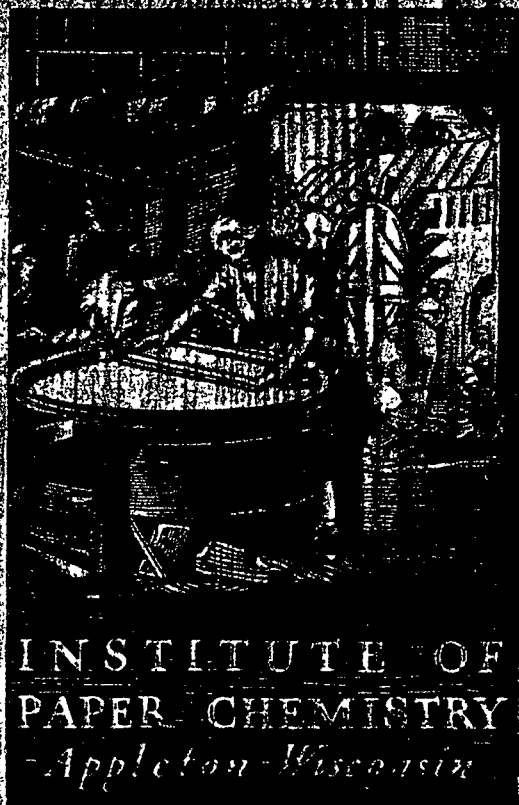


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**A KINETIC STUDY OF CARBON OXIDATION IN AN
ALKALI CARBONATE MELT**

Project 3473-I

**Report Three
A Progress Report
to**

MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

January 31, 1965

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

A KINETIC STUDY OF CARBON OXIDATION IN AN ALKALI CARBONATE MELT

Project 3473-1

Report Three

A Progress Report

to

MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

January 31, 1985

EXECUTIVE SUMMARY

This is one report in a series describing the fundamental processes occurring within a kraft recovery furnace. This report describes the kinetics of simultaneous carbon oxidation and sulfide reduction in an environment similar to that present in the bed of a recovery furnace.

Carbon oxidation is only part of the complex process of black liquor combustion. However, knowledge of carbon oxidation is valuable in itself. Such knowledge provides a basis for informed decisions on how to meet recovery boiler operating objectives such as improved reduction, bed control, and blackout prevention. The greatest potential benefit would be the ability to achieve enhanced burning rates of large particles of liquor which in turn would allow increased hearth loadings with minimum carryover. This could result in significant capacity improvement.

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Appleton, Wisconsin

A KINETIC STUDY OF CARBON OXIDATION IN AN ALKALI CARBONATE MELT

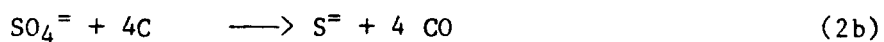
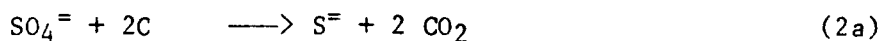
SUMMARY

In a kraft recovery furnace, carbonaceous char is produced during the pyrolysis of kraft black liquor. In the char bed, oxidation of the carbon content of this char occurs simultaneously with sulfate reduction. Despite the obvious importance of the oxidation and reduction reactions, there is little information available concerning their fundamental nature. Earlier reports (1,2) have described carbon oxidation by sulfate (sulfate reduction). This report describes a kinetic study of air oxidation of carbon in alkali carbonate-sulfate melts.

Although carbon oxidation is only part of the complex process of black liquor combustion, knowledge of carbon oxidation is valuable in itself. Such knowledge provides a basis for informed decisions on how to meet recovery boiler operating objectives such as improved reduction, bed control, and blackout prevention. The greatest potential benefit would be the ability to achieve enhanced burning rates of large particles of liquor which in turn would allow increased hearth loadings with minimum carryover. This could result in significant capacity improvement.

In this report, the mechanism for simultaneous carbon oxidation and sulfate reduction during kraft char oxidation is described. Rate controlling parameters for these reactions are determined, rate expressions are developed, and appropriate rate constants are determined for these reactions.

There are two possible basic mechanisms for the oxidation of the carbon content of kraft black liquor char. These mechanisms are direct oxidation of the carbon with oxygen, generating either carbon monoxide or carbon dioxide, Eq. (1a, 1b) or oxidation through a sulfide-sulfate cycle, Eq. (2a, 2b, 3).



In the sulfate-sulfide cycle, sulfate oxidizes carbon, forming sulfide and carbon dioxide or carbon monoxide. This sulfide is then reoxidized by oxygen to sulfate, completing the cycle.

To determine which of these basic mechanisms is responsible for kraft char oxidation in a carbonate melt, oxidation of various carbons (pulverized graphite, soda char, and kraft char) was studied with and without sulfur added to the melt. For pulverized graphite and soda, the magnitude of the sulfate-sulfide cycle during air oxidation was determined by comparing the oxidation rate with sulfur present to that without sulfur present. For kraft char the effect of the sulfate-sulfide cycle was determined by comparing the air oxidation rate to the sulfate oxidation rate.

One reaction which occurs during carbon oxidation in a carbonate melt containing sulfur is the oxidation of sulfide to sulfate. To determine if this reaction would limit the rate of the sulfate-sulfide mechanism, sulfide oxidation with air was studied by purging air through a sodium carbonate melt containing sulfide and was found to be extremely fast. The oxidation rate of the

sulfide was limited only by the availability of oxygen until the sulfide was nearly completely oxidized.

To determine the magnitude of the sulfate-sulfide cycle in carbon oxidation, air oxidation of pulverized graphite and soda char was studied in carbonate melts with and without sulfur present. Without sulfur present, air oxidation of pulverized graphite and soda char carbon was determined to be first order in the carbon concentration and independent of the oxygen partial pressure. Air oxidation of these carbons is described by the following rate expression.

$$\frac{d[C]}{dt} = - K[C] e^{-\Delta E/RT} \quad (4)$$

Here [C] is the carbon concentration, mole/L;

K is a constant;

ΔE is the activation energy;

R is the ideal gas constant; and

T is the absolute temperature.

It was found that adding sulfur to the melt increased the air oxidation rate of pulverized graphite by a factor of two at 1600°F and increased the air oxidation rate of soda char by a factor of six at 1450°F. These results demonstrate that the sulfate-sulfide cycle significantly enhances the air oxidation rate of pulverized graphite and soda char in a carbonate melt.

The magnitude of the sulfate-sulfide cycle during kraft char oxidation was determined by comparing the air oxidation rate of kraft char to the sulfate oxidation rate of kraft char. The air oxidation rate of kraft char was found to be essentially the same as the sulfate oxidation rate. At 1450°F there was less

than a 2% difference between the air and sulfate oxidation rates for kraft char. Also, over the temperature range of this study both the air oxidation rate expression, Eq. (4) for kraft char and the previously developed sulfate oxidation rate expression for kraft char (2) predict nearly identical oxidation rates.

These results demonstrate that the air oxidation rate for kraft char is the same as the sulfate oxidation rate. Therefore air oxidation of kraft char occurs exclusively through the sulfate-sulfide cycle. When air is added to a melt containing kraft char, the air oxidizes the sulfur present in the char to sulfate, which then oxidizes the carbon in the char. Since there is no enhancement in the oxidation rate over the sulfate oxidation rate, there is no direct oxidation of the carbon by oxygen.

The major conclusions of this report are summarized below.

1. Air oxidation of sulfide in a carbonate melt is an extremely fast reaction. In the experimental system used in this study, sulfide oxidation was limited only by the availability of oxygen.
2. Air oxidation of pulverized graphite and soda char in an alkali carbonate melt without sulfur present is first order in the carbon concentration and independent of the oxygen partial pressure. The air oxidation rate constants for these carbons and for kraft char and the predicted reaction rate at 1520°F are shown in Table 1.
3. Without sulfur present, air oxidation of pulverized graphite or soda char is a relatively slow reaction. The faster air oxidation rate for kraft char is due to the presence of sulfur and resulting sulfate-sulfide cycle.

Table 1. Oxidation rates of carbon in an alkali carbonate melt.

$$\frac{d[C]}{dt} = -K [C] e^{-\Delta E/RT}$$

Carbon Type	K (sec ⁻¹)	ΔE (cal/mole)	Rate at 1520°F (1100°K) [C] = 0.37 moles/L (moles/L-s) x 10 ⁴
Pulverized graphite	123 ± 9.0	27,950 ± 800	1.27
Soda char	172 ± 7.0	26,420 ± 1000	3.58
Kraft char	3910 ± 360	30,167 ± 2000	14.7

4. The air oxidation and sulfate oxidation rates for kraft char are the same. A comparison of separate experiments at 1450°F for these reactions demonstrated that both oxidation reactions are first order in carbon and have the same rate constants within 2%. Assuming that carbon dioxide is the principal product from sulfate oxidation of kraft char, the models for both air oxidation and sulfate oxidation of kraft char also predict the same carbon oxidation rate.

5. Air oxidation of kraft char occurs through a sulfate-sulfide cycle. Here, sulfide is oxidized by air to sulfate, which then oxidizes the carbon content of kraft char, forming sulfide and principally carbon dioxide.

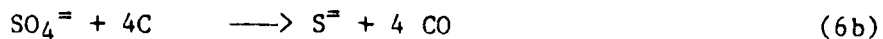
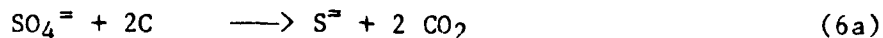
INTRODUCTION

This is the third in a series of reports concerned with the kinetic processes occurring in the bed of a kraft recovery furnace. Earlier reports (1,2) described sulfate reduction (carbon oxidation by sulfate) with various forms of carbon including kraft black liquor char. This report describes a kinetic study of air oxidation of different forms of carbon (kraft char, soda char, and pulverized graphite) in alkali carbonate melts with and without sulfur present.

In a kraft recovery furnace, carbonaceous char is produced from the pyrolysis of kraft black liquor. In the char bed, oxidation of the carbon content of this char occurs simultaneously with reduction of sulfate to sulfide. Although sulfate contained in the black liquor supplies some of the oxygen necessary for oxidation of the carbon, combustion air is the principal source of oxygen.

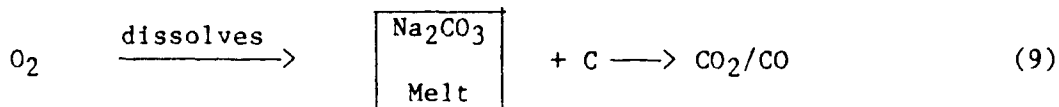
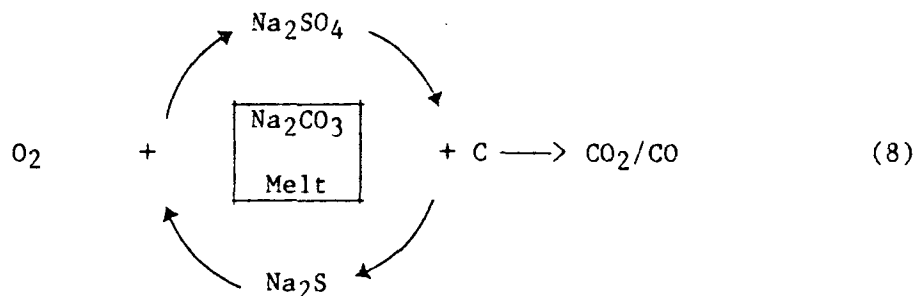
Since the temperature of the chemically active layer in the char bed is above the melting point of the salts present in the char, this section of the char bed may be perceived as discrete carbon particles covered with molten smelt. Carbon oxidation in the bed of the furnace then occurs within a molten smelt environment. This report presents a kinetic study of carbon oxidation within such an environment.

There are two possible basic mechanisms for the oxidation of the carbon content of kraft black liquor char in the bed of the furnace. These are direct oxidation of the carbon by oxygen, Eq. (5a), (5b), generating carbon dioxide or carbon monoxide, or oxidation of the carbon through a sulfate-sulfide cycle, Eq. (6a), (6b), (7).



The sulfate-sulfide cycle for the oxidation of carbon in a Na_2CO_3 melt containing sulfur was first proposed by Stelman, et al. (3). In this cycle, the carbon is oxidized by sulfate generating sulfide and carbon dioxide or carbon monoxide. The sulfide formed is then reoxidized by oxygen to sulfate, completing the cycle.

As illustrated by Eq. (8), sulfur in this cycle serves as a carrier of the oxygen from the air to the carbon in the Na_2CO_3 melt. This contrasts to direct oxidation of the carbon where oxygen dissolves in the melt and directly oxidizes the carbon, Eq. (9).



In this report, the mechanism for simultaneous carbon oxidation and sulfate reduction during kraft char oxidation is described.

PROJECT OBJECTIVES

The project objectives are to obtain fundamental kinetic data on the oxidation of carbon in carbonate melts, to define the effect that sulfur has on this process, and to define the process through which carbon present in the molten smelt in a kraft recovery furnace is burnt. The fundamental kinetic data include experimental data on the effects of temperature, sulfur level, oxygen partial pressure, and form of carbon.

Kinetic data were obtained on carbon oxidation for pulverized graphite, soda char, and kraft char. The pulverized graphite is a form of carbon that is more easily characterized than the kraft or soda chars. If it can be shown that the oxidation of pulverized graphite in a carbonate melt is similar to the oxidation of char, the mechanistic insights gained using pulverized graphite can be applied to defining the oxidation mechanism for char. Studying air oxidation of both kraft and soda char enabled the effect of sulfur on char oxidation to be isolated.

EXPERIMENTAL OBJECTIVE

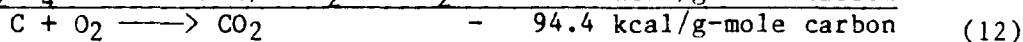
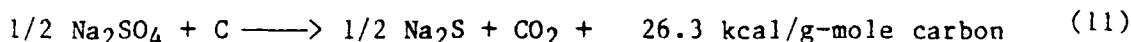
The major experimental objectives are summarized below:

1. Design an experimental system to study air oxidation of carbon in a carbonate melt. Such a system includes methods for uniformly dispersing the carbon in the carbonate melt.
2. Develop experimental procedures for producing consistent char samples.
3. Obtain kinetic data on char oxidation in a carbonate melt. Such data would include the effects of temperature, oxygen partial pressure, sulfur, carbon loading, and form of carbon.

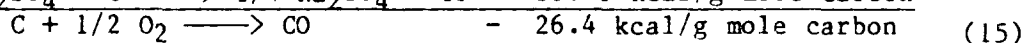
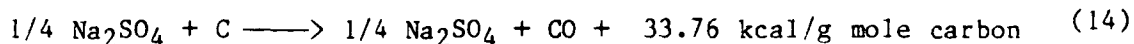
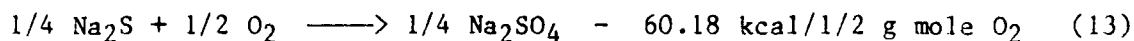
CHEMISTRY OF CARBON OXIDATION IN A CARBONATE MELT

BASIC CHEMISTRY

In the char bed of a kraft recovery furnace, char oxidation to form carbon monoxide and carbon dioxide occurs simultaneously with sulfate reduction. In fact, the main route for carbon oxidation may be the sulfate-sulfide cycle, Eq. (10)-(15).



or



In this mechanism sodium sulfide is oxidized to sulfate; the sulfate then acts as a carrier for oxygen and oxidizes carbon. The oxidation of sulfide is an exothermic reaction and sulfate reduction is an endothermic reaction. The net result of this cycle is an exothermic reaction with the magnitude of the exotherm being dependent on whether carbon monoxide or carbon dioxide is formed as the product gas.

REVIEW OF SULFATE REDUCTION WORK

Sulfate reduction (carbon oxidation by sulfate) is one step in the sulfate-sulfide oxidation cycle of carbon. The other step in this cycle is the oxidation of the sulfide by air to sulfate. In Progress Reports One and Two of

this series (1,2), the kinetics of sulfate reduction in a carbonate melt with graphite rods, pulverized graphite, and kraft char as reducing agents were presented.

To assess the magnitude of the sulfate-sulfide cycle in the oxidation of the carbon content of kraft black liquor char, it is necessary to know the rate of sulfate reduction with kraft black liquor char. By comparing the rate of sulfate oxidation to that of air oxidation of kraft char, the extent of oxidation occurring through the sulfate-sulfide cycle can be determined. Progress Report Two (2) contains the rate expression and parameters necessary to evaluate the function of sulfate oxidation of carbon during the combustion of kraft black liquor char.

The reduction reactions were conducted in alumina crucibles containing either 1.5 L or 0.04 L of melt. The crucibles were contained within steel retorts that were heated by either an electric furnace (in the case of the larger crucible) or by a radio frequency induction furnace (in the case of the smaller crucible). Reduction was initiated by adding graphite rods to the molten salts or by rapidly heating a mixture of carbon and alkali carbonate-sulfate salts to the desired reaction temperature. The reduction rate was measured through quantitative analysis of the carbon dioxide and carbon monoxide concentrations in the off-gases from the reaction, using an infrared spectrophotometer.

