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PROCEDURE FOR THE ESTIMATION OF CARBON OXIDATION RATES IN POROUS SPENT OIL SHALE

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PROCEDURE FOR THE
ESTIMATION OF CARBON OXIDATION RATES
IN POROUS SPENT OIL SHALE

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ABSTRACT

The rate of consumption of oxygen in the oxidation of carbon residues in porous particles of spent oil shale can be estimated from the free stream oxygen concentration and temperature. The procedure consists of calculating the reaction rate based on the free stream parameters

$$R_s = 6.53 \times 10^5 \sqrt{T} \exp \left[\frac{-44000 \text{ cal./mole}}{RT} \right] \frac{2\varepsilon}{r_p} C_s \frac{\text{moles/sec}}{\text{m}^3 \text{ of particles}}$$

and applying the correction

$$\Gamma = \frac{R_p}{R_s} = \frac{\eta}{\frac{1}{(1-\alpha)} + \frac{\eta}{3} \phi^2 \frac{1 - (1-\alpha)^{1/3}}{(1-\alpha)^{1/3}}}$$

R_p is the actual reaction rate within the porous particle;
 R_s is the rate evaluated at the free stream temperature and oxygen concentration; η is the effectiveness factor; α the total fraction of carbon consumed; and ϕ is the Thiele modulus.

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INTRODUCTION

The oxidation of carbonaceous residues which remain on the interstitial surfaces of spent or retorted oil shale is expected to provide the heat needed for in situ retorting processes. In the modeling of an in situ retort, the rate of carbon oxidation must therefore be calculated or estimated from such variables as the oxygen partial pressure and temperature. Only free stream or bulk flow variables are calculated in the macro model being developed by B. R. Bowman, but the direct calculation of the carbon oxidation rate without accounting for the differences in partial pressure and temperature between the bulk stream and the interior of the porous rock where the oxidation actually occurs can result in large errors. It is proposed that the oxidation of carbonaceous residues can be considered to be equivalent to heterogeneous catalyses where reactions occur at the interstitial surfaces of a catalyst. The analysis presented here is directed toward providing a method of calculating the ratio of the actual oxidation rate to the rate which would occur if all carbon were exposed to the free stream temperature and oxygen partial pressure. Since the calculation of the rate from free stream variables is straight forward, the method presented here will provide a simple method for calculating the actual rate.

Assumptions

It is assumed that in an underground or in situ retort, the oxidation of either carbon residues or hydrocarbons produced from retorting will be limited by the oxygen supply. In the process most commonly envisioned, the gases containing oxygen will be supplied to the top of a rubble chimney and will initially encounter spent shale containing carbonaceous residues at relatively high temperatures. For this type of process the following assumptions appear to be reasonable

and simplify the calculation of the oxidation rate.

- 1) All oxygen consumed in the oxidation of carbonaceous residues is consumed in spent shale. The oxidation of carbon in raw or partially retorted shale can be ignored. Rather, the oxidation of hydrocarbons produced from retorting will occur preferentially if oxygen is available at pieces of partially retorted shale.
- 2) The oxidation of carbonaceous residues reaches a quasi-steady state. Transients in diffusion of oxygen into the porous rocks and transient heating of the rocks can be neglected.
- 3) Spent oil shale particles are spherical and of uniform porosity.

These approximations permit an energy balance and a material balance equation to be written which govern the temperature and oxygen partial pressure within the shale particles. These equations can be considered to be time independent since the transients within the particles are assumed to be fast compared to changes in corresponding free stream variables.

