ANALYSIS OF MULTIPLE GAS-SOLID REACTIONS DURING THE GASIFICATION OF CHAR IN OIL SHALE BLOCKS

Robert L. Braun, Richard G. Mallon and Hong Yong Sohn
Lawrence Livermore National Laboratory
Livermore, CA 94550

ABSTRACT
In combustion retorting of oil shale, the required process energy is largely supplied by the combustion of char (the residual organic carbon and hydrogen from kerogen pyrolysis). Efficient use of this char is required in avoiding excessive combustion of oil. Accurate prediction of oil yield requires a good understanding of the important reactions of carbon with O₂, CO₂ and H₂O. In this paper we focus on the latter two gasification reactions.

A mathematical model is presented for the major high-temperature chemical reactions occurring in the absence of O₂ within a block of spent oil shale: decomposition of dolomite and calcite, char pyrolysis, carbon gasification with CO₂ and H₂O, water-gas shift, and intrablock diffusive and convective flow of CO₂, CO, H₂ and H₂O. To establish the validity of the computer model, experiments were performed on cylindrical blocks of oil shale having a mass of about 8 kg. The blocks were heated in an electric furnace and swept with heated gas of controllable composition that included steam. Maximum block surface temperatures of 750°C and 815°C were used.

The computer model produced excellent simulations of the experimental carbon gasification reactions, not only with respect to total carbon reacted but also with respect to the radial distribution of the unreacted char. Accurate simulation of the carbon gasification reactions required the use of intrinsic rate coefficients that were substantially lower than those previously measured for powdered samples. The water-gas shift had an almost negligible effect on the rate of carbon gasification in all runs. The rigorous block model described here will be a useful tool for exploring a wide range of operating conditions and for developing a simple model that can more readily be included in a comprehensive model of an entire retort.

INTRODUCTION
In combustion retorting of oil shale, a hot zone is maintained in the rubble bed by injection of air, possibly diluted by steam and recycle gas. A major portion of the required process energy is supplied by combustion of char (the residual organic carbon and hydrogen from kerogen pyrolysis) and oil vapor. An ideal retorting process would maximize the combustion of char so as to minimize the combustion of oil. Therefore, the gasification and combustion of char are important aspects of combustion retorting.

Since in many retorting processes a major portion of the shale is in pieces which are larger than 1 cm, the char reactions will be strongly influenced not just by chemical reaction kinetics, but also by gas transport conditions within the pieces. The reaction of char is primarily with O₂, CO₂, and H₂O. Since decomposition of carbonate minerals is an important source of CO₂, this decomposition must be considered in studying char reactions. The reaction of char with O₂ and CO₂ in blocks has been described previously (Mallon and Braun, 1976). In this paper we describe the simultaneous reaction with H₂O and CO₂ in blocks.

*Consultant to LLNL: is with Departments of Metallurgy and Metallurgical Engineering and of Mining and Fuels Engineering, University of Utah, Salt Lake City, UT 84112.
The study of these char reactions was performed by a combination of computation and experimentation, with the two aspects of the study closely coordinated. The mathematical forms used in computation were, as far as possible, based on fundamental principles. The geometry of the experiments was chosen so as to facilitate a simple and exact mathematical description.

EXPERIMENTATION

The experiments to be described here consisted of exposure of shale blocks to high temperature in an atmosphere of controlled composition. Each block was exposed to a different combination of atmosphere and temperature. The oil shale used in these experiments came from the mine at Anvil Points, Colorado. The shale blocks were in the shape of right circular cylinders 14.6 cm in diameter and about 25 cm in length. The cylinder axis was perpendicular to the shale bedding planes. The mass of each block was about 8 kg. All of the blocks were cut by coring from a single large slab of shale. We took all of the cores from the same strata of shale in order for them to be virtually identical. Analysis of cuttings from holes drilled the full length of the centerline of the blocks showed that organic carbon ranged among the blocks from 15.11% to 15.26% of the raw shale mass. This implies that the shale grade was about 135 l/Mg (Smith, 1966). The CO₂ release by acid treatment of the raw shale was about 20% of the shale mass.