The reduction reactions were found to be first order with respect to carbon and to be zero order with respect to sulfate at high sulfate concentrations. At low sulfate concentrations, sulfate reduction with the graphite rods became distinctly first order in sulfate. With pulverized graphite and

kraft char, the rate of sulfate reduction decreased at low sulfate concentrations, but did not exhibit clearly the first order behavior observed with the graphite rods. Depending on the type of carbon used, the activation energy for sulfate reduction varied from 50,000 cal/mol to 30,000 cal/mol.

To explain these results, a mechanism based on the adsorption and reduction of sulfate on an active surface site was proposed. In this mechanism, the active site was perceived to be an adsorbed oxygen on the carbon surface, formed by the reaction of carbon dioxide with the carbon. The sulfate then adsorbed on this site and was reduced, forming carbon dioxide and sulfide, which then desorbed from the carbon surface. Based on this mechanism, the following rate equation describing sulfate reduction with carbon was derived, Eq. (16).

$$\frac{d[SO_4]}{dt} = \frac{-K[SO_4][C]}{1 + K_4[SO_4]} e^{-\Delta E/RT} \quad (16)$$

Here, $[SO_4]$ is the sulfate concentration;

$[C]$ is the carbon concentration;

ΔE is the activation energy;

R is the ideal gas constant;

T is the absolute temperature; and

K and K_4 are constants.

Of the carbons used as reducing agents, only the graphite rods exhibited autocatalytic behavior. This autocatalytic behavior was shown to be due to an increase in active sites on the rod's surfaces as reduction proceeded. To account for this autocatalytic behavior, Eq. (16) was modified for the graphite rods by multiplying the right side by a function describing this increase in active surface sites.

The rate constants for sulfate reduction with pulverized graphite and kraft char and the predicted reaction rates for the listed concentrations of sulfate and carbon are listed in Table 2. With the exception of the rates being calculated at a higher carbon level, this table is the same as Table 10 in Progress Report Two (2). The rate constants for the three types of carbon used for reduction are listed in several areas of Progress Report Two. However, in Table 11 on Page 78 there is a typographical error in the value of K for pulverized graphite and kraft black liquor char. The correct values are shown in Table 2 of this report and in Tables 7 through 10 of Progress Report Two.

CATALYTIC EFFECT OF ALKALI CARBONATE

In Progress Report Two (2), it was shown that sulfate reduction with carbon is strongly catalyzed by the carbonate melt. The rate of sulfate reduction with the three carbons studied in Progress Report Two (2) (graphite rods, pulverized graphite, and kraft char) was considerably slower in either sodium chloride-sodium sulfate or pure sodium sulfate than in sodium carbonate-sodium sulfate melts. Based on an apparent initial catalytic effect of carbon dioxide, the catalytic nature of the carbonate melts was attributed to the formation of an adsorbed oxygen on the carbon surface. This oxygen on the carbon surface then served as an active site. Reduction was proposed to occur by fast reversible adsorption of the sulfate on these sites, followed by reduction, and a slower rate determining desorption of the products.

The catalytic effect of alkali carbonates in the reactions involving coal char is well known. Among the reactions which alkali carbonates are known to catalyze are the gasification reactions of coal char with steam, oxygen, and carbon dioxide (4,5). It is likely that the mechanism by which alkali

Table 2. Sulfate reduction rates with pulverized graphite and kraft black liquor char.

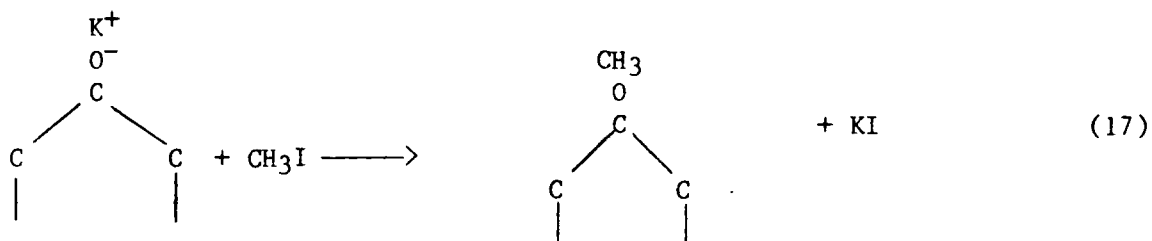
$$\frac{d[SO_4]}{dt} = \frac{-K[SO_4][C]}{1 + K_4[SO_4]} e^{-\Delta E/RT}$$

Conditions $[SO_4] = 0.60$ mol/L
 $[C] = 1.20$ mol/L
 $T_1 = 1400^\circ F$ (1033°K)
 $T_2 = 1600^\circ F$ (1144°K)

	K (liter/mol-s)	K ₄ (liter/mol)	ΔE cal/mol	BET Surface Area (m ² /g)	Rate (mol/liter-s) at T ₁	Rate (mol/liter-s) at T ₂
Pulverized graphite	1.92 x 10 ⁶	38.9	44,000	19.7	2.80 x 10 ⁻⁵	2.23 x 10 ⁻⁴
Kraft black liquor char	5.96 x 10 ⁴	45.6	29,200	580	1.00 x 10 ⁻³	3.99 x 10 ⁻³
Ratio graphite/char					0.028	0.056

carbonates catalyze these reactions is similar to that by which alkali carbonates catalyze sulfate oxidation of carbon (sulfate reduction).

Recently, progress has been made in determining the mechanism by which alkali carbonates catalyze the carbon gasification reactions. Mims and Pabst (6) have shown that potassium carbonate reacts with coal char or carbon to form surface salt complexes such as phenoxide groups. By surface methylation and solid NMR, such surface complexes were correlated with the rate of gasification reactions of the carbon. The surface methylation reaction was represented as:



By this technique, it was demonstrated that the rate of the gasification reactions is correlated to the number of these oxygen sites on the carbon surface. This is consistent with these sites being active sites for the gasification reactions. Therefore, an important characteristic of the catalytic nature of alkali carbonate is the formation and stabilization of these oxygen groups. Based on these results, Mims and Pabst proposed that the mechanism for the carbon gasification reactions involved these surface oxygen sites serving as active sites, with gasification occurring through a rapid reversible oxidation of these sites, followed by a slower desorption step.

This mechanism, based on the identification of oxygen bonded to the carbon surface as active sites, is basically the same as that proposed for sulfate reduction by carbon in Progress Report Two (2). In both mechanisms, the catalytic effect of the carbonate results from the formation and stabilization of a carbon-bonded oxygen on the carbon surface.

ATOMICS INTERNATIONAL RESEARCH

To support their molten salt coal gasification process, Atomics International has conducted a considerable amount of research on coal oxidation in molten Na_2CO_3 . This coal gasification process consists of the partial oxidation of coal in molten Na_2CO_3 . With this process, a low Btu gas is produced and any sulfur present in the coal is converted to Na_2SO_4 and Na_2S . The federal government has been one of the major sponsors of this research, and a number of papers describing reactions in this process have been published. These papers can be divided into two areas: those relating to the study of carbon oxidation in a Na_2CO_3 melt (3,7-9) and electrochemical studies of Na_2CO_3 melts (10-14).

Carbon Oxidation Studies in Sodium Carbonate Melt

The papers describing carbon oxidation in carbonate melt were published over a five-year period (1976-1981). As might be expected, the last paper published (9) is the most comprehensive of this series. This paper describes carbon oxidation by oxygen with and without sulfur present and sulfate reduction by carbon. The experimental design, results, and conclusions are summarized below.

Using two different size reactors (one containing 5500 g of melt and one containing 125 g), they studied carbon oxidation with either sulfate or oxygen in sodium carbonate-sodium sulfate melts. Spectrographic grade powdered graphite sieved to produce a particle 0.15 mm to 0.18 mm in diameter was used as the carbon source and the reactions were studied from 1650 to 1900°F.

The experimental results from this study are summarized below:

1. Temperature Dependence

- a. Air oxidation of carbon in carbonate-sulfate melt:
Activation energy was 50 cal/mole in the large reactor and 76 cal/mole in the small reactor.
- b. Reduction of sulfate: Activation energy was 57 cal/mole in the larger reactor and 64 cal/mole in the small reactor.
- c. Air oxidation of carbon in pure carbonate: Activation energy was 32 cal/mole in the large reactor and 28 cal/mole in the small reactor.

The difference in activation energies between the two reactors indicates that mixing the melt and carbon may have been a problem.

2. Oxygen Dependence for Carbon Oxidation

For pure carbonate melts, the oxygen dependence was half-order. For melts containing sulfate, the dependence was approximately zero order (0.1 to 0.2). These values were obtained with only two levels of oxygen: pure air and pure oxygen.

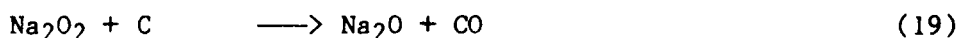
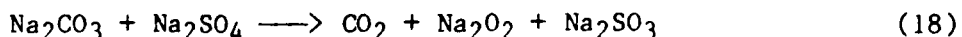
3. Carbon Dioxide Dependence

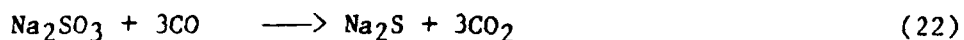
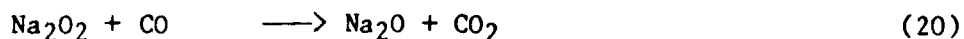
A slight decrease was observed in carbon combustion in pure carbonate melt when carbon dioxide was added to the purge.

4. Graphite Surface Area Dependence for Carbon Oxidation

Depending on the sulfate and carbon level, the carbon surface area dependence varied from 0.45 to 1.0 order, based on the initial surface area.

Depending on the reactions (sulfate reduction, carbon oxidation in pure carbonate, etc.) rather complex mechanisms were proposed. These mechanisms are based on a series of sulfur and sodium oxide intermediates. Typical of these mechanisms is the oxidation of carbon in a carbonate-sulfate melt with air, Eq. (18)-(24).





The catalytic effect of carbonate is explained by Reaction (18).

Support for the other reactions is based on the shift in carbon dependence and on the sodium oxides being known species in carbonate melts.

The addition of sulfur to an alkali carbonate melt significantly increased the air oxidation rate. Based on this catalytic effect, Stelman et al. (3) proposed the sulfate-sulfide cycle.

Electrochemical Studies of Graphite Oxidation in Sodium Carbonate Melt

Four of the Atomics International papers (10-14) describe an electrochemical technique for determining the ionic species present in sodium carbonate melts. This technique is used to determine the species present in carbonate melt under various atmospheres and the intermediate species present during carbon oxidation in carbonate melt.

A. Experimental Design

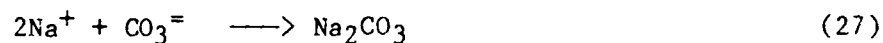
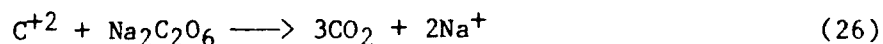
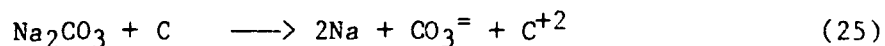
The experimental apparatus used in this study is well described. It consists of an electrochemical cell contained in an electric tube furnace. Product gases from this reactor are passed through O_2 , CO_2 , and CO analyzers and a gas chromatograph. Therefore, in addition to the electrochemical measurements, the reactions can be followed from gas analysis.

B. Results

The electrochemical waves generated were quite complex and were analyzed through the use of computer synthesized curves. This analysis showed that all experimental electrochemical measurements could be described by eight electrochemical waves.

The intermediates in the carbonate melt during carbon oxidation by oxygen were determined by following changes in the peak currents after the addition of the graphite. Based on the behavior of the electrochemical wave assigned to peroxydicarbonate ion ($C_2O_6^{=}$) when comparing oxidation and control experiments, the peroxydicarbonate ion was proposed to react directly with carbon.

The oxidation rate of a graphite electrode was increased by application of a positive potential and decreased by application of a negative potential. This suggests that the rate limiting step of carbon oxidation in a carbonate melt involves an ionic species. A sequence of reactions proposed for the oxidation of carbon in a carbonate melt is shown below.



Here, the catalytic effect of carbonate is due to the reaction of carbonate with carbon to form elemental sodium and a positively charged carbon site. Peroxydicarbonate then reacts with this positive site, and the elemental sodium is oxidized by oxygen. In this mechanism, oxidation occurs through an elemental sodium intermediate.

The use of electrochemical techniques in these systems appears to be quite complex. The resolution of the electrochemically observed waves required the construction of these waves from computer generated theoretical waves. Due to the complexity of this technique, it is difficult to evaluate the validity of the proposed mechanisms. However, some of the proposed intermediate species appear to have been identified. This technique may provide valuable insights into the intermediate species present in carbonate melts.

EXPERIMENTAL APPROACH

The principal objective of this study was to define the process through which the carbon content of the char is burnt in a kraft recovery furnace. This process occurs in the bed of the recovery furnace at temperatures in excess of 1400°F. This is above the melting point of the inorganic salts contained in the kraft char, and oxidation of the carbon content of the char may be considered to occur in a molten salt environment. Therefore, to define the kinetics of the combustion process, carbon oxidation was studied in molten alkali carbonate-sulfate systems.

Air oxidation of three different types of carbon - pulverized graphite, soda char, and kraft char - in carbonate melts with and without sulfur added is described in this report. The pulverized graphite was used, since this is a more readily characterized carbon than the chars. If the carbon oxidation process can be defined using this carbon, and if it can be shown that the same mechanism is responsible for char oxidation, the insights obtained using pulverized graphite can be applied to understanding the oxidation reaction of char.

To aid the reader in understanding the experimental program, 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. Sulfate Reduction with Soda Char: One method of determining the effect of the sulfate-sulfide cycle would be to compare oxidation with and without sulfur present. Since kraft char contains sulfur, it is not possible to study air oxidation

of kraft char without sulfur present. Therefore, to make this comparison for char, air oxidation of soda char was studied with and without sulfur present. Since the rate of soda char oxidation with sulfate (or sulfate reduction rate with soda char) was not previously determined and was required for this comparison, it was determined in this experimental section.

3. Sulfide Oxidation: One of the reactions occurring in the sulfate-sulfide cycle is air oxidation of sulfide to sulfate. The study of this reaction is described in this section.
4. Carbon Oxidation without Sulfur Present: In this section, air oxidation of pulverized graphite and soda char in a carbonate melt with no sulfur present is described. The effects of oxygen partial pressure and carbon loading are determined and suitable rate expressions are developed. These expressions will be used in comparing the rates of air oxidation of sulfur- and nonsulfur-containing melts and in determining the magnitude of the sulfate-sulfide cycle.
5. Carbon Oxidation with Air in Carbonate Melts Containing Sulfur: In this section the results from the study of air oxidation with sulfur present of the three carbons used in this study - pulverized graphite, soda char, and kraft char - are described. These results are compared to air oxidation without sulfur present. Based on these comparisons, the significance of the sulfate-sulfide cycle is determined.

EXPERIMENTAL SYSTEM

The experimental reactor used to study carbon oxidation is illustrated in Fig. 1. The reactor vessel consisted of a ceramic crucible 2-1/2 inches in diameter and 4 inches high contained in a stainless steel retort. The steel retort was heated by an induction heating coil energized by a 20-kw Lepel high frequency power supply. The ceramic crucible was then heated by thermal radiation from the steel retort. Various mixtures of air and nitrogen were bubbled through the purge tube illustrated in Fig. 1. To keep the melt well mixed and to ensure good liquid and gas content, the gas purge rate was maintained at a flow rate of 1 L/minute or more. The temperature of the melt was monitored using a chromel-alumel thermocouple.

To prepare for a carbon oxidation experiment in a carbonate melt, anhydrous reagent-grade alkali carbonates and sulfate (for the experiments with sulfur present) were mixed and dried under vacuum for 2 hours at 300°F. The carbon was then added to these salts, and this mixture was placed in the alumina crucible. This mixture was then rapidly heated to the desired reaction temperature under a nitrogen purge. Approximately 5 to 10 minutes were required to melt the salts (melting point 1200 to 1300°F) and an additional 15 minutes to reach the desired reaction temperature. Shortly before the desired reaction temperature was reached, air was added to the purge stream.

