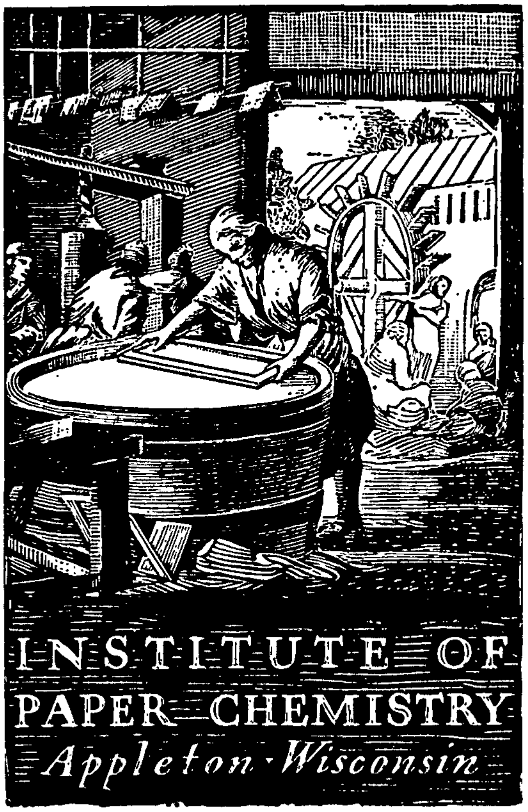

A KINETIC STUDY OF SULFATE REDUCTION WITH CARBON

Project 3473-1

Report Two
A Progress Report
to
MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

June 6, 1983

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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SUMMARY

One of the key chemical reactions occurring within a kraft recovery furnace is the reduction of sodium sulfate to sodium sulfide. Despite the obvious importance of this reaction, relatively little fundamental information is known about it. This report is the second of two describing the results of a fundamental study of sulfate reduction with various forms of carbon, including black liquor char.

Sulfate reduction in molten salts is very similar for all forms of carbon and occurs through a common mechanism. Carbon dioxide in the melt reacts with a carbon surface site to form two molecules of adsorbed carbon monoxide. These sorbed carbon monoxide molecules serve as active sites for the adsorption of sulfate. Sorbed sulfate is then reduced to form carbon dioxide and a reduced sulfur compound which can then desorb. The rate-limiting step is the reduction of the adsorbed sulfate.

Black liquor char is very reactive with sulfate, apparently due to its very high surface area. Reduction rates with char were found to be proportional to the surface area in agreement with the proposed mechanism. Char is so reactive that reduction can proceed at significant rates at temperatures of 1400°F or less.

The effect of sulfate concentration on the reduction rate can be described by an adsorption isotherm. The rate is independent of sulfate concentration until low levels of sulfate are reached and then gradually becomes first order in sulfate. For black liquor char this transition begins at about 3 wt.% Na_2SO_4 in the melt, which corresponds to a reduction efficiency of about 90-95%.

Sulfate reduction by carbon is catalyzed by sodium carbonate. Reduction rates are about one order of magnitude lower in carbonate-free melts. This is probably due to the relatively high level of carbon dioxide in carbonate melts and is in agreement with the proposed mechanism.

No differences were found between sulfate reduction using commercial smelts and reduction using reagent-grade chemicals. No catalytic effects or unusual reactions were observed with commercial smelt. The reactions studied in this program are those responsible for reduction in a kraft recovery furnace.

Rate expression and appropriate rate constants were developed for sulfate reduction with black liquor char, pulverized graphite, and graphite rods. These can be used to predict reduction rates under a wide variety of conditions.

Sulfate reduction with black liquor char or pulverized graphite is not an autocatalytic reaction, in contrast to the behavior with graphite rods. The autocatalytic nature of reduction with graphite rods is due to an increase in active surface sites as reduction proceeds. The new active sites are formed by the reduction process. This behavior is not observed with char and pulverized graphite because they already have a sufficiency of active sites.

INTRODUCTION

This is the second in a series of reports concerned with the kinetic processes occurring in the bed of a kraft recovery furnace. One of the key reactions occurring in the kraft chemical process is the reduction of sodium sulfate in the presence of carbon. An earlier report (1) described sulfate reduction with relatively large graphite rods. In this report, the kinetic study has been extended to reduction with micronized graphite particles and kraft black liquor char. Based on the results obtained in these studies, a common mechanism for sulfate reduction with all forms of carbon is proposed.

In a kraft recovery furnace, reduction occurs in a melt consisting principally of sodium carbonate, sodium sulfate, sodium sulfide, and carbon at temperatures in excess of 1400°F. Here, molten sulfate reacts with carbon to form sulfide, carbon dioxide, and carbon monoxide. Although sulfate reduction by carbon is one of the key reactions occurring in the kraft chemical recovery process, little information is available concerning its mechanism or controlling parameters. This lack of information is due to the difficulty of studying a reaction involving three phases (solids, liquids, and gases), the high temperature required, and the corrosive nature of the reaction system.

PROJECT OBJECTIVES

The project objectives are to obtain fundamental kinetic data on sulfate reduction with various forms of carbon and to define the process by which sulfate reduction occurs in the hearth zone of a kraft recovery furnace. The fundamental kinetic data include experimental data on the effects of sulfate and sulfide concentrations, melt composition, possible catalysts, temperature, and form of carbon.

In a kraft recovery furnace, the carbon, essential for sulfate reduction, is formed from the pyrolysis of kraft black liquor. Kinetic data were obtained on forms of carbon that are readily characterized, such as powdered graphite, as well as on carbon formed from the pyrolysis of kraft black liquor. Here, the objective was to define the sulfate reduction mechanism with these readily characterized carbons. If it can be shown that reduction with char is similar to reduction with these readily characterized carbons, the mechanistic insights gained with these carbons can be applied to defining the reduction mechanism with char.

To understand the process through which sulfate reduction occurs in the kraft recovery furnace, it is necessary to define the mechanism through which carbon reduces sulfate. In Report One of this series (1), sulfate reduction using graphite rods as the source of carbon was described. During this study, experimental data were obtained on the effects of carbon surface area, sulfate and sulfide concentrations, melt composition, catalysts, and temperature. Based on these experimental results, a sulfate reduction mechanism was proposed. One of the objectives of the current study is to further refine this mechanism using kinetic data obtained from different forms of carbon. By obtaining experimental information on sulfate reduction with small carbon particles and carbonaceous char, the similarities or differences in sulfate reduction with graphite rods or char can be defined and an understanding of the sulfate reduction mechanism with char obtained.

EXPERIMENTAL OBJECTIVES

The main experimental objectives are summarized below:

1. Design an experimental system to acquire experimental data on sulfate reduction with various types of carbon over a

wide range of experimental conditions. Such a system will include a method of dispersing fine carbon particles in molten smelt.

2. Develop a method of producing a uniform and consistent carbonaceous char to be used as the reducing agent. This char should simulate the char found in a kraft recovery furnace.
3. Determine if the composition of commercial kraft smelt compared with a synthetic smelt significantly affects sulfate reduction.
4. Obtain kinetic data including composition and temperature effects on sulfate reduction with various forms of carbon.

SULFATE REDUCTION CHEMISTRY

BASIC CHEMISTRY

The reduction of sodium sulfate to sulfide can be written as:

$$Na_2SO_4 \rightarrow Na_2S + 2O_2 \qquad (1)$$

The basic step in reduction is removal of oxygen from sulfur. However, due to an unfavorable equilibrium, this reaction will not proceed as written. A reducing agent must be present to bind with and remove the oxygens from the sulfur. The fundamental requirement of this reducing agent is that it have a greater affinity for oxygen than sulfide has for oxygen.

The principal reducing agents found in a recovery furnace are hydrogen, carbon monoxide, and carbon. Table I illustrates the various reduction reactions for sulfate in the presence of these reducing agents plus the oxidation of sulfide and the heat of reaction.

TABLE I

REDUCTION REACTIONS OF SODIUM SULFATE

Reaction	ΔH, heat of reaction, Btu/lb Na_2SO_4	
Temperature	1340°F	1880°F
$Na_2SO_4 + 2C \rightarrow 2CO_2 + Na_2S$	542	506
$Na_2SO_4 + 4C \rightarrow 4CO + Na_2S$	1576	1521
$Na_2SO_4 + 4CO \rightarrow 4CO_2 + Na_2S$	-491	-509
$Na_2SO_4 + 4H_2 \rightarrow 4H_2O + Na_2S$	-70	-122
$Na_2S + 2O_2 \rightarrow Na_2SO_4$	-2934	-2901

Although all these reactions may be occurring in a recovery furnace, reduction in a recovery furnace is an endothermic reaction because carbon is the principal reducing agent. Reoxidation of sulfide, which occurs in the oxidizing environment at the bed's surface and in the smelt stream from the recovery furnace, is a highly exothermic reaction.

REVIEW OF SULFATE REDUCTION WITH GRAPHITE RODS

Report One in this series (1) presented a study of the kinetics of sulfate reduction in molten carbonate salts using graphite rods as the reducing agent. Among the variables studied were temperature, sulfate and sulfide concentration, carbon surface area, and melt composition.

Reduction reactions were carried out in a semibatch mode using an alumina crucible containing about 1.5 L of smelt. The crucible was contained within an iron retort in a cylindrical electric furnace. Nitrogen gas was bubbled through the molten smelt to keep the mass stirred and to sweep off product gases. Reduction was initiated by adding graphite rods about one inch in length to the reactor. The reduction rate was measured by quantitative analysis of carbon dioxide and carbon monoxide concentrations in the off-gases using an infrared spectrophotometer.

Characteristic sulfate reduction data from this study are illustrated in Fig. 1. The carbon dioxide and carbon monoxide generation rates were determined from the carbon dioxide and carbon monoxide in the off-gases and the nitrogen purge rate, and the sulfate reduction rate was calculated from the carbon dioxide and carbon monoxide generation rates. Sulfate reduction begins with an initial period from 6 to 8 min during which no reduction is observed, followed by a period of rapidly increasing rate. The reduction rate then peaks and gradually decreases due to the depletion of the sulfate and carbon. In these reports the initial period from 0 to

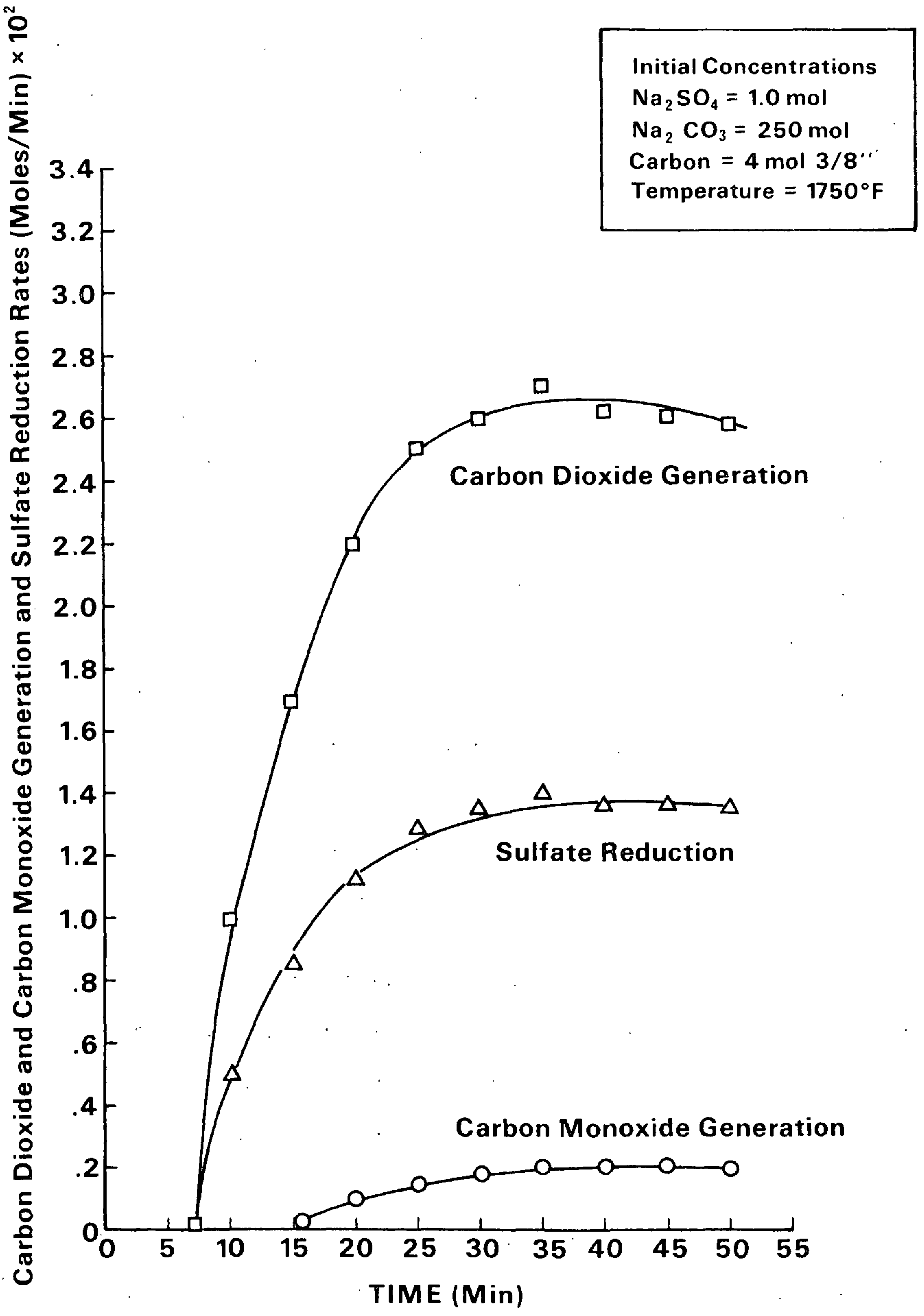

Figure 1. Sulfate reduction with graphite rods in large reactor.

8 min, during which no reduction is observed, is referred to as the induction period, and the period of increasing rate as the autocatalytic period.

Carbon dioxide added to the melt before the introduction of the graphite rods shortened the induction period. By adding initial amounts of sulfide to the reactor, it was determined that the autocatalytic behavior was not due to the increase in sulfide during reduction. By varying the amount of sulfate added to the reactor, it was determined that sulfate reduction with carbon is first order in sulfate at low sulfate concentrations but zero order at high sulfate concentrations. By varying the amount of carbon added, the rate of reaction was found to be proportional to the square root of the carbon surface area. The activation energy for sodium sulfate reduction in a sodium carbonate melt was determined to be approximately 53 kcal/g mole. Reaction kinetics were not appreciably influenced by the nature of the carbonate cation and hence by the melting point of the smelt or smelt fluidity.

To explain these experimental results, a mechanism based on a carbon dioxide-carbon monoxide cycle was proposed. In this mechanism, carbon dioxide adsorbs on the surface of the carbon and reacts with the carbon to form two molecules of adsorbed carbon monoxide. This carbon monoxide then desorbs from the carbon surface into the melt where it reduces the sulfate to sulfite, forming additional quantities of carbon dioxide and completing the cycle. It was proposed that the sulfite, being an unstable compound, then rearranges with itself to form sulfate and sulfide.

In this report, the results from reduction experiments with pulverized graphite and kraft black liquor char are presented. Because these results differ from the previous results with graphite rods, the nature of sulfate reduction with graphite rods was reexamined and a new interpretation of the experimental results proposed.

EXPERIMENTAL APPROACH

The principal objective of this study was to define the process through which sulfate reduction with char occurs in the bed of a kraft recovery furnace. Since the primary reducing agent in sulfate reduction with char is carbon, sulfate reduction with char should be similar to sulfate reduction with other forms of carbon.

Sulfate reduction with three different types of carbon - graphite rods, pulverized graphite, and kraft black liquor char - is described in this report. Graphite rods and pulverized graphite are more readily characterized than kraft black liquor char. If the sulfate reduction process can be defined using these readily characterized carbons, and if it can be shown that the same mechanism is responsible for sulfate reduction with kraft black liquor char, the insights obtained using these readily characterized carbons can be applied to understanding sulfate reduction with kraft black liquor char.

In addition to the experiments conducted to identify the effects of the basic variables such as temperature, sulfate level, and carbon level on sulfate reduction, several experiments were conducted to clarify certain experimental observations. To aid the reader, a basic outline of the experimental section is given below.

1. Experimental System: In this section the experimental apparatus used for this study is described.
2. Effect of Reactor Configuration: Since the experimental reactor used in this study contained only 3% of the melt contained in

the reactor used in the earlier study, numerous experiments were conducted to determine if both systems produced similar experimental results. The change in reactor size and experimental design also allowed any mass transfer effects in sulfate reduction with carbon to be identified. No differences in experimental results were observed with the two experimental systems.

3. Carbonaceous Reducing Agents: The types of carbon used in this study are described.
4. Typical Experimental Results: The experimental techniques are discussed, and typical experimental results for pulverized graphite and kraft black liquor char are presented. The kraft black liquor char was considerably more reactive than either the graphite rods or pulverized graphite. The autocatalytic behavior observed in sulfate reduction with graphite rods was not seen with either pulverized graphite or kraft black liquor char.
5. Autocatalytic Nature of Sulfate Reduction with Graphite Rods: As described in the introduction, sulfate reduction with graphite rods is a strongly autocatalytic reaction. However, this autocatalytic behavior was not observed with either pulverized graphite or kraft black liquor char. Therefore, this autocatalytic behavior of sulfate reduction with graphite rods was reexamined and found to be due to an increase in active surface sites as reduction proceeds.
6. Effect of Carbon on Sulfate Reduction: Using the three types of carbon studied, the effect of carbon level on sulfate

reduction is presented in this section. The effect of carbon rod surface area was evaluated based on the nature of autocatalytic effect. From these results, it was determined that sulfate reduction is directly proportional to the active surface sites on the carbon.

7. Effect of Sulfate on Sulfate Reduction: The effect of sulfate level on sulfate reduction with pulverized graphite and char is presented in this section. Similar to reduction with graphite rods, reduction with either pulverized graphite or char was found to be zero order in sulfate at high sulfate levels. With pulverized graphite and char, the reduction rate declined at low levels of sulfate. Based on these results, it was concluded that the sulfate level has a similar effect on reduction with all forms of carbon studied.
8. Effect of Temperature on Sulfate Reduction: The activation energies for sulfate reduction with pulverized graphite and kraft black liquor char are presented in this section.
9. Effect of Carbon Dioxide on Sulfate Reduction: During the study of sulfate reduction with graphite rods, carbon dioxide added to the melt prior to the introduction of the graphite rods was found to initially catalyze sulfate reduction. Since carbon dioxide is relatively soluble in carbonate melts and is present from the decomposition of the carbonate, the comparison of reduction in noncarbonate melts with reduction in carbonate melts enabled the effect of carbon dioxide on reduction to be determined. During these experiments, sulfate reduction with all forms of carbon studied was found to be

approximately one order of magnitude slower in noncarbonate melts than in carbonate melts. These results demonstrate that sulfate reduction is strongly catalyzed by carbonate melts. This catalytic effect of carbonate melts appears to be due to the dissolved carbon dioxide. Based on these results, it was concluded that since sulfate reduction with all forms of carbon studied involves the catalytic action of carbonate, the same mechanism is responsible for sulfate reduction with these different types of carbon. It was also concluded that carbon dioxide has a significant role in the sulfate reduction mechanism.

10. Effect of Commercial Smelt: The sulfate reduction rates in a commercial smelt were found to be very close to those in synthetic smelts. No catalytic or unexpected effects were observed using commercial smelt. This demonstrates that the sulfate reduction reactions studied during this program are those responsible for reduction in a kraft recovery furnace.
11. Carbon Monoxide Reduction of Sulfate: The product gas from sulfate reduction with carbon consisted principally of carbon dioxide with a carbon monoxide content averaging about 10% of the carbon dioxide level. However, this carbon monoxide, as it passes through the melt, will also reduce sulfate. Therefore, sulfate reduction with carbon monoxide will also occur during reduction with carbon. A student research program was organized to study sulfate reduction with carbon monoxide, and the results of this program are presented in this section.