Since the mathematical treatment of the experiments was to be limited to a single spatial dimension, the blocks were prepared so as to minimize axial transport of both heat and fluids. An insulating and sealing cap was attached to each end of each block. These caps were formed of multiple layers of sheet asbestos bonded together with ceramic cement. This cement was also used to bond the caps to the ends of the blocks. The caps were about 3 cm thick and equal in diameter to the blocks. Temperature measurements within the blocks during the high-temperature treatment indicated that axial heat flow was negligible. Since the ceramic cement was not damaged by the high temperature, we conclude that axial flow of fluids was also negligible.

Temperatures were measured with chromel-alumel thermocouples in 1.6-mm-diam stainless-steel sheaths. Figure 1 is a section diagram through the block showing the thermocouple locations. Three thermocouples were cemented in the hole on the block centerline. The two thermocouples on the surface were on the midplane diametrically opposite each other.

The blocks were individually heated in an electric oven and were oriented so that shale bedding planes were horizontal. Figure 2 is a diagram of the oven and ancillary equipment. Gas to be passed through the oven was preheated and injected at the top. Gas was discharged at the bottom of the oven. In these experiments the gas entering the oven was either pure nitrogen or a mixture of nitrogen and steam. The nitrogen flow rate was metered downstream of the control valve. The steam was produced in a flash boiler. Water was delivered to the boiler by a constant displacement pump with adjustable stroke length. The weight of the water reservoir was continuously monitored, and the rate of change of this weight was taken as the steam flow rate.

For each block, we chose a temperature for study of char reactions. This temperature was considerably above that required to complete shale retorting. The block surface was heated to the selected temperature, and then held constant at that value. During the temperature increase, pure

Figure 1. Section diagram of a block.
temperatures for an experiment in which the selected temperature was 750 °C. On this figure, time zero has been chosen as the time at which the block surface temperature reached the selected temperature for char reaction. As shown on the figure, steam was added to the flowing gas from 2 h to 8 h after time zero.

After a shale block had cooled, the oven was disassembled, thermocouples were cut off, and the sides of the block were wrapped with plastic tape to prevent disintegration during handling. The end caps were removed and samples of the shale were taken for chemical analysis. This sampling was done by drilling parallel to the cylinder axis at various radial positions. Each sample hole was drilled the full length of the block, and the material from each hole was thoroughly mixed before analysis.

Four experiments were performed. Two of these had steam in the flowing gas and two did not. The two non-steam experiments were intended as calibration or reference for evaluation of the two experiments in which steam was present. Tables 1 through 4 show experimental conditions and initial and final organic carbon and mineral CO₂ fractions. The carbon and CO₂ values are expressed as mass percent of the total raw shale mass. The final carbon and CO₂ values are presented for four different radial positions.

Samples of the discharge gas were taken during the experiments, and were analyzed by mass spectrophotometer for CO₂, CO₂ and H₂. Results for CO and CO₂ during the non-steam experiments are shown on Figures 4 and 5. Figure 6 shows the comparison of H₂ production with and without steam for blocks tested at 750 °C. The time scale on these figures is the same as used previously in Figure 3. The ordinate on the figures is the number of moles of each gas per hour per cubic meter of shale.

Measurements of CO₂ from the experiments using steam were impossible since condensed moisture in the gas sample containers was slightly alkaline and therefore absorbed CO₂.

MATHEMATICAL MODEL

Background

Major reactions taking place within an oil shale block during combustion retorting include:

1. the release of bound water,
2. the pyrolysis of kerogen into oil, gas, and char,
TABLE 1. Temperatures and steam volume fractions in the four experiments.

<table>
<thead>
<tr>
<th>Experiment designation</th>
<th>Char reaction temperature (^\circ)C</th>
<th>Steam volume fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-15</td>
<td>750</td>
<td>0</td>
</tr>
<tr>
<td>T-17</td>
<td>750</td>
<td>0.39</td>
</tr>
<tr>
<td>T-18</td>
<td>815</td>
<td>0.39</td>
</tr>
<tr>
<td>T-19</td>
<td>815</td>
<td>0</td>
</tr>
</tbody>
</table>

TABLE 2. Initial concentrations of organic carbon and mineral CO\(_2\) in shale blocks.

