AIR OXIDATION OF GRAPHITE IN MOLTEN SALTS

D. Stelman, A. J. Darnell, J. R. Christie
and S. J. Yosim

Atomics International Division
8900 De Soto Avenue
Canoga Park, California 91304

ABSTRACT

The rate of oxidation of graphite particles by air in Na$_2$CO$_3$, NaCl, and Na$_2$CO$_3$-Na$_2$SO$_4$ melts was investigated. For sulfate-free melts, carbon and oxygen appear to be the only chemically reactive species. The reaction tends to be limited by the transport of oxygen over most of its course giving rise to a plateau in the oxidation curves. When the carbon is nearly consumed, the system becomes carbon surface area-limited. The reaction was found to be 1/2 order in O$_2$ and the effective activation energies were found to be 30.6 ±0.8 kcal/mole in the oxygen transport-limited regime and 49.9 ±0.4 kcal/mole in the carbon surface-limited regime. For sulfate-containing melts, the results are consistent with a regenerative SO$_4$/S$^-$ cycle, i.e., SO$_4^-$ + C —> S$^-$ + CO$_x$ (slow) and S$^-$ + 2O$_2$ —> SO$_4^-$ (fast). Compared to oxidation in pure Na$_2$CO$_3$, the reaction of dissolved SO$_4^-$ with graphite occurs much faster than the transport of O$_2$ to the carbon particle. Therefore, the addition of sulfate causes the plateau to disappear, and the reaction becomes surface-limited.
INTRODUCTION

Because of growing shortage of economical fuels, there is increasing pressure to develop environmentally acceptable methods of utilizing our coal reserves for power generation. The current practice of adding SO\textsubscript{2} stack gas scrubbers to conventional steam power generation cycles significantly increases the cost of the energy produced and can produce large amounts of sludge for disposal. Therefore, increasing emphasis is being given to the low-Btu gas fueled combined gas turbine-steam cycle. In this process, the sulfur is removed prior to combustion of the gas rather than after combustion. In general, low-Btu coal gasification involves partial oxidation of coal with air to produce a hot fuel gas containing CO and H\textsubscript{2} as well as sulfur which is usually present as H\textsubscript{2}S. To maximize the thermal efficiency of the cycle, the H\textsubscript{2}S should preferably be removed from the fuel at the gasification temperature. Suitable high temperature methods of H\textsubscript{2}S removal are now actively being sought.

In the Atomics International Molten Salt Coal Gasification Process, this problem is avoided because the sulfur is removed during gasification. The process consists of partial oxidation of coal in a bed of molten sodium carbonate. Virtually all of the sulfur remains behind in the molten salt as sodium sulfide. Furthermore, the presence of Na\textsubscript{2}S or Na\textsubscript{2}SO\textsubscript{4} in molten Na\textsubscript{2}CO\textsubscript{3} is found to catalyze the gasification.

Because of the increasing interest in gasification of coal with molten salts, there is a need for a basic understanding of the mechanism of gasification in molten salts. As a first step in understanding the kinetics of this system, the rate of oxidation of carbon by air in molten salts is being investigated. The salts in this study were Na\textsubscript{2}CO\textsubscript{3}, NaCl, and Na\textsubscript{2}CO\textsubscript{3}-Na\textsubscript{2}SO\textsubscript{4} mixtures. The Na\textsubscript{2}CO\textsubscript{3} was chosen because it is the salt upon which the Molten Salt Coal Gasification Process is based. Sodium chloride was selected to determine whether or not the CCl ion participated in the reaction, and the sulfate mixtures were chosen because the Na\textsubscript{2}SO\textsubscript{4} is known to catalyze the oxidation of carbon.

Spectroscopic grade graphite was selected as a source of carbon because of its low ash content, low sulfur content, low porosity, and low reactivity with air.