EXPERIMENTAL SYSTEM

In a kraft recovery furnace, reduction occurs in an environment consisting primarily of molten sodium carbonate, sodium sulfide, sodium sulfate, and carbonaceous char. To obtain kinetic data on sulfate reduction with various forms of carbon, an experimental system was designed to contain these molten salts, allow the carbon to be introduced, and monitor the carbon dioxide and carbon monoxide product gases. With graphite rods as the reducing agent, sulfate reduction was a relatively slow reaction and the rods were readily dispersed in the molten salts. However, with powdered graphite or carbonaceous char as the reducing agent, an experimental system had to be designed to disperse these materials in the molten salts and to follow a reaction that is relatively fast.

Figure 2 illustrates the experimental reactor used to study sulfate reduction with the various forms of carbon. The reaction vessel consists of a ceramic crucible 2-1/2 inches in diameter and 4 inches high, which is contained in a stainless steel retort. The steel retort is heated with an induction heating coil energized by a 20-kW Lepel high frequency power supply. The ceramic crucible is then heated by radiation from the steel retort.

To prepare for a sulfate reduction experiment, anhydrous, reagent-grade alkali carbonates and sodium sulfate were mixed, dried at 150°C under vacuum for 2 hr, and then added to the alumina crucible. A typical charge consisted of 0.51 mole of sodium carbonate, 0.26 mole of potassium carbonate, and 0.01 mole of sodium sulfate. This mole ratio of sodium sulfate produced a reduction rate that could be monitored, and the mole fraction of sulfate used approximates that found in a kraft recovery furnace as reduction nears completion.

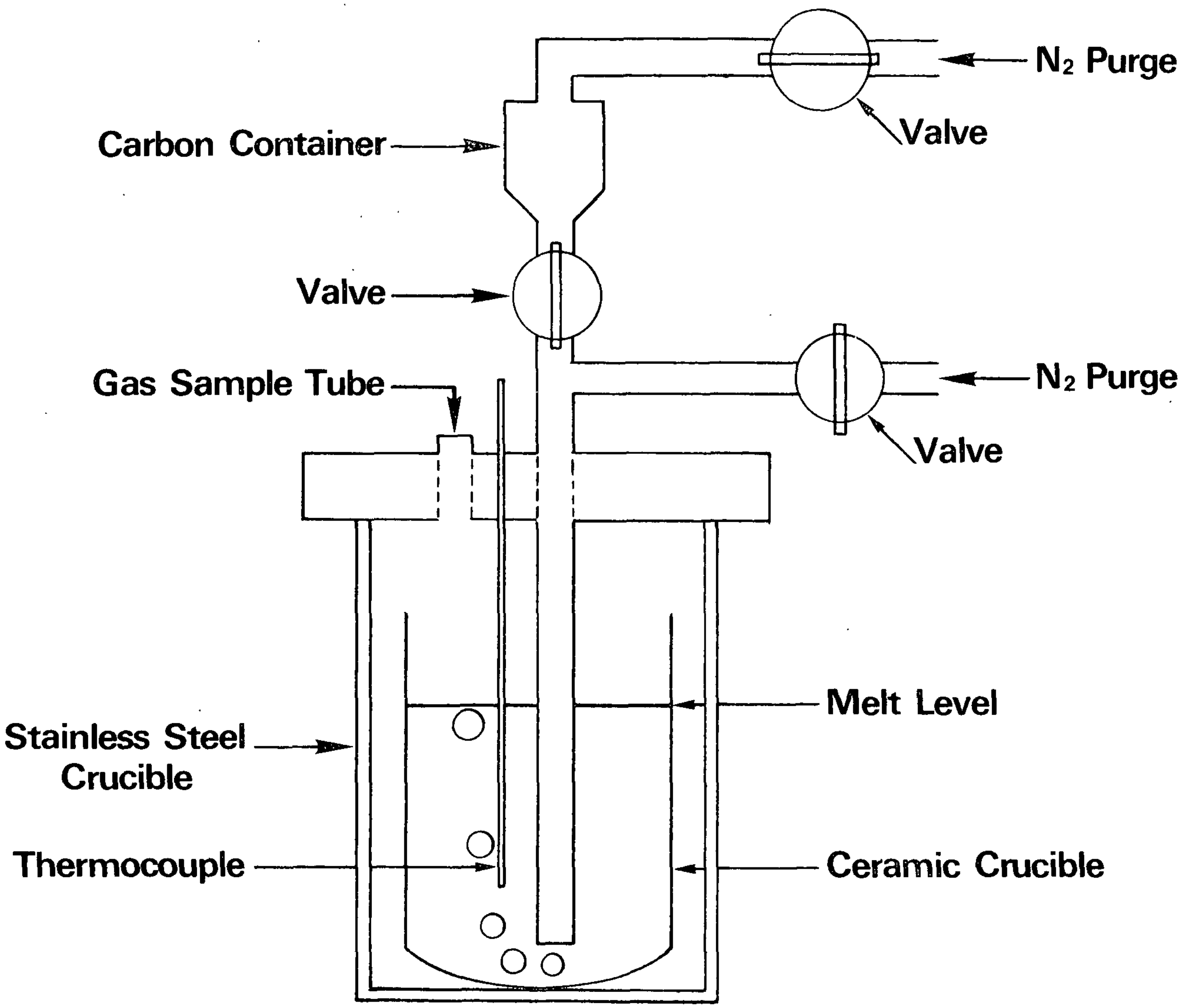

Figure 2. Experimental reactor.

Two methods of introducing carbon or carbonaceous char into the melt were used with this reactor. In the first method, the carbon was premixed with the carbonate and sulfate salts and placed in the reactor. This mixture was then rapidly heated to the desired reaction temperature. The sulfate-carbonate mixture normally required 5 to 10 minutes to melt and 15 additional minutes to reach a steady temperature. Although the temperature of the reactants is continually increasing, the effects of the sulfate and carbonate concentrations can be identified and the activation energy for the reduction reaction determined.

In the second method of adding carbon, the alkali carbonate and sulfate salts were mixed, added to the alumina crucible, and brought to a temperature slightly above the desired reaction temperature; reduction was then initiated by introducing the carbon through the purge tube using the valves shown in Fig. 2. After the carbon was added, approximately 2 minutes was required for complete mixing of the carbon and the melt. Using this approach a small amount of carbon was blown through the sample port and lost from the reactor. Since this loss of carbon caused some difficulty in the quantitative interpretation of the reduction data, most of the data contained in this report were obtained by premixing the carbon and salts.

Figure 3 illustrates the configuration of the experimental system. To accurately measure the flow rate of the nitrogen purge stream, the nitrogen was metered from a pressurized gas cylinder through a thermal mass flowmeter. This flowmeter provided an instantaneous reading of gas flow rate and a 0 to 5-V output signal. A mercury manometer monitored purge pressure and served as a pressure release valve. If the purge line from the reactor became plugged, the mercury in this manometer would be blown into a vial, releasing the purge pressure and preventing overpressurization of the reactor.

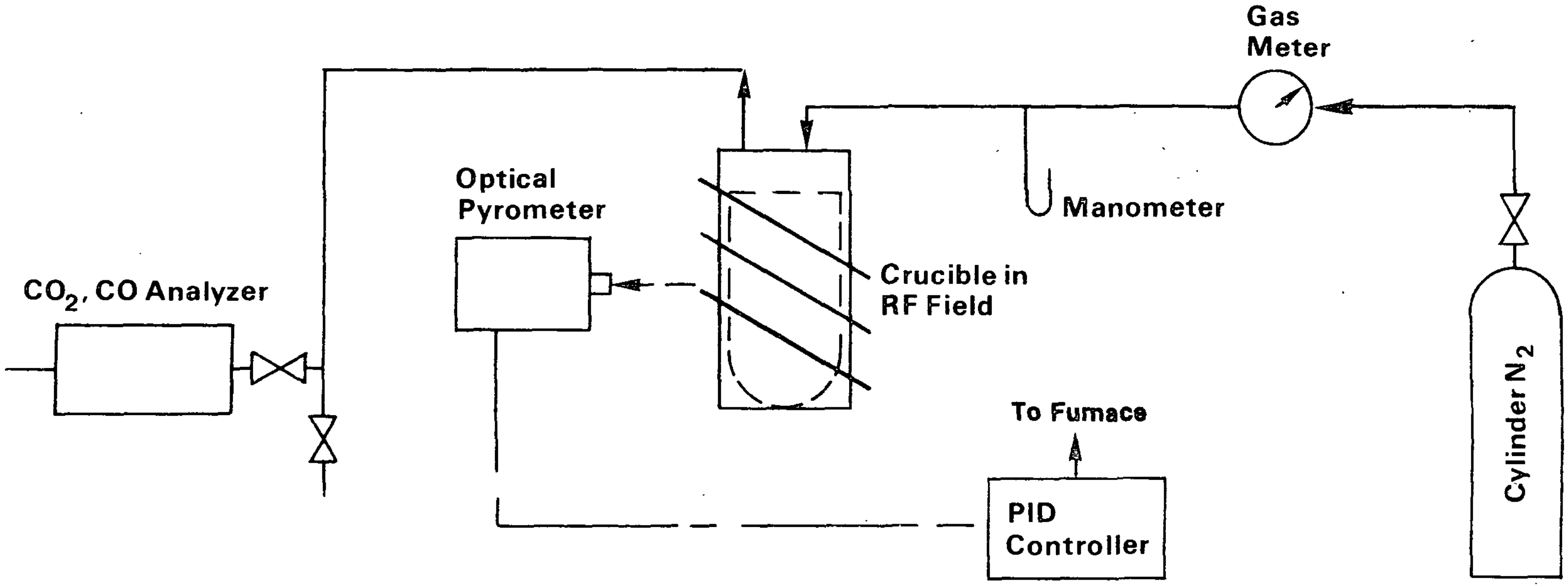

Figure 3. Experimental system.

The nitrogen purge stream plus any carbon dioxide or carbon monoxide generated by the reduction reaction was conveyed from the reactor in a 1/4-inch steel tube. This gas stream then passed through a filter to remove any particles and to a carbon monoxide-carbon dioxide gas analyzer (Model IR 702-703, Infrared Industries, Inc., Santa Barbara, California). This infrared analyzer could simultaneously measure both the carbon monoxide and carbon dioxide concentrations over a 0 to 30% range and provided a 0 to 100-mV output signal.

Using the optical pyrometer in Fig. 3 to monitor the temperature of the steel retort, the control system regulated furnace power, maintaining the steel retort at a constant temperature. By controlling the temperature of the steel retort, the desired melt temperature was maintained.

Since sulfate reduction with carbon produces carbon dioxide and carbon monoxide as products, the reduction was followed by monitoring the rate of carbon dioxide and carbon monoxide generation. From the nitrogen purge rate and the percentages of carbon dioxide and carbon monoxide in the sample gas, the carbon dioxide and carbon monoxide production rates and the sulfate reduction rate were determined.

The data acquisition system is illustrated in Fig. 4. In this system, the analog inputs from the infrared gas analyzer, melt thermocouple, optical pyrometer, and mass flowmeter are first converted to digital inputs. These inputs are then sampled several times a second, and an average value over a set time interval is recorded. During an experimental trial, the data acquisition program integrates the reaction rates, determines the melt composition, and provides a printed copy of the input data, reaction rates, and melt composition.

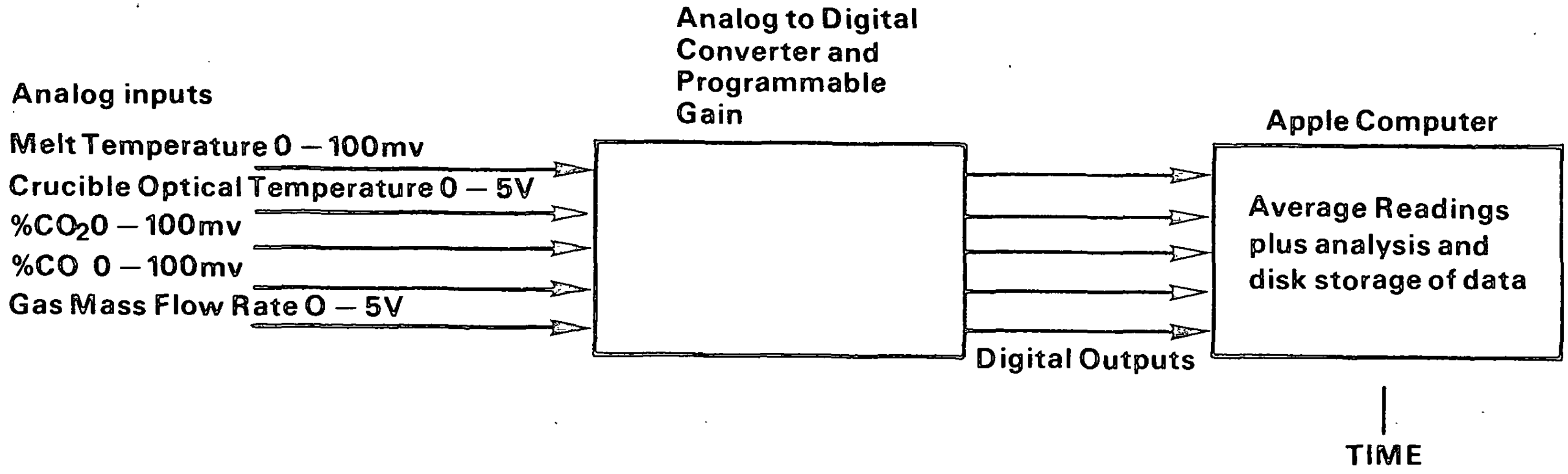

Figure 4. Data acquisition system.

EXPERIMENTAL RESULTS

EFFECT OF REACTOR CONFIGURATION ON EXPERIMENTAL RESULTS

The reactor heated by the induction furnace contained only 3.5% of the smelt contained in the large electrically heated reactor, while the product gases from the reduction reaction were removed with 10% of the nitrogen purge rate used with the large electrically heated reactor. Therefore, the gas flow rates per smelt volume are three times as great in the smaller reactor. To determine if the small reactor would produce experimental data similar to those obtained with the relatively large electrically heated reactor, several of the reduction experiments with graphite rods previously conducted in the large reactor were repeated using the small reactor.

Since the reactor configurations, melt mixing patterns, and purge rates are significantly different in the two reactors, comparison of the experimental data from the two systems will indicate what effect these variables have on the observed sulfate reduction rates. Any mass transfer influences on the reaction kinetics should also be evident in comparing the experimental data from the two reactor systems.

Sulfate reduction rates, determined from carbon dioxide and carbon monoxide generation for the two reactors, are shown in Fig. 5. Here, the level of carbon rods used in the small induction-heated reactor was selected to maintain the same ratio of carbon surface area per volume of melt to sulfate concentration in the two reactor systems. Therefore, the only experimental variable was the size of the reactors, with the large reactor containing 28.3 times more reactants than the smaller reactor.

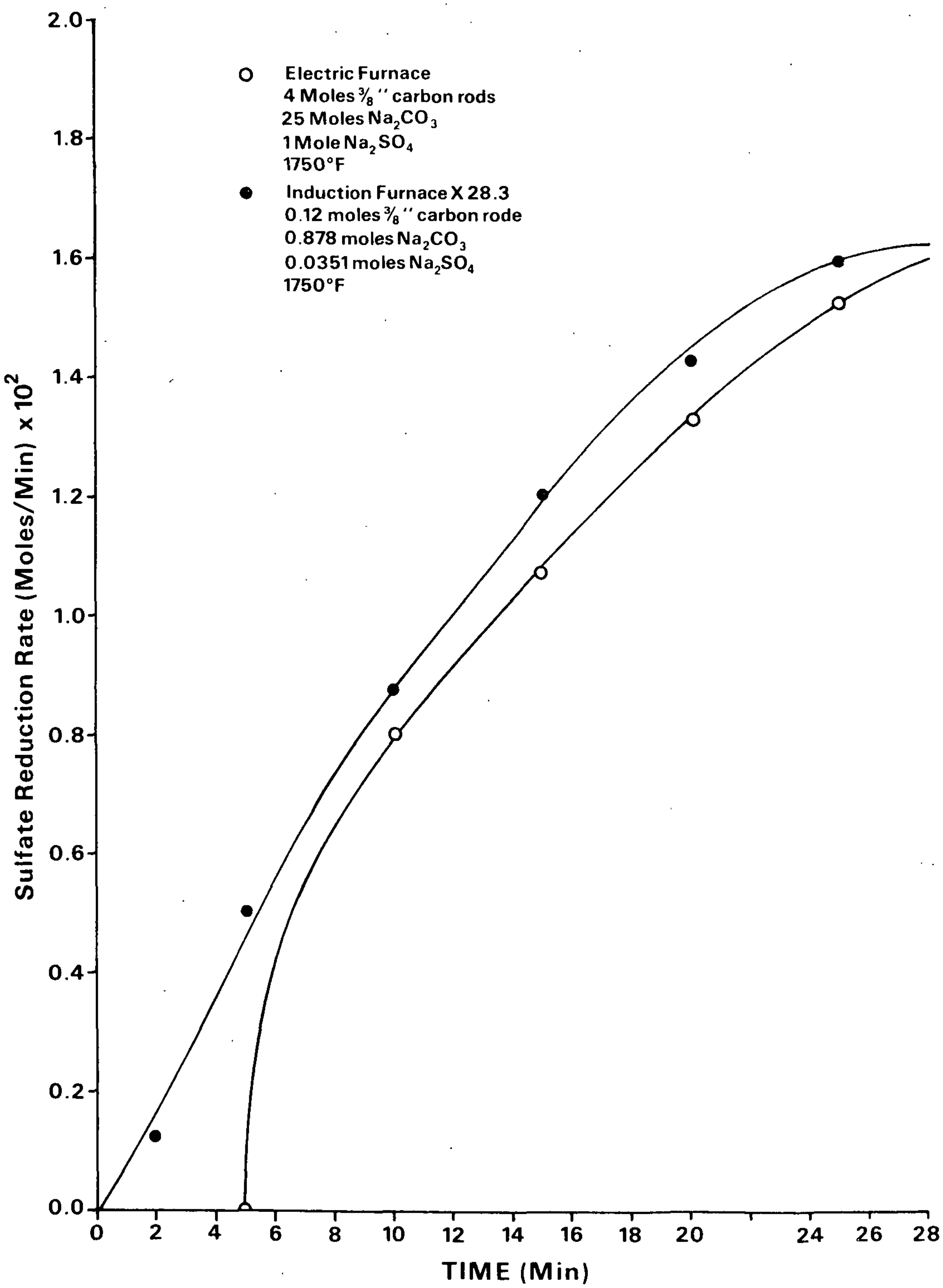

Figure 5. Effect of experimental system on sulfate reduction.

In Fig. 5, the sulfate reduction rate in the large electrically heated reactor is plotted directly against time, whereas the sulfate reduction rate in the smaller reactor is multiplied by the ratio of the two reaction systems (28 to 1) and then plotted vs. time. The relative reduction rates in the two reactor systems are nearly equal, with the maximum rate being only 3.7% higher in the smaller reactor. This difference in reduction rates is within the normal experimental variation with either reactor system.

One evident difference in the sulfate reduction rates in Fig. 5 is the lack of an induction period with the small reactor. With the large electrically heated reactor, a period of 5 to 7 min was required before any carbon dioxide or carbon monoxide generation was detected. With the small reactor in the induction furnace, carbon dioxide was observed almost immediately after the addition of the graphite rods. This difference in induction period was apparently due to the initial level of carbon dioxide in the melt. With the large furnace several hours were required to melt the salts and reach the desired reaction temperature. During this period, any carbon dioxide generated from the decomposition of the alkali carbonates was removed from the melt. With the small reactor in the induction furnace, only 10 to 15 min was required to melt the smelt and reach the desired temperature. Therefore, a considerably greater amount of carbon dioxide was being evolved from the small reactor when the carbon rods were added. Since carbon dioxide was previously found to initially catalyze sulfate reduction with carbon (1), it is likely that the greater level of carbon dioxide in the small reactor accounts for the lack of an induction period.

In both reactor systems, the dead time (volume of reactor, lines, and filter divided by the volumetric flow rate) is less than 30 sec and has little effect on either rate curve in Fig. 5. To verify the cause of this induction period, in one experiment the molten salts in the small reactor were held at temperature for two hours before introducing the graphite rods. Here, a five-minute induction period was observed, demonstrating that the induction period results from stripping the melt of carbon dioxide.