<table>
<thead>
<tr>
<th>Experiment designation</th>
<th>Concentration of organic carbon (mass %)</th>
<th>Concentration of mineral CO(_2) (mass %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-15</td>
<td>15.20</td>
<td>19.35</td>
</tr>
<tr>
<td>T-17</td>
<td>15.26</td>
<td>18.97</td>
</tr>
<tr>
<td>T-18</td>
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<td>T-19</td>
<td>15.25</td>
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</table>

TABLE 3. Final concentration of organic carbon in samples at different distances from the centerline. Concentration is expressed as mass percent on a raw shale basis.

<table>
<thead>
<tr>
<th>Experiment designation</th>
<th>Sample distances from centerline (mm)</th>
<th>Concentration of organic carbon (mass %)</th>
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<tbody>
<tr>
<td>T-15</td>
<td>9.5</td>
<td>2.99</td>
</tr>
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<td>35.0</td>
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<td>70.6</td>
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<td></td>
<td>70.6</td>
<td>1.16</td>
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TABLE 4. Final concentration of mineral CO\(_2\) in samples at different distances from the centerline. Concentration is expressed as mass percent on a raw shale basis.

<table>
<thead>
<tr>
<th>Experiment designation</th>
<th>Sample distances from centerline (mm)</th>
<th>Concentration of mineral CO(_2) (mass %)</th>
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<td>2.19</td>
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<tr>
<td></td>
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</tr>
<tr>
<td></td>
<td>70.6</td>
<td>0.60</td>
</tr>
</tbody>
</table>
(3) the coking of oil,
(4) the evolution of \( \text{H}_2 \) from char,
(5) the decomposition of carbonate minerals,
(6) the reaction of char with \( \text{O}_2, \text{CO}_2, \) and \( \text{H}_2\text{O} \), and
(7) the water-gas shift.

A comprehensive retort model that includes these reactions, the chemical reactions in the bulk-gas stream, and numerous important physical processes is under development (Braun, 1981). The model described here is concerned only with the intrablock reactions.

Among the reactions listed above, the first three occur at considerably lower temperatures (<500 °C) than all the other reactions (>500 °C) and therefore can be treated separately. It is the purpose of this work to simulate the chemical reactions taking place inside an oil shale block at the higher temperature range. Figure 7 schematically shows these various reactions. Previous block models have addressed carbonate decomposition as well as some of the carbon gasification reactions. Specifically, Mallon and Braun (1976) discussed the reactions with \( \text{O}_2 \) and \( \text{CO}_2 \), and Gregg, Campbell and Taylor (1979) discussed the reaction with \( \text{CO}_2 \). The present model will focus on the reactions with \( \text{H}_2\text{O} \) and \( \text{CO}_2 \). This situation is encountered in the retorting process immediately following kerogen decomposition before the oxygen front reaches the region. Furthermore, the analysis of this simpler reaction system in the absence of \( \text{O}_2 \) provides a better opportunity to test the model for the char-\( \text{H}_2\text{O} \) reaction.

The analysis of this reaction system, even in the absence of \( \text{O}_2 \), is complicated due to the fact that a net bulk flow of gas is generated inside the block. Steam must diffuse into the solid against this bulk flow to react with char. A considerable amount of research has been done on the analysis of gas-solid reactions in recent years (Szekely, Evans and Sohn, 1976; Sohn, 1978, 1979). Most of the previous work, however, has been on single gas-solid reactions without the effect of bulk flow. Among the exceptions are the studies of Sohn and Braun (1980), Rehmat and Saxena (1977), and Wen and Wei (1971) on simultaneous gas-solid reactions; Sohn and Rajamani (1977) on successive gas-solid reactions; and Sohn and Sohn (1980) on the bulk-flow effects on single gas-solid reactions.

Our modeling philosophy was to formulate a predictive model based on fundamental principles. This would allow maximum use of information on individual reactions and processes obtained from separate, isolated experiments. This is a much more satisfactory approach than a correlative model based on empirical parameters that may include the combined effects of several phenomena. Extension to different systems can be made with greater confidence using the more fundamental model. This is important, since it is our ultimate objective to use the results of the analysis of intrablock reactions to improve the overall oil shale retort model.

Mathematical Formulation

The events taking place in spent shale involve a complex network of chemical reactions, diffusion in a multicomponent gas mixture, the bulk flow of gases, and heat transfer. We make the following simplifications and assumptions to facilitate the mathematical analysis of the reaction system:

1. The diffusion of gaseous species can
be described using pseudobinary diffusivities.

(2) The total gas pressure in the solid is uniform and equal to the ambient pressure.