Material Balance Equation

FIG. 1 Spherical Oil Shale Particle

If an oxygen material balance is written for the spherical shell shown schematically in Figure 1, the following equation is obtained.⁽⁵⁾ (See the Table of Nomenclature for the definition of the terms.)

$$D_e \left[\frac{d^2 C}{dr^2} + \frac{2}{r} \frac{dC}{dr} \right] = \rho S_g k C \quad (1)$$

The oxidation rate is considered to be proportional to oxygen partial pressure and to the surface area coated with carbon.⁽²⁾

Equation 1 has the following simple analytical solution at constant temperature (which implies constant k) for the boundary condition of constant oxygen concentration at the surface of the particle. The validity of ignoring temperature gradients in the particle will be treated later.

$$\frac{C}{C_s} = \frac{r_s}{r} \frac{\sinh \left[\frac{\phi (r/r_s)}{r_s} \right]}{\sinh \phi} \quad (2)$$

The subscript s signifies the value at the particle surface or in the

free stream and the parameter ϕ is defined as follows:

$$\phi = r_s \sqrt{\frac{\rho S_g k}{D_e}} \quad (3)$$

The actual rate of oxygen consumption is equal to the rate at which it enters the particle at the surface

$$R_p = 4\pi r_s^2 D_e \left(\frac{dC}{dr}\right)_s \quad (4)$$

and the rate which would be observed if all carbon were available at the bulk or free stream temperature and oxygen pressure is

$$R_s = 4/3\pi r_s^3 \rho S_g k C_s \quad (5)$$

Therefore the ratio of actual rate to the rate which would apply at free stream conditions is simply

$$\eta = \frac{R_p}{R_s} = \frac{3 D_e \left(\frac{dC}{dr}\right)_s}{r_s \rho S_g k C_s} \quad (6)$$

If the derivative in Equation 6 is evaluated from Equation 2 and substituted, the expression for the effectiveness factor η reduces to

$$\eta = \frac{3}{\phi} \left[\coth \phi - \frac{1}{\phi} \right] \quad (7)$$

This ratio can be computed rapidly since the data needed to calculate ϕ is available or can be estimated with reasonable accuracy.

Exhaustion of Carbon Supply

FIGURE 2

Particle with Carbon Partially Consumed

The examination of retorted oil shale samples indicates that the carbon near the surface is oxidized while that deep inside the particle is not, leaving a configuration similar to that shown schematically in Figure 2. The depletion of carbon near the surface and the shrinking of the boundary between oxidized and unoxidized carbon suggest a phenomenon analogous to pore mouth poisoning of a catalyst.⁽⁵⁾ To relate the rate of the oxidation in the partially unreactive particle to that of the fully reactive particle it can be assumed that diffusion through the outer unreactive portion of the sphere is rapid compared to the rate of shrinking of the carbon boundary. The reaction rate can then be written as the rate at which oxygen crosses the outer boundary.⁽⁵⁾

$$R_p = D_e (4\pi r^2) \left(\frac{dC}{dr} \right) \quad (8)$$

Since this rate of diffusion is constant between r_o and r_s , Equation 8 can be integrated to obtain

$$R_p = \frac{4\pi D_e r_s r_c}{(r_s - r_c)} (C_s - C_c) \quad (9)$$

For a particle in which the carbon has been partially consumed the carbon oxidation rate can be written as

$$R_p = (4/3\pi r_c^3) \rho S_g k C_c \eta. \quad (10)$$

If the concentration C_c is eliminated between Equations 9 and 10, the actual rate in terms of the surface concentration can be obtained. The derivation of the ratio of the actual reaction rate for a partially depleted particle to the ideal rate which would occur if all carbon were exposed to the bulk stream oxygen partial pressure and temperature is straight forward and leads to the result

$$\Gamma = \frac{\eta}{\left(\frac{1}{1-\alpha}\right) + \frac{\eta}{3} \phi^2 \left[\frac{1-(1-\alpha)^{1/3}}{(1-\alpha)^{1/3}} \right]} \quad (11)$$

In Equation 11, α is the fraction of internal surface area depleted and its relationship to r_c is shown in Equation 12.

$$\alpha = 1 - \left(\frac{r_c}{r_s}\right)^3 \quad (12)$$

When $\alpha = 0$, Equation 11 reduces to $\Gamma = \eta$ which is the case initially derived. If the total amount of carbon residue initially present is known, the fraction consumed can be computed at each time increment as the calculation proceeds.