Figure 2 illustrates the configuration of the experimental system. To accurately measure the nitrogen and air flow rates, these gases were metered from pressurized gas cylinders through thermal mass flowmeters. These flowmeters provided an instantaneous reading of flow rates and 0 to 5-V output signals. A mercury manometer in the nitrogen line monitored the purge pressure

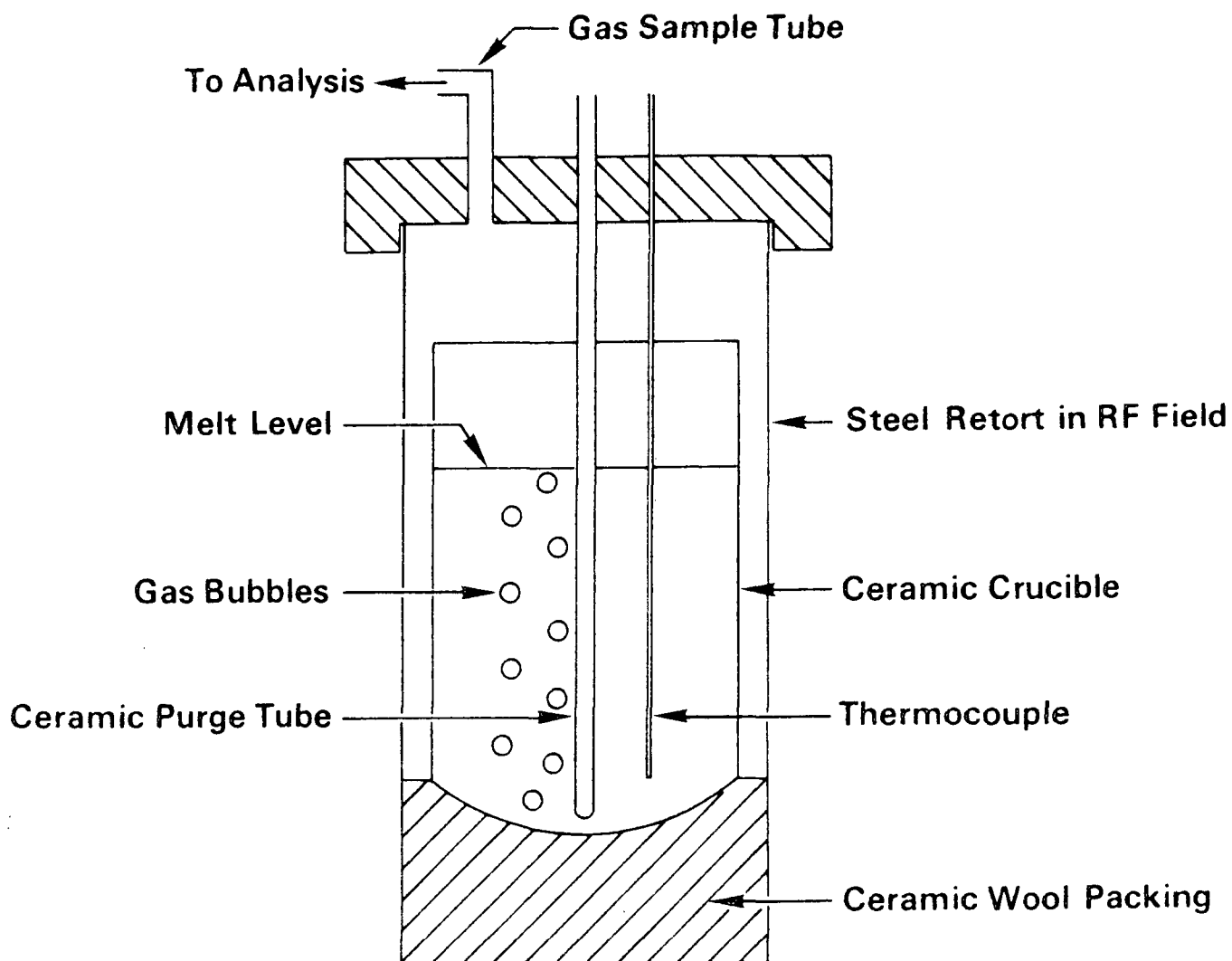


Figure 1. Experimental reactor.

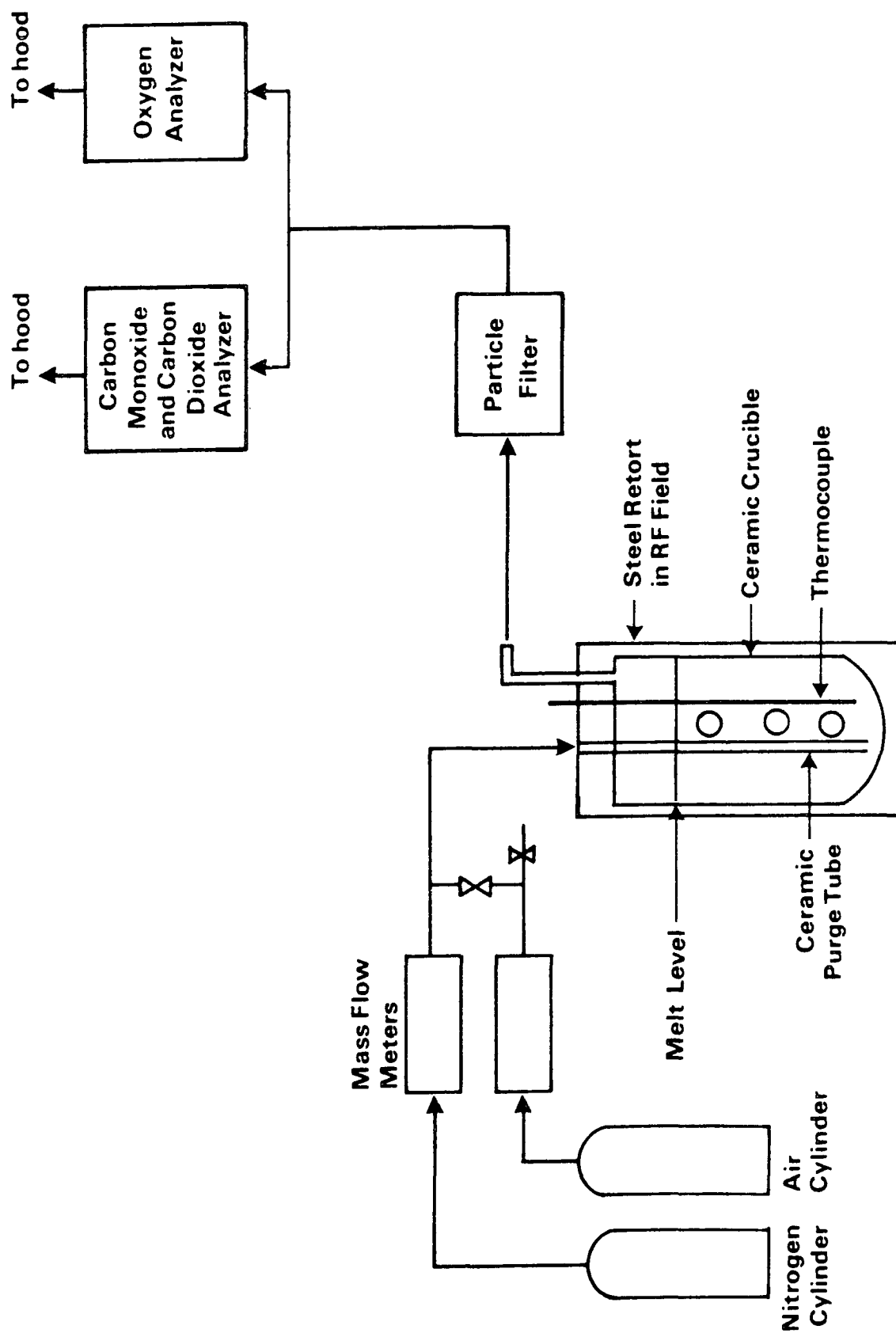


Figure 2. Experimental system.

and served as a pressure release valve. If the purge line from the reactor were to become plugged, the mercury in this manometer would be blown into a vial, releasing the purge pressure and preventing overpressurization of the reactor.

After the flow rates of the gases were measured, the air and nitrogen were mixed and entered the reactor through the purge tube. The gases exited the reactor through a 1/4-inch steel line located at the top of the steel retort. These gases then passed through an infrared carbon monoxide and carbon dioxide analyzer (Model IR 702-703, Infrared Industries, Santa Barbara, California) and an electrochemical oxygen analyzer (Model 326A, Teledyne, City of Industry, California). Both these meters provided instantaneous readings and d.c. voltage output signals.

The voltage signals from the mass flowmeters, thermocouple, carbon monoxide/dioxide analyzer, and oxygen analyzer were converted to digital signals and sampled several times a second using an Apple Computer. Average values of these signals were then recorded over a set time interval. The data acquisition system also integrated the reaction rate, calculated the melt composition, and provided a printed copy of input data, reaction rates, and melt composition.

REAGENTS

CARBONS

During this project, the oxidation of three forms of carbon - pulverized graphite, soda char, and kraft char - in a carbonate melt was studied. The pulverized graphite was produced by pulverizing graphite rods obtained from the Becker Brothers Carbon Corporation, Cicero, Illinois, into micron sized particles. Oxidation of pulverized graphite was studied, since this is a readily characterized carbon and the mechanistic insights obtained here can be applied to understanding char oxidation.

The soda and kraft chars were obtained by pyrolyzing dried soda and kraft liquors. The soda liquor was produced from a laboratory soda cook, whereas the kraft liquor was a mill liquor obtained from the Thilmany Pulp and Paper Co., Kaukauna, Wisconsin. The liquors were first dried under vacuum at 150°C and then pyrolyzed in a covered ceramic crucible at 950°C for 7 minutes. This pyrolyzing procedure is based on that recommended for determination of the volatile content of coal (15). During the pyrolysis of the dried liquors, approximately 35% of the liquor was volatilized.

The results of elemental analyses of the chars by Hoffman Laboratories, Inc., Wheat Ridge, Colorado, are shown in Table 3.

From the carbon dioxide and carbon monoxide generated during char oxidation, it was found that the total carbon evolved was 25.5% of the kraft char and 26.9% of the soda char.

Table 3. Elemental analysis of chars.

Element	Kraft Char Weight %	Estimated Standard Deviation	Soda Char Weight %	Estimated Standard Deviation
Carbon	29.4	± 0.15	33.4	± 0.15
Hydrogen	0.65	± 0.15	0.53	± 0.15
Oxygen	33.8	± 0.5	35.9	± 0.5
Sulfur	2.12	± 0.1	0.03	± 0.03
Chlorine	0.56	± 0.15	--	--
Potassium	3.39	± 0.20	0.27	± 0.02
Sodium	<u>26.0</u>	± 1.3	<u>29.4</u>	± 1.5
Total	95.9		99.5	

To determine the surface areas of the chars, the chars were first washed to remove the inorganic salts. The surface areas were then measured by nitrogen gas absorption utilizing a gas-flow sorptometer and reference sample of titanium (IV) oxide (surface area $10.3 \text{ m}^2/\text{g}$). The surface areas of the pulverized graphite, unwashed kraft char, and washed kraft and soda chars are shown in Table 4.

Table 4. Surface area of pulverized graphite and chars.

Carbon	BET Surface Area, m^2/g
Pulverized graphite	19.7
Unwashed kraft char	25.2
Washed kraft char	580
Washed soda char	569

MELT COMPOSITION

The melts used in this study typically consisted of 0.51 mole Na_2CO_3 , 0.26 mole K_2CO_3 and 0.01 mole Na_2SO_4 . The addition of K_2CO_3 lowered the melting point of the melts to a range where the char oxidation reactions could be studied.

The rate expressions developed in this report are based on a melt density of 1.92 kg/liter. This density is based on the density of $\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ melts (16) and $\text{Na}_2\text{CO}_3\text{-Na}_2\text{S}$ melts (17) in the temperature range of this study. The addition of K_2CO_3 and Na_2S to a Na_2CO_3 melt has little effect on melt density. For example, at 1700°F the difference in density between a 100% Na_2CO_3 melt and a 70% $\text{Na}_2\text{CO}_3\text{-30% K}_2\text{CO}_3$ is 0.8% and the difference between a 100% Na_2CO_3 and a 70% $\text{Na}_2\text{CO}_3\text{-30% Na}_2\text{S}$ melt is 1.5%.

EXPERIMENTAL RESULTS

SULFATE REDUCTION WITH SODA CHAR

To determine the magnitude of the sulfate-sulfide cycle in carbon oxidation, it was necessary to study air oxidation of carbon in a carbonate melt with and without sulfur present. Since kraft char contains sulfur, a soda char was prepared to study the oxidation of char without sulfur present. To determine the effect of sulfur on the oxidation of soda char, it was necessary to define sulfate reduction with soda char.

Similarly to sulfate reduction with pulverized graphite and kraft char, reduction with soda char was found to be independent of the sulfate concentrations until low levels of sulfate were reached and directly proportional to the carbon content of the melt. Therefore, the reaction mechanism for sulfate reduction with soda char appeared to be the same as that for sulfate reduction with pulverized graphite and kraft char. As expected, the rate expression, Eq. (30), describing sulfate reduction with pulverized graphite and kraft char also described sulfate reduction with soda char.

$$\frac{d[SO_4]}{dt} = \frac{-K[SO_4][C]}{1 + K_4[SO_4]} \times e^{-\Delta E/RT} \quad (30)$$

Here, $[SO_4]$ is the sulfate concentration, moles/L;

$[C]$ is the carbon concentration, moles/L;

ΔE is the activation energy;

R is the ideal gas constant;

T is the absolute temperature; and

K and K_4 are constants.

The three constants in Eq. (30) (K , K_4 , and ΔE) for soda char were determined using a nonlinear regression analysis program (18) to fit experimental data obtained over a large variation in experimental conditions to the kinetic equation for sulfate reduction, Eq. (30). The ability of this kinetic equation to describe sulfate reduction with soda char is illustrated in Fig. 3. Here, the reduction rate model, Eq. (30), is compared to the actual sulfate reduction rate from a typical reduction experiment.

Contained in Table 5 are the rate constants for the three carbons (pulverized graphite, kraft char, and soda char) used in this study and the predicted reduction rates at 1340 and 1520°F. Although the kinetic constants describing reduction for kraft char and soda char are different, the reduction rates for these chars are of the same order of magnitude, whereas the reduction rate for pulverized graphite is only 2 to 4% that of the chars.

SULFIDE OXIDATION

One of the objectives of this project is to define the mechanism through which the carbon in the smelt of a kraft recovery furnace is burnt. One possible mechanism for the oxidation of this carbon is the sulfate-sulfide cycle proposed by Stelman et al. (3). Since sulfide is a highly reactive species and may have an essential part in the carbon oxidation mechanism, the oxidation of sulfide was investigated.

Two experimental techniques were employed to study sulfide oxidation. As described in Progress Report One (1), sulfide oxidation was studied using a relatively large reactor containing 2500 grams of sodium carbonate and, initially, 78 grams of sodium sulfide. With this reactor, the sulfide was oxidized

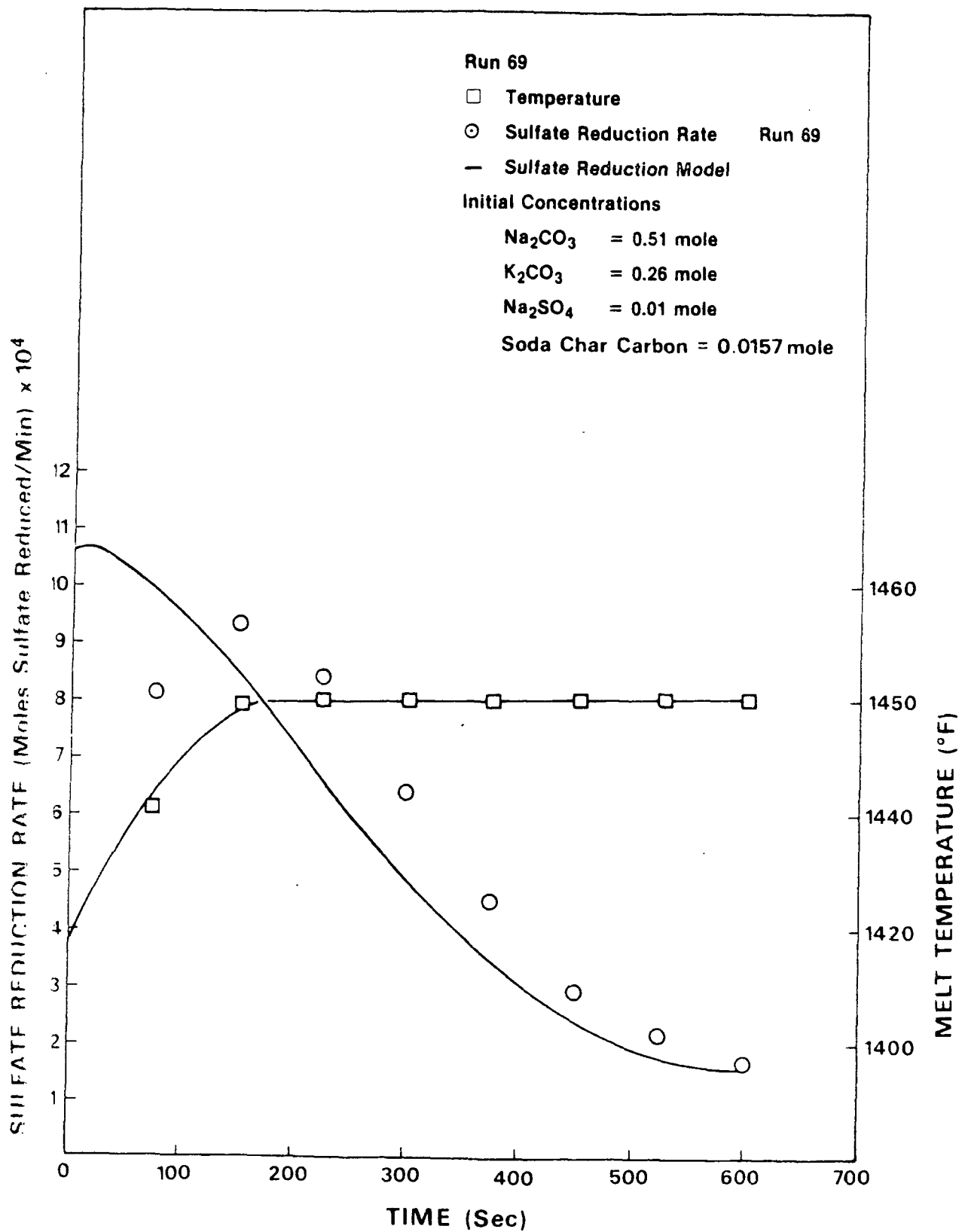


Figure 3. Sulfate reduction with soda char.