(3) The gas composition is that composition which would eventually develop if the gas sources and boundary conditions were held fixed at the values which they have at each time in the calculation (pseudosteady-state approximation).

(4) Heat is mainly transferred through the solid phase, and thermal equilibrium exists between the gas and the solid.

Rigorous treatment of multicomponent diffusion requires the use of the Stefan-Maxwell equation (Bird, Stewart and Lightfoot, 1960). In the system under investigation, all the gases have similar diffusivities except for H₂, which exists in relatively low concentrations. (At the beginning of the char gasification, the H₂ concentration is high because of evolution from char pyrolysis. This evolution is nearly complete in a relatively short time.) Thus assumption (1) was used by assigning a diffusivity value based on a CO₂-H₂O mixture to all species except H₂. For H₂, the binary diffusivity for an H₂-CO₂ mixture was used. In all cases, the effective diffusivities for transport parallel to the shale bedding planes were obtained from those theoretical binary diffusivities as used previously by Mallon and Braun (1976). The resulting effective diffusivities were \( D_{\text{CO}} = D_{\text{H₂O}} = 2.5 \times 10^{-10} \text{m}^2/\text{s} \), and \( D_{\text{H₂}} = 7.4 \times 10^{-10} \text{m}^2/\text{s} \), where \( T \) is the temperature in Kelvin.

Assumption (2) is justified because spent shale has rather high permeability. Assumptions (3) and (4) are generally valid for gas-solid reactions. With these assumptions, the species balance equations can be written as follows:

\[
\nabla \cdot \mathbf{N}_i = R_i, \quad \text{for } i = 1, 2, \ldots, n, \tag{1}
\]

where \( \mathbf{N}_i \) is the superficial molar flux of the \( i \)th species and \( R_i \) is the molar rate of production of the \( i \)th species per unit volume of the porous solid. In the absence of oxygen, the gas species are CO₂, H₂O, CO, H₂ and N₂. Under assumption (3) the flux of nitrogen is zero, and its concentration is obtained by difference. Thus, the mass balance equations are required only for the first four species.

With the use of an effective binary diffusivity for the diffusion of gas species \( i \) in a mixture, \( N_i \) is related to the concentration gradient by (Bird, Steward and Lightfoot, 1960)

\[
N_i = -D_{ij} \nabla \chi_i + \sum_{j=1}^{n} N_j, \quad \text{for } i = 1, 2, \ldots, n, \tag{2}
\]

where \( C \) is the molar concentration of the total gas and \( \chi_i \) is the mole fraction of gas species \( i \).

We now consider the local rates of the chemical reactions per unit volume of shale.

(a) Decomposition of carbonate minerals

Two mineral CO₂ components are considered. The first (\( W_1 \)) is the CO₂ from the MgCO₃ portion of dolomite, and the second (\( W_2 \)) is the CO₂ from the CaCO₃ portion of dolomite as well as from the initial free calcite. The rate of decomposition of dolomite is (Campbell, 1978)

\[
-\frac{\partial W_1}{\partial t} = V_1 = k_1 W_1, \tag{3}
\]

where \( k_1 = 1.7 \times 10^{10} \exp(-29090/T) \text{ s}^{-1} \).

Campbell (1978) proposed a more detailed scheme for modeling the rate of CaCO₃ decomposition. In the present model, however, we found that a simple first-order reaction adequately simulated the reaction. That is, the rate of CaCO₃ decomposition is

\[
-\frac{\partial W_2}{\partial t} = V_2 = k_2 W_2, \tag{4}
\]

where \( k_2 = 1.52 \times 10^8 \exp(-29330/T) \text{ s}^{-1} \).

This value for \( k_2 \) is based on previous block studies (Mallon and Braun, 1976) and on Campbell's (1978) kinetics for a CO₂ pressure of 0.5 atm. Steam is known to increase the rate of carbonate decomposition in powdered samples of oil shale (Burnham, 1979a). However, modeling these reactions for the present block experiments was successful using the above kinetics.