Using the large electrically heated reactor, sulfate reduction with graphite rods had an activation energy of approximately 50,000 cal/g-mole in Na_2CO_3 or Na_2CO_3/K_2CO_3 melts. To determine if sulfate reduction in the small reactor would have a similar temperature dependence, a series of reduction experiments with graphite rods at different temperatures was conducted. The reduction rate at each temperature was measured with 60% of the sulfate converted to sulfide. Here, an activation energy of approximately 51,000 ± 1600 cal/g-mole for sulfate reduction with graphite rods was obtained.

In comparing the two reactor systems, no differences were found in the experimental results from sulfate reduction with carbon rods. Therefore, any mixing or mass transfer effects appear to be minimal.

CARBONACEOUS REDUCING AGENTS

Three forms of carbon - graphite rods, pulverized graphite, and carbonaceous char - were studied as reducing agents. The graphite rods, obtained from Becker Brothers Carbon Corporation, Cicero, Ill., were 3/8-inch in diameter and cut to 0.48-inch in length. With the exception of the length, these rods were the same as those used with the large electrically heated reactor.

One of the essential differences between reduction in a kraft recovery furnace and the previous study of sulfate reduction with the graphite rods is size of the carbon particle. To produce small carbon particles, the graphite rods were pulverized to particles a few microns in diameter. The use of this material as the reducing agent enabled the effect of particle size to be identified with a carbon that could be readily characterized.

Carbonaceous black liquor char was produced by first drying kraft black liquor under vacuum at 150°C and then pyrolyzing the dried solids in a covered ceramic crucible at 950°C for 7 min. This pyrolyzing procedure is based on that recommended for determination of the volatile content of coal (2). During the pyrolysis of the dried black liquor, approximately 50% was volatilized. Different batches of char prepared in this manner provided very reproducible experimental data.

The results of an elemental analysis of the kraft black liquor char by Hoffman Laboratories, Inc., Wheat Ridge, Colorado, are shown in Table II. The elements in Table II total 96%. In addition to the elemental analysis, the char was analyzed for the major inorganic compounds, and the results of this analysis are also shown in Table II. By washing the char, it was found that 77% of the char was water soluble. This may be compared to the major inorganic compounds identified in Table II which constitute 65% of the char.

TABLE II

ELEMENTAL ANALYSIS OF CHAR

Elemental		Inorganic Compounds	
Element	Weight, %	Inorganic Compound	Weight, %
Carbon	29.36	Na_2CO_3	59.8
Hydrogen	0.65	Na_2S	2.9
Oxygen	33.78	Na_2SO_4	1.76
Sulfur	2.12		
Chlorine	0.56		
Potassium	3.39		
Sodium	26.0		
Total	95.9		64.5

The average particle size of the carbonaceous char and pulverized graphite was determined by measuring the particles with the aid of an electron microscope. The surface areas of the washed char and powdered graphite were measured by nitrogen gas absorption utilizing a gas-flow sorptometer and a reference sample of TiO_2. The surface area of the reference sample was 10.3 m^3/g. The particle size and surface area measurements for pulverized graphite and char are shown in Table III.

TABLE III

PARTICLE SIZE AND SURFACE AREA OF PULVERIZED GRAPHITE AND CHAR

Compound	Mean Particle Diameter, microns	BET Surface Area, m^2/g
Pulverized graphite	11.1 ± 11.3	19.7
Unwashed char	12.5 ± 7.55	25.2
Washed char	7.4 ± 4.7	580.1

From the carbon dioxide and carbon monoxide generated by sulfate reduction with char, it was found that the maximum total carbon evolved was 25.5% of the char. By subtracting the carbon content of the sodium carbonate in the char from the elemental carbon, the carbon which is not contained in the carbonate should be 22.7%, which is slightly less than that determined by product gas analysis.

Although the carbonate, sulfate, and sulfide were reported as sodium salts, approximately 10% of these compounds are potassium salts. From the carbonate, sulfate, and sulfide analysis, the potassium and sodium weigh 29.0% of the char, which compares closely with the 29.4% in the elemental analysis. The total sulfur in the sulfate and sulfide is 1.6% compared with 2.1% in the elemental analysis.

TYPICAL EXPERIMENTAL RESULTS

To study sodium sulfate reduction with either pulverized graphite or char, the pulverized graphite or char was premixed with the sodium sulfate and alkali carbonate salts and heated in the induction furnace. Since the melting point of sodium carbonate is 1563°F and reduction with char is quite rapid in a melt at 1450°F, a large fraction of the char in a sodium carbonate system would be consumed as the system melts. Therefore, with char as the reducing agent, the majority of the experimental data was acquired in a K_2CO_3/Na_2CO_3 system with a melting point of approximately 1300°F.

Typical sulfate reduction rates with pulverized graphite and char, illustrated by carbon dioxide and carbon monoxide generation in a K_2CO_3/Na_2CO_3 melt, are shown in Fig. 6 and 7. Here, the pulverized graphite and char were premixed with K_2CO_3, Na_2CO_3, and Na_2SO_4 salts and rapidly brought to the desired reaction temperature with the induction furnace. As the mixture was heated, the nitrogen purge stream continually removed any carbon dioxide and carbon monoxide generated in

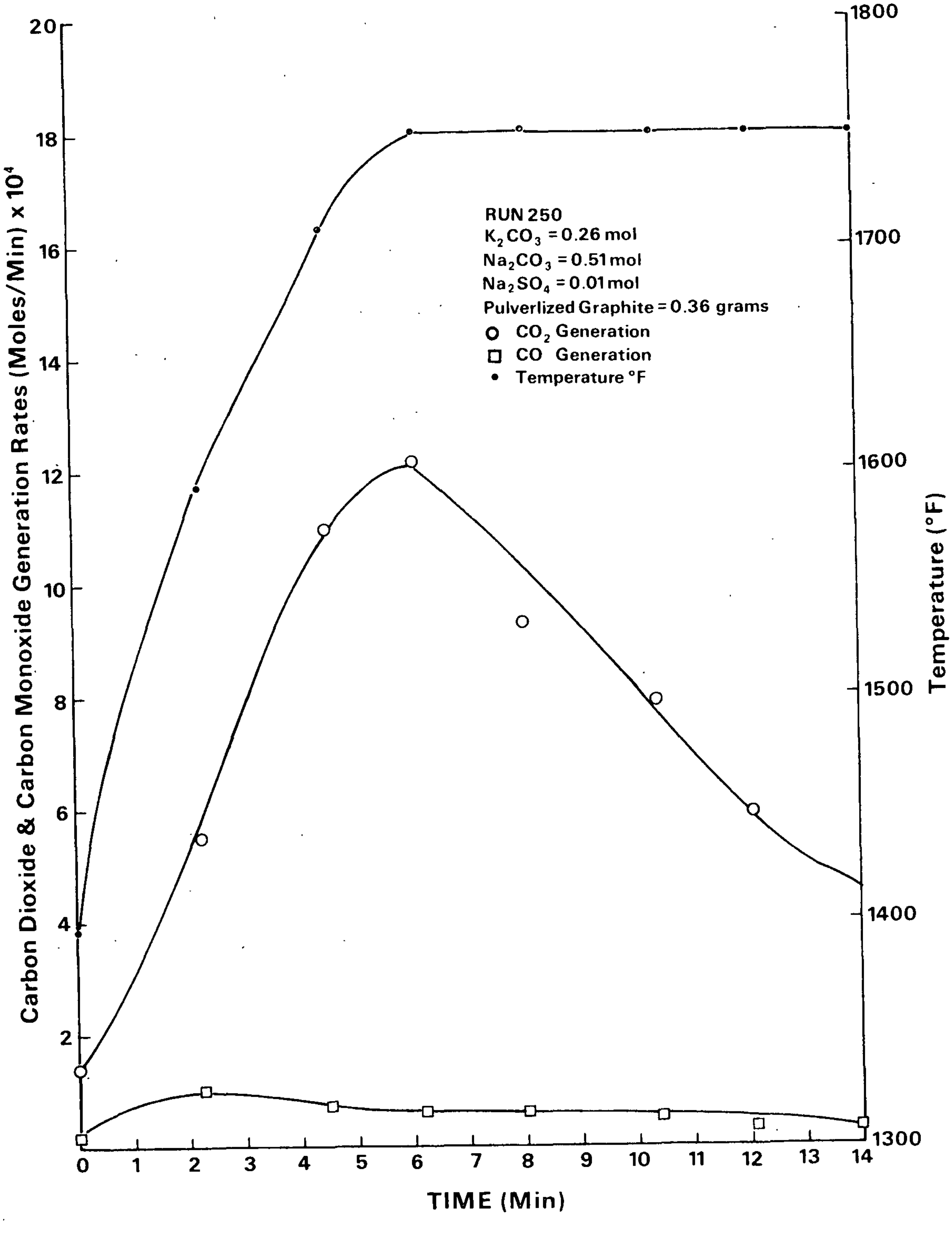

Figure 6. Sulfate reduction with pulverized graphite.

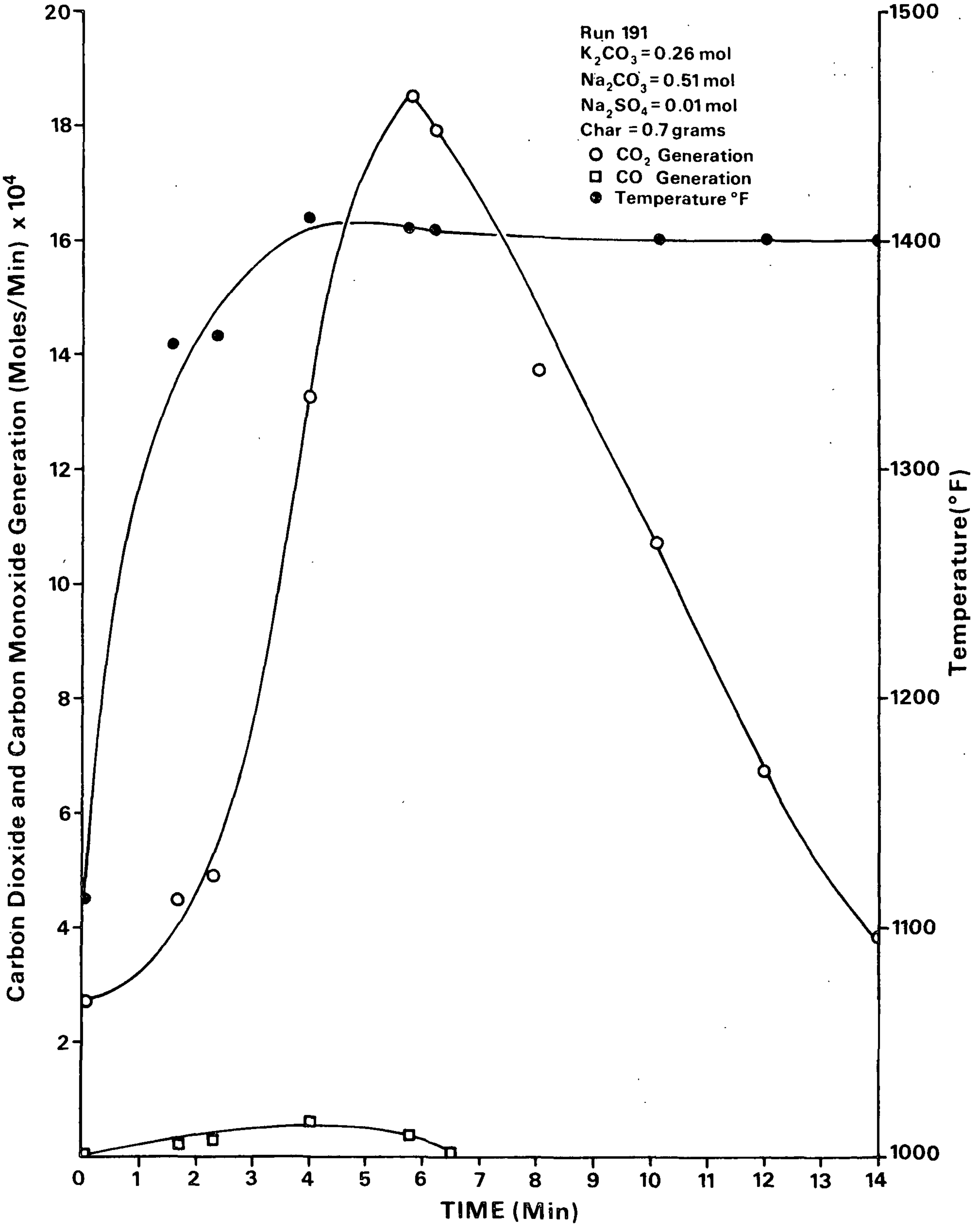

Figure 7. Sulfate reduction with kraft black liquor char.

the reactor. Little carbon dioxide and carbon monoxide gas was generated below the melting point of the salts. The desired reaction temperature, as seen in Fig. 6 and 7, was reached a few minutes after a molten state was achieved.

As the melt temperature increased, the carbon dioxide and carbon monoxide generation rates increased. Once the maximum melt temperature was reached, the carbon dioxide and carbon monoxide generation rates decreased due to the depletion of the carbon and sulfate in the reactor. As seen in Fig. 6 and 7, the sulfate reduction rate with char at 1400°F is the same order of magnitude as the rate with pulverized graphite at 1750°F. As illustrated in these figures, sulfate reduction with kraft black liquor char is a considerably faster reaction than sulfate reduction with pulverized graphite.

During the heating period, the temperature of the salts continually increases until the melting point of the system is reached. At this point, the temperature of the system remains constant for 1 to 2 minutes as the salts melt. In the K_2CO_3/Na_2CO_3 system, the melting point occurs at approximately 1300°F. Although the reduction rate is slow before a molten state is reached, the generation rates of carbon dioxide and carbon monoxide are recorded as the salts are heated through the melting point. These data allow the sulfate and sulfide composition of the melt to be determined at any time during the reaction.

The experimental data used to define the reduction reactions were obtained at temperatures where a homogeneous molten system was believed to exist. The existence of this homogeneous molten phase was confirmed in one experiment by inspecting the reactor immediately after the melting point of the system was exceeded.

One of the characteristics of sulfate reduction with graphite rods was the autocatalytic nature of this reaction (Fig. 1). In the experiments where the pulverized graphite and kraft black liquor char were premixed with the alkali carbonate and sodium sulfate salts (Fig. 6 and 7), it was difficult to determine if an autocatalytic reaction was occurring due to the continually increasing temperature; but there did not appear to be an autocatalytic effect.

To determine if sulfate reduction with either pulverized graphite or kraft black liquor char was an autocatalytic reaction, two experiments were conducted where these carbons were injected into the molten salts. Illustrated in Fig. 8 and 9 are the carbon dioxide and carbon monoxide generation rates and sulfate reduction rate with pulverized graphite and kraft black liquor char injected into the molten salts.

Approximately one minute was required for mixing of the carbon and the melt and for the generated product gases to reach the infrared carbon dioxide and carbon monoxide analyzer. As shown in these figures, the reduction rates continually decrease without any discernible autocatalytic effect. Therefore, sulfate reduction with either pulverized graphite or char is not an autocatalytic reaction.

Autocatalytic Nature of Sulfate Reduction with Graphite Rods

To define the nature of sulfate reduction with carbon and use the experimental information from the study of sulfate reduction with graphite rods, it is necessary to characterize the nature of the autocatalytic behavior of sulfate reduction with graphite rods. In the previous report on sulfate reduction with graphite rods, the autocatalytic nature of this reaction was ascribed to a continual increase in carbon dioxide in the melt. Although carbon dioxide appears to initially catalyze sulfate reduction with carbon, as noted in the comparison of the two reactor

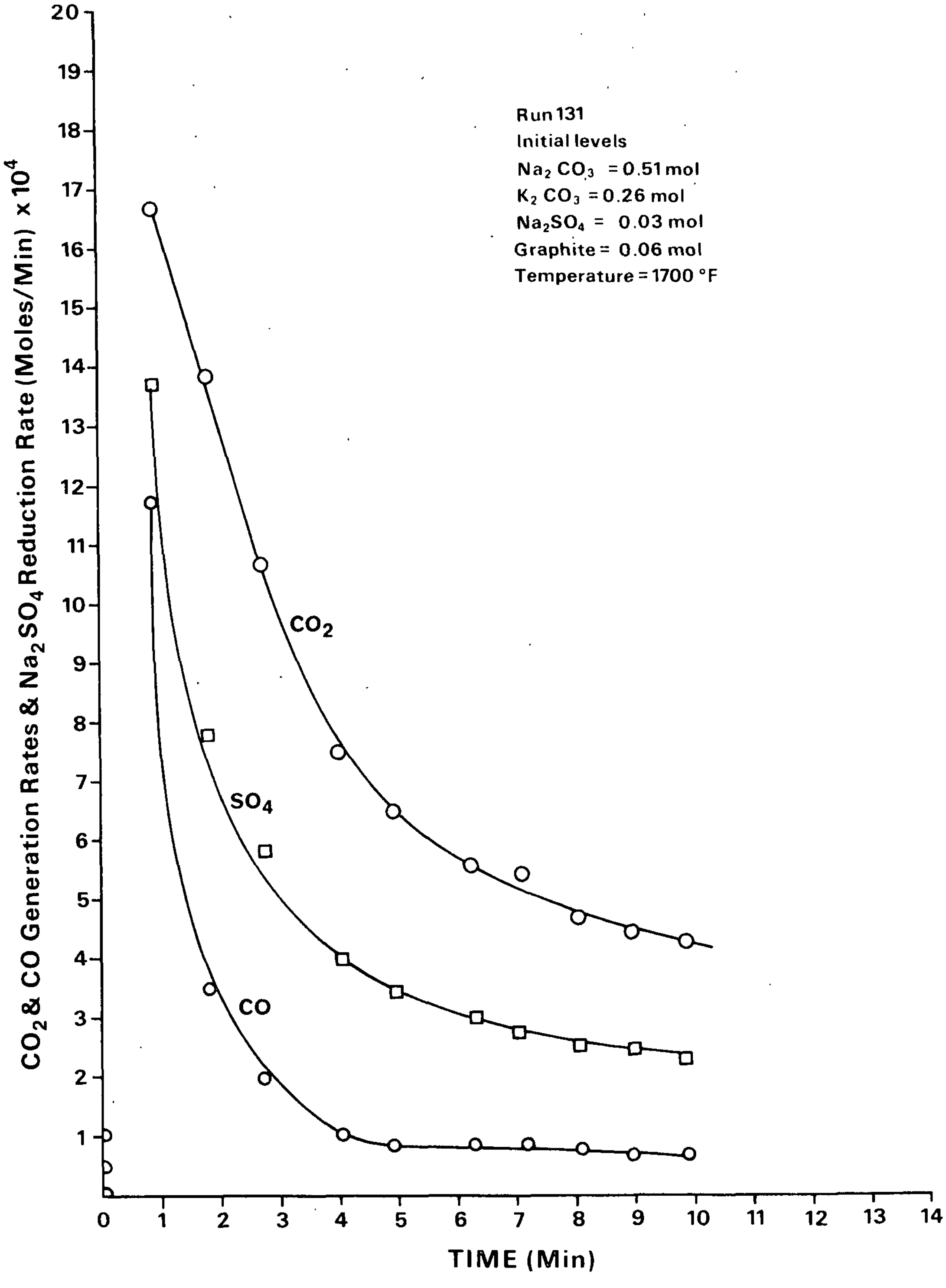

Figure 8. Sulfate reduction with pulverized graphite injected into melt.