Table 5. Effect of form of carbon on sulfate reduction rate.

Carbon Type	K L/mole-s	K_4 L/mole	ΔE cal/mol	BET Surface Area, m ² /g	Rate at	
					[SO ₄] 1340°F (1000°K)	[C] = 1 1520°F (1100°K) moles/L-s
Pulverized graphite	(1.92 ± 0.32) x 10 ⁶	38.9 ± 7.2	44,000 ± 1200	19.7	9.48 x 10 ⁻⁶	7.1 x 10 ⁻⁵
Kraft char	(5.96 ± 1.86) x 10 ⁴	45.6 ± 17.1	29,200 ± 1000	580	4.45 x 10 ⁻⁴	1.69 x 10 ⁻³
Soda char	(7.46 ± 1.8) x 10 ⁶	24.5 ± 7.5	39,850 ± 1500	569	4.22 x 10 ⁻⁴	2.6 x 10 ⁻³

$$\frac{d[\text{SO}_4]}{dt} = \frac{-K[\text{SO}_4][\text{C}]}{1 + K_4[\text{SO}_4]} e^{-\Delta E/RT}$$

by bubbling air through the melt. The degree of oxidation was followed by periodically removing smelt samples from the reactor and analyzing them for sulfate and sulfide. Typical experimental results obtained using this reactor are illustrated in Fig. 4. Here, the amount of sulfate remaining in the melt is plotted against time. As illustrated in this figure, the rate of sulfide oxidation is limited only by the amount of oxygen supplied to the melt. Essentially all the oxygen supplied to the melt is consumed by the oxidation of the sulfide.

The second experimental apparatus used to study sulfide oxidation consisted of the smaller induction heated reactor and an oxygen analyzer. Approximately 80 grams of alkali carbonates and 0.8 to 4.0 grams of sodium sulfide were melted in the reactor, and the sulfide was oxidized by bubbling nitrogen and air mixtures through the melt. The rate of oxygen consumption was followed by monitoring the amount of oxygen in the off-gas from the reactor. The rate of sulfide oxidation was then calculated from an oxygen balance around the reactor.

Figure 5 illustrates the rate of sulfide oxidation from 1450 to 1600°F. Here, the sulfide oxidation rate was stoichiometrically limited to 6.5×10^{-3} moles/minute by the availability of oxygen until the level of sulfide in the melt reached approximately 0.15 mole/liter. At this concentration, the sulfide oxidation rate rapidly decreased. This rapid decrease in rate may represent a transition from an oxygen supply-controlled to a kinetically-controlled reaction. The melt temperature had little effect on the rate of sulfide oxidation. Although data points for 1450, 1500, and 1550°F are only shown for sulfide concentrations less than 0.20 mole/L, the oxidation rate at these temperatures was recorded starting at 1.0 mole/L and falls on the curve shown in this figure.

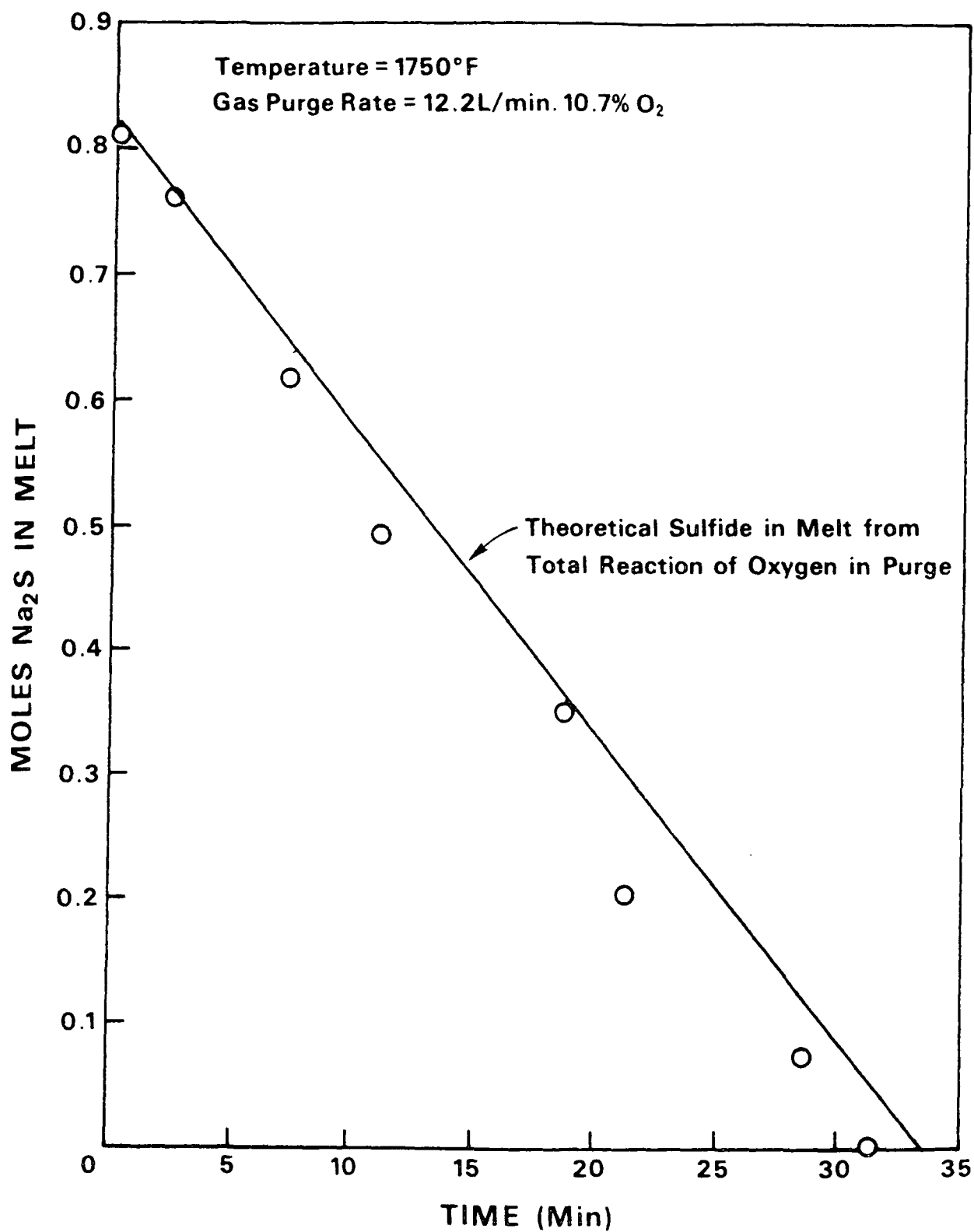


Figure 4. Oxidation of sodium sulfide.

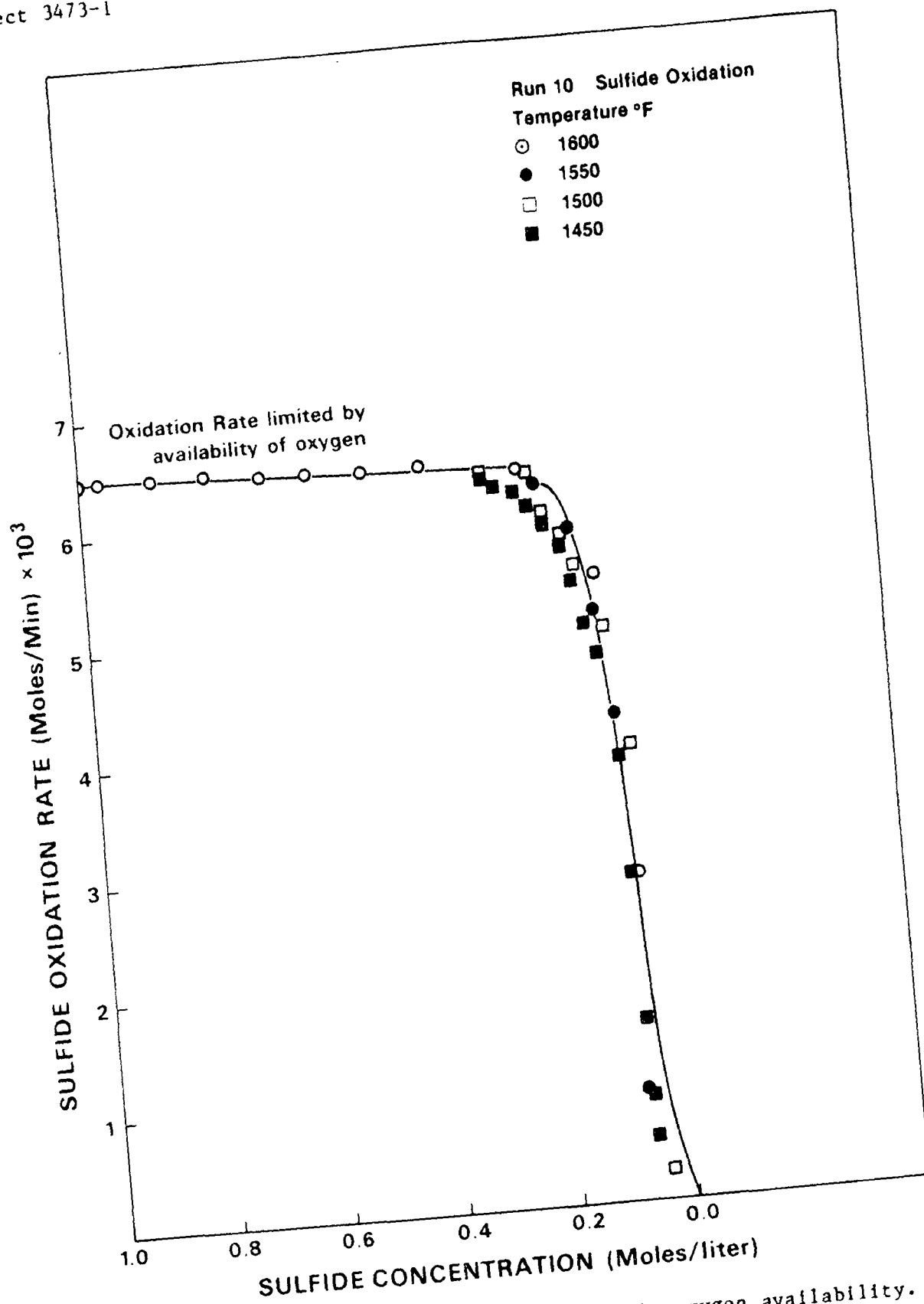


Figure 5. Sulfide oxidation rate limited by oxygen availability.

Based on these results, it is concluded that at the temperature range used in this study (1400 to 1850°F) sulfide oxidation is limited only by the availability of oxygen, until the sulfide concentration reaches a low level (less than 0.15 mole/L). For comparison, smelt with a 25% sulfidity based on T.T.A. has a sulfide concentration of approximately 5 moles/L. Sulfide oxidation is an extremely fast reaction at these temperatures, and a melt containing sulfide will consume, through sulfide oxidation, essentially all the oxygen supplied.

TYPICAL EXPERIMENTAL OXIDATION RESULTS

With the experimental system used in this study, the rate of carbon oxidation could be followed with either of two methods: through the rate of carbon dioxide and carbon monoxide generation or through the rate of oxygen consumption. Typical experiments obtained for the oxidation of pulverized graphite are illustrated in Fig. 6.

Here, the oxidation rates calculated using both methods are illustrated. Both methods of calculating the oxidation rate produced similar rate curves. However, the carbon monoxide/dioxide method generally provided a more accurate measure of the oxidation rate and was therefore used for the majority of the data analysis. There are two major reasons for the greater accuracy of the carbon monoxide/dioxide method of monitoring the oxidation rate. First, the carbon monoxide/dioxide monitor appeared to be a more accurate analyzer than the oxygen monitor. Second, the carbon monoxide/dioxide method was a direct measurement as opposed to the difference method used in the oxygen balance around the system.

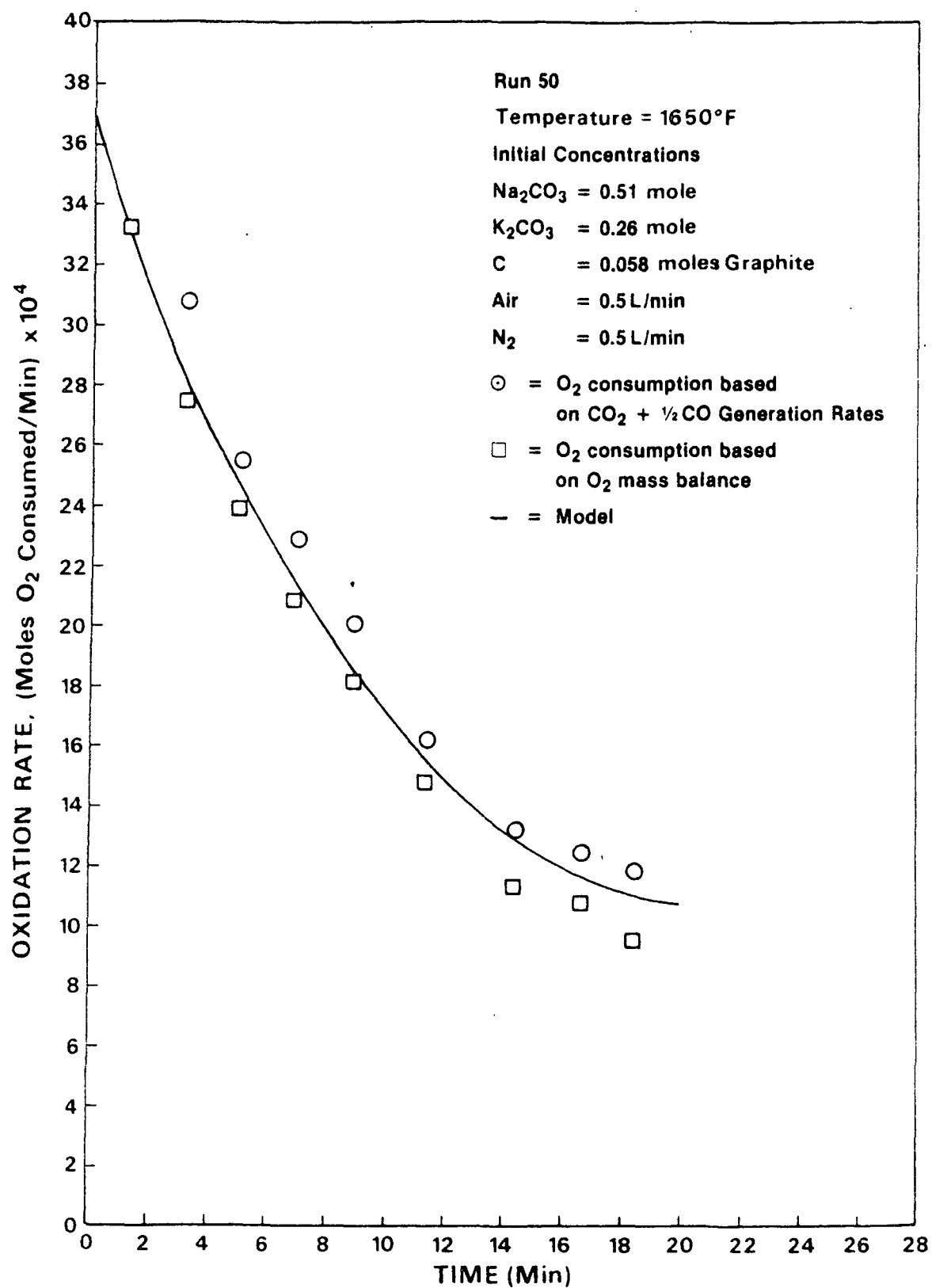


Figure 6. Air oxidation of pulverized graphite.