The experiments were performed in a 15 cm ID batch reactor. Air was bubbled through the graphite-melt mixture at a velocity high enough to produce turbulent mixing in the bed. The course of the reaction was followed by analyzing the exhaust gas...
for CO₂, CO, and O₂ as a function of time. Melt samples were taken as a function of time during the Na₂SO₄ experiments.

In this paper, the experimental data for the oxidation of graphite in pure Na₂CO₃ melts as well as in pure NaCl and in Na₂CO₃-Na₂SO₄ melts are evaluated on the basis of various hypothetical mechanisms.

THEORETICAL CONSIDERATIONS

In the case of sulfate-free melts it was found that the results are consistent with a mechanism where carbon and oxygen are the only chemically reactive species (i.e., the melt does not participate chemically in the reaction). The theoretical model consists of three phases (solid graphite particles, liquid Na₂CO₃, and gas bubbles) and three boundary layers (liquid films at the melt-graphite and at the melt-gas bubble interfaces, and a gas film at the gas bubble-melt interface). Transport of oxygen or COₓ product was assumed to be solely by physical processes involving diffusion through the boundary layers, and turbulent mixing in the bulk melt. The chemical reaction was assumed to occur on the carbon surface. Figure 1 outlines the sequence of physical and chemical steps.

While the differential rate equation for the complete sequence of events in Figure 1 is very complicated, there are two limiting cases which were solved analytically. One limiting case occurs when one of the steps on the bubble side is the slowest reaction in the system (Steps 1, 2, or 3 in Figure 1). This case will be called the oxygen transport-limited case. In this case, the rate of reaction will not depend on the carbon surface area, but will depend on the oxygen pressure and the gas flowrate. The system can always be forced into the oxygen transport-limited case by using a very large excess of carbon, so that the dissolved oxygen is consumed as fast as it dissolves.

The other limiting case occurs when the reaction of oxygen on the carbon surface is the slowest step (Step 7 in Figure 1). This case will be called the carbon surface limited case. In this case the rate of reaction will depend on the carbon surface area and on the dissolved oxygen concentration. As the reaction proceeds the carbon surface area decreases and the dissolved oxygen concentration increases. For spherical particles both limiting cases are described by the differential equation

301
\[
\frac{dm}{dt} = -k(4\pi r^2)^A p_0^B
\]  

(1)

where \(m\) and \(r\) are the instantaneous mass and radius of a single carbon particle, \(p_0\) is the instantaneous oxygen pressure in the bed, \(t\) is the time, and \(A\), \(B\), and \(k\) are constants. All the particles are initially of the same size. The rate constant \(k\) is a function of temperature and flowrate. The distinction between the two cases is that in the oxygen transport-limited case \(A = 0\), and in the carbon surface reaction limited case \(A = 1\). If the product of the reaction is a mixture of CO and CO\(_2\) rather than a single oxide,* then equation (1) is not sufficient to determine the course of the reaction. The kinetics of the conversion of CO into CO\(_2\) would also have to be included. However, the end product in the present experiments was CO\(_2\) with very little CO. Therefore, the kinetics of the conversion of CO into CO\(_2\) can justifiably be neglected. Equation (1) was solved assuming CO\(_2\) was the only product.** The error introduced by this assumption is less than 3%. The solutions to the differential equation are plotted in Figure 2 for six combinations of exponents, \(A = 0\) and 1, \(B = 0, 1/2\) and 1.*** The CO\(_2\) pressure in the exhaust gas is plotted as a function of time. The six curves are normalized to the same initial amount of carbon and the same burnout time. When \(A = 0\), the curves for \(B = 0, 1/2\) and 1 all coincide. The shape of the curves is dominated by the dependence on carbon surface area (\(A = 0\) or 1), with the dependence on oxygen order (\(B = 0, 1/2, 1\)) having little or no effect.

*The question of the identity of the initial product of combustion of solid carbon has been studied extensively in systems which do not contain molten salt. There was considerable controversy as to whether the initial product was CO or CO\(_2\). According to a review by Thring and Essenhigh(4), the currently accepted view is that CO is the initial product, and the oxidation of CO to CO\(_2\) takes place in the gas phase.