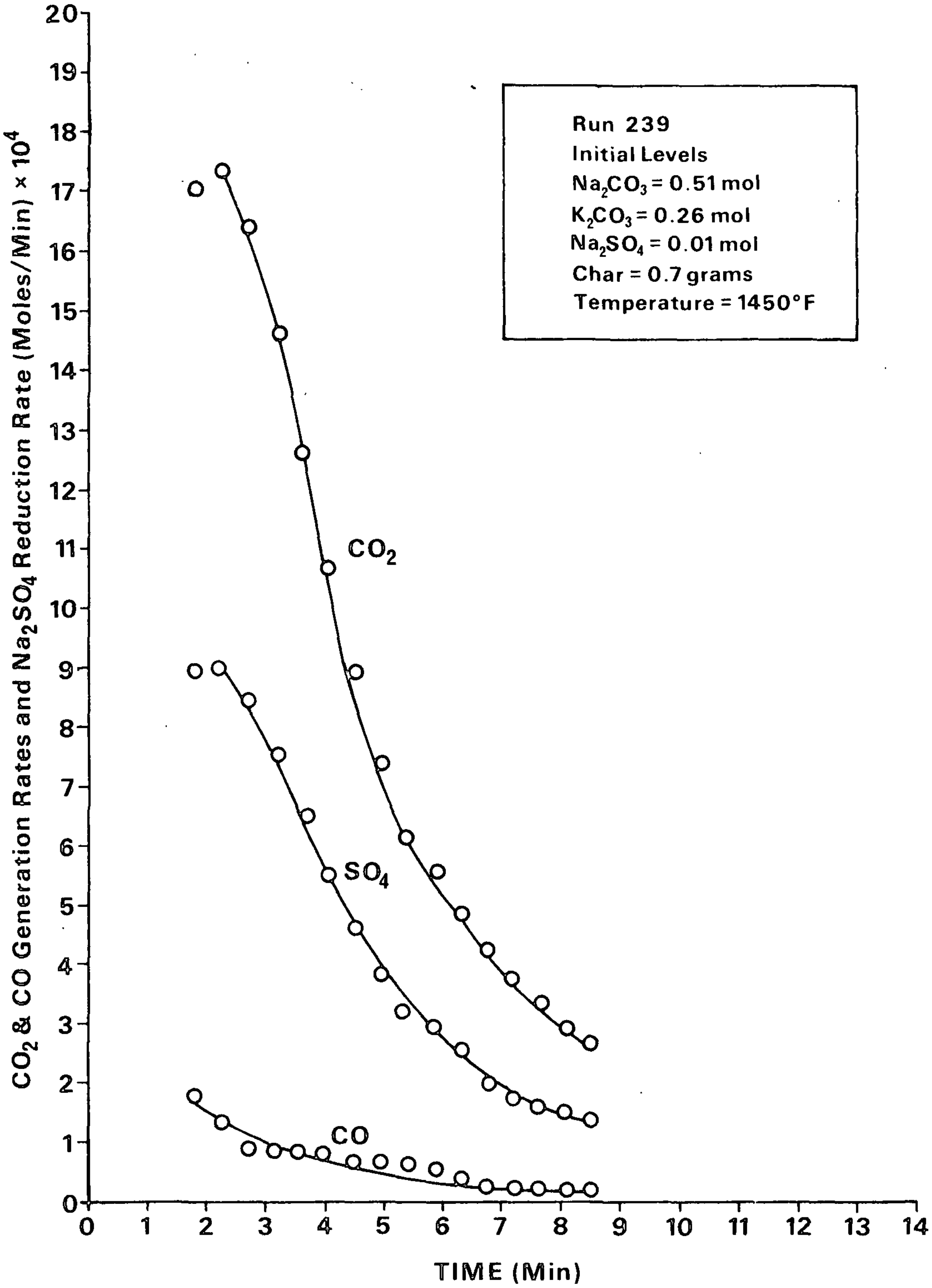

Figure 9. Sulfate reduction with kraft black liquor char injected into melt.

systems, increasing carbon dioxide in the melt does not appear to account for the autocatalytic nature of reduction with graphite rods. If the autocatalytic effect resulted from an increase in carbon dioxide, sulfate reduction with pulverized graphite and char (Fig. 8 and 9) should also be autocatalytic reactions. Therefore, to define the mechanism responsible for the autocatalytic nature of sulfate reduction with graphite rods, several additional reduction experiments using graphite rods were conducted.

With the reactor configuration used in the induction furnace, the graphite rods can be removed from the melt during a reduction experiment. Due to the experimental configuration, used in the previous reactor, this could not be accomplished during the earlier study of sulfate reduction with graphite rods. By using graphite rods that have been previously reacted with sulfate, any changes in reaction rate due to surface changes on the graphite can be identified.

In Fig. 10, the sulfate reduction rate for a previously reacted graphite rod is compared with the rate for an unreacted rod. Since the melt in these experiments was rapidly brought to the desired reaction temperature, a considerable amount of carbon dioxide from the decomposition of the alkali carbonates was being generated at the time of the carbon addition. Therefore, both reduction rates in Fig. 10 begin at relatively high levels. However, the sulfate reduction rate for the previously reacted graphite rod initially increases very rapidly followed by almost a plateau, while the sulfate reduction rate with the unreacted rod gradually increases. This demonstrates that a considerable amount of the autocatalytic nature of sulfate reduction with graphite rods is due to changes in the nature of the graphite surface.

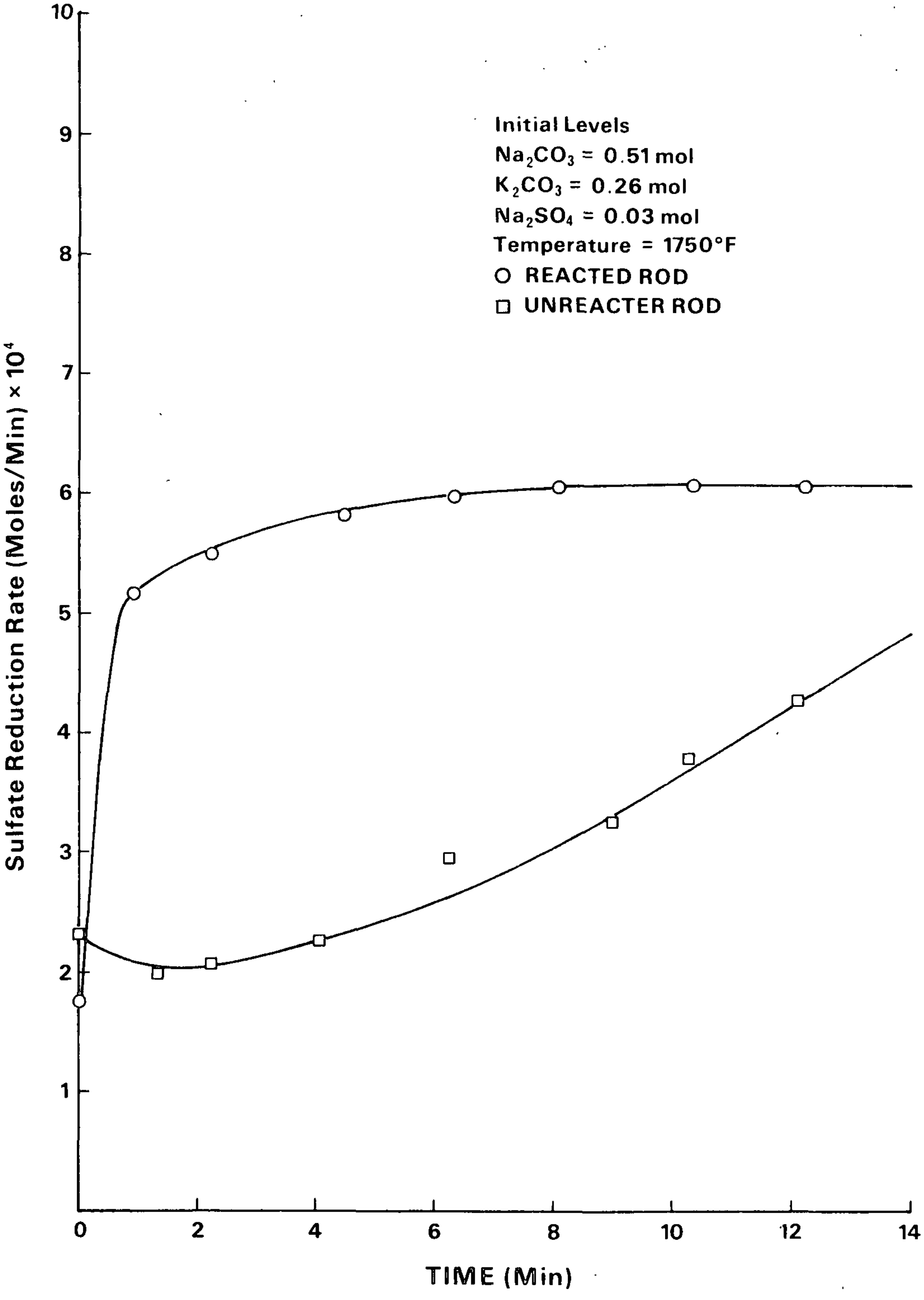

Figure 10. Effect of graphite rod surface oxidation by sulfate on sulfate reduction.

In the previous report on sulfate reduction with graphite rods (1), the effect of surface area on the reaction rate was determined by measuring the reduction rate at different levels of surface area and all other variables constant. Since the only variable was surface area, the order of the reaction in terms of surface area can be calculated. However, for this analysis to be valid, all surfaces must have the same degree of reactivity.

As shown in Fig. 10, the reactivity of the graphite rods is dependent on the extent of oxidation of the graphite. Therefore, to determine the effect of carbon surface area on the sulfate reduction rate, it is necessary to measure the rate at the point in time where the graphite rods have experienced the same degree of oxidation per unit surface area. Figure 11 illustrates the effect of carbon surface area on the rate of sulfate reduction with graphite rods. Here, each unit surface area on the graphite rods has been oxidized to the same extent by the sulfate.

The melts in Fig. 11 initially contained the same level of sulfate but different levels of graphite rods. For each unit surface area on the graphite rods to be oxidized to the same extent at the time the reduction rate was measured required that the rate be measured with the extent of sulfate reduction proportional to the graphite surface area in the melt. Therefore, if the number of carbon rods for a particular run was doubled, the reduction rate was measured with twice the amount of sulfate reduced. The melts in Fig. 11 contained a relatively high level of sulfate, and it was previously found that at high levels of sulfate the reduction rate is independent of the sulfate concentration. Therefore, although the rate measurements were made with different levels of sulfate, this had no effect on the sulfate reduction rate.

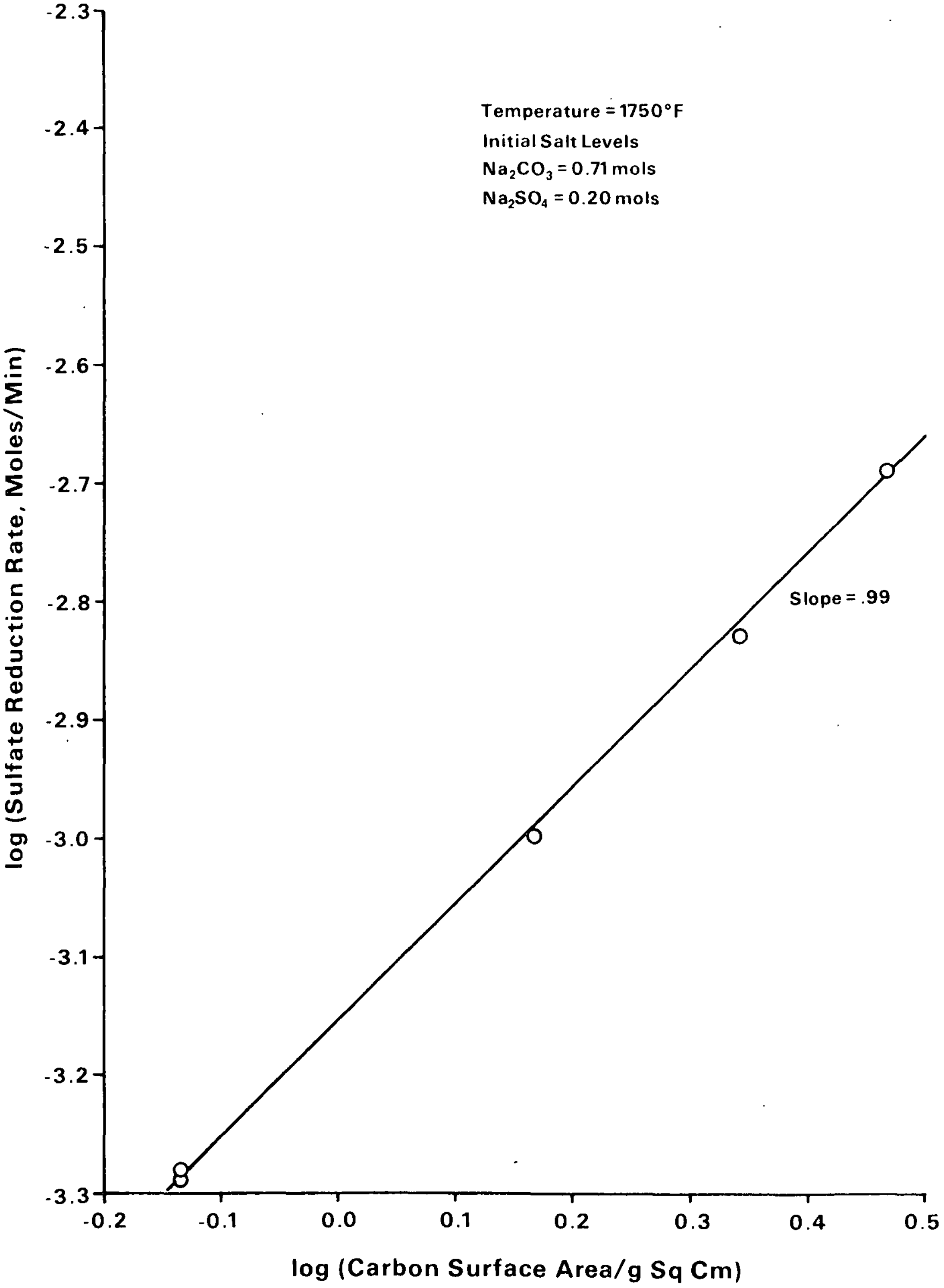

Figure 11. Effect of carbon surface area on sulfate reduction with graphite rods.

In Fig. 11, the log of the sulfate reduction rate is plotted vs. the log of the carbon surface. Since the slope of the curve in this plot is one, the sulfate reduction rate is directly proportional to the carbon surface area.

The autocatalytic nature of sulfate reduction with graphite rods results from an increase in reactivity of the graphite surface. This increase in reactivity is due to an increase in active sites resulting from the oxidation of the surface by sulfate. With all surfaces oxidized to the same extent, ensuring that all surfaces contain the same number of active sites, sulfate reduction is proportional to the surface area. This demonstrates that reduction is proportional to the number of active sites on the carbon surface.

EFFECT OF CARBON LEVEL ON SULFATE REDUCTION

In contrast to the behavior of sulfate reduction with graphite rods, no autocatalytic effect was observed in sulfate reduction with either pulverized graphite or black liquor char. To determine the effect of varying levels of pulverized graphite on sulfate reduction, the sulfate reduction rate was measured at 1700°F with different initial amounts of graphite present. The effect of pulverized graphite level on sulfate reduction was then determined by measuring the rate of reduction with the same amount of sulfate reduced. This ensured that the only experimental variable was the level of pulverized graphite. As shown in Fig. 12, the sulfate reduction rate was directly proportional to the amount of graphite present. If the moles of graphite in the reactor were doubled, the sulfate reduction rate also doubled.

The effect of the black liquor char level on sulfate reduction was also determined by varying the initial level of char present and measuring the reduction

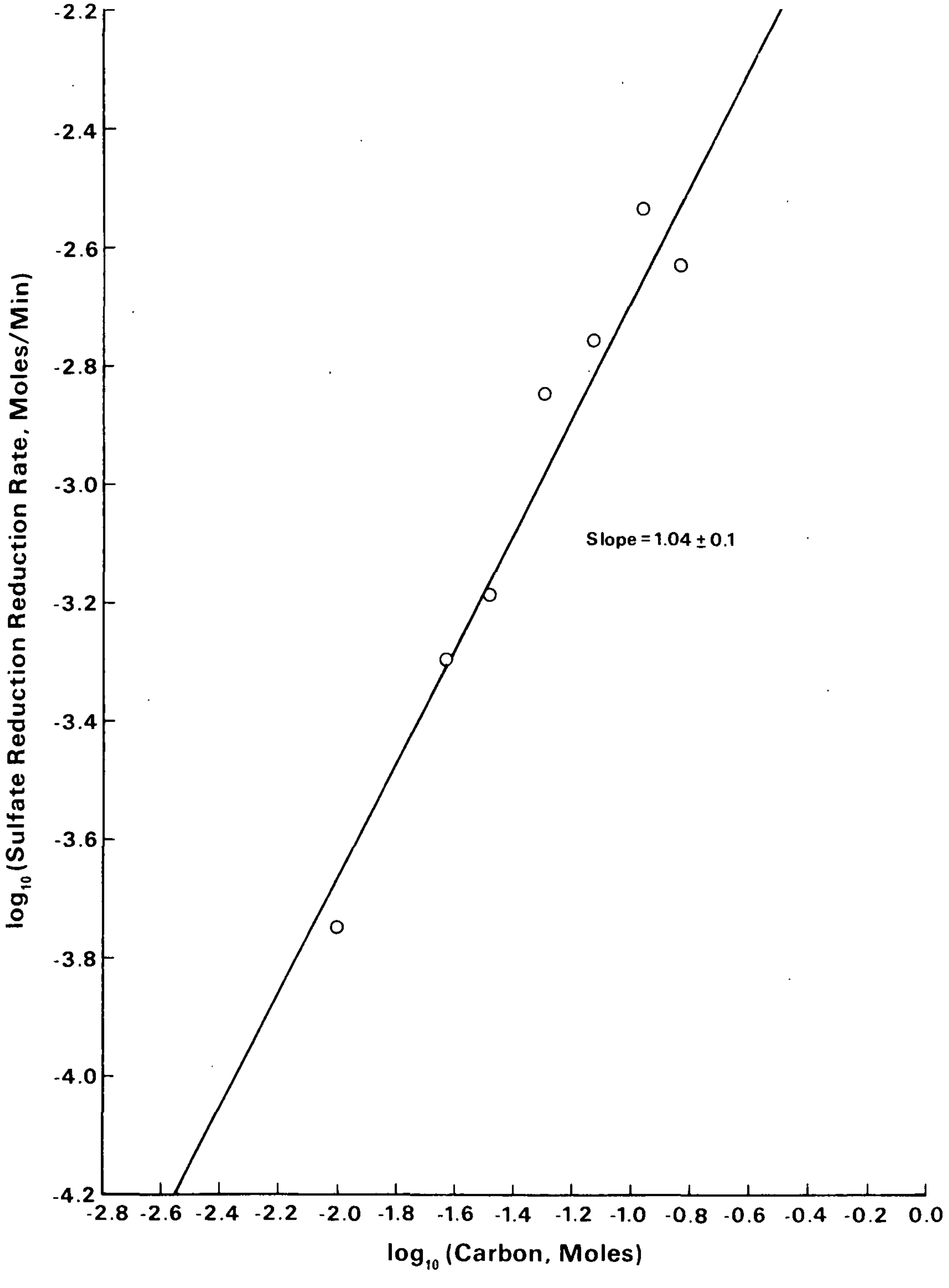

Figure 12. Effect of pulverized graphite level on sulfate reduction.

rate with the same amount of sulfate reduced. The effect of the level of char on the sulfate reduction rate is shown in Fig. 13. Again, the sulfate reduction rate was directly proportional to the amount of char.

Here, the rate of sulfate reduction with either pulverized graphite or kraft black liquor char was determined to be first order in terms of the amount of carbon present. Previously, sulfate reduction with graphite rods was found to be first order in terms of rod surface area, once all surfaces were oxidized to the same extent. This change in dependence on surface area to dependence on mass results from the use of small irregular graphite and char particles compared with large regular rods. Scanning electron microscope photographs of the pulverized graphite and char reveal these particles to be a few microns in diameter, highly fractured, and irregularly shaped. With such particles, the ratio of surface area to particle mass remains relatively constant as the particles are oxidized by sulfate, and reduction can be expressed as first order in carbon mass.

EFFECT OF SULFATE LEVEL ON SULFATE REDUCTION

During the previous sulfate reduction studies using graphite rods (1), the sulfate reduction rate varied from zero order in sulfate at high sulfate levels to first order in sulfate at low sulfate levels. At sodium sulfate levels greater than 7 wt.% sodium sulfate in the melt, the level of sulfate had no effect on the rate of sulfate reduction with graphite rods, and at sulfate levels less than 3.3 wt.%, the rate of sulfate reduction was directly proportional to the level of sulfate in the melt.