(b) \( C + H₂O = CO + H₂ \)
Burnham (1979b) has studied the intrinsic chemical kinetics of this reaction and interpreted the results assuming two simultaneous reactions, both of which are first order with respect to carbon. His results can also be closely approximated by assuming a single reaction that carries a more complex carbon dependence (Burnham, 1980a).

That is, the rate of the carbon-steam reaction is

\[ V_3 = \frac{k_3 P_X H_2 O}{1 + k_4 P_X H_2 + k_5 P X H_2 O} \left( \frac{W_3^2}{W_{3,0}} \right), \]  

(5)

where \( W_3 \) is the concentration of organic carbon residue, with an initial value of \( W_{3,0} \) after kerogen pyrolysis. In this equation, we have also incorporated the Langmuir-Hinshelwood dependence on the internal gas composition to account for the internal inhibition effects (absent in Burnham's powder experiments, but present in block experiments). The total pressure, \( P \), is assumed to be constant and the adsorption coefficients are taken from Long and Sykes (1948) as \( k_4 = 3.26 \times 10^{-4} \) Pa\(^{-1} \) and \( k_5 = 0.313 \exp(-10120/T) \) Pa\(^{-1} \). The rate coefficient was obtained by reinterpretation of Burnham's data as \( k_3 = 1.25 \times 10^5 \exp(-28000/T) \) s\(^{-1}\)Pa\(^{-1} \).

We will later note that a substantial decrease had to be made in the pre-exponential factor of this coefficient in the present block analyses.

(c) \( C + CO_2 = 2CO \)

Burnham (1979c, 1979d) has also studied the intrinsic kinetics of this reaction and interpreted the results assuming two simultaneous first-order reactions. More recently, Burnham (1980b) has shown that his results can also be adequately interpreted assuming a single first-order reaction if a lower activation energy is used. To account for CO inhibition effects, we used the Ergun (1956) equation, which is an accurate simplification for the Langmuir-Hinshelwood adsorption kinetics for this reaction. Thus, the rate of the carbon-CO\(_2\) reaction is

\[ V_4 = \frac{k_4 W_3}{1 + \frac{X_{CO}}{X_A CO_2}}, \]  

(6)

where Burnham's single first-order rate coefficient is \( k_6 = 3.6 \times 10^5 \exp(-20130/T) \) s\(^{-1} \) and the equilibrium constant for the oxygen exchange reaction is \( \exp(-11420/T) \).

We will later note that the pre-exponential factor for \( k_6 \) also had to be decreased appreciably in the present block analyses.

In the recent block model of Gregg et al. (1979) the gasification of carbon by CO\(_2\) was analyzed by a simplification of equation (6) in which the denominator was assumed to be constant, to obviate the need for knowing the internal gas composition. While that assumption may have been valid for their conditions of a linear heating rate, it is not generally valid for typical conditions encountered in an actual retort.

From equations (5) and (6), the net rate of gasification of the residual organic carbon is

\[ \frac{\partial W_3}{\partial t} = V_3 + V_4. \]  

(7)

(d) \( H_2 \) evolution from char pyrolysis

Campbell et al. (1980) studied this reaction and found that this secondary emission of \( H_2 \) from char pyrolysis occurred over a broad temperature range. It could mathematically be described best by using a distribution of activation energies. However, for the shale heating rate used here, the broad evolution of \( H_2 \) from char pyrolysis can also be adequately modeled by using a single first-order reaction with a relatively low activation energy. That is, the rate of \( H_2 \) evolution is

\[ \frac{\partial W_4}{\partial t} = V_5 = k_7 W_4, \]  

(8)

where \( W_4 \) is the concentration of organic hydrogen residue and \( k_7 = 10.7 \exp(-10190/T) \) s\(^{-1} \). This rate expression is not accurate at very low heating rates.