**When CO\(_2\) is the only product, the problem is greatly simplified because there is no change in the gas volume as a result of the reaction, and the flowrate remains constant throughout the run.

***Because of space limitations, the details of the solution of the differential equations will be published elsewhere.
Later in the paper when theoretical and experimental curves are compared, the presence of small amounts of CO are taken into account by plotting the experimental value of $P'^{\text{CO}_2}$

$$P'^{\text{CO}_2} = \frac{P_{\text{CO}_2} + P_{\text{CO}}}{1 - \frac{1}{2}P_{\text{CO}}/P}$$

(2)

where $P'^{\text{CO}_2}$ is the value of the CO$_2$ pressure that would exist if the CO present in the exhaust gas were converted to CO$_2$. P is the total pressure.

EXPERIMENTAL

The materials used in these experiments were Union Carbide SP2Z Spectroscopic grade graphite (99.999% C) with a specific surface area of 1.307 m$^2$/g (by the B.E.T. technique), Baker reagent grade anhydrous sodium carbonate (99.5%, 20 ppm SO$_4$), Baker reagent grade sodium sulfate (99.0%), Morton food grade sodium chloride (99.9%), Airco breathing air, oxygen (99.6%), nitrogen (99.995%), and carbon dioxide (99.8%). The water content in all the gases was 10 ppm (dew point - 60°C). The vessel was made of Coors 99.8% alumina.

The quiescent melt height was 15 cm in all the experiments, corresponding to 5.45 kg of Na$_2$CO$_3$ or 4.14 kg of NaCl in the 15 cm ID reactor. Prior to each run the bed was sparged with CO$_2$ to remove any Na$_2$O or NaOH that might be present. Then, with N$_2$ bubbling through the melt, 410 g of -70 +80 mesh spectroscopic grade graphite was added. Unless stated otherwise, 410 g of graphite was used in all the experiments. In the sulfate experiments, the sulfate was added last. Air or pure O$_2$ was bubbled through the melt at 77.8 standard liters per minute (SLM) corresponding to a superficial velocity of 1 fps at 900°C (except in one run which was at 50.7 SLM). The turbulent bed expanded by 75%, giving a contact time of about 0.9 seconds for the air.

The CO$_2$ and CO concentrations were measured with a NDIR analyzer, Horiba Model MEXA 304. The O$_2$ concentration was measured with a Teledyne Oxygen Meter, Model 320AX, whose sensing element is a fuel cell.
RESULTS

A. Pure Na$_2$CO$_3$

Figure 3 shows the oxidation of graphite with air in pure Na$_2$CO$_3$ at 990°C. P'CO$_2$ which includes the contribution from CO is plotted versus time. For comparison the CO concentration is also plotted. The solutions to equation (1) for A = 0 and 1, B = 1/2 are also plotted in the figure.

The number of moles of CO$_2$ + CO produced equals the original number of moles of carbon within the experimental accuracy, 101 ±1%, indicating that decomposition of the melt (Na$_2$CO$_3$→Na$_2$O + CO$_2$) does not contribute a significant amount of CO$_2$ to the exhaust gas.

The shape of the experimental curve is consistent with the mechanism shown in Figure 1. Apparently the system is intermediate between the two limiting cases. Of the two cases, the system seems to be closer to the oxygen transport-limited case. Based on the bed expansion, the initial mole ratio of C to O$_2$ in the bed is 8900:1. In addition, the carbon particles are smaller than the air bubbles, 0.2 mm compared to 5-10 mm. The large excess of carbon present tends to make the system nearly zero order in carbon surface area, resulting in the long plateau. After ~95% of the carbon is consumed, the system makes a transition becoming pseudo carbon surface area-limited resulting in the more rapid decline of P'CO$_2$ at the tail end.