For pulverized graphite and char, the effect of sulfate on the reduction rate was determined by measuring the reduction rate at the same level of carbon present but at different sulfate levels. Figure 14 illustrates the sulfate effect on

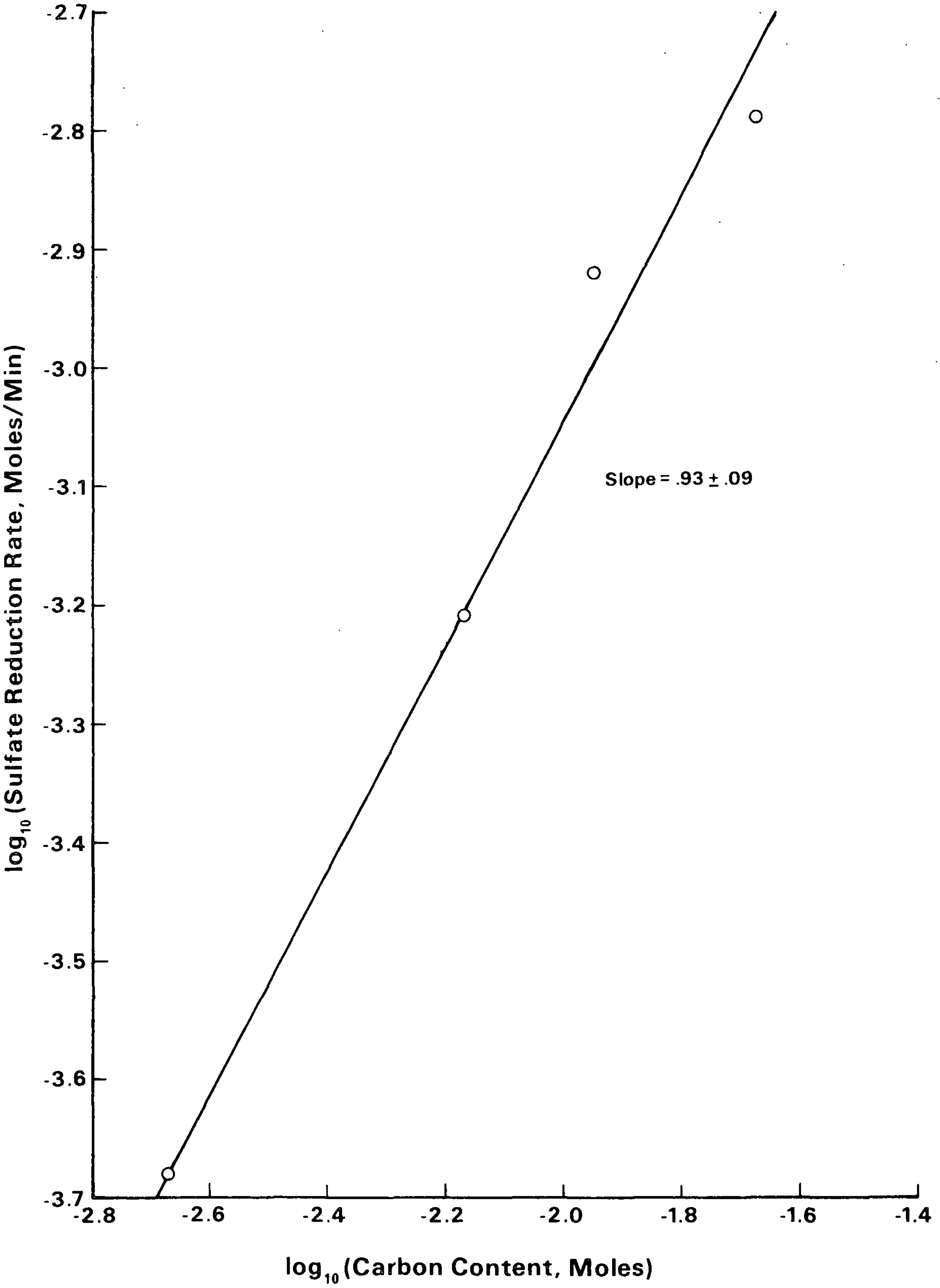

Figure 13. Effect of kraft black liquor char level on sulfate reduction.

sulfate reduction with pulverized graphite. Here, the sulfate reduction rate was measured at 1750°F with 0.006 mole of the initial sulfate converted to sulfide. All the experimental systems shown in Fig. 14 initially contained 0.51 mole of Na_2CO_3, 0.26 mole of K_2CO_3, 0.06 mole of graphite, and varying levels of Na_2SO_4.

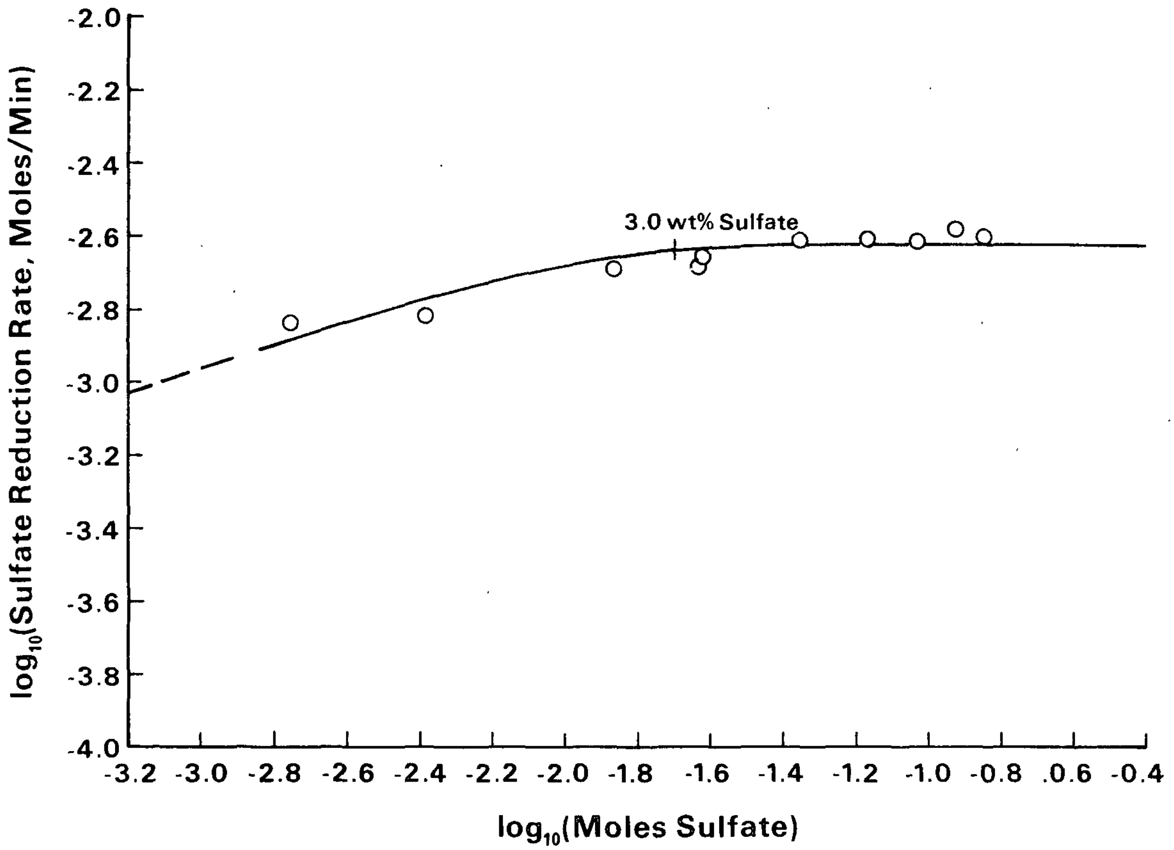

Figure 14. Effect of sulfate level on sulfate reduction with pulverized graphite.

With the exception of a slight decrease in the sulfate reduction rate at low levels of sulfate, the reduction rate with pulverized graphite is essentially independent of the sulfate level. Although the level of sulfate in Fig. 14 varies by two orders of magnitude, the sulfate reduction rates show only a slight variation.

Figure 15 illustrates the sulfate effect on sulfate reduction with kraft black liquor char. Here, the sulfate reduction rate was measured at 1400°F with 0.0025 mole of the initial sulfate converted to sulfide. All the experimental systems shown in Fig. 15 initially contained 0.51 mole of Na_2CO_3, 0.26 mole of K_2CO_3, 0.70 gram of char, and varying levels of Na_2SO_4.

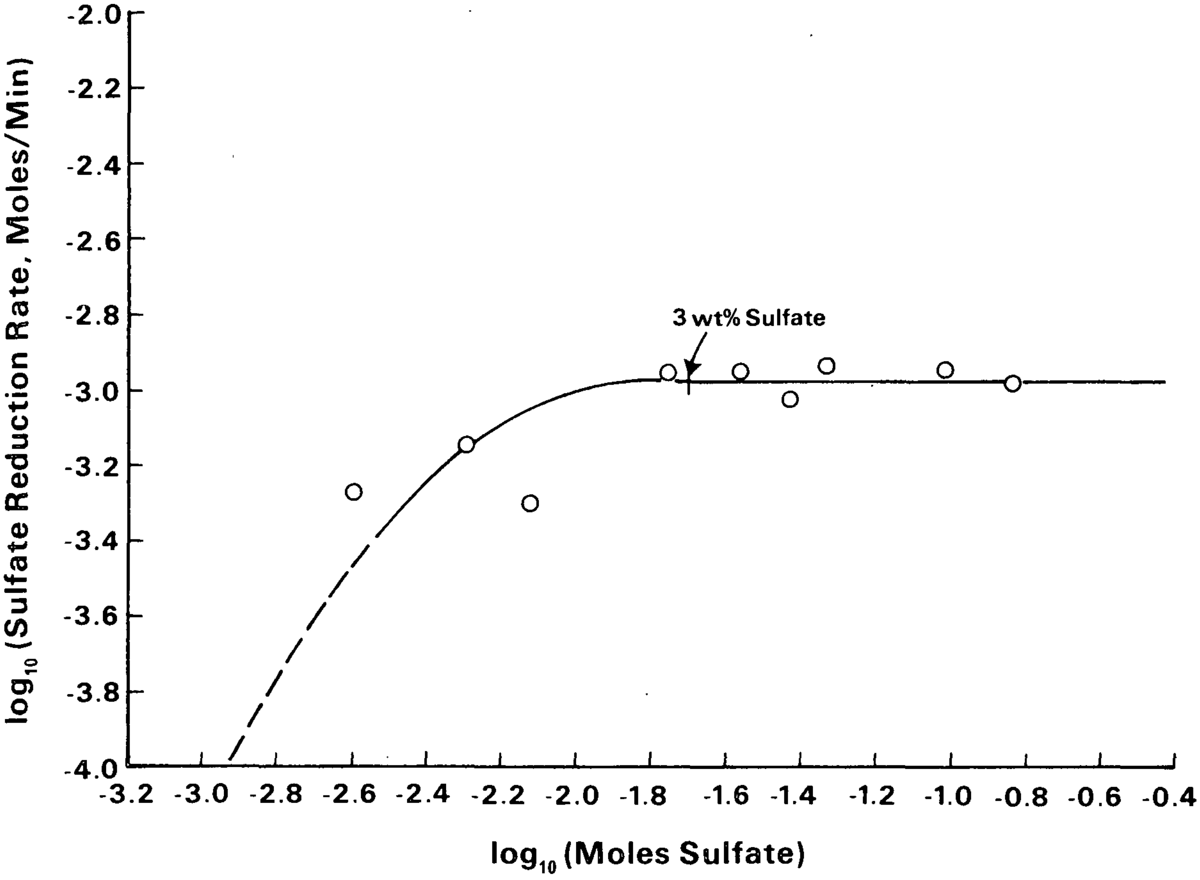

Figure 15. Effect of sulfate level on sulfate reduction with kraft black liquor char.

Again, with the exception of a slight decrease in the sulfate reduction rate at low levels of sulfate, the reduction rate with black liquor char is essentially independent of the sulfate level. While the sulfate level in Fig. 15 varies by two orders of magnitude, the sulfate reduction rate shows only a slight variation.

The effect of the sulfate on reduction with either pulverized graphite or char is similar. With both types of carbon, reduction is independent of the sulfate level until the sulfate level in the melt is less than 3.0 wt.% Na_2SO_4. [At a 30% sulfidity and with sulfidity defined as $Na_2S/(Na_2S + NaOH + Na_2CO_3)$ all expressed as Na_2O, a 3 wt.% Na_2SO_4 is equivalent to a reduction efficiency of 93%.] Therefore, at levels of sulfate greater than 3 wt.%, the reduction rate with either pulverized graphite or char is dependent only on the amount of carbon present and the temperature.

EFFECT OF TEMPERATURE ON SULFATE REDUCTION

To determine the effect of temperature on sulfate reduction with pulverized graphite and kraft black liquor char, the rate of sulfate reduction was measured at various temperatures in a melt consisting of Na_2CO_3, K_2CO_3, and Na_2SO_4. These salts produced a system with a melting point of 1300°F and generate only a trace of carbon dioxide from the decomposition of the carbonates. In Report One of this study (1), it was shown that the addition of K_2CO_3 to a Na_2CO_3/Na_2SO_4 melt had no effect on the activation energy. The rate of sulfate reduction with pulverized graphite was studied over a temperature range from 1600 to 1850°F, while sulfate reduction with char was studied over a temperature range from 1400 to 1550°F.

The activation energies for sulfate reduction with pulverized graphite and kraft black liquor char were calculated assuming that the temperature dependency can be represented by Arrhenius' Law [Eq. (2)].

$$\text{Rate} = K_o e^{-\Delta E/RT} f(\text{composition}) \qquad (2)$$

where K_o is the frequency factor

ΔE is the activation energy

R is the ideal gas constant

T is the absolute temperature

f(composition) represents the composition-dependent terms

The activation energies were calculated using a least squares fit of the natural logarithm of the sulfate reduction rate, moles/minute, vs. the reciprocal of the absolute temperature, $°K^{-1}$. The activation energies for sulfate reduction with pulverized graphite and kraft black liquor char were based on the reduction rates at 50% of the sulfate converted to sulfide. Since the initial concentrations of reactants were the same in each experiment, at 50% conversion the composition-dependent terms in Eq. (2) are constant and the reaction rates are a function only of temperature. Table IV illustrates the activation energies for sulfate reduction with the three forms of carbon studied.

TABLE IV

EFFECT OF TEMPERATURE ON SULFATE REDUCTION

Carbon Form		Graphite Rods	Pulverized Graphite	Black Liquor Char
Composition, mole%	Na_2CO_3	57.7	63.4	65.4
	K_2CO_3	38.5	32.5	33.3
	Na_2SO_4	3.8	3.8	1.3
Temperature range, °F		1600-1850	1600-1850	1400-1550
Activation energy, Kcal/mol		51.0 ± 1.7	44.0 ± 1.2	29.0 ± 1.0

EFFECT OF CARBON DIOXIDE ON SULFATE REDUCTION

In the previous study of sulfate reduction with graphite rods (1), it was found that carbon dioxide added to the melt would initially catalyze sulfate reduction, and the autocatalytic nature of sulfate reduction with graphite rods was then ascribed to an increase in carbon dioxide in the melt. However, it later determined that this autocatalytic behavior is due to changes in the nature of the graphite surface. Therefore, to understand the sulfate reduction mechanism with carbon, it was necessary to reexamine the role of carbon dioxide in this reaction.

With an alkali carbonate melt, there is a relatively high level of carbon dioxide dissolved in the melt from the decomposition of the carbonate,

$$Na_2CO_3 \rightleftharpoons Na_2O + CO_2(g)$$

If sulfate reduction is catalyzed by carbon dioxide, the rate of sulfate reduction with carbon should be considerably reduced in a noncarbonate melt where little carbon dioxide would be present. The solubility of carbon dioxide, reported as Henry's law constants, Table V, is significantly lower in sodium chloride than in sodium carbonate, and no carbon dioxide would be present from decomposition reactions in sodium chloride. To estimate the dissolved carbon dioxide content of the carbonate melts used in this study, the partial pressure of carbon dioxide was measured over these melts without carbon present. Sodium carbonate initially generated a partial pressure of approximately 0.004 atm. carbon dioxide as it was heated from its melting point to 1800°F. Using the Henry's law constant for sodium carbonate in Table V and this partial pressure, the estimated dissolved carbon dioxide content of this melt is 4×10^{-8} mol CO_2/cc of melt. Since noncarbonate melts generate no carbon dioxide, they would initially have no dissolved carbon dioxide present.

TABLE V

SOLUBILITY OF CARBON DIOXIDE IN SODIUM CHLORIDE AND SODIUM CARBONATE

Melt	Temp., °C	CO_2 Solubility, mol/cc-atm	Reference
Na_2CO_3	880	$(9.6 \pm 2.3) \times 10^{-6}$	(<u>3</u>)
NaCl	950	$(0.99 \pm 0.18) \times 10^{-6}$	(<u>4</u>)
	1000	$(1.01 \pm 0.12) \times 10^{-6}$	

To determine the effect of reduced levels of carbon dioxide, sulfate reduction rates with graphite rods, pulverized graphite, and char were measured in sodium chloride-sodium sulfate melts. In Fig. 16, the sulfate reduction rate with graphite rods in sodium chloride is compared with the reduction rate in sodium carbonate. As illustrated in this figure, sulfate reduction is considerably slower in a sodium chloride melt compared with a sodium carbonate melt. Fourteen minutes after the addition of the graphite rod, the sulfate reduction rate in sodium chloride is approximately only 10% of the rate in sodium carbonate.

In Fig. 17, the sulfate reduction rate with pulverized graphite in sodium chloride is compared with the reduction rate in sodium carbonate. Again, the reduction rate in sodium carbonate is an order of magnitude greater than the reduction rate in sodium chloride. Since there is little autocatalytic effect with pulverized graphite, the reaction rates in both melts decrease as the carbon and sulfate are consumed.

In Fig. 18, the sulfate reduction rate with char in sodium chloride is compared with the reduction rate in sodium carbonate. In these experiments, the char was first washed to remove as much of the carbonate as possible and then injected into the melt at the desired reaction temperature. With char, the reduction rate was also an order of magnitude lower in the sodium chloride melt.

These results demonstrate that sulfate reduction with all forms of carbon studied is catalyzed by carbonate melts. This catalytic action of carbonate appears to be due to the level of dissolved carbon dioxide in these melts. However, carbon dioxide appears to be only an initiating catalyst. If relatively high levels of carbon dioxide continued to catalyze sulfate reduction, reduction with pulverized graphite and char should be autocatalytic reactions. Also, if increasing levels of carbon dioxide continued to produce a catalytic effect, it is unlikely that the first order rate dependence of reduction on carbon previously described for

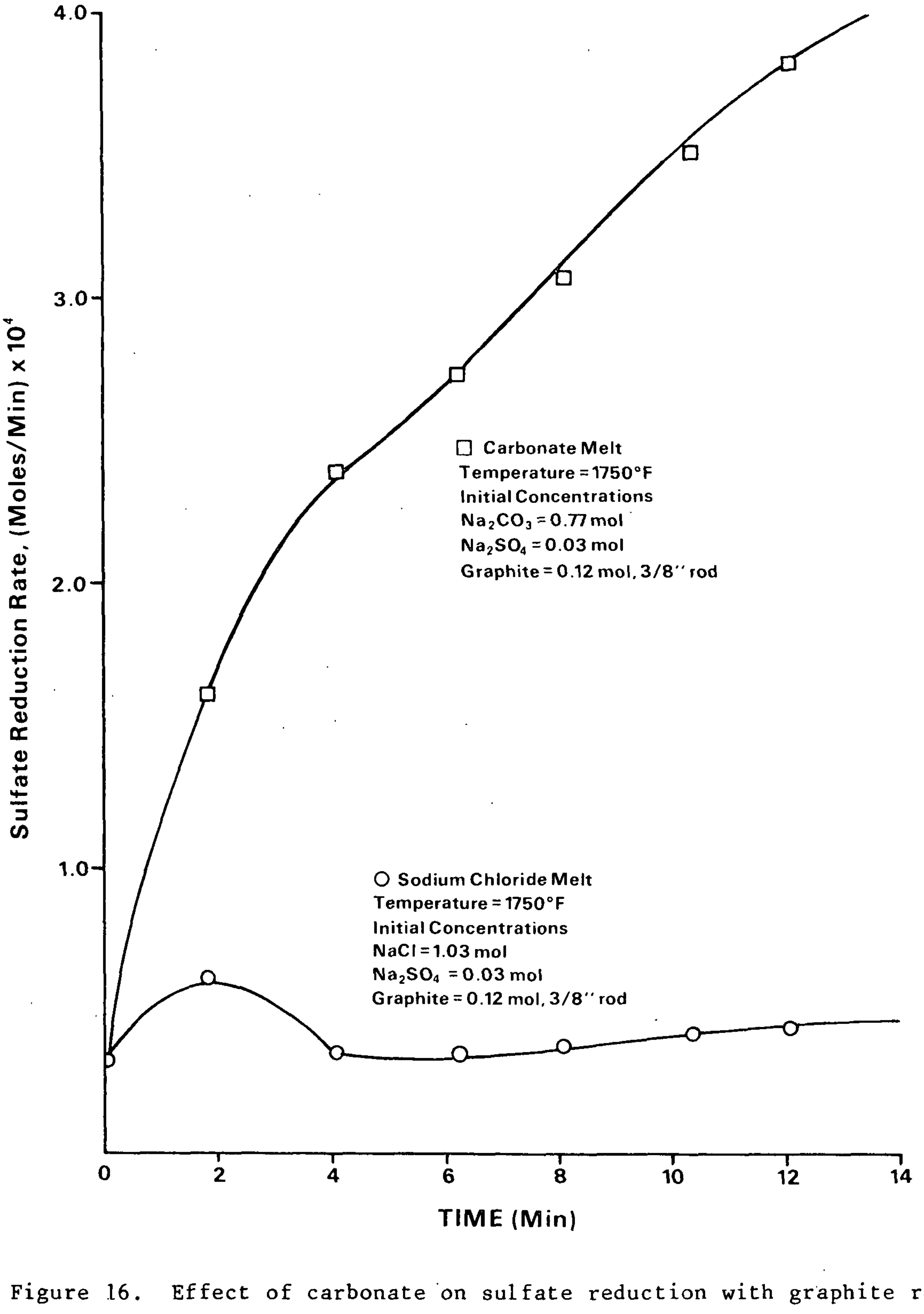

Figure 16. Effect of carbonate on sulfate reduction with graphite rods.