(e) Water-gas shift reaction \( (CO + H_2 O = \text{CO}_2 + H_2) \)

Experimental work on this reaction in the presence of spent oil shale has begun by Thomson (1980) and Steward (1980). The preliminary results of Steward are qualitatively similar to kinetics measured by Grebenshchikova (1957) in the presence
of coal ash. Therefore, until more complete investigations are made for this reaction in the presence of oil shale, we will use the coal ash data fit to first order with respect to all four gases. The net reaction rate is then

$$V_6 = k_8 \left( X_{H_2O}X_CO - X_{CO_2}X_{H_2}/k_B \right)(P/RT)^2 \varepsilon^3$$  \hspace{1cm} (9)$$

where the rate coefficient for the forward reaction is $k_8 = 375 \exp(-7300/T)$ m$^3$/mol$\cdot$s, the equilibrium constant is $k_B = 0.017 \exp(4400/T)$, the gas constant is $R = 8.3143$ J/mol$\cdot$K, and the shale porosity is $\varepsilon$.

Now, the terms $R_1$ to be used in equation (1) are

$$R_{CO_2} = V_1 + V_2 - V_4 + V_6'$$  \hspace{1cm} (10)$$

$$R_{H_2O} = -V_3 - V_6'$$  \hspace{1cm} (11)$$

$$R_{CO} = V_3 + 2V_4 - V_6'$$  \hspace{1cm} (12)$$

and

$$R_{H_2} = V_3 + V_5 + V_6'$$  \hspace{1cm} (13)$$

The boundary conditions of the four gas species for equations (1) and (2) are:

at $r = 0$, $N_i = 0$  \hspace{1cm} (14)$$

and

at $r = r_o'$, $X_i = X_{i1b}'$  \hspace{1cm} (15)$$

where $r$ is the radial location in the cylindrical block, $r_o$ is the block radius, and $X_{i1b}$ is the mole fraction of gas species $i$ in the external gas stream.

The initial conditions of the four solid species for equations (3), (4), (7) and (8) are:

at $t = 0$, $W_i = W_{i10}'$  \hspace{1cm} (16)$$

Solution Procedure

Temperature equation. In this work we did not actually solve an energy balance equation. Rather, the temperature at any desired radial location in the shale cylinder was obtained from the measured temperatures at the external surface ($T_s$) and the center ($T_c$) of the block by interpolation as

$$T = T_c + \left( r/r_o' \right)^2 (T_s - T_c).$$  \hspace{1cm} (17)$$

This was done for two reasons. First, the difference between the surface and center temperatures was not large. Second, the main emphasis in this work was to develop a mathematical description of the chemical reaction rate under the influence of mass transfer including the effect of bulk flow. It was thought that the use of measured temperatures would increase the sensitivity of the comparison between the experimental data and the model calculations for the carbon gasification reactions. The validity of equation (17) was verified for a block in which the internal temperatures were measured during heating to 900 °C.

Solid-species equations. Equations (3), (4), (7), and (8) were solved as a function of time and radial location by the following method. A constant time increment and equivalent radial zoning was used. At the start of each time increment, the gas composition was first calculated as a function of radial location (see next section). For the remainder of each time increment, this gas composition was assumed to be constant and equations (3), (4), (7), and (8) could be integrated by means of algebraic equations.

The initial conditions for the two carbonate species were based on the data in Table 2 and on x-ray diffraction data which indicated that approximately 90% of the CO$_2$ was in dolomite and 10% was in calcite. The initial condition for the organic carbon residue (after kerogen pyrolysis) was determined in two ways. Indirectly, from established correlations of oil yield as a function of heating rate (Campbell et al., 1977), and carbon residue as a function of oil yield (Stout et al., 1976), one can calculate that, for these experiments, 22% of the organic carbon in the raw shale should be left as carbon residue. More directly (from integration of the carbon oxides in the offgas, the initial and final inorganic carbon in the shale, and the final organic carbon in the shale), the data for experiment T-15 also indicated that 22% of the organic carbon in the raw shale was left as carbon residue. Finally, the initial condition for the organic hydrogen residue was based on an assumed char formula of CH$_{0.5}$. The carbon gasification calculations are very insensitive to
this assumption, since most of the hydrogen is evolved before steam was introduced.

Gas composition and flow equations. Equations (1) and (2) were solved by a collocation method to give $N_i$ and $X_i$ as a function of radial location at each time increment. We used the Fortran subroutine COLSYS, which was written by Ascher et al. (1977) to solve a multipoint boundary value problem for a mixed-order system of nonlinear ordinary differential equations. This subroutine automatically selects the number of collocation points and for this problem it required up to 96 subintervals in order to reach convergence.