The activation energy in the plateau region was determined by comparing two oxidation curves at 900°C and 1000°C for six different values of carbon surface area (i.e., at 30, 40, 50, 60, 70, 80% of the carbon consumed). An activation energy of 30 ±3 kcal/mole was obtained in the plateau region.*

The activation energy in the tail region was determined with a melt containing a small amount of carbon. Figure 4 shows how the reaction rate varies as the temperature is lowered from 1000°C to 890°C with 29 grams of carbon in the bed. A least squares fit gives an activation energy of 49.9 ±0.4 kcal/mole.

*Additional experiments are planned so that the activation energy can be determined from more than two temperatures.
The apparent difference in effective activation energies during the plateau and the tail is consistent with two different processes dominating the two regions.

The existence of a plateau means that the rate of reaction is not controlled by the carbon surface area in this region. On the other hand, the tail end of the reaction appears to be first order in carbon as determined by oxidizing 10, 30, and 40 grams of carbon added to 5.45 kg of Na$_2$CO$_3$.

Using air and pure O$_2$, the reaction was found to be half order in oxygen ($B = 0.53$) with a small amount of carbon in the bed. We have not yet measured the order in the plateau region, but we believe it is also half order in oxygen based on results in NaCl melts to be discussed later.

Even though the experimental results are consistent with the mechanism outlined in Figure 1, frequently more than one mechanism can agree with experiment. Therefore, alternative mechanisms involving reactions of the Na$_2$CO$_3$ melt have also been explored. For example, it is known that carbon reacts with Na$_2$CO$_3$ in a CO or inert atmosphere (N$_2$, He, Ar) to form Na$_2$C$_2$. A possible mechanism involving Na$_2$C$_2$ as an intermediate is illustrated by the following reactions.

\begin{align*}
\text{CO}_3^+ + 4\text{C} & \rightarrow \text{C}_2^+ + 3\text{CO} \\
\text{C}_2^+ + 2\text{O}_2 & \rightarrow \text{CO}_3^+ + \text{CO} \\
4\text{CO} + 2\text{O}_2 & \rightarrow 4\text{CO}_2
\end{align*}

There are three likely possibilities, reaction (3) is slowest, reaction (4) is slowest, or (3) and (4) are comparable. If reaction (3) is the slowest reaction, then the CO$_2$ evolution would follow the carbon surface area and there would be no plateau. If reaction (4) is the slowest reaction, the instantaneous amount of CO$_2$ evolved would not equal the instantaneous amount of O$_2$ consumed. Initially the C$_2^+$ concentration would be zero. Reactions (3) and (5) would produce twice as much CO$_2$ as the amount of O$_2$ consumed. Toward the end of the run, the carbon would be completely consumed by reaction (3) while C$_2^+$ would still be present. At this point the O$_2$ consumed would be 2.5 times greater than the CO$_2$ evolved. Figure 5 shows that the amount of O$_2$ consumed is accounted for by the CO$_2$ and CO evolved within experimental accuracy. Thus, the results do not support
either limiting case involving $C_2^-$ . However, an intermediate case might conceivably produce the proper curve. To investigate this point, the experiments were repeated in pure NaCl where $C_2^-$ would not be expected to form.

B. NaCl

The experiments with NaCl were hampered by the excessively high vapor pressure of the salt. Because NaCl is very volatile at 1000°C, the gas sampling lines and particulate filter plugged with NaCl in about five minutes, necessitating frequent disassembly and cleaning of the sampling lines. Because of this problem, the oxidation reaction was not followed to completion.

Figure 6 shows the results. The oxidation curves for Na$_2$CO$_3$ and NaCl melts are given as a function of the mass of carbon consumed. This corresponds to comparing the two systems at approximately the same carbon surface area. The rate of oxidation in NaCl is about half that in Na$_2$CO$_3$. However, differences in viscosity, etc., would be expected to influence the hydraulic properties of the bed, and therefore influence the overall reaction rate. The shapes of the two curves appear to be the same, however. The activation energy in the plateau region is also the same.