CARBON OXIDATION WITHOUT SULFUR PRESENT

To define the mechanism by which carbon is burned in a carbonate melt, the oxidation of pulverized graphite and soda char was initially studied without sulfur present. Since no sulfur was present, the direct oxidation of these carbons in the absence of the sulfate-sulfide cycle could be defined.

To characterize the direct oxidation mechanism of carbon in a carbonate melt, the effects of carbon level, oxygen partial pressure, and temperature were determined. Based on these experimental results, rate equations describing direct oxidation were developed.

Oxygen Effect

To determine the effect of the oxygen partial pressure on the oxidation rate of carbon in a carbonate melt, the oxidation rates of pulverized graphite and soda char were measured with different levels of oxygen in the purge gas. For these experiments, the alkali carbonates and carbon were premixed and the melt was heated to the desired reaction temperature under a nitrogen purge. The oxidation of the carbon was then initiated by adding air to the purge. The oxygen, carbon monoxide, and carbon dioxide partial pressures in the off gas were measured, and based on the rate of carbon monoxide and carbon dioxide generation, the carbon oxidation rate was calculated. The effect of oxygen partial pressure on the rate of carbon oxidation is shown in Table 6. As illustrated here, the rate of carbon oxidation is independent of the oxygen partial pressure.

Table 6. Effect of oxygen partial pressure on oxidation rate of carbon.

Pulverized Graphite

Initial Conditions

Na_2CO_3 = 0.51 mole
 K_2CO_3 = 0.26 mole
 Graphite = 0.0583 mole
 Purge rate = 1.0 L/min

Rate is measured at 0.030 mole carbon evolved from melt

Run No.	Temperature, °F	O ₂ in Purge to Reactor, %	O ₂ in Off Gas from Reactor, %	Oxidation Rate Based on CO ₂ and CO Evolution (moles/min) x 10 ⁴
9C	1696	4.2	0.81	17.7
8C	1698	8.4	5.0	16.2
7C	1698	12.6	8.7	18.4
6C	1701	16.8	13.1	16.3
10C	1700	21.0	16.1	20.6

Soda Char

Initial Conditions

Na_2CO_3 = 0.51 mole
 K_2CO_3 = 0.26 mole
 Char carbon = 0.016 mole
 Purge rate = 1.0 L/min

Rate is measured at 0.005 mole of carbon evolved from melt

Run No.	Temperature, °F	O ₂ in Purge to Reactor, %	O ₂ in Off Gas from Reactor, %	Oxidation Rate Based on CO ₂ and CO Evolution (moles/min) x 10 ⁴
142C	1501	2.10	1.04	6.42
143C	1499	6.23	5.49	6.37
144C	1501	14.7	13.8	6.72
145C	1502	20.9	17.7	6.42

Carbon Effect

To determine the order of carbon oxidation with respect to the carbon concentration, the rate of carbon oxidation was measured in a carbonate melt with different initial carbon loadings. Similarly to the study of oxygen effect, the alkali carbonate and carbon were premixed and heated to the desired reaction temperature under a nitrogen purge. This nitrogen purge prevented any oxidation occurring during this heating period and assured that the carbonate and carbon were well mixed. Once the desired reaction temperature was reached, oxidation was initiated by adding air to the purge stream.

For pulverized graphite and soda char, the effect of carbon concentration on the rate of oxidation is illustrated in Fig. 7 and 8. Here, the log of the carbon oxidation rate is plotted vs. the log of the carbon content in the melt. These figures were obtained with melts containing different initial levels of carbon. These carbons were then oxidized with a nitrogen-air mixture, and the oxidation rate was measured at 500 sec after oxidation was initiated. As illustrated in these figures, the rate of oxidation of both pulverized graphite and soda char is approximately first order with respect to the amount of carbon in the melt.

Rate Equation for Carbon Oxidation Without Sulfur Present

Since the rate of carbon oxidation for pulverized graphite and soda char was first order in the level of carbon and independent of the oxygen partial pressure, Eq. (31) was used to describe carbon oxidation by oxygen in a carbonate melt.

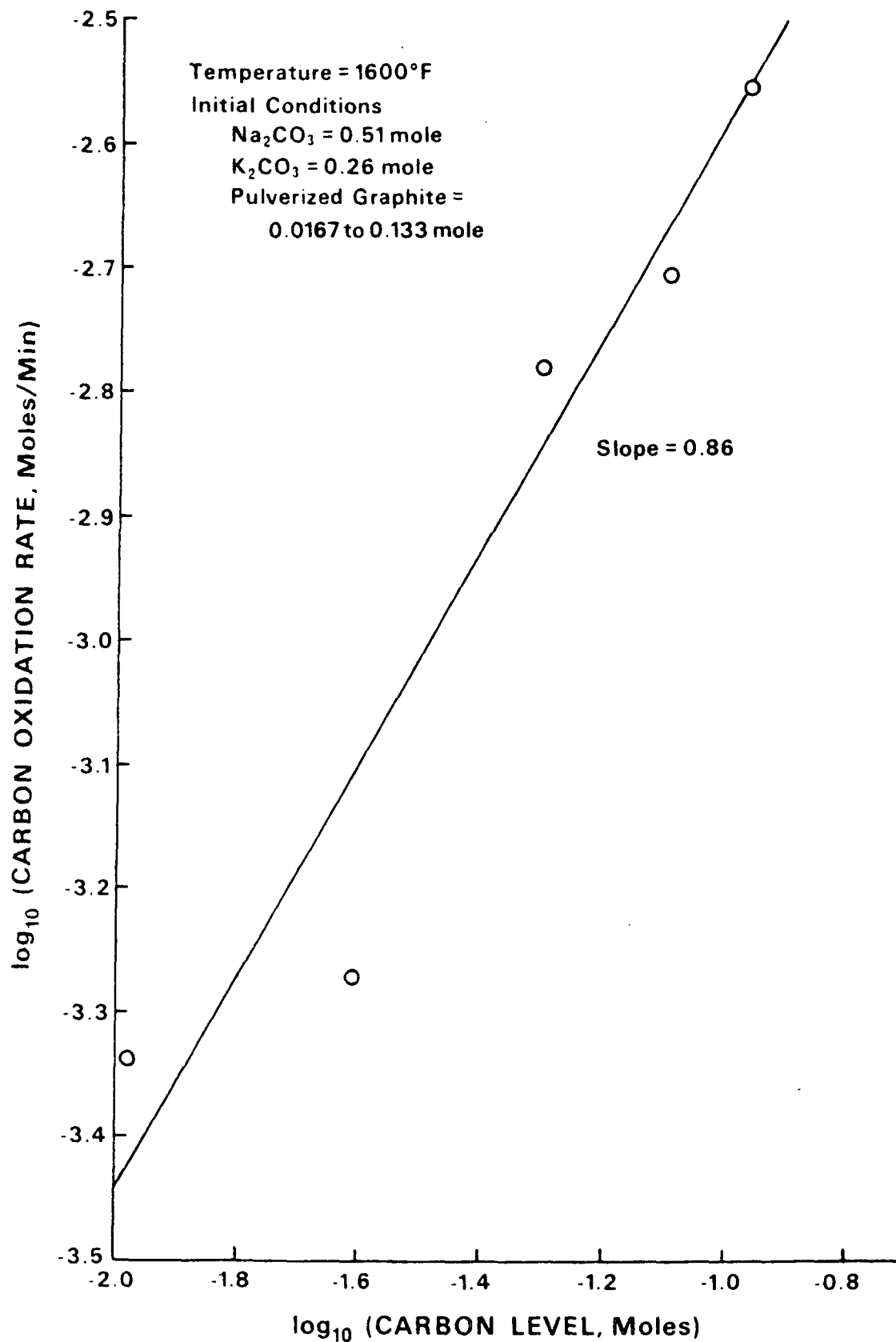


Figure 7. Effect of pulverized graphite level on air oxidation rate.

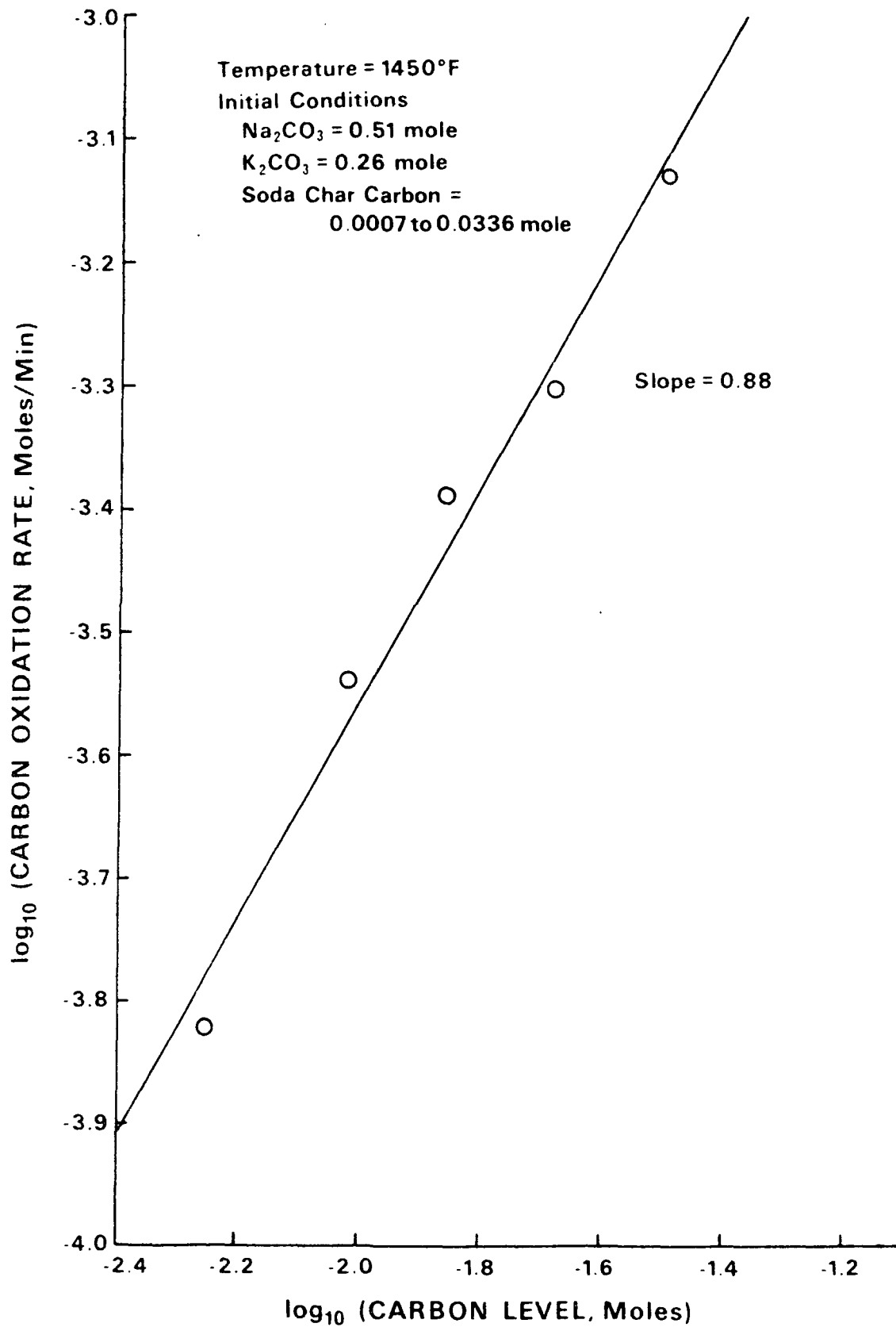


Figure 8. Effect of soda char level on air oxidation rate.

$$\frac{d[C]}{dt} = - K[C] e^{-\Delta E/RT} \quad (31)$$

Here [C] is the carbon concentration;

K is a constant;

ΔE is the activation energy;

R is the ideal gas constant; and

T is the absolute temperature.

Using a nonlinear regression analysis program (18), the constants, K and ΔE , which describe carbon oxidation for pulverized graphite and soda char, were determined. The temperature effect on the rate of oxidation was determined by monitoring the oxidation rate at temperatures from 1450 to 1650°F and fitting this data to rate Eq. (31).

The constants for these carbons and the predicted oxidation rates at 1520°F are shown in Table 7. Figures 9 and 10 illustrate the ability of the oxidation rate expression Eq. (31) to describe the oxidation of these carbons.

Table 7. Oxidation of carbon in a carbonate melt without sulfur present.

Carbon Type	$\frac{d[C]}{dt} = - K[C] e^{-\Delta E/RT}$		
	K (sec ⁻¹)	ΔE (cal/mole)	Rate at 1100°K (1520°F) [C] = 0.37 mole/L (moles/L-s) x 10 ⁴
Pulverized graphite	123 ± 9.0	27,950 ± 800	1.27
Soda char	172 ± 7.0	26,420 ± 1000	3.58

CARBON OXIDATION WITH AIR IN A CARBONATE MELT CONTAINING SULFUR

In this section, the results of air oxidation of the three carbons—pulverized graphite, soda char, and kraft char—with sulfur present are

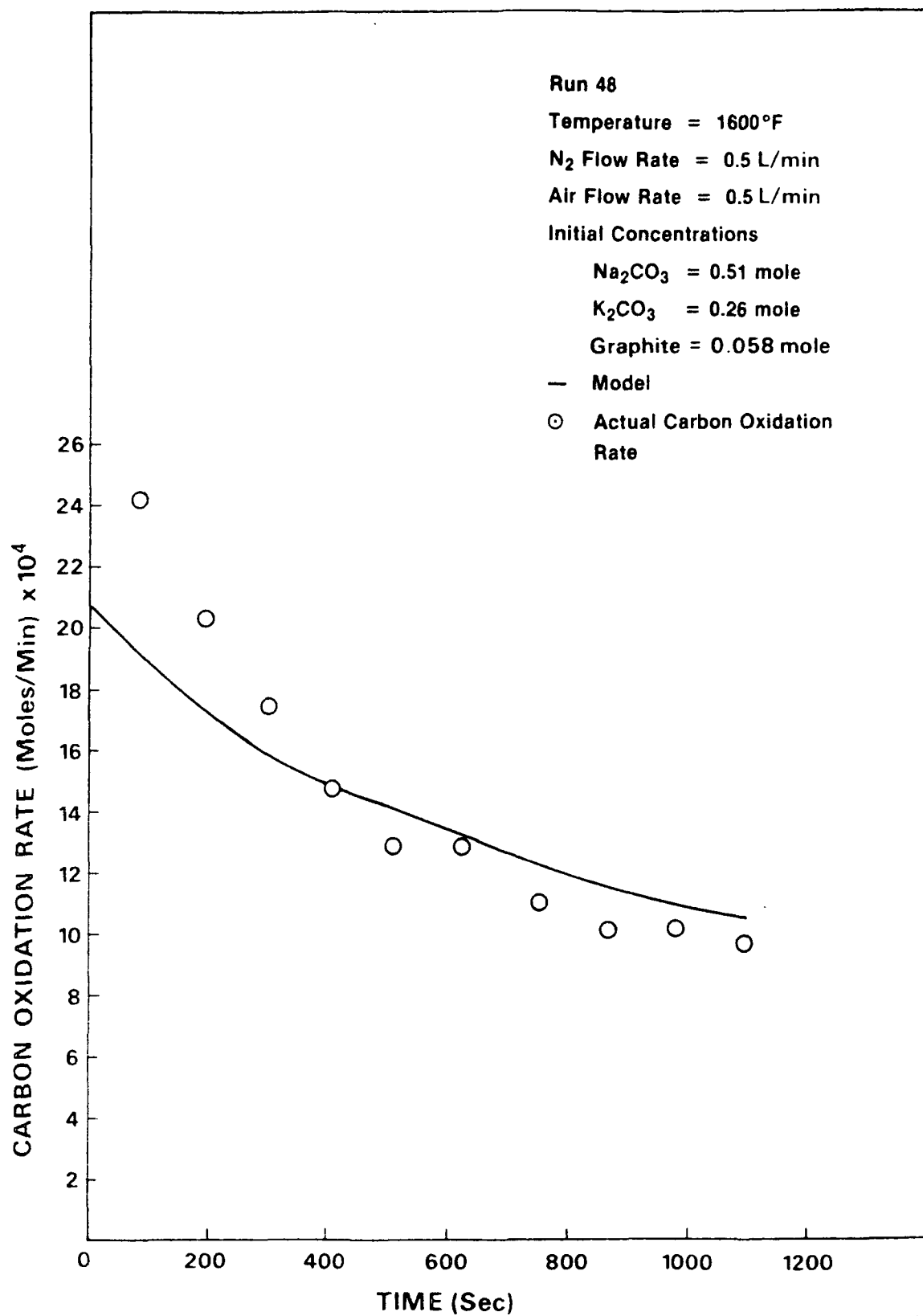


Figure 9. Air oxidation of pulverized graphite in a carbonate melt without sulfur present.