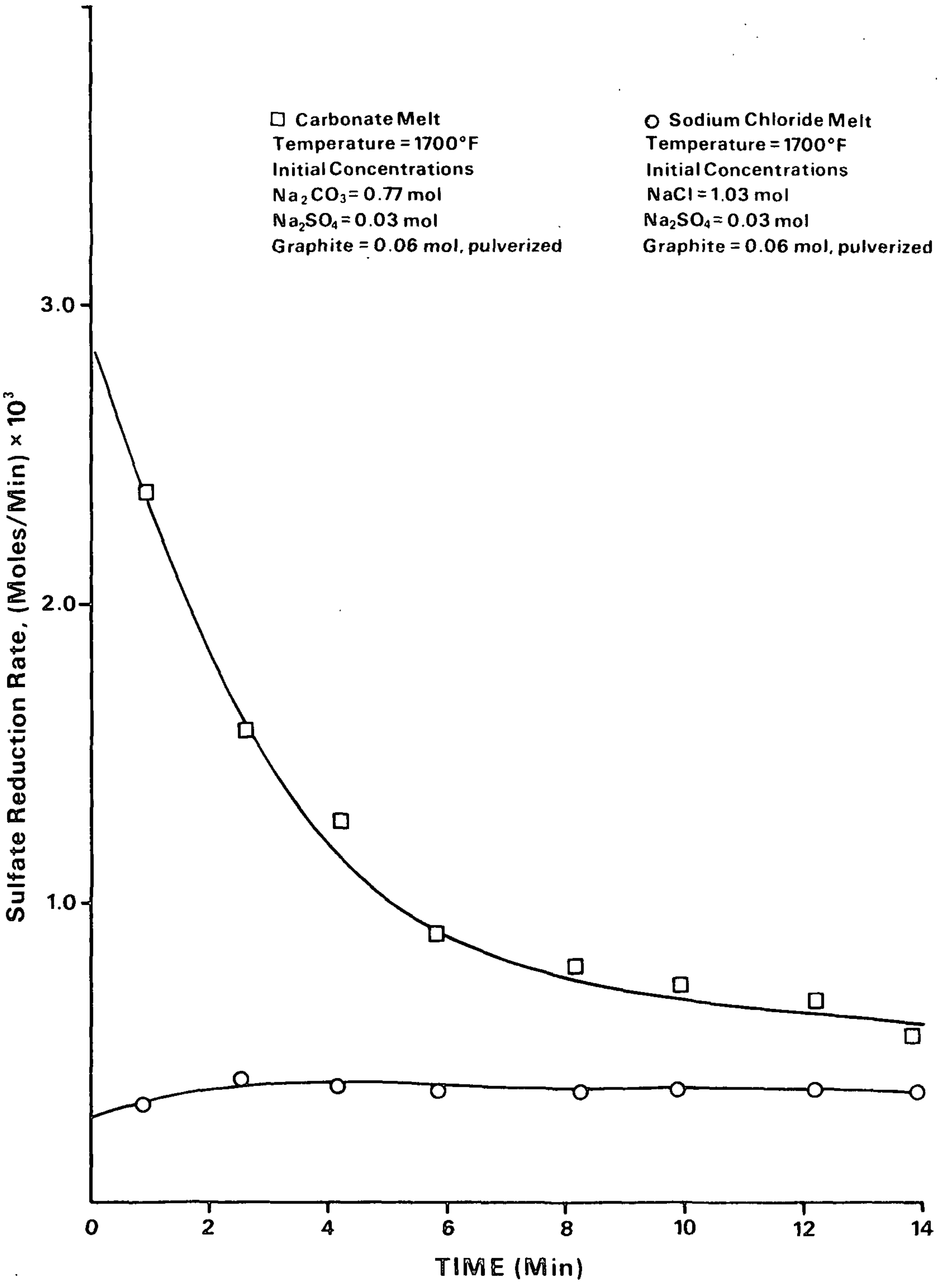

Figure 17. Effect of carbonate on sulfate reduction with pulverized graphite.

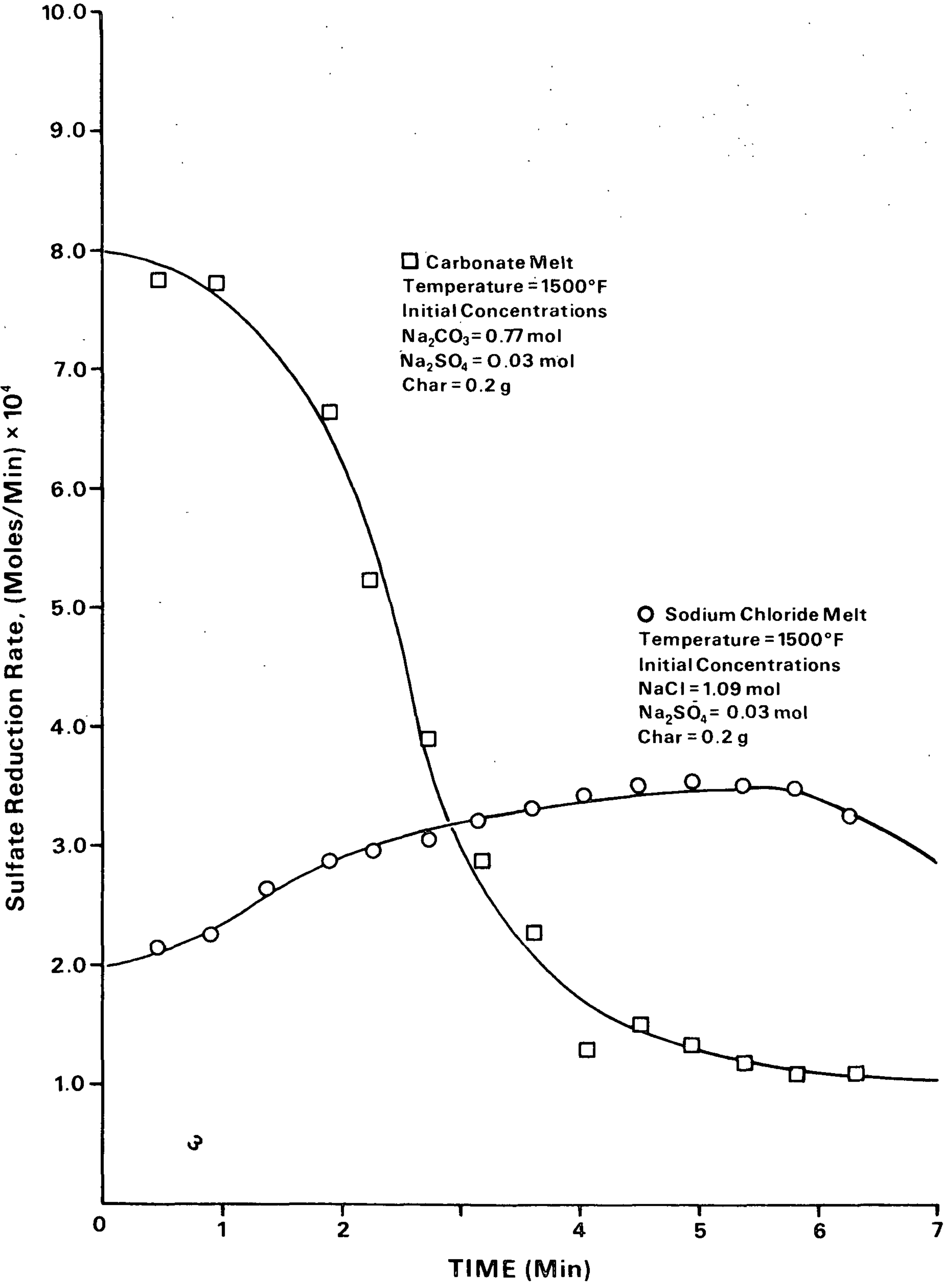

Figure 18. Effect of carbonate on sulfate reduction with kraft black liquor char.

pulverized graphite and char (Fig. 12 and 13) would be seen. In these figures, the reduction rate, based on carbon dioxide generation, is shown to be directly proportional to the carbon level. Since at higher carbon levels more carbon dioxide is generated, a continual catalytic effect of carbon dioxide would also increase the reduction rate, resulting in it being improbable that the distinctly first order dependence of reduction on carbon would be observed.

Therefore, only an initiating level of carbon dioxide is required to produce the full catalytic effect. Once this level is exceeded, no additional increase in reduction rate is observed with increasing carbon dioxide level. This limit is apparently not reached in the noncarbonate melts, due to the lower carbon dioxide solubility in these melts and the slower reduction rate. The Henry's law constant for carbon dioxide is an order of magnitude lower in sodium chloride than sodium carbonate, and the rate of carbon dioxide generation from reduction is also an order of magnitude lower. Therefore, the level of carbon dioxide present in a sodium chloride melt during these reduction reactions would be approximately two orders of magnitude lower than the level in a carbonate melt. At these levels, apparently not enough carbon dioxide is present to fully catalyze reduction.

The catalytic effect of carbonate on sulfate reduction was observed with all carbons used in this study. Therefore, a common mechanism is responsible for reduction with these various forms of carbon.

EFFECT OF COMMERCIAL SMELT

One of the assumptions made in this study was that sulfate reduction in a synthetic smelt consisting of alkali carbonates and sulfates would not be significantly different from reduction in a commercial smelt obtained from a kraft recovery furnace. This assumption is that the reactions studied during this experimental program are those responsible for reduction in a kraft recovery furnace. To verify this assumption, kraft smelt was obtained from the Thilmany Pulp and Paper Co., Kaukauna, Wisconsin, and sulfate reduction in this smelt compared with reduction in a synthetic smelt.

The Thilmany smelt was analyzed for sodium sulfate, sodium sulfide, and sodium carbonate, and the results of this analysis are shown in Table VI. At high sulfate levels, sulfate reduction was previously found to be principally dependent on the carbon level. Therefore, to obtain accurate reduction data, it was necessary to remove any free carbon from the Thilmany smelt. To remove the carbon, the smelt was oxidized, which also converted the sulfide to sulfate. Based on the initial analysis of this smelt, it was calculated that after oxidizing, the smelt contained 62 wt.% alkali carbonates and 38% sodium sulfate. After oxidation, this smelt was brought to the desired reduction temperature. A carbon rod, 3/8-inch in diameter and 1/2-inch in length was added, and reduction followed through the evolution of carbon dioxide and carbon monoxide. This reduction rate was then compared with that obtained with a synthetic smelt containing a high level of sulfate, Fig. 19.

TABLE VI

ANALYSIS OF THILMANY SMELT

Compound	Wt.%	Analytical Method
Na_2CO_3	73.21	CO_2 evolution
Na_2SO_4	3.22	T-624
Na_2S	22.7	Specific ion
Total	99.1	

Since at high sulfate concentrations, sulfate reduction with carbon is independent of sulfate, the difference in sulfate levels for the two experiments in Fig. 19 had no effect on the reduction rates. Both reduction rates started at a low level and showed the autocatalytic behavior associated with sulfate reduction using graphite rods. The sulfate reduction rate in the commercial smelt eventually reached a level 14% above that obtained in the synthetic smelt. This is only a slight difference in reduction rates, corresponding to the difference that would result from a 12°F increase in temperature. Therefore, sulfate reduction in a synthetic smelt is similar to reduction in a commercial smelt.

This experiment demonstrates that the sulfate reduction in a synthetic smelt is the same as reduction in a commercial smelt. There are no catalytic effects or unexpected reactions due to the commercial smelt, and the reactions investigated during this program are those responsible for reduction in a kraft recovery furnace.

CARBON MONOXIDE REDUCTION OF SULFATE

The principal product gas from sulfate reduction with the three types of carbon used in this study was carbon dioxide. The carbon monoxide content of the product gas usually averaged 5 to 10% of the carbon dioxide level and was correlated with the carbon and sulfate levels of the melt. At high carbon content and low sulfate levels, relatively high levels of carbon monoxide were produced. (For example, in a melt containing 3.5 mol/L of pulverized graphite and 0.7 mol/L of sulfate, carbon monoxide levels of 20 to 30% of the carbon dioxide were observed.)

A possible source of the carbon monoxide is the reaction of carbon dioxide with carbon, Eq. (3).

$$CO_2 + C \longrightarrow 2CO \tag{3}$$

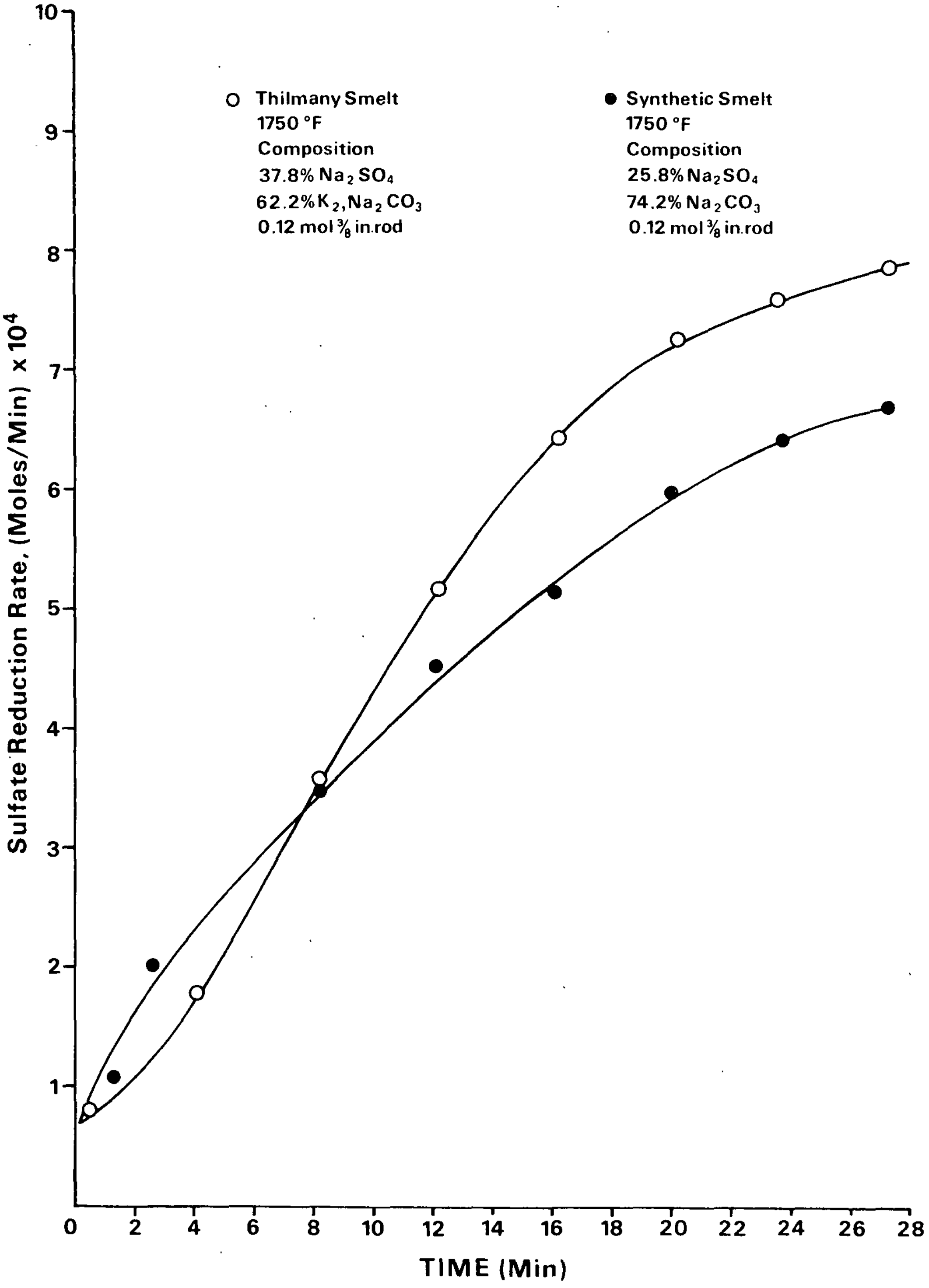

Figure 19. Effect of commercial smelt on sulfate reduction.

To confirm this reaction, carbon dioxide was bubbled through a sodium carbonate melt containing graphite rods. During this experiment less than 5% of carbon dioxide was converted to carbon monoxide. In a melt containing sulfate, some of the carbon monoxide formed on the carbon would reduce sulfate as it passed through the melt. Therefore, reduction of sulfate by carbon monoxide will occur during reduction of sulfate with carbon. However, from the low carbon monoxide levels in the gas phase, carbon monoxide reduction of sulfate appears to be a secondary reaction.

Since carbon monoxide reduction of sulfate occurred during this study and is a possible path for sulfate reduction in a kraft recovery furnace, a student research program was conducted by Sjoberg (5) to study sulfate reduction with carbon monoxide. In this study sulfate reduction was followed by bubbling carbon monoxide through the melt and monitoring the amount of carbon dioxide formed. The major conclusions of this study are:

1. The sodium sulfate content of the melt has no effect on the rate of sulfate reduction.
2. The rate of sulfate reduction is proportional to the carbon monoxide partial pressure.
3. Sulfate reduction with carbon monoxide has an Arrhenius type activation energy of approximately 30,000 cal/mol.

During this study, the normal conversion of carbon monoxide to carbon dioxide at 1750°F was 20 to 25% of the entering carbon monoxide. From these results it was concluded that although reduction with carbon monoxide does occur, it appears to be a relatively slow reaction compared with reduction with kraft black liquor char or pulverized graphite.

DISCUSSION

The experimental results for sulfate reduction with the three forms of carbon used in this study - graphite rods, pulverized graphite, and black liquor char - were quite similar. With graphite rods, sulfate reduction had an activation energy of 51,000 cal/mol, varied from zero order in sulfate at high sulfate concentrations to first order at low sulfate concentrations, and with all graphite surfaces oxidized to the same degree, was first order in graphite surface area. With pulverized graphite, reduction had an activation energy of 44,000 cal/mol, was zero order in sulfate until very low sulfate levels were reached, and was first order in the amount of graphite present. With kraft black liquor char, sulfate reduction had an activation energy of 30,000 cal/mol, was zero order in sulfate until very low levels of sulfate were reached, and was first order in the amount of char present.

Although sulfate reduction with graphite rods was a highly autocatalytic reaction, no autocatalytic behavior was observed with either pulverized graphite or kraft black liquor char. The autocatalytic behavior of sulfate reduction with graphite rods was found to be due to increased reactivity of the graphite surface as the reaction proceeded.