Figure 7 shows the effect of temperature in the plateau region of NaCl over the interval of 837° to 1000°C. The temperature was decreased (circles) then increased (triangles). Nitrogen was sparged through the melt while waiting for the temperature to stabilize at a new value. There were 360 g of carbon at the start and 16.5 g were consumed during the experiment, corresponding to a 3% reduction in surface area. A least squares fit gave an activation energy of 30.6 ±0.8 kcal/mole which is the same as the value found in the plateau of Na$_2$CO$_3$ (30 ±3 kcal/mole). The fact that the shape of the oxidation curve and the activation energies are the same for NaCl and Na$_2$CO$_3$ suggest that the mechanism is also the same in both systems. Consequently, the $C_3^-$ ion does not appear to be involved in the reaction, ruling out a $C_3^-/C_2^-$ cycle.

Using air and pure O$_2$ with 340 g of carbon present, the rate oxidation was found to be half order in oxygen ($B = 0.498$) in the plateau region of NaCl. Since the shape of the curves and the activation energies are the same for NaCl and Na$_2$CO$_3$, it is assumed that the reaction is probably also half order in the plateau region of Na$_2$CO$_3$. (The tail region of Na$_2$CO$_3$ was previously determined to be half order in O$_2$).

306
Even though $\text{CO}_3^-$ does not appear to be involved in the reaction, $\text{Na}^+$ could have a role. It is known that impregnating coke with $\text{Na}_2\text{CO}_3$ accelerates the rate of combustion.\(^{(6)}\) It is also known that carbon reacts with $\text{Na}_2\text{CO}_3$ in an inert atmosphere to form Na and $\text{CO}$:\(^{(7)}\)

$$\text{Na}_2\text{CO}_3 + 2\text{C} \rightarrow 2\text{Na} + 3\text{CO}$$

An analogous reaction in $\text{NaCl}$ would have to involve $\text{Cl}^-$ as well as $\text{Na}^+$ in order to maintain charge neutrality. We did not look for any $\text{Cl}$ compounds in the exhaust gases, however any halogen reactions would have to be consistent with the observation that the $O_2$ consumption equalled the $CO_2$ evolution. A cyclic reaction would satisfy this requirement. In any event, the present experiments did not determine whether $\text{Na}^+$ plays a role in the combustion mechanism.

C. $\text{Na}_2\text{CO}_3 - \text{Na}_2\text{SO}_4$ Melts

Sodium sulfate is known to catalyze the oxidation of carbon.\(^{(2)}\) Figure 8 shows the catalytic effect of 10% wt $\text{Na}_2\text{SO}_4$ compared to pure $\text{Na}_2\text{CO}_3$. The same amount of carbon is consumed approximately ten times faster. In fact, the rapidity of the reaction and the associated rapid heat evolution in the sulfate runs made it difficult to control the temperature. The furnace had such a large thermal mass that it took several hours to reach thermal equilibrium after a change in the heat load. The system could not reject the heat liberated in the sulfate runs fast enough. As indicated in Figure 8 next to the sulfate curve, the temperature rose sharply at the beginning of the run, then remained within a 10°C interval (970°C-980°C) until the reaction was nearly complete and then fell rapidly. To slow down the reaction in order to avoid the nearly 100°C temperature rise and fall, the experiment was repeated with only 1 wt% $\text{Na}_2\text{SO}_4$. Figure 9 shows the oxidation curve and the temperature fluctuations for 1 wt% $\text{Na}_2\text{SO}_4$ in $\text{Na}_2\text{CO}_3$ at 900°C (air flow rate = 50.7 SLM). The temperature still rose 30°C initially and then oscillated in a ±6°C temperature band before a new thermal equilibrium could be established. Note that there is a one-to-one correspondence in the fluctuations of the two curves. Even though the fluctuation of the absolute temperature is only ±0.5% there is a relatively large fluctuation in the rate of the reaction. From the size of the fluctuations in $P_{\text{CO}_2}$, the activation energy has been estimated to be approximately 50 kcal/mole.
In spite of the temperature control problem, the 1 wt% Na$_2$SO$_4$ oxidation curve still sheds some light on the reaction mechanism. It has been suggested that the catalytic effect is due to a SO$_4^{\text{-}}$/S$^\text{=}$ cycle.\(^{(2)}\)