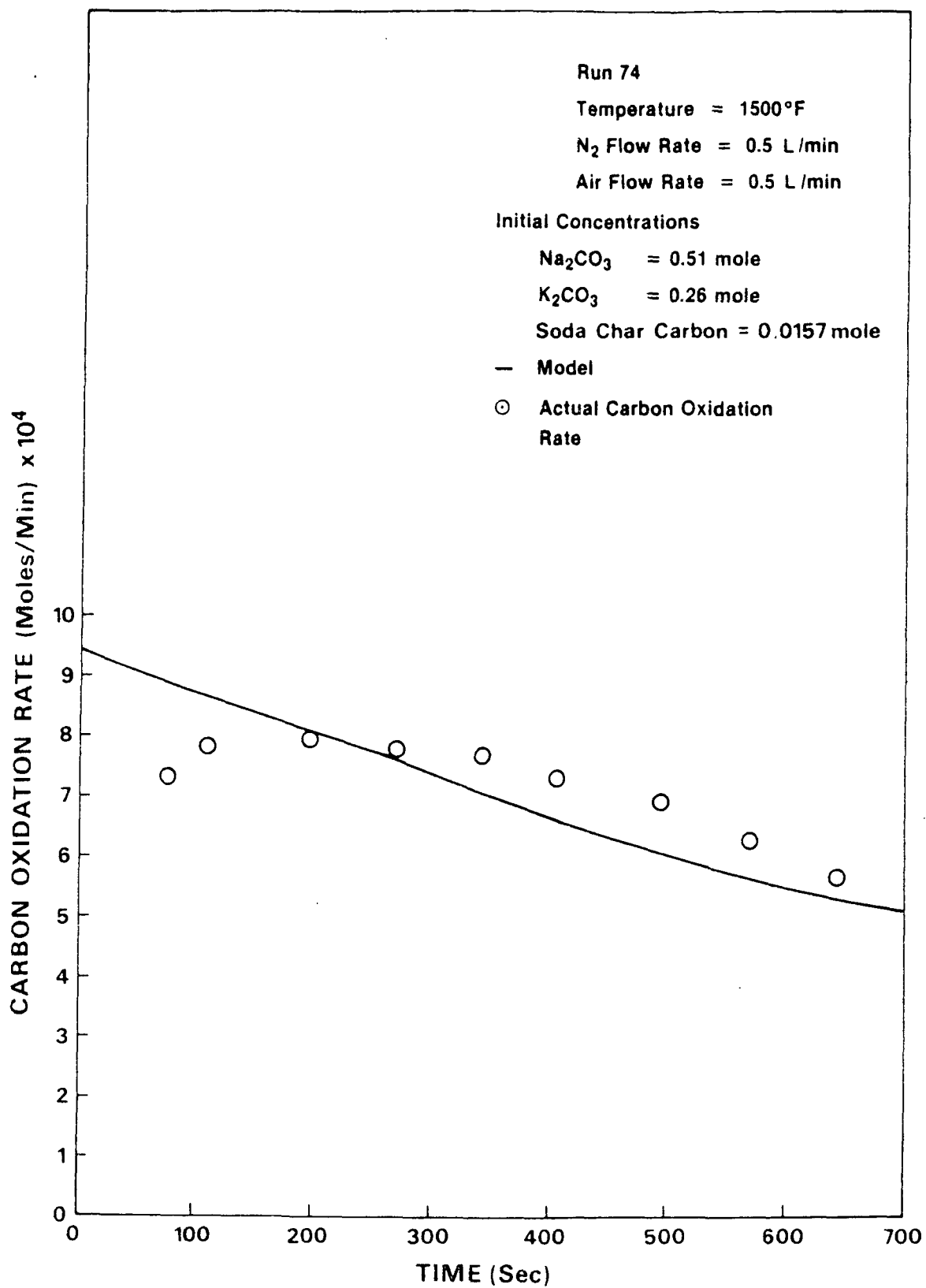


Figure 10. Air oxidation of soda char in a carbonate melt without sulfur present.

described. To study this type of oxidation, the alkali carbonate, sodium sulfate, and carbon were premixed and heated under a nitrogen purge to a predetermined temperature. Once this temperature was reached, the nitrogen purge was replaced with an air or air/nitrogen purge.

During the heating period, the rate of carbon dioxide and carbon monoxide evolution was continuously monitored. These rates were recorded by the computer and the amount of carbon remaining in the melt was calculated. When air was added to the purge, the rate of the combination of sulfate and air oxidation could then be determined for a given level of carbon in the melt.

Pulverized Graphite

The carbon dioxide generation rate from air oxidation of pulverized graphite in a carbonate melt containing sulfate is shown in Fig. 11. Also shown in Fig. 11 are the predicted carbon dioxide generation rates for sulfate oxidation of carbon (sulfate reduction) and air oxidation of carbon without sulfur present. The air oxidation rate of carbon with sulfur present is greater than either sulfate oxidation of carbon or air oxidation of carbon without sulfur present. Once air is added to the purge, the carbon dioxide generation rate rapidly increases until it approximately equals the sum of the two predicted carbon dioxide generation rates. This increase in the carbon dioxide generation rate during the first few minutes is due principally to the system dead time (time required for a purge composition change to register).

Since the total oxidation rate is approximately equal to the sum of the two individual oxidation rates, these oxidation reactions, sulfate and air oxidation, appear to be occurring independently of each other. In this system, both sulfate and air are oxidizing the carbon.

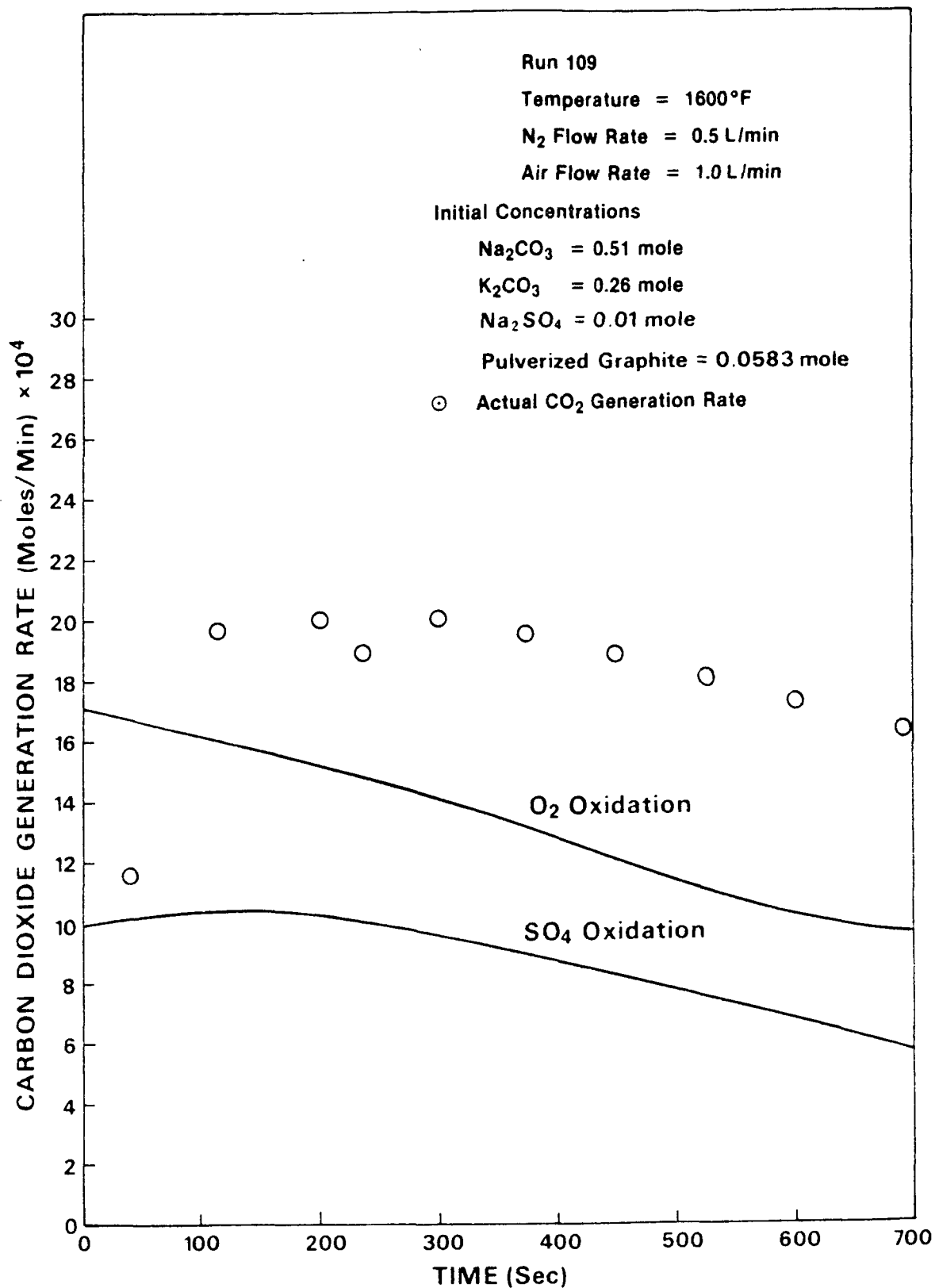


Figure 11. Air oxidation of pulverized graphite in a carbonate melt with sulfur present.

Soda Char

The carbon dioxide generation rate from air oxidation of soda char with sulfur present is illustrated in Fig. 12. Also shown in Fig. 12 are the predicted carbon dioxide generation rates for sulfate oxidation of soda char and for air oxidation of soda char without sulfur present. The predicted carbon dioxide generation rate from air oxidation of soda char without sulfur present is only 16% of the predicted carbon dioxide generation rate from sulfate oxidation of soda char. The predicted carbon dioxide generation rate for sulfate oxidation of soda char closely matches the observed rate for sulfate and air oxidation of soda char. Therefore, the major mechanism for oxidation of soda char with sulfur present is the sulfate-sulfide cycle. There may be some direct air oxidation of the soda also occurring together with the sulfate oxidation. However, since the rate of direct oxidation of soda char is low compared to the rate of sulfate oxidation of the soda char, any increase in carbon dioxide generation due to the presence of air would be difficult to detect.

One difference between air oxidation of pulverized graphite and soda char in the presence of sulfur is that during oxidation of pulverized graphite both air and sulfate oxidation were observed to occur simultaneously, while with soda char only sulfate oxidation was observed. This difference in behavior may be due to the relative rates of sulfate and air oxidation for pulverized graphite and soda char. While the sulfate and air oxidation rates of pulverized graphite are roughly equal, the sulfate oxidation rate of soda char is 6 times that of air oxidation at 1450°F. Therefore with pulverized graphite, both air and sulfate oxidation would be readily observable; but with soda char, air oxidation would be difficult to detect during sulfate oxidation.

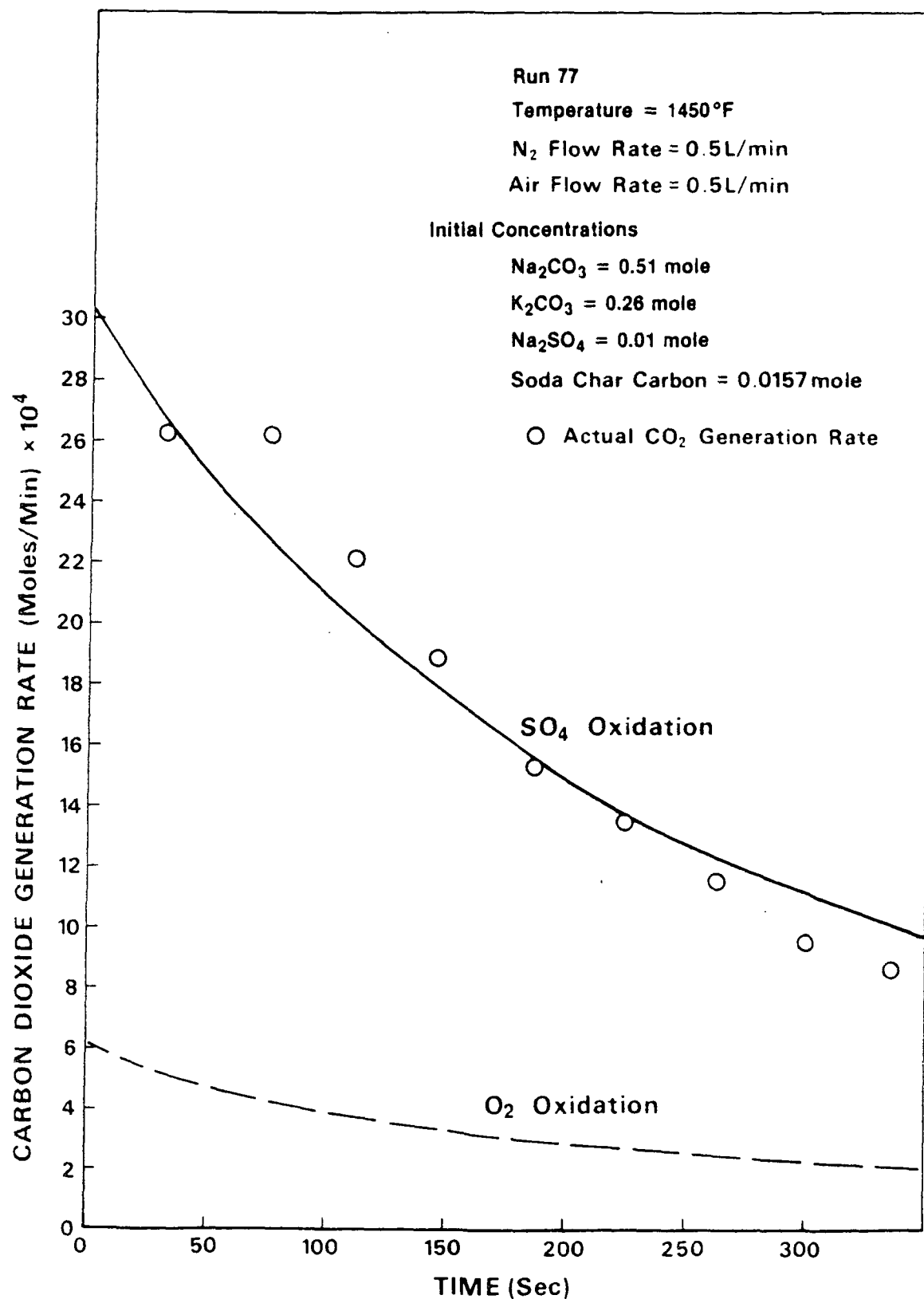


Figure 12. Air oxidation of soda char in a carbonate melt with sulfur present.

Also, simultaneous direct oxidation and sulfate oxidation will only occur when all sulfide in the melt is oxidized to sulfate. If any sulfide is present in the melt, it will react with the oxygen, preventing direct oxidation of the carbon. With the chars, the sulfate reduction rate is apparently faster than the rate at which oxygen diffuses into the melt. Therefore, the melt always contains an excess of sulfide and no direct oxidation is observed. Due to the slower sulfate reduction rate with pulverized graphite, oxygen enters the melt faster than sulfate is reduced by pulverized graphite, and simultaneous direct oxidation and sulfate oxidation are observed.

Kraft Char

Kraft char oxidation was studied in alkali carbonate melts containing no sulfur other than that present in the char. The rate expression, Eq. (31), that described air oxidation of soda char and pulverized graphite was also found to describe air oxidation of kraft char. The constants K and ΔE in Eq. (31) were determined for kraft char by measuring the carbon oxidation rate over a large range of experimental conditions and are shown in Table 8. The ability of this rate expression to describe air oxidation of kraft char is illustrated in Fig. 13.

