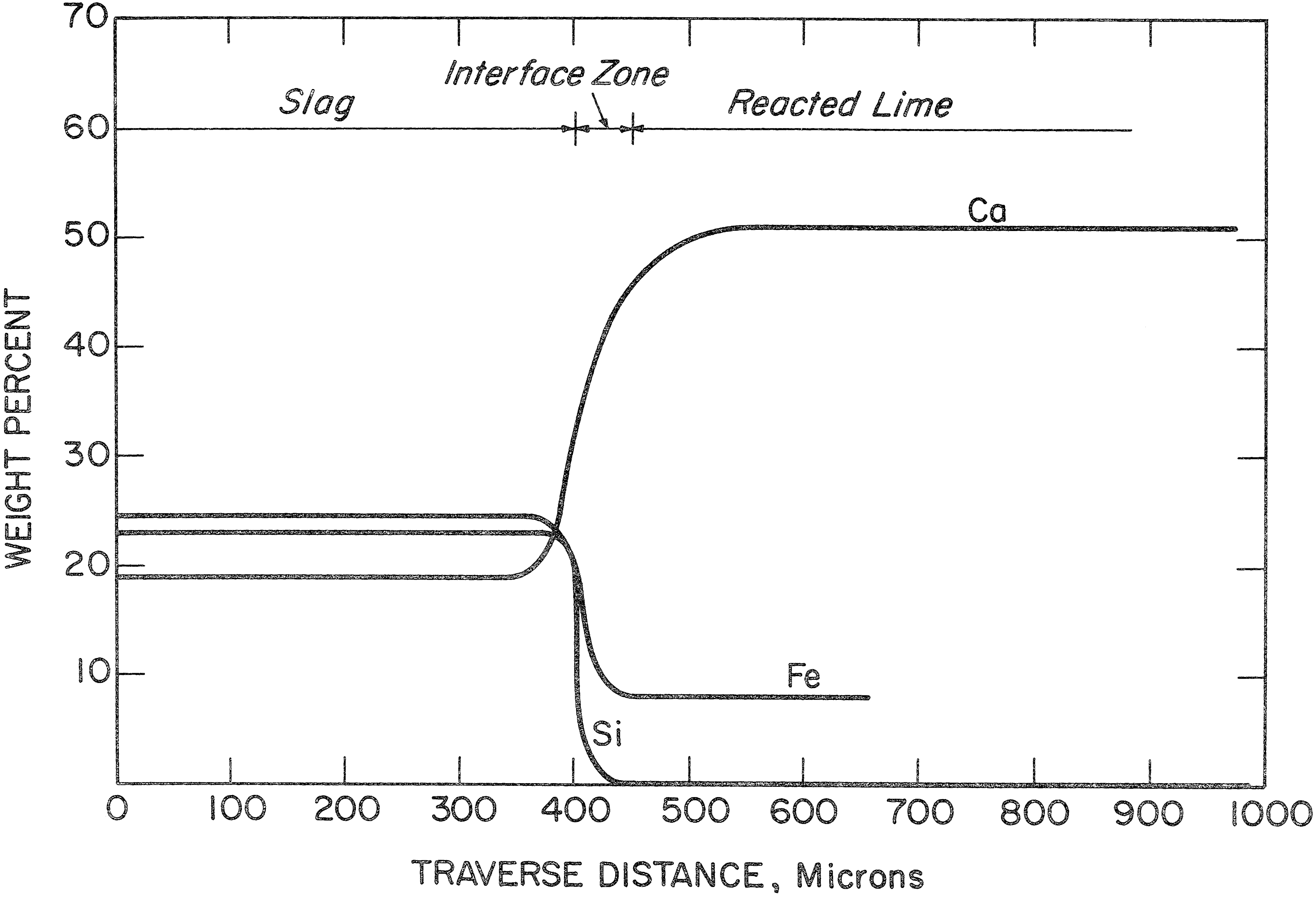

Figure 14: Microprobe Analysis of Sample Shown in Figure 13