\[
\begin{align*}
\text{SO}_4^{\text{-}} + 2\text{C} & \rightarrow S^\text{=} + 2\text{CO}_2 \quad (6) \\
S^\text{=} + 2\text{O}_2 & \rightarrow \text{SO}_4^{\text{-}} \quad (7) \\
2\text{C} + 2\text{O}_2 & \rightarrow 2\text{CO}_2
\end{align*}
\]

Some of the steps associated with this mechanism are illustrated schematically below.

Sixteen melt samples were taken during the course of the reaction and analyzed for sulfide, S$^\text{=}$. None was detected in any of the samples, indicating the sulfide concentration in the melt was less than 10 ppm, (the detection limit). This indicates that reaction (6) is the controlling step. Thus, the unreactive spectroscopic grade graphite is attacked by sulfate at a much slower rate than the sulfide is oxidized. Since the initial mole ratios (C:SO$_4$:O$_2$) = (8200:93:1) would have favored the formation of S$^\text{=}$, reaction (6) must be very much slower than reaction (7) and the overall reaction is controlled by reaction (6) on the surface area of the carbon.\(^{(8)}\) Since the dynamic sulfide concentration is practically zero, the reaction should appear to be pseudo zero order in SO$_4^{\text{-}}$ and O$_2$. That is, the reaction should
follow equation (1) with $A = 1$, $B = 0$. The theoretical curve is drawn in Figure 9 normalized to the same amount of carbon, that is, the experimental and theoretical curves have the same area under them. As a consequence of constraining the two curves to the same area, the disturbance caused by the initial 30° temperature rise must be compensated for at the tail. Taking this fact into account as well as the other temperature fluctuations, the agreement between theory and experiment is reasonably good.

If the activation energy of the $S^-$ oxidation reaction is lower than that of the $SO_4^{2-}$ reduction reaction, the system may undergo a transition from carbon surface-limited to oxygen transport-limited at higher temperatures.

CONCLUSIONS

(1) The $CO_3^{--}$ ion does not appear to be involved in the air oxidation of graphite in pure $Na_2CO_3$.

(2) Whether the $Na^+$ ion plays a role in the reaction is unresolved.

(3) The experimental results in pure $Na_2CO_3$ and $NaCl$ are consistent with a mechanism in which C and $O_2$ are the only reactive species. According to this mechanism, for the C to $O_2$ mole ratio and particle size used in these experiments, the reaction tends to be limited by the transport of oxygen initially giving rise to a plateau in the oxidation curve. When the carbon is nearly consumed the system makes a transition to the carbon surface area-limited case.

*On the basis of this mechanism, one would predict the increased gas-liquid contact area with increasing flowrate would have no effect on the reaction rate. The simultaneous decrease in the boundary layer thickness would only have an effect if the rate of diffusion through the boundary layer is nearly as slow as the rate of the surface reaction. Thus, it is likely that the flow rate will have little or no effect on this reaction.
(4) The data for sulfate catalysis at 900°C are consistent with the reactions.

\[ \text{SO}_4^{2-} + C \rightarrow S^{2-} + \text{CO}_x \] (SLOW reaction occurring on carbon surface)

\[ S^{2-} + 2\text{O}_2 \rightarrow \text{SO}_4^{2-} \] (FAST reaction occurring at bubble)

Compared to the experiments in pure Na$_2$CO$_3$, the reaction of dissolved SO$_4^{2-}$ with C occurs with much greater speed than the transport of O$_2$ from the gas phase through the melt to the particle surface. Therefore, at 900°C, the addition of sulfate causes the plateau associated with oxygen transport to disappear, and the reaction changes from oxygen transport-limited to surface-limited.