A total execution time of approximately 4 min was needed for solving the complete set of equations (1)-(17) on a CRAY computer for a reaction time of 13 h. Most of this time was spent in the COLSYS subroutine. This long execution time for solving the reactions of a single block of oil shale illustrates the unacceptability of using a rigorous solution procedure, such as this, in a general retort model in which hundreds of shale blocks must be calculated for much longer reaction times than 13 h. This rigorous block model will be useful, however, in developing simpler models that can readily be used in an overall retort model.

Comparisons between model calculations and experimental data

Model calculations were first done for the two non-steam experiments T-15 and T-19. Comparison of the calculated and measured organic carbon residue at the end of these experiments indicated that too much carbon had reacted in the model. The rate coefficient for the $C + CO_2$ reaction was lowered by a factor of 6.3 to $k_6 = 5.7 \times 10^4 \exp(-20130/T)$ s$^{-1}$. This brought the final organic carbon concentrations into good agreement for both experiments. It is interesting to note that this rate coefficient is now very close to the one used in the previous block analyses by Mallon and Braun (1976). Gregg et al. (1979) found that the rate coefficient for the $C + CO_2$ reaction in their block model also had to be lowered by a factor of approximately five from the initial one they tried, which was based on measurements of the reaction kinetics in powdered samples of oil shale.

Model calculations were then done for the two steam experiments T-17 and T-18, using the new lower value for $k_6$. Comparison of the calculated and measured organic carbon residue at the end of these experiments again indicated that excessive carbon had reacted in the model. Therefore, one additional adjustment was made. The rate coefficient for the $C + H_2O$ reaction was lowered by a factor of 12.5 to $k_3 = 1 \times 10^4 \exp(-28000/T)$ s$^{-1}$ Pa$^{-1}$. This brought the final organic carbon concentrations into excellent agreement for both experiments.

These four comparisons are illustrated in Fig. 8 for the two experiments having a maximum temperature of 750 °C, and in Fig. 9 for the two experiments having a maximum temperature of 815 °C. The model results can be computed as a function of time for the entire reaction period, whereas the measured results for residual organic carbon are available only at the end of the experiment.

A more stringent test of the validity of the model can be obtained by comparing the radial distribution of unreacted carbon. Radial distributions are shown in Figure 10 for the two non-steam experiments and in Figure 11 for the two steam experiments. Except for the non-steam experiment T-15 at the lower temperature, excellent agreement is seen. In these graphs, an abscissa of equivolume increments ($r^2$) is used to give a better appreciation of the importance of the radial variations.

Figure 8. Residual organic carbon as a function of time for experiments at a maximum temperature of 750 °C.
It should be emphasized that only two parameters used in the model were adjusted: namely, the pre-exponential factors for the C + CO₂ rate coefficient and for the C + H₂O rate coefficient. It appears that the use of slightly lower activation energies for these two coefficients is also indicated. However, we made no adjustments in those quantities or in other physical or chemical parameters.

The need in block analyses for using carbon gasification rate coefficients that are substantially lower than indicated by kinetics measurements in powdered samples is not understood. There may be additional inhibition effects not addressed by the block models or, as suggested by Gregg et al. (1979), the carbon residue in blocks may simply be less reactive.

The importance of the water-gas shift reaction on the extent of carbon gasification was studied by letting the forward and reverse rate coefficients be zero in one case and essentially infinite in another case. The results are given in Figure 12 for experiment T-18, illustrating that the water-gas shift has almost negligible effect on the carbon gasification. The same was true for the other three experiments. The composition of the effluent gas, to be sure, was affected by the water-gas shift.
SUMMARY AND CONCLUSIONS

A mathematical model is presented for the major high-temperature reactions occurring in the absence of $O_2$ within a block of spent oil shale. To establish the validity of the computer model, four experiments were performed on cylindrical blocks, each having a mass of about 8 kg. The model produced excellent simulations of the experimental carbon gasification reactions with $CO_2$ and $H_2O$. Accurate simulation of the carbon gasification reactions required the use of intrinsic rate coefficients that were substantially lower than those previously measured for powdered samples. The water-gas shift had almost negligible effect on the rate of carbon gasification in all runs. The block model described here will be a useful tool for exploring a wide range of operating conditions and for developing a simpler model that can more readily be included in a comprehensive model of an entire retort.

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