Table 8. Air oxidation of kraft char.

$$\frac{d[C]}{dt} = - K[C]e^{-\Delta E/RT}$$

Carbon Type	K (sec^{-1})	ΔE (cal/mole)
Kraft char	3910 ± 360	$30,167 \pm 2000$

To determine if sulfate oxidation of kraft char and air oxidation of kraft char occurred through the same mechanism, a series of experiments were

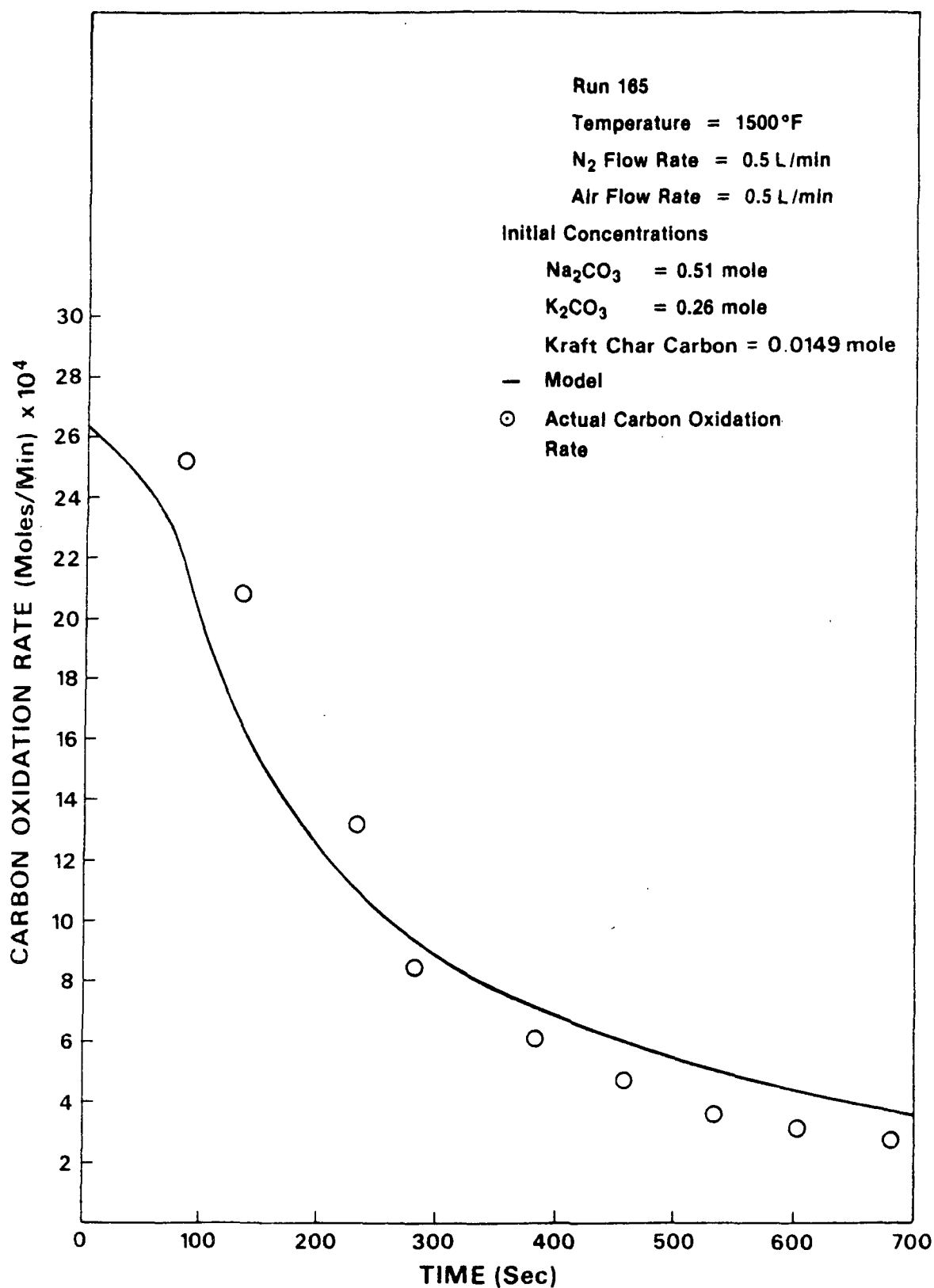


Figure 13. Air oxidation of kraft char in a carbonate melt.

conducted to compare these oxidation rates. In Table 9 the carbon oxidation rate is illustrated for sulfate oxidation of kraft char and for air oxidation of kraft char in a carbonate melt with sulfate added to the melt. Also shown in this table is the amount of carbon evolved from the melt calculated through integration of the carbon dioxide and carbon monoxide generation rates.

In these experiments, the alkali carbonates, sodium sulfate, and char were premixed and heated with nitrogen purging through the melt to the selected experimental temperature. The zero time in these experiments was chosen to be the point in time where the melt temperature reached 1000°F. However, only a slight degree of carbon oxidation occurred below 1400°F. Table 9 illustrates the reaction as the melt temperature approaches the desired experimental temperature of 1450°F. In air oxidation of kraft char, with additional sulfur present, Run 191, the nitrogen purge was replaced with an air purge when the melt temperature reached approximately 1430°F. In this experiment, the temperature of the melt reached the selected run temperature of 1450°F approximately 60 seconds after the addition of the air.

To compare the oxidation rates in Table 9, these rates must be compared when both melts contain the same level of carbon (when the same amount of carbon has been evolved from each melt). As illustrated in this table, the air oxidation rate is initially greater than the sulfate oxidation rate, but after a few minutes, the rates are similar.

An easier method of comparing these rates is given by the following derivation. The sulfate oxidation rate for carbon has previously been shown to be described by Eq. (32).

Table 9. Carbon dioxide generation rates for air oxidation of kraft char with sulfur present and for sulfate oxidation of kraft char.

Run 186, Air oxidation of kraft char with sulfur present

Conditions

Temperature = 1450°F (1060°K)
 Na_2CO_3 = 0.51 mole
 K_2CO_3 = 0.26 mole
 Na_2SO_4 = 0.01 mole
 Kraft char carbon = 0.015 mole
 N_2 flow rate = 1.0 L/min to 500 sec
 Air flow rate = 1.0 L/min after 500 sec

Time, sec	Temperature, °F	CO_2 and CO Generation Rate (moles/min) $\times 10^4$	Carbon Evolved from Melt (moles)
532	1430	30.28 ^a	0.00464
570.2	1444	23.10 ^a	0.00619
607.8	1451	17.28	0.00746
645.3	1451	13.40	0.00845
682.9	1450	10.18	0.00922
720.5	1447	7.44	0.00979
758.1	1450	5.89	0.01021
795.5	1451	5.27	0.01056

Run 191, Sulfate oxidation of kraft char

Conditions

Temperature = 1450°F (1060°K)
 Na_2CO_3 = 0.51 mole
 K_2CO_3 = 0.26 mole
 Na_2SO_4 = 0.01 mole
 Kraft char carbon = 0.015 mole
 N_2 flow rate = 1.0 L/min

Time, sec	Temperature, °F	CO_2 and CO Generation Rate (moles/min) $\times 10^4$	Carbon Evolved from Melt (moles)
681	1444	18.11 ^a	0.00552
719	1450	18.86	0.00665
756	1451	19.27	0.00785
794	1452	17.40	0.00898
831	1452	14.43	0.00998
869	1452	11.31	0.01078
906	1452	8.534	0.01140
944	1451	6.080	0.01185
981	1450	4.852	0.01219

^aRate corrected for temperature difference to 1450°F.

$$\frac{d[SO_4]}{dt} = \frac{-K [SO_4][C]}{1 + K_4[SO_4]} e^{-\Delta E/RT} \quad (32)$$

For $K_4[SO_4] \gg 1$, Eq. (32) becomes

$$\frac{d[SO_4]}{dt} = -\frac{K}{K_4} [C] e^{-\Delta E/RT} \quad (33)$$

For carbon oxidation with sulfate, carbon dioxide is the principal product gas with only a small amount of carbon monoxide evolved. Therefore, approximately two moles of carbon are burnt per mole of sulfate reduced and the rate of carbon oxidation is given by Eq. (34).

$$\frac{d[C]}{dt} = -\frac{2K}{K_4} [C] e^{-\Delta E/RT} = -K(T) [C] \quad (34)$$

Here, $K(T)$ is a temperature dependent rate constant.

For an isothermal reaction, Eq. (34) may be written as:

$$\frac{d[C]}{dt} = -k[C] \quad (35)$$

$$\ln[C] = \ln[C_0] - kt \quad (36)$$

$$\text{or} \quad [C] = [C_0] e^{-kt} \quad (37)$$

Here, $[C_0]$ is the initial carbon concentration at time equal zero.

Substituting this expression into Eq. (37) gives:

$$\frac{d[C]}{dt} = -k[C_0] e^{-kt} = -\text{rate of carbon dioxide evolution} \quad (38)$$

Taking the ln of both sides gives

$$\ln (\text{rate}) = \ln (k [C_0]) - kt \quad (39)$$

Therefore, a plot of the ln (rate of carbon dioxide evolution) vs. time should be a straight line with a slope equal to $-k$. A similar derivation could also be made for air oxidation of kraft char in a carbonate melt.

In Fig. 14, the ln (carbon oxidation rate is plotted vs. time for the two oxidation experiments described in Table 9. The major observations concerning kraft char oxidation that are illustrated in Fig. 14 are described below.

1. There is a considerable offset in time between the two curves. This is due to the faster heating rate of air oxidation of kraft char compared to sulfate oxidation of kraft char. Since sulfate oxidation of char is an endothermic reaction and air oxidation is exothermic, the melt in the air oxidation experiment reaches the selected temperature (1450°F) faster than the melt in the sulfate oxidation experiment.
2. The first couple of data points in the sulfate oxidation experiment fall below the curve. This lag in the carbon oxidation rate with sulfate may be due to temperature effects.
3. As illustrated in Fig. 14, both the curve for sulfate oxidation of carbon and air oxidation of carbon with sulfur present are straight lines. This demonstrates that for isothermal conditions, the oxidation rate for both types of oxidation is only dependent on the carbon

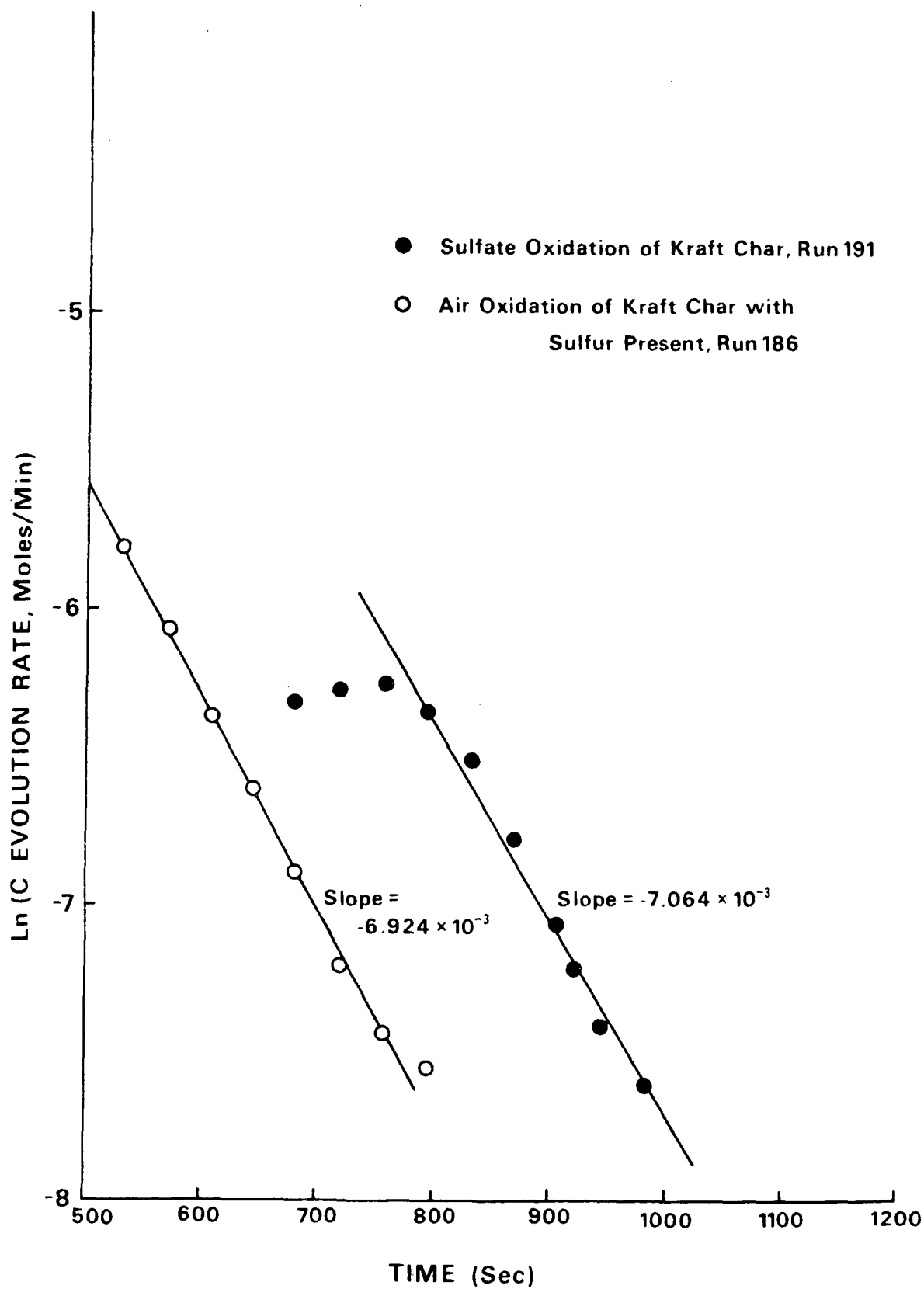


Figure 14. Comparison of air and sulfate oxidation of kraft char.

concentration. A rate equation first order in carbon concentration would accurately describe kraft char oxidation with either oxygen or sulfate for the experimental conditions used in this study.

4. The most significant result illustrated in this figure is that the rate constant for air oxidation of kraft char with sulfur present is the same (within 2%) as the rate constant for sulfate oxidation of kraft char. As previously derived, the rate constants are equal to the negative slope of the curves in Fig. 14. Since both curves have the same slope, the rate constants for both reactions are the same.

Previously, kinetic rate expressions and parameters were determined for sulfate and air oxidation of kraft char. In this section, the predicted oxidation rate constants from these models are calculated for the experimental conditions of Fig. 14 and compared with the rate constants derived from this figure.

The sulfate oxidation rate of kraft char is given by Eq. (40).

$$\frac{-d[\text{SO}_4]}{dt} = \frac{K[\text{SO}_4][\text{C}]}{1 + K_4[\text{SO}_4]} e^{-\Delta E/RT} \quad (40)$$

Since two moles of carbon dioxide are evolved for every mole of sulfate reduced, the negative slope of the curves in Fig. 14 should be equal to twice the rate constant of Eq. (40) multiplied by the volume (0.0469 L) of melt used in Fig. 14.

$$-\text{Slope (Fig. 14)} = \frac{2 K [\text{SO}_4]}{1 + K_4[\text{SO}_4]} e^{-\Delta E/RT} \times \text{vol} \quad (41)$$

Here $K = 5.96 \times 10^4$ (L/mole-s)

$K_4 = 45.6$ (L/mole); and

$\Delta E = 29,200$ cal/mole

For the experimental conditions used in Fig. 14,

$[SO_4] = 0.213$ mole/L;

$T = 1450^\circ F = 1061^\circ K$; and

vol = 0.0469L.

$$\begin{aligned}
 -\text{slope} &= \frac{2}{\text{mole-s}} \left| \frac{5.96 \times 10^4 \text{ L}}{\text{mole-s}} \right| \frac{60 \text{ s}}{\text{min}} \left| \frac{0.213 \text{ mole/L}}{(1 + 45.6 \text{ L/mole} \times 0.213 \text{ mole/L})} \right| \frac{0.0469 \text{ L}}{\text{min}} \times \\
 &\quad e^{-\left(\frac{29,200 \text{ cal}}{\text{mole}} \left| \frac{\text{Mole } ^\circ K}{1.987 \text{ cal}} \right| \frac{1}{1061^\circ K} \right)} \\
 &= 6.44 \text{ to } 10^{-3} \text{ L/min}
 \end{aligned}$$

Earlier it was shown that the air oxidation rate of kraft char in a carbonate melt without any additional sulfur present is described by Eq. (42).

$$\frac{d[C]}{dt} = -K[C] e^{-\Delta E/RT} \quad (42)$$

Therefore, the negative slope of the curves in Fig. 14 should also be equal to the rate constant in Eq. (42) multiplied by the volume of melt used in Fig. 14.

$$-\text{Slope} = K e^{-\Delta E/RT} \times \text{vol} \quad (43)$$

Here $K = 3910 \text{ sec}^{-1}$ and;

$\Delta E = 30,167$ cal/mole.

For the experimental conditions used in Fig. 13,

$$T = 1450^{\circ}\text{F} = 1061^{\circ}\text{K}$$

$$\text{vol} = 0.0469\text{L}$$

$$\begin{aligned} -\text{Slope} &= \frac{3910}{\text{s}} \left| \frac{60 \text{ s}}{\text{min}} \right| \frac{0.0469 \text{ L}}{\text{min}} \left| e^{-\left(\frac{30,167 \text{ cal}}{\text{mole}} \left| \frac{\text{mole}^{\circ}\text{K}}{1.987 \text{ cal}} \right| 1061^{\circ}\text{K} \right)} \right| \\ &= 6.72 \times 10^{-3} \text{ L/min} \end{aligned}$$

In Table 10, the slope of the two curves in Fig. 14 (sulfate oxidation of kraft char, Run 191, and air oxidation of kraft char with additional sulfur present, Run 186) are compared to the rate constants for sulfate oxidation of kraft char, Eq. (41), and air oxidation of kraft char, Eq. (43), both at 1450°F.

Table 10. Kraft char oxidation rate constants.