ACKNOWLEDGEMENT

Funding for this work was provided by the U.S. Energy Research and Development Administration, Division of Physical Research, under contract AT(04-3)-701, Task 30.
REFERENCES

1. C. A. Trilling, Coal Gasification by Atomics International's Rockgas Process, Winter Annual Meeting of ASME, November 17-22, 1974. Paper 74-WA/PWR-11.

2a. P. A. Lefrancois and K. M. Barclay, U.S. Patent 3,567,412 (1971)
2b. J. R. Birk and D. A. Huber, U.S. Patent 3,708,270 (1973); J. R. Birk, U.S. Patent 3,710,737 (1973)

3. J. R. Fair, Chem. Eng. 74 (14) 67 (1967). Fair showed that the transition from the quiescent regime to the turbulent regime occurs in the superficial velocity interval of 0.20 to 0.25 fps for water. The present experiments were performed at 1 fps. According to Fair, in the turbulent regime, the performance is not affected by the design of the gas distributor. Since molten Na$_2$CO$_3$ beds may differ from H$_2$O beds, a graphite oxidation experiment was done with two different sparge tubes, one with a single 1-1/2 inch hole and the other with four equally spaced 1/8 inch holes. The two sparge tubes gave the same oxidation curves, indicating the bed is turbulent.

4. H. H. Lowry, Chemistry of Coal Utilization, Supplementary Volume, Chapter 17 (John Wiley & Sons, Inc., New York, 1963)

5. J. E. Witmer, A. C. Thadam, and D. S. Chang, Office of Coal Research, R&D Report 33, PB235301, August 1968.

6. G. W. Lee, Chem & Ind. 1963, 1060

7. R. Bibaud and W. S. Graves, Process Specifications Carbothermic Production of Sodium, Vitro Engineering, N. Y., December 14, 1956.

8. J. Birk and W. Vaux, PB191957, have studied reaction (6) in the absence of reaction (7) by reducing S$O_4^-$ with coke in an He atmosphere in alkali carbonate eutectic melts between 600 and 800°C. Using their results one calculates an activation energy of 49 kcal/mole for reaction (6). This agrees with the crude estimate of activation energy determined from the fluctuations in Figure 9.
Figure 1

OUTLINE OF A POSSIBLE MECHANISM FOR THE OXIDATION OF GRAPHITE IN MOLTEN SODIUM CARBONATE

1. Diffusion of oxygen from bulk gas to the surface of the bubble.
2. Absorption of oxygen into the liquid surface.
3. Diffusion of dissolved oxygen into the bulk liquid.
4. Turbulent mixing of dissolved oxygen throughout the liquid.
5. Diffusion of dissolved oxygen from the bulk liquid to the fluid at the exterior surface of the carbon.
6. Adsorption of oxygen onto the exterior and pore surfaces of the particle.
7. Reaction of adsorbed oxygen with carbon. The carbon particle diameter decreases as the reaction proceeds.
8.-13. Reverse of Steps 6 through 1, respectively, for the product.
FIGURE 2. SOLUTION OF THE DIFFERENTIAL RATE EQUATION IN MOLTEN Na2CO3 AT 990°C

\[
\frac{dm}{dt} = k (4\pi r^2) P_{O2}
\]

FIGURE 3. AIR OXIDATION OF GRAPHITE IN MOLTEN Na2CO3 AT 990°C

FIGURE 4. EFFECT OF TEMPERATURE ON THE RATE OF GRAPHITE OXIDATION IN THE TAIL REGION WITH Na2CO3

\[ E_a = 49.9 \pm 0.4 \text{ kcal/mole} \]

FIGURE 5. INSTANTANEOUS BALANCE BETWEEN O2 CONSUMED AND O2 RELEASED AS CO2 AND CO FOR GRAPHITE OXIDATION IN Na2CO3 AT 990°C

\[ \text{Based on unreacted } O_2, 0.209 - P_{CO} / P_{CO2} \]

\[ \text{Based on CO}_2 \text{ CO formed } P_{CO2} / P_{CO} \]

313