The autocatalytic nature of sulfate reduction with graphite rods may be the result of increasing edge carbons on the graphite rods. Many studies have shown that essentially all surface reactions with pure carbons occur at the carbon edges rather than basal planes (6,7). Walker et al. (6) have shown that depending on the degree of graphitization the reactivity of the carbon edges is two to three orders of magnitude greater than that of the basal carbon (6,8). Therefore, if the oxidation of the graphite rods by sulfate results in increased edge carbons, one would expect to observe an increase in reactivity. However, with pulverized graphite or char, the initial number of edge carbons is relatively high and any increase in the number of edge carbons from the oxidation of the carbon would be relatively small and no autocatalytic effect observed.

With graphite rods, sulfate reduction was found to be proportional to the number of active sites on the graphite surface. However, as sulfate reacts with the graphite rods, the number of active sites increases, resulting in sulfate reduction with carbon being an autocatalytic reaction. An increase in active sites has been observed with other reactions involving carbon. Walker (7) states that in the reaction of carbon dioxide with carbon, the number of active sites formed for each carbon monoxide molecule desorbed from the carbon may be 0, 1, or 2. If one to two active sites are formed per carbon monoxide molecule desorbed, an autocatalytic effect will be observed. When all surfaces of the graphite rods are oxidized to the same extent, the sulfate reduction rate is proportional to the surface area. If the surface area of the graphite rods is doubled, the sulfate reduction rate also doubles.

With the small pulverized graphite and kraft black liquor char particles, sulfate reduction was found to be proportional to the mass of carbon present. Here, the ratio of surface area to particle mass remains constant as the particles are oxidized.

For all carbons, the rate of sulfate reduction was zero order in sulfate over a wide range of sulfate concentrations. For graphite rods, the shift from zero order to first order occurred at approximately 5 wt.% sodium sulfate remaining in the melt. However, for pulverized graphite and kraft black liquor char, the reduction rate was zero order in sulfate at 3 wt.% and decreased only slightly from 3 wt.% to 0.3 wt.%. (As described in the experimental section, at 30% sulfidity, 3%

sodium sulfate in the melt corresponds to a reduction efficiency of 93%.) Therefore, sulfate reduction for pulverized graphite and char can be described as zero order in sulfate until low levels of sulfate are reached.

The shift in the rate dependence on sulfate from zero order to first order can be described by a Langmuir type adsorption isotherm, Eq. (4), indicating that sulfate reduction with carbon occurs through adsorption of sulfate on an active carbon site.

$$(SO_4)_{ads} = \frac{[SO_4]}{K_4[SO_4] + 1} \tag{4}$$

Here, $(SO_4)_{ads}$ is adsorbed sulfate

$[SO_4]$ is the sulfate concentration in the melt.

At high sulfate concentrations, the level of adsorbed sulfate is independent of the sulfate concentration, and at low levels of sulfate, the adsorbed sulfate is directly proportional to the sulfate concentration. The effect of sulfate on reduction with the three types of carbon used in this study is effectively described by Eq. (4).

As discussed in the experimental section, sulfate reduction with carbon is strongly catalyzed by carbonate melts. Sulfate reduction with all carbons studied was found to be an order of magnitude faster in alkali carbonate/sodium sulfate melts than in sodium chloride/sodium sulfate or pure sodium sulfate melts. Since sulfate reduction with all carbons studied is catalyzed by carbonate melts, a common mechanism is responsible for reduction with these carbons. The experimental information obtained on reduction using graphite rods and pulverized graphite can then be applied to reduction with char and to defining the reduction process occurring in the bed of a kraft recovery furnace.

This catalytic effect of carbon dioxide may be due to the reaction of carbon dioxide with the carbon to form two adsorbed oxygen atoms. These oxygen sites then serve as active sites for the adsorption of sulfate. Many researchers have reported that the reactivity of coal char with oxygen and hydrogen is correlated with its oxygen content and that active carbon sites result from the inclusion of oxygen in the coal char (9,10). If the carbon atom in the adsorbed carbon monoxide is considered to be part of the carbon matrix, the adsorbed carbon monoxide is then equivalent to an adsorbed oxygen. This adsorbed oxygen in kraft black liquor char may have an effect similar to oxygen in coal char and catalyze reduction. Since these oxygen sites result from the reaction between carbon dioxide and carbon, melts with a low carbon dioxide content would produce few oxygen sites on the carbon and reduction would occur at a slower rate.

Only in melts where there is a relatively low carbon dioxide level is the carbon dioxide effect observed. With sulfate reduction in carbonate melts, there is no effect of increasing carbon dioxide. Therefore, carbon dioxide is only an initiating catalyst and at high levels has no additional effect on reduction. Since a relatively high level of carbon dioxide normally is present in carbonate melts, reduction in these melts is independent of the carbon dioxide level.

The most significant difference between sulfate reduction with kraft black liquor char and the two forms of graphite - rods and pulverized graphite - is the high reactivity of the char. Much of this high reactivity may be the result of the relatively high surface area of the char.

PROPOSED MECHANISM FOR SULFATE REDUCTION WITH CARBON

With pulverized graphite and char, sulfate reduction is first order with respect to the mass or moles of the carbon, and for graphite rods with the same degree of oxidation per unit surface area, reduction is first order with respect to the graphite surface area. For graphite rods, the sulfate reduction rate with respect to sulfate varies from zero order at high sulfate concentrations to first order at low sulfate concentrations. For pulverized graphite and kraft black liquor char, sulfate reduction is zero order with respect to sulfate at high concentrations, and the rate decreases at low sulfate concentrations. These results suggest that sulfate reduction occurs through adsorption of sulfate on an active carbon site, a reaction involving this adsorbed sulfur, and desorption of a reduced sulfur species.

The rate of sulfate reduction with all forms of carbon used in this study was approximately one order of magnitude lower in a noncarbonate melt than in a carbonate melt, demonstrating that sulfate reduction is catalyzed by carbonate. It was also shown in an earlier report (1) that the addition of carbon dioxide to a carbonate melt containing a low level of carbon dioxide would initially catalyze sulfate reduction with graphite rods. This suggests that the catalytic effect of carbonate melts is due to the high level of carbon dioxide in these melts.

Based on the experimental results presented in this report, the following mechanism for sulfate reduction with carbon is proposed. Dissolved carbon dioxide in the melt reacts with a carbon site to form two carbon monoxide molecules on the carbon surface. These carbon monoxide molecules then serve as active sites for the adsorption of sulfate. Sulfate adsorbs on these carbon monoxide sites and reacts, forming a reduced sulfur compound and carbon dioxide. The reduced sulfur compound then undergoes a series of fast reduction reactions to form sulfide. This proposed sulfate reduction mechanism is described in more detail in the following paragraphs.

Sulfate reduction with carbon was found to be catalyzed by carbonate. This catalytic effect appears to be due to the high carbon dioxide level in carbonate melts, suggesting that carbon dioxide has a key role in sulfate reduction. One method by which carbon dioxide could influence reduction is through the reaction of carbon dioxide with carbon, forming adsorbed carbon monoxide on the carbon surface. These adsorbed carbon monoxide molecules could then act as active sites for the adsorption of sulfate. In the reaction between carbon dioxide and carbon, one molecule of carbon dioxide would adsorb on the carbon and react to form two molecules of carbon monoxide, Eq. (5) and (6).

$$CO_2 + C_f \overset{K_1}{\rightleftharpoons} C(CO_2)_{ads} \tag{5}$$

$$C(CO_2)_{ads} \overset{K_2}{\rightleftharpoons} 2(CO)_{ads} \tag{6}$$

Here CO_2 is carbon dioxide in the melt

C_f is a free active carbon site

$(CO)_{ads}$ is adsorbed CO

$C(CO_2)_{ads}$ is adsorbed CO_2

This reaction of one molecule of carbon dioxide with carbon to form two adsorbed carbon monoxide molecules is consistent with the mechanism proposed by Darken and Turkdogan (11) for the reaction of gaseous carbon dioxide with carbon.

The total number of active carbon sites is equal to the sum of the free active carbon sites and those occupied by adsorbed carbon monoxide and carbon dioxide, Eq. (7).

$$C_T = C_f + C(CO_2)_{ads} + (CO)_{ads} \qquad (7)$$

Here C_T is total active carbon sites per unit surface area.

Solving Eq. (5), (6), and (7) for the adsorbed carbon monoxide in terms of carbon dioxide in the melt and total carbon sites yields Eq. (8).

$$(CO)_{ads} = \left(-1 + \left[1 + 4 \frac{K_1[CO_2] + 1}{K_1K_2[CO_2]} \times C_T\right]^{1/2}\right)\frac{K_1K_2[CO_2]}{2(K_1[CO_2] + 1)} \qquad (8)$$

At high levels of carbon dioxide, the adsorbed carbon monoxide becomes independent of the carbon dioxide content of the melt. This agrees with the experimental observation that the carbon dioxide content of the melt only affects reduction when it is present at low levels.

The adsorbed carbon monoxide molecules serve as active sites for the adsorption of sulfate and in the future will be referred to only as active sites. The adsorption of sulfate on these active sites can be represented by Eq. (9).

$$[SO_4] + C_f' \overset{K_4}{\rightleftharpoons} C(SO_4)_{ads} \qquad (9)$$

$$\text{with } C(SO_4)_{ads} = K_4[SO_4]\ C_f' \qquad (10)$$

Here $[SO_4]$ is the sulfate in the melt

C_f' represents an active site resulting from the adsorbed carbon monoxide, $(CO)_{ads}$

$C(SO_4)_{ads}$ is adsorbed sulfate

The total number of active carbon sites available for the adsorption of the sulfate, C_T', is the sum of the free active carbon sites and those occupied by the sulfate, Eq. (11).

$$C_T' = C_f' + C(SO_4)_{ads} \tag{11}$$

Here C_T' is the total number of active carbon sites resulting from adsorbed carbon monoxide per unit surface area

By combining Eq. (10) and (11) and eliminating the free active carbon site term C_f', the adsorbed sulfate can be expressed in terms of sulfate concentration and total active carbon sites, Eq. (12).

$$C(SO_4)_{ads} = \frac{K_4[SO_4]}{1 + K_4[SO_4]} \times C_T' \tag{12}$$

At low sulfate concentrations, the adsorbed sulfate is proportional to the sulfate concentration, but at high sulfate concentrations, the adsorbed sulfate becomes independent of the sulfate concentration. Therefore, the effects of the sulfate concentration on sulfate reduction with carbon are described by the rate of sulfate reduction being dependent on the level of adsorbed sulfate.

The rate-limiting step in sulfate reduction then is the reduction of the adsorbed sulfate on the carbon surface forming carbon dioxide and a reduced sulfur compound. Since the rate-limiting step is the reduction of adsorbed sulfate, the reduction rate is proportional to the amount of adsorbed sulfate and can be described by Eq. (13).

$$\frac{d[SO_4]}{dt} = - \frac{K[SO_4]}{1 + K_4[SO_4]} \times e^{-\Delta E/RT} \times C_T' \tag{13}$$

Here $[SO_4]$ is the bulk sulfate concentration

ΔE is the activation energy

K is an effective rate constant

R is the gas constant

T is the absolute temperature

Here, the rate of sulfate reduction with carbon in a carbonate melt is proportional to the sulfate concentration at low sulfate levels, independent of the sulfate concentration at high sulfate levels, and proportional to the number of active carbon sites.

MECHANISM FOR SULFATE REDUCTION WITH GRAPHITE RODS

Equation (13) effectively describes sulfate reduction for pulverized graphite or kraft black liquor char where the number of active carbon sites per carbon mass is constant, but not sulfate reduction with graphite rods where the number of active sites increases as reduction proceeds. To account for the increase of active sites with graphite rods, another term must be added to the rate expression.

To describe the increase in the reactivity of the graphite resulting from sulfate reduction, the surface of the graphite rods was considered to consist of two types of carbon sites; active sites and inactive sites capable of becoming active. The sum of the inactive and active sites per unit surface area is referred to as total sites and is assumed to be constant, Eq. (14).

$$NT = NA + NI \tag{14}$$

Here NT is total number of sites per unit surface area

NA is the number of active sites per unit surface area

NI is the number of inactive sites per unit surface area

The increase in active sites results from the reduction of sulfate on the carbon surface. This reduction reaction is assumed to occur on an active site and in the reduction process may convert an inactive site to an active site. The rate of increase of active sites per unit carbon surface area is then proportional to the rate of sulfate reduction multiplied by the fraction of inactive sites per unit surface area, Eq. (15).

$$\frac{d[NA]}{dt} = K' \ FI \left[\frac{-d[SO_4]}{dt} \right] \tag{15}$$

Here K' is the proportionality constant

FI is the fraction of inactive sites $= \frac{NI}{NT}$

SO_4 is sulfate per unit surface area of carbon

Since the fraction of inactive sites plus the fraction of active sites equals one, Eq. (15) can be written in terms of the fraction of active sites, FA, as:

$$\frac{d[FA]}{dt} = \frac{-K}{NT} (1-FA) \frac{d[SO_4]}{dt} \tag{16}$$

By multiplying both sides of Eq. (16) by dt, integrating, and applying the initial conditions, the fraction of active sites can be expressed in terms of sulfate reduced or sulfide formed per unit carbon surface area, Eq. (20)

$$\ln (1-FA) \Big|_{FAI}^{FA} = \frac{K'}{NT} \quad SO_4 \Big|_{SO_4I}^{SO_4} \tag{17}$$

Initial Conditions

At $SO_4 = SO_4I$ (initial sulfate concentration per unit surface area)

FA = FAI (initial fraction of active sites)

Applying these limits, Eq. (17) becomes

$$\ln (1-FA) - \ln (1-FAI) = \frac{K'}{NT} [SO_4-SO_4I] \tag{18}$$

Since SO_4I-SO_4 is the moles of sulfide formed per unit carbon surface area, Eq. (18) can be written as

$$\ln (1-FA) - \ln (1-FAI) = \frac{K' \, SI}{NT} \tag{19}$$

Here, SI is the moles of sulfide formed per unit surface area.

The fraction of active carbon sites can now be expressed as:

$$FA = 1 - (1-FAI)\, e^{-\frac{K' \, SI}{NT}} \tag{20}$$

The nature of the active carbon site was previously ascribed to adsorbed carbon monoxide on the carbon surface. The active sites described here would also be adsorbed carbon monoxide. Sulfate reduction could either result directly in adsorbed carbon monoxide at a neighboring carbon or in a carbon site that would react with carbon dioxide to form adsorbed carbon monoxide. In either case, these active sites would be the same as those previously described.

Combining Eq. (13) and (20), the rate of sulfate reduction with graphite rods can be described by Eq. (21).

$$\frac{d[SO_4]}{dt} = - \frac{K \, [SO_4]}{1+K_4[SO_4]} \, e^{-\Delta E/RT} \times [1 - (1-FAI)e^{-\frac{K' \, SI}{NT}}][CSA] \tag{21}$$

Here, SI is the amount of sulfide formed per unit surface area

CSA is the carbon surface area per liter of melt.

With five experimentally determined parameters, K, K_4, ΔE, (1-FAI), and $\frac{K'}{NT}$, Eq. (21) describes sulfate reduction with graphite rods over a wide range of experimental conditions. The activation energy, ΔE, for sulfate reduction with graphite rods was previously found as described in the experimental section to be 51,000 ± 1670 cal/mol. To determine the validity of this rate expression and the other four experimental parameters, data from six representative reduction experiments were fit to this rate expression using a nonlinear regression analysis computer program. These parameters and their estimate of standard deviation obtained from this analysis are shown in Table VII.

TABLE VII

EXPERIMENTAL PARAMETERS DESCRIBING SULFATE REDUCTION WITH GRAPHITE RODS

Parameter	Value	Linear Estimate of Standard Deviation
K (liters/cm^2-sec)	9.96×10^7	1.26×10^7
K_4 (liters/mol)	10.4	2.0
(1-FA)	0.832	0.016
$\frac{K'}{NT}$ (cm^2/mol)	1.30×10^3	0.2×10^3
ΔE (cal/mol)	51,050	1,670

Here, ΔE and its standard deviation were determined as described in the experimental section from independent experimental data. The six reduction experiments used to determine the other parameters represent a large range of sulfate concentrations, carbon surface areas, and temperatures. Illustrated in Fig. 20 is a typical reduction experiment showing the actual and predicted reduction rates. As illustrated by this figure, the rate expression for sulfate reduction with graphite rods, Eq. (21), accurately describes sulfate reduction. The treatment of the active sites results in a rate expression that closely fits the observed autocatalytic behavior of sulfate reduction with graphite rods.

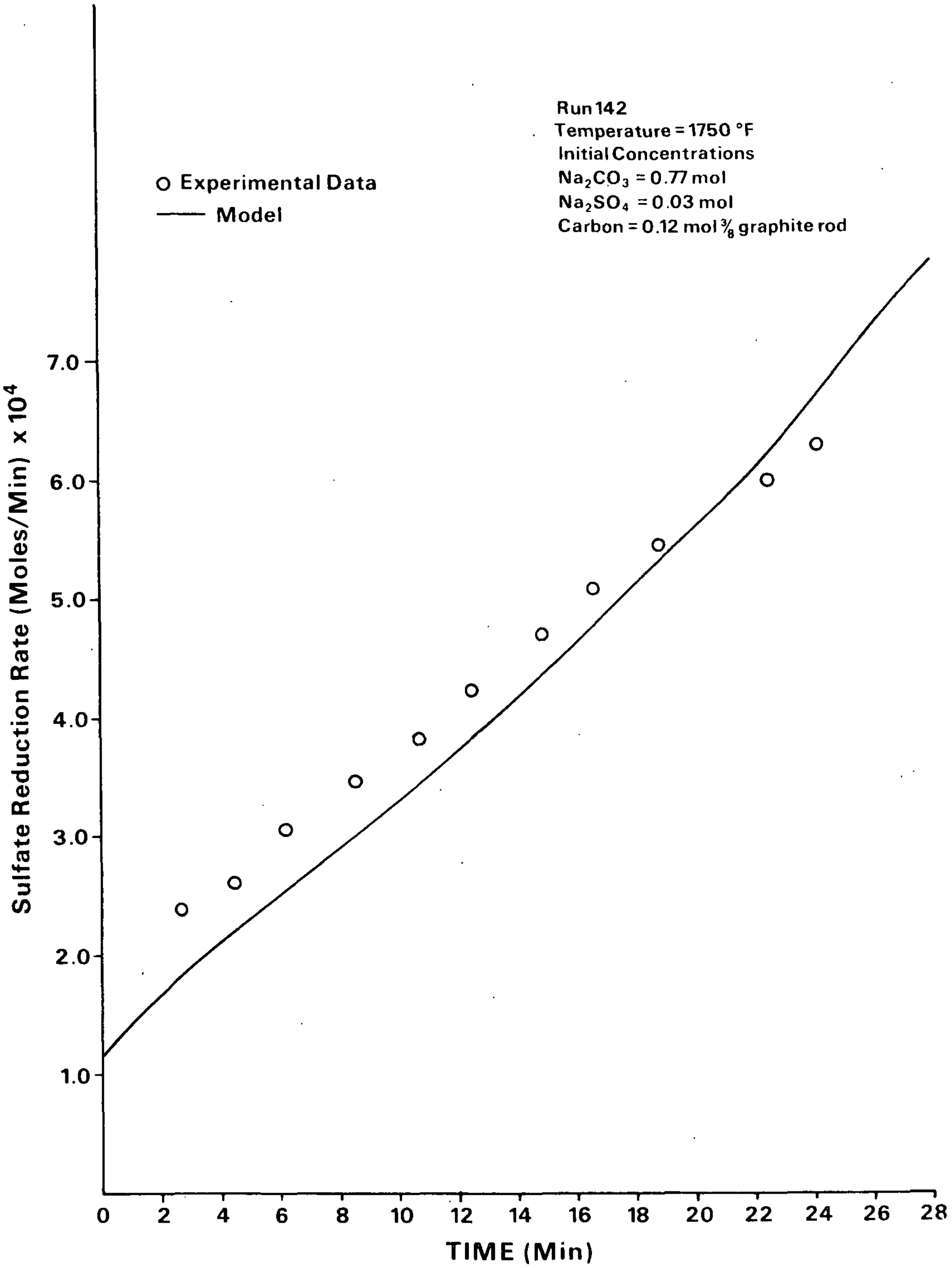

Figure 20. Model for sulfate reduction with graphite rods.