Source	Rate Constant L/min x 10 ³
Figure 14, Run 191 Sulfate oxidation	6.92
Figure 14, Run 186 Air oxidation	7.06
Model sulfate oxidation at 1450°F	6.45
Model air oxidation at 1450°F	6.72

The units on the rate constants in Table 10 are L/min; multiplying this by the carbon concentration (mole/L), the carbon oxidation rate becomes moles/min.

The rate constants from all four derivations are essentially the same. From this, one can conclude that

- 1) The two oxidation rate equations adequately describe air and sulfate oxidation of kraft char for the experimental system used in this study. Although the oxidation experiments illustrated in Fig. 14 were not used to determine the kinetic parameters for the two oxidation rate equations, the rate constants in this figure are approximately the same as those derived from the rate equations.
- 2) Sulfate and air oxidation of kraft char occur through the same mechanism. Both the oxidation rate equations and the oxidation experiments illustrated in Fig. 14 show that the two types of oxidation have the same reaction rate. It is extremely unlikely that these oxidation rates would be equal unless both types of oxidation occur through the same mechanism. Therefore, air oxidation of kraft char occurs through the sulfate-sulfide cycle, with the rate controlling reaction in this cycle being the oxidation of kraft char carbon content by sulfate.

Comparison of Air Oxidation of Kraft Char with Air Oxidation of Soda Char and Pulverized Graphite

In this section, the oxidation rate of kraft char in an alkali carbonate melt is measured and compared to the oxidation rates of soda char and pulverized graphite. In these experiments, kraft char oxidation was studied in melts containing no sulfur other than that present in the char.

The constants for kraft char and predicted oxidation rate at 1520°F are shown and compared with those for soda char and pulverized graphite in Table 11.

Table 11. Comparison of kraft char oxidation with soda char and pulverized graphite.

$$\frac{d[C]}{dt} = -K[C] e^{-\Delta E/RT}$$

Carbon Type	K (sec ⁻¹)	ΔE (cal/mole)	Rate at 1520°F (1100°K)
			[C] = 0.37 mole/L (moles/L-s) x 10 ⁴
Pulverized graphite	123 ± 9.0	27,950 ± 800	1.27
Soda char	172 ± 7.0	26,420 ± 1000	3.58
Kraft char	3910 ± 360	30,167 ± 2000	14.7

As illustrated in this table, the air oxidation rate for kraft char is nearly four times that for soda char. Since the major difference between kraft char and soda char is the sulfur contained in the kraft char, this greater air oxidation rate for kraft char is a result of its sulfur content and the resulting sulfate-sulfide oxidation cycle.

PRODUCT GAS FROM KRAFT CHAR OXIDATION

While carbon dioxide was the major product gas from both sulfate and air oxidation of carbon, some carbon monoxide was observed. The carbon monoxide generation rate was usually extremely low, but under certain experimental conditions it reached approximately 10% of the carbon dioxide generation rate. The ratio of carbon monoxide to carbon dioxide increased with temperature and melt carbon content and decreased with an increase in sulfate concentration or oxygen partial pressure.

As described in Progress Report Two (2), the active sites on the carbon surface are believed to be adsorbed oxygens. It is possible that these sites can either serve as sites for sulfate adsorption and consequential reduction or desorb from the carbon as carbon monoxide. If sulfate is reduced at these sites, the product gas from reduction is carbon dioxide. The ratio of carbon monoxide to carbon dioxide is then proportional to the fraction of sites that form carbon monoxide divided by the fraction that serve as sites for sulfate reduction.

In the mechanism for sulfate reduction with carbon, the total number of active sites was equal to those containing oxygen and those containing adsorbed sulfate at these oxygen sites, Eq. (44).

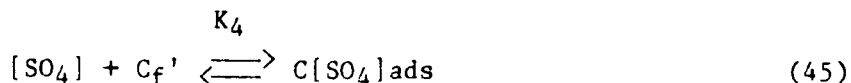
$$C_t' = C_f' + C[SO_4]_{ads} \quad (44)$$

Here C_t' represents the total active carbon sites,

C_f' represents the available sites containing only oxygen, and

$C[SO_4]_{ads}$ represents the sites containing adsorbed sulfate.

Sulfate reduction occurs through adsorption of sulfate on the sites containing oxygen, Eq. (45).



By combining Eq. (44) and (45) and eliminating the sites containing only oxygen, the adsorbed sulfate is expressed in terms of sulfate concentration and total active carbon sites, Eq. (46).

$$C[SO_4]_{ads} = \frac{K_4 [SO_4]}{1 + K_4 [SO_4]} \times C_t' \quad (46)$$

The rate of sulfate reduction and hence the rate of carbon dioxide generation is then described by Eq. (47).

$$\frac{-d[SO_4]}{dt} = 1/2 \frac{d[CO_2]}{dt} = \frac{K[SO_4]}{1 + K_4 [SO_4]} \times C_t' \times e^{-\Delta E_1/RT} \quad (47)$$

The rate of carbon monoxide generation is equal to the rate of desorption of the carbon monoxide from the surface of the carbon, Eq. (48).

$$\frac{d[CO]}{dt} = K_3 C_f' e^{-\Delta E_2/RT} \quad (48)$$

Combining Eq. (44), (45), and (48), the carbon monoxide generation rate can be expressed in terms of the sulfate concentration and total active carbon sites, Eq. (49).

$$\frac{d[CO]}{dt} = \frac{K_3 C_t'}{1 + K_4 [SO_4]} \times e^{-\Delta E_2/RT} \quad (49)$$

The ratio of the carbon monoxide to carbon dioxide in the product gas is equal to the carbon monoxide generation rate divided by the carbon dioxide generation rate, Eq. (50).

$$\frac{d[CO]/dt}{d[CO_2]/dt} = \frac{\frac{K_3 C_t'}{1 + K_4 [SO_4]} \times e^{-\Delta E_2/RT}}{\frac{2K[SO_4]C_t'}{1 + K_4 [SO_4]} \times e^{-\Delta E_1/RT}} \quad (50)$$

$$\frac{d[CO]}{d[CO_2]} = \frac{K_3}{2K[SO_4]} e^{[-\Delta E_2 + \Delta E_1]/RT} \quad (51)$$

$$\frac{d[CO]}{d[CO_2]} = \frac{K'}{[SO_4]} e^{[-\Delta E_2 + \Delta E_1]/RT} \quad (52)$$

This analysis predicts that the carbon monoxide/carbon dioxide ratio should be independent of the melt carbon content and inversely proportional to the melt sulfate concentration. To test this prediction, the carbon monoxide/carbon dioxide ratio from several different pulverized graphite oxidation experiments with sulfate was plotted against the inverse of the melt sulfate concentration, Fig. 15. The straight line in this figure illustrates the ideal inverse relationship.

As illustrated in this figure, the predicted relationship between the carbon monoxide/carbon dioxide ratio and the melt sulfate concentration appears to be valid for the carbon loadings normally used in this study (2.0 moles/L or less). However, the carbon monoxide/carbon dioxide ratio tends to increase as the carbon loading increases. This increase in carbon monoxide with increased carbon loading is illustrated in Fig. 15 by the higher carbon monoxide/carbon dioxide ratio generated from the melt initially containing 1.92 moles/L carbon compared to the melts initially containing 1.28 moles/L carbon. This increase in

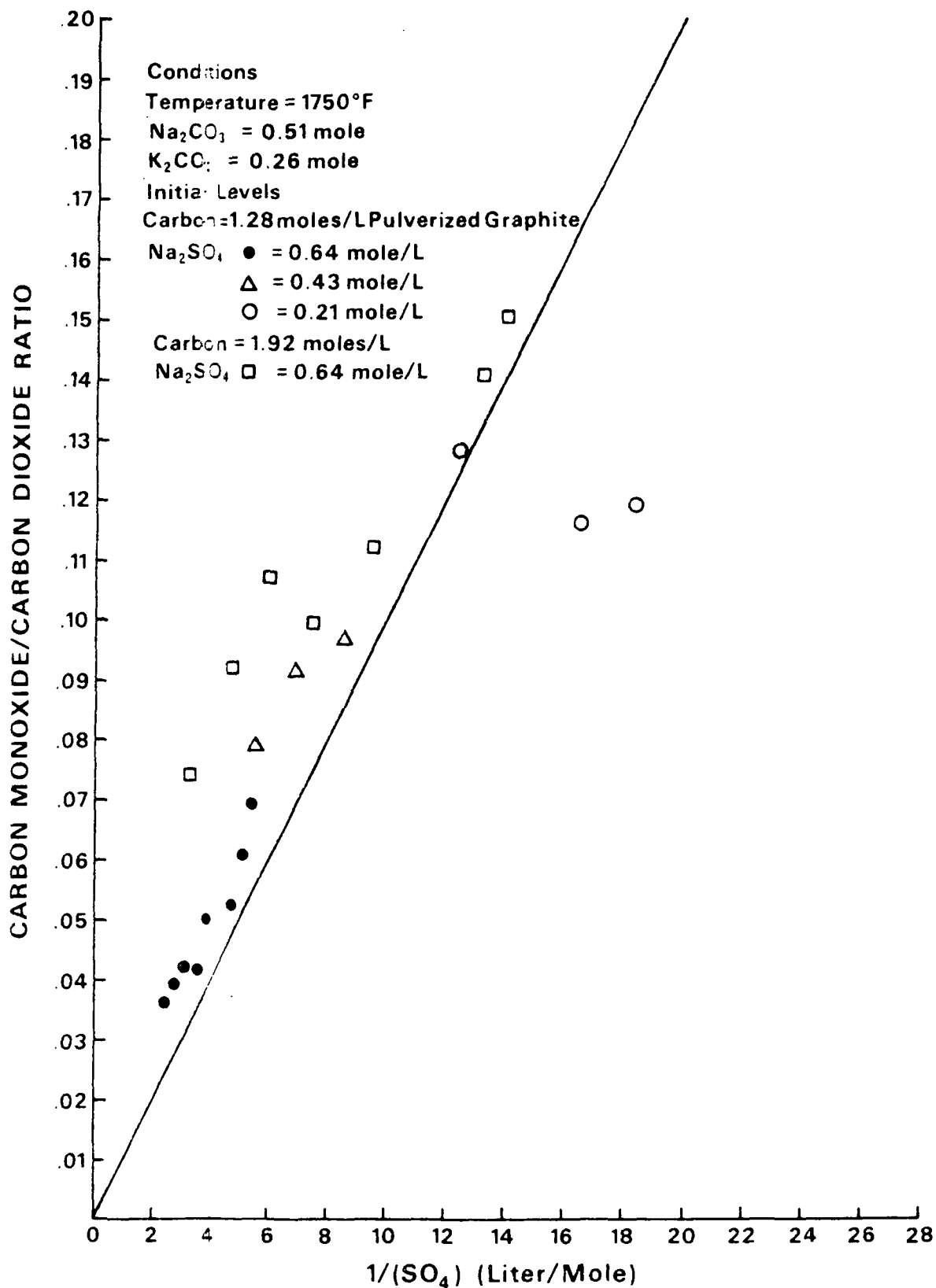


Figure 15. The effect of sulfate concentration on the CO/CO₂ ratio from sulfate reduction.

the carbon monoxide generation rate may be due to other reactions occurring within the melt. For example, the reaction between carbon dioxide and carbon forming carbon monoxide can occur in the melt and would become more significant as the melt carbon content increased.

DISCUSSION

A mechanism which is consistent with the reaction rate data has been proposed for sulfate oxidation of carbon. In this mechanism, sulfate is adsorbed on an active carbon site and is reduced, forming sulfide and carbon dioxide, which then desorb from the carbon surface. The rate limiting step consistent with the reaction rate data is the desorption of sulfide from the carbon surface.

The active carbon site is believed to be an adsorbed oxygen on the carbon surface. The catalytic nature of the alkali carbonates is due to the formation and stabilization of this adsorbed oxygen. This concept of the catalytic nature of alkali carbonates is directly supported by the work of Mims and Pabst (6), which demonstrated that the catalytic action of alkali carbonates in carbon gasification is due to the formation of adsorbed oxygens on the carbon surface.

Air oxidation of pulverized graphite and soda char was studied in alkali carbonate melts without sulfur present. Here, the oxidation rate was found to be proportional to the carbon concentration in the melt and independent of the oxygen partial pressure. Although kraft char contains sulfur, kraft char oxidation was also studied in these carbonate melts. It was found that the rate of carbon oxidation for all three types of carbon could be described by the following rate equation.

$$\frac{d[C]}{dt} = - K[C] e^{-\Delta E/RT} \quad (53)$$

Over the temperature range studied (1340 to 1520°F), the soda char oxidation rate with air was approximately 25% of the kraft char oxidation rate with

air. This faster air oxidation rate for kraft char is due to the sulfur present in the char and the resulting sulfate-sulfide cycle.

Air oxidation of soda char was also studied in an alkali carbonate melt containing sulfur. Here, the air oxidation rate of soda char was approximately five times as fast as the air oxidation rate without sulfur present. This demonstrates that the sulfate-sulfide cycle significantly enhances the air oxidation rate of soda char in an alkali carbonate melt.

Perhaps the clearest support for the sulfate-sulfide mechanism for carbon oxidation with air in melts containing sulfur is the comparison of the rates of kraft char oxidation with air and sulfate. These rates were compared for two experiments in this study and found to be within 2% of each other at 1450°F. It was also determined that the sulfate and air oxidation rate equations for kraft char (obtained using totally different experimental conditions) predict the same oxidation rate. It is extremely unlikely that this would occur unless the same mechanism was responsible for both types of kraft char oxidation.

Air oxidation of kraft char occurs entirely through the sulfate-sulfide cycle. Simultaneous direct oxidation and sulfate oxidation of carbon will only occur when all the sulfide present in the melt is oxidized to sulfate. If sulfide is present, it will scavenge the oxygen, forming sulfate and preventing direct oxidation of the carbon.

It is clearly demonstrated by these experimental results that the mechanism for air oxidation of kraft char in an alkali carbonate melt is the sulfate-sulfide cycle. In this mechanism, air contacting a reduced smelt

rapidly oxidizes this sulfide to sulfate. This sulfate then adsorbs on an active carbon site and oxidizes the carbon, forming sulfide and carbon dioxide. The sulfide then desorbs from the carbon, completing the cycle.

CONCLUSIONS

1. Air oxidation of sulfide in a carbonate melt is an extremely fast reaction. In the experimental system used in this study, sulfide oxidation was limited only by the availability of oxygen.

2. Air oxidation of pulverized graphite and soda char in an alkali carbonate melt without sulfur present is first order in the carbon concentration and independent of the oxygen partial pressure. The air oxidation rate constants for these carbons and for kraft char and the predicted reaction rate at 1520°F are shown in Table 12.

Table 12. Oxidation rates of carbon in an alkali carbonate melt.

$$\frac{d[C]}{dt} = -K [C] e^{-\Delta E/RT}$$

Carbon Type	K (sec ⁻¹)	ΔE (cal/mole)	Rate at 1520°F (1100°K) [C] = 0.37 mole/L (moles/L-s) x 10 ⁴
Pulverized graphite	123 ± 9.0	27,950 ± 800	1.27
Soda char	172 ± 7.0	26,420 ± 1000	3.58
Kraft char	3910 ± 360	30,167 ± 2000	14.7

3. Without sulfur present, air oxidation of pulverized graphite or soda char is a relatively slow reaction. The faster air oxidation rate for kraft char is due to the presence of sulfur and the resulting sulfate-sulfide cycle.

4. The air oxidation and sulfate oxidation rates for kraft char are the same. A comparison of separate experiments at 1450°F for these reactions demonstrated that both oxidation reactions are first order in carbon and have the same rate constants within 2%. Assuming that carbon dioxide is the principal product from sulfate oxidation of kraft char, the models for both air

oxidation and sulfate oxidation of kraft char also predict the same carbon oxidation rate.

5. Air oxidation of kraft char occurs through a sulfate-sulfide cycle.

Here, sulfide is oxidized by air to sulfate, which then oxidizes the carbon content of kraft char, forming sulfide and principally carbon dioxide.

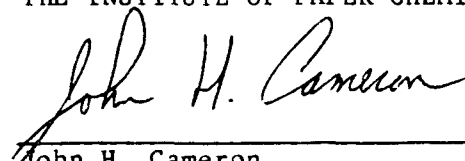
NOMENCLATURE

[C]	Carbon concentration
C_f'	Unoccupied active sites containing oxygen
C_t'	Total active carbon sites
$[C_0]$	Initial carbon concentration
ΔE	Activation energy
$K's$	Constants
R	Ideal gas constant
$[SO_4]$	Sulfate concentration
$[SO_4]_{ads}$	Adsorbed sulfate
vol	Volume of melt

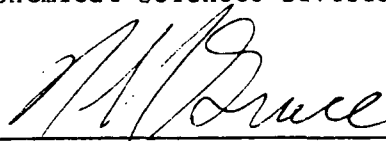
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John H. Cameron
Research Associate
Recovery Group
Chemical Sciences Division



Thomas M. Grace
Group Leader, Recovery
Pulping Sciences
Chemical Sciences Division