MECHANISM FOR SULFATE REDUCTION WITH PULVERIZED GRAPHITE

With the micronized graphite, the ratio of active sites to particle mass remained constant as reduction occurred. Therefore, the number of active surface sites is proportional to the mass or moles of the graphite particles, and Eq. (13) can be rewritten as Eq. (22).

$$\frac{d[SO_4]}{dt} = \frac{-K[SO_4]}{1 + K_4 [SO_4]} \times e^{-\Delta E/RT} \times CM \qquad (22)$$

Here, CM is the moles of pulverized graphite per liter of melt.

The rate of sulfate reduction with graphite rods and the rate with pulverized graphite are described by the same general rate expression. For pulverized graphite, the fraction of initial active sites, FAI, equals one and the active sites are proportional to the carbon mass. Under these conditions, Eq. (21) reduces to Eq. (22).

The activation energy, ΔE, was previously determined, as described in the experimental section to be 44,000 cal/mol ± 1200 cal/mol. To determine the validity of this rate expression for sulfate reduction with pulverized graphite and define the two remaining experimental parameters, experimental data from several reduction experiments were fit to this equation again using a nonlinear regression analysis program. These parameters and their estimate of standard deviation are shown in Table VIII.

TABLE VIII

EXPERIMENTAL PARAMETERS DESCRIBING SULFATE REDUCTION WITH PULVERIZED GRAPHITE

Parameter	Value	Linear Estimate of Standard Deviation
K (liters/mol-sec)	1.92×10^6	$\pm 0.32 \times 10^6$
K_4 (liters/mol)	38.9	± 7.2
ΔE (cal/mol)	44,000	± 1200

Again, the reduction experiments used to determine these parameters represent a large range of sulfate concentrations, carbon surface areas, and temperatures. Illustrated in Fig. 21 is a typical reduction experiment showing the actual rate and predicted rate vs. time.

Figure 21 demonstrates that sulfate reduction with pulverized graphite is effectively described by Eq. (22). While Fig. 21 is only one data set, it illustrates the ability of the reaction model to describe sulfate reduction with pulverized graphite. With the same experimental parameters used in Fig. 21, Eq. (22) can accurately describe sulfate reduction over the entire range of experimental conditions investigated in this study.

MECHANISM FOR SULFATE REDUCTION WITH KRAFT BLACK LIQUOR CHAR

In terms of the effects of sulfate concentration and carbon loading, sulfate reduction with kraft black liquor char was found to be similar to reduction with pulverized graphite. Therefore, rate equation (22), which was used to describe sulfate reduction with pulverized graphite, was also used to describe sulfate reduction with kraft black liquor char.

Sulfate reduction with kraft black liquor char was previously determined, as described in the experimental section, to have an activation energy of 29,000 ± 1000 cal/mol. Using this activation energy, several sets of addition data, and a regression analysis program, the two remaining parameters (K and K_4) were determined. The value of the three parameters and their estimate of standard deviation are shown in Table IX.

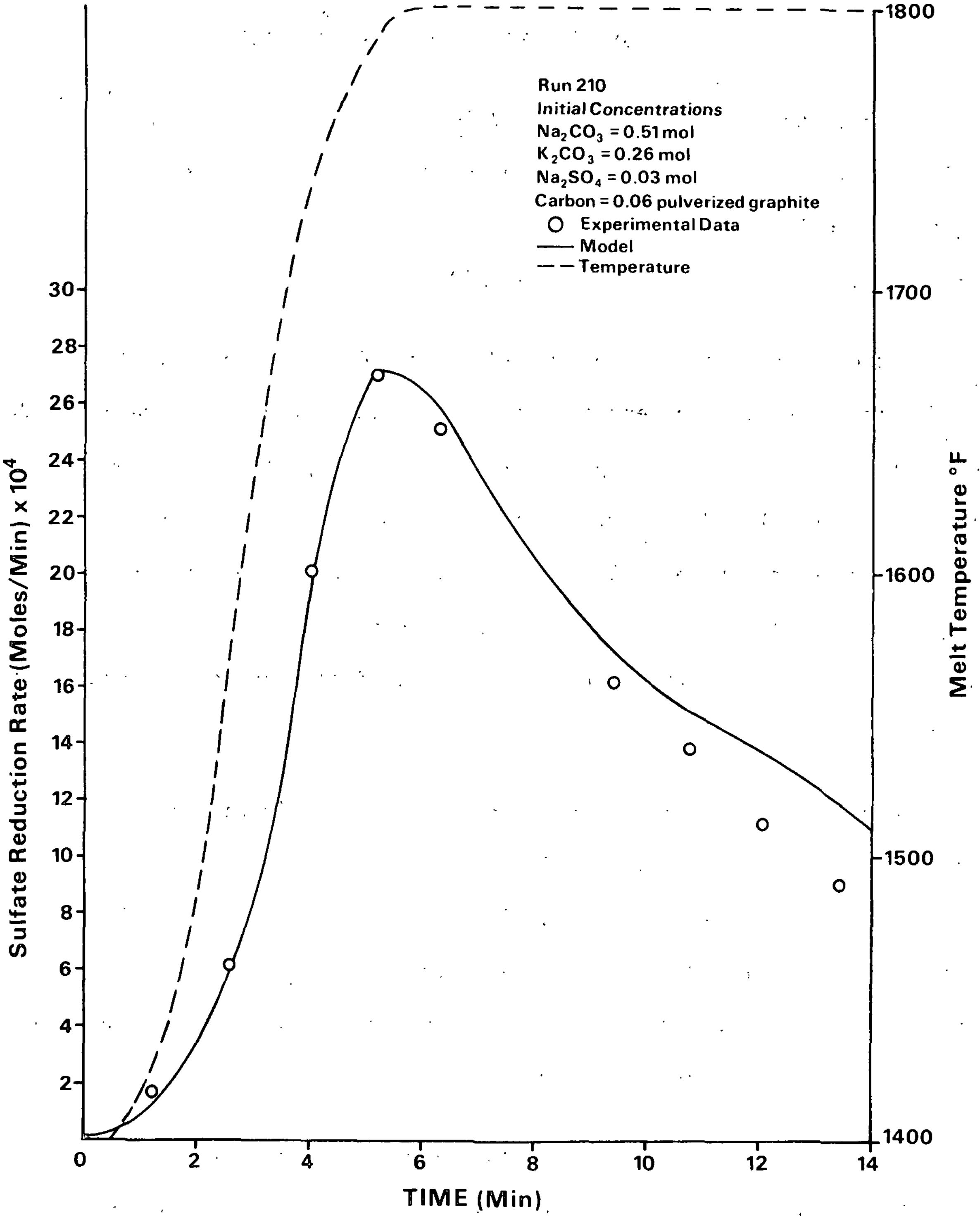

Figure 21. Model for sulfate reduction with pulverized graphite.

TABLE IX

EXPERIMENTAL PARAMETERS DESCRIBING SULFATE REDUCTION WITH KRAFT BLACK LIQUOR CHAR

Parameter	Value	Linear Estimate of Standard Deviation
K (liters/mol-sec)	5.96×10^4	$\pm 1.88 \times 10^4$
K_4 (liters/mol)	45.6	± 17.1
ΔE (cal/mol)	29,200	± 1000

These parameters were determined using reduction experiments over a wide range of initial sulfate concentrations, carbon loading, and temperature. The activation energy, ΔE, was previously determined from independent experimental data and the rate parameters K and K_4 were determined using a nonlinear regression analysis program and comparing the actual level of sulfate reduced to that predicted by a rate equation [Eq. (22)]. A typical reduction experiment used for this analysis is shown in Fig. 22. Here, the actual amount of sulfate reduced is compared with that predicted by the rate equation.

To ease the transfer of data from the data acquisition computer to the regression analysis program, the sulfate reduction with char data was analyzed in the form of total sulfate reduced _vs_. time. For reduction with graphite rods and pulverized graphite, the data were analyzed using the reduction rate _vs_. time. Both methods of analyzing the data are valid and only affect the form of the typical reduction experiment, illustrating goodness of fit.

Sulfate reduction with kraft black liquor char is accurately described by by Eq. (22), a rate equation. Although Fig. 22 represents only one reduction experiment, the reaction model with the parameters in Table IX accurately fits the experimental data over the entire range of experimental conditions investigated during this study.

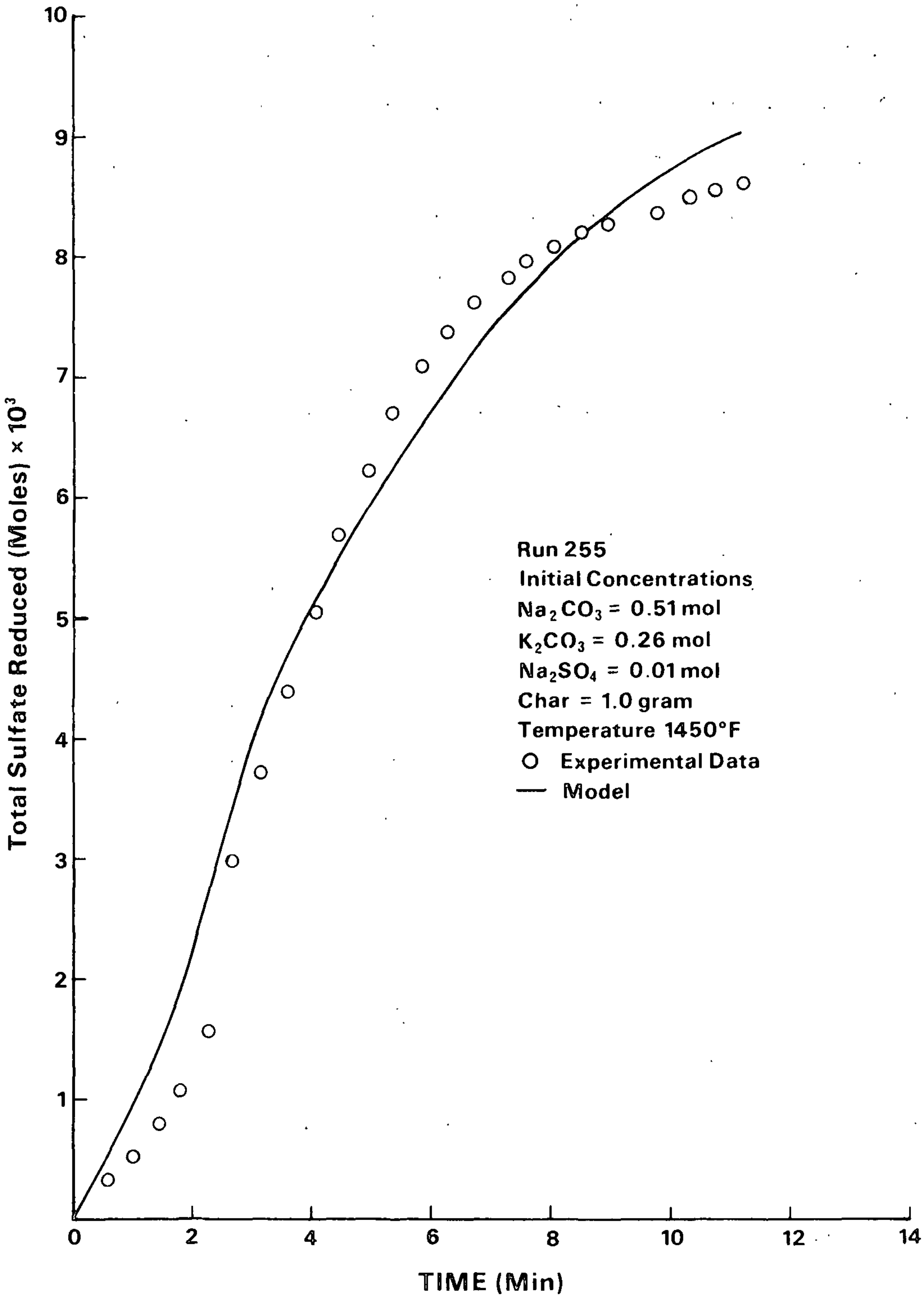

Figure 22. Model for sulfate reduction with kraft black liquor char.

DISCUSSION OF SULFATE REDUCTION MECHANISM

The proposed reaction model accurately describes sulfate reduction with the three types of carbon studied over a large variation in experimental conditions. The autocatalytic behavior of reduction with graphite rods was closely fit through the use of a term describing an increase in active surface sites. The representative data sets for sulfate reduction with the three types of carbons demonstrate that the rate equations closely predict the experimentally observed reduction rates.

Sulfate reduction with kraft black liquor char was found to be a considerably faster reaction than reduction with pulverized graphite. Surface area measurements of pulverized char also revealed that char has a considerably greater surface area than pulverized graphite. Therefore, the increase in reduction rate with char may be a result of this increased surface area. To calculate the extent that the increase in rate results from increased surface area, the predicted sulfate reduction rates with pulverized graphite and char were compared at 1400°F and 1600°F. These rates were calculated using the previously determined rate parameters and are illustrated in Table X.

As illustrated in Table X, the predicted sulfate reduction rate for pulverized graphite is approximately 3% of the predicted rate for char at 1400°F and 6% at 1600°F. However, the surface area for pulverized graphite is only 3.4% of the surface area for char. Therefore, the difference in reduction rates for pulverized graphite and char can be accounted for by the difference in surface areas between the two types of carbon.

The mechanism proposed in this report for sulfate reduction with carbon is similar to that described in the previous report on sulfate reduction with graphite rods. In both mechanisms sulfate is reduced by carbon through a carbon monoxide

TABLE X

SULFATE REDUCTION RATES WITH PULVERIZED GRAPHITE AND KRAFT BLACK LIQUOR CHAR

$$\frac{d[SO_4]}{dt} = \frac{-K[SO_4]}{1 + K_4[SO_4]} \times e^{-\Delta E/RT} \times CM$$

Conditions $[SO_4] = 0.60$ mol/L
$CM = 0.02$ mol/L
$T_1 = 1400°F = 1033°K$
$T_2 = 1600°F = 1144°K$

	K (liter/mol/s)	K_4 (liter/mol)	ΔE cal/mol	BET Surface Area (m^2/g)	Rate (mol/s) at T_1	Rate (mol/s) at T_2
Pulverized Graphite	1.92×10^6	38.9	44,000	19.7	4.66×10^{-7}	3.71×10^{-6}
Kraft black liquor char	5.96×10^4	45.6	29,200	580	1.68×10^{-5}	6.65×10^{-5}
Ratio graphite/char				0.034	0.028	0.056

intermediate. In the previous study, it was proposed that carbon dioxide reacted with the carbon to form carbon monoxide. This carbon monoxide then desorbed from the carbon and reduced the sulfate in the melt. In the mechanism proposed in this report, carbon dioxide again reacts with the carbon to form adsorbed carbon monoxide. But instead of desorbing from the carbon, these carbon monoxide molecules act as active sites for the adsorption of the sulfate. Sulfate then adsorbs on these sites and is reduced forming carbon dioxide and a reduced sulfur compound. Unlike the mechanism proposed in Progress Report One (1), this mechanism does not require the bulk decomposition of sulfite.

CONCLUSIONS

1. Sulfate reduction with carbon is described by the following mechanisms. Carbon dioxide in the melt reacts with a carbon surface site to form two molecules of carbon monoxide on the carbon surface. These carbon monoxide molecules then serve as active sites for the adsorption of sulfate. Sulfate adsorbs on these sites and is reduced to form a reduced sulfur compound and carbon dioxide. This reduced sulfur compound and the carbon dioxide then desorb from the carbon into the melt. The rate-limiting step in sulfate reduction is the reaction of adsorbed sulfate on the carbon surface.

2. The sulfate effect on the rate of sulfate reduction with carbon can be described by an adsorption isotherm. At high sulfate concentrations, the rate of sulfate reduction is zero order with respect to sulfate; at low concentrations, of sulfate it becomes first order. With kraft black liquor char and pulverized graphite, the rate of sulfate reduction is essentially independent of the sulfate concentration until low levels of sulfate (less than 3 wt.% Na_2SO_4 in the melt) are reached.

3. The sulfate reduction rate is directly proportional to the number of active sites on the carbon surface. With kraft black liquor char and pulverized graphite, the number of active sites remains proportional to the carbon mass as reduction proceeds. For these carbons, the sulfate reduction rate is proportional to the amount of carbon present. With graphite rods, the number of active sites increases during sulfate reduction, resulting in an autocatalytic reaction. This increase in active sites results from the oxidation of the graphite surface by sulfate.

4. A common rate equation, Eq. (23), describes sulfate reduction with either pulverized graphite or kraft black liquor char.

$$\frac{d[SO_4]}{dt} = \frac{-K\ [SO_4]}{1 + K_4[SO_4]} \times e^{-\Delta E/RT} \times CM \qquad (23)$$

Using different parameters for pulverized graphite and char (Table XI), this rate equation effectively describes sulfate reduction over a large variation in experimental conditions. By modifying Eq. (23) by a term that accounts for the increase in active surface sites on the graphite rods, Eq. (23) can also describe sulfate reduction with graphite rods. This revised rate equation, Eq. (24), contains five experimentally determined parameters and effectively describes sulfate reduction with graphite rods over a large variation in experimental conditions.

$$\frac{d[SO_4]}{dt} = \frac{-\ K[SO_4]}{1 + K_4[SO_4]} \times e^{-\Delta E/RT} \times [CSA] \times [1-(1-FAI) \times e^{-\frac{K'\ SI}{NT}}] \qquad (24)$$

Table XI also contains the five experimentally determined parameters used to describe sulfate reduction with graphite rods.

TABLE XI

PARAMETERS DESCRIBING SULFATE REDUCTION WITH CARBON

Carbon Type	K	K_4	ΔE	(1-FAI)	$\frac{K'}{NT}$
Kraft black liquor char	$1.92 \times 10^6 \pm 0.32 \times 10^6$ L/mol-sec	45.6±17.1 liters/mol	29,200±1000 cal/mol	--	--
Pulverized graphite	$5.69 \times 10^6 \pm 0.96 \times 10^6$ L/mol-sec	38.9±7.2 liters/mol	44,000±1200 cal/mol	--	--
Graphite rods	$9.97 \times 10^7 \pm 1.26 \times 10^7$ L/cm^2-sec	10.4±2.0 liters/mol	51,050±1670 cal/mol	0.83±0.02	$1.3 \times 10^3 \pm 0.2 \times 10^3$ cm^2/mol

5. Sulfate reduction with all carbons occurs through a common mechanism. The effects of carbon loading and sulfate concentration were similar with all carbons

used in this study. Similar rate expressions were able to accurately describe sulfate reduction with the three types of carbon. Also, for all types of carbon studied, the sulfate reduction mechanism involved the catalytic action of carbonate. In noncarbonate melts, the sulfate reduction rate with all forms of carbon was approximately an order of magnitude slower than in carbonate melts. Since reduction with all carbons studied is catalyzed by carbonate and can be described by a common rate equation, a common mechanism appears responsible for reduction with these various carbons.

6. The most significant difference between sulfate reduction with graphitic carbon and char is the high reduction rate with char. This high reactivity of char may be accounted for by its high surface area relative to pulverized graphite. Although char at 1400°F is approximately 30 times more reactive than pulverized graphite, its BET surface area is also 30 times as great.

7. Sulfate reduction in commercial smelt is essentially identical to sulfate reduction in synthetic smelt using reagent-grade chemicals. No catalytic effects or unusual reactions were observed with commercial smelt. The reactions investigated during this program are those responsible for reduction in a kraft recovery furnace.

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NOMENCLATURE

$C(A)_{ads}$	Adsorbed A
C_f	Free active carbon site
C_f'	Free active carbon site resulting from adsorbed carbon monoxide
CSA	Carbon surface area
C_T	Total active carbon sites per unit surface area
C_T'	Total active carbon sites resulting from adsorbed carbon monoxide per unit surface area
ΔE	Activation energy
FA	Fraction of active sites
FAI	Initial fraction of active sites
FI	Fraction of inactive sites
K_0	Frequency factor for Arrhenius' Equation
K'	Proportionality constant for Eq. (15)
K_4	Equilibrium constant for Eq. (9)
NA	Number of active sites per unit surface area
NI	Number of inactive sites per unit surface area
NT	Total number of sites per unit surface area
R	Ideal gas constant
SI	Amount of sulfide formed per unit surface area
SO_4I	Initial sulfate concentration per unit surface area
T	Absolute temperature, °K

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