Justification For Ignoring Thermal Gradients Within Particle

In energetic reactions such as the oxidation of carbon, thermal gradients frequently form within catalytic particles and can drastically effect the global reaction rate. If non-isothermal effects are considered, the following heat balance equation must accompany the oxygen material balance of Equation 1.⁽⁵⁾

$$\frac{d^2T}{dr^2} + \frac{2}{r} \frac{dT}{dr} - \frac{\rho S_g k C}{k_e} \Delta H_r = 0 \quad (13)$$

where k_e is the effective thermal conductivity of the porous rock. Inasmuch as the reaction rate constant is a strong function of temperature normally expressed by the Arrhenius equation,

$$k = k_o \exp (-E/RT) , \quad (14)$$

the simultaneous solution of Equation 1 and Equation 13 must be obtained numerically. These equations have been solved by Weisz and Hicks.⁽⁹⁾ The results of their computations are expressed as relationships between η and ϕ as a function of two parameters, γ and β , which are defined below.

$$\gamma = \frac{E}{RT} \quad (15)$$

$$\beta = \frac{(-\Delta H_r) C_s D_e}{k_e T_s} \quad (16)$$

$$\phi = r_s \sqrt{\frac{\rho S_g k}{D_e}} \quad (17)$$

The actual results of Weisz and Hicks calculations are included in Appendix B.

When $\beta = 0$, the value of η predicted from the numerical solution of Weisz and Hicks is identical to that obtained from the analytical solution shown in Equation 7. For positive values of β less than 0.01, the results of Equation 7 lie within 3% of those from the more cumbersome numerical solution, and for β less than 0.05, the approximation of Equation 7 is within 20% of the numerical solution when γ is less than 30. Happily, for the oxidation of carbon, γ will exceed 30 only at temperatures below about 850°F where the rate constant is very small. The details of estimating β for oxidation of carbon residues on oil shale are given in Appendix A, but the results are tabulated in Table I. Since β is relatively insensitive to temperature variation, tabulated values are shown only at 1000°F. At 1400°F, it is about 5% lower.

TABLE I

Values of β at 1000°F

$$\beta = \frac{-\Delta H_r C_s D_e}{k_e T_s}$$

Oil Shale Grade and O ₂ Partial Pressure	For Oxidation to CO		For Oxidation to CO ₂	
	β Perpendicular to Bedding Plane	β Parallel to Bedding Plane	β Perpendicular to Bedding Plane	β Parallel to Bedding Plane
15 gpt 0.2 atm O ₂	.0033	.0048	.0061	.0088
15 gpt 0.05atm O ₂	.0008	.0012	.0015	.0022
25 gpt 0.2 atm O ₂	.0093	.018	.017	.033
25 gpt 0.05atm O ₂	.0023	.0044	.0043	.0083
35 gpt 0.2 atm O ₂	.018	.049	.034	.090
35 gpt 0.05atm O ₂	.0046	.012	.0086	.022

Summary and Conclusion

The overall rate of consumption of oxygen in the oxidation of the carbon residues can be calculated by first estimating the rate which would occur if all carbon were at the free stream temperature and oxygen partial pressure and then multiplying the result by the correction factor Γ .

The rate based on free stream or bulk variables is shown in Equation 18

$$R_s = (6.53 \times 10^5 \sqrt{T} \exp\left[\frac{-44000}{RT}\right]) \left(\frac{2}{r_p}\right) (C_s) \frac{\text{moles } O_2/\text{sec}}{\text{m}^3 \text{ of particles}} \quad (18)$$

The correction factor Γ is defined by Equation 11 and repeated as Equation 19 below

$$\Gamma = \frac{R_p}{R_s} = \frac{\eta}{\left(\frac{1}{1-\alpha}\right) + \frac{\eta}{3} \phi^2 \frac{1-(1-\alpha)}{(1-\alpha)^{1/3}}} \quad (19)$$

The correct oxidation rate is therefore

$$R_p = \Gamma R_s \quad (20)$$

TABLE OF NOMENCLATURE

C	oxygen concentration	moles/m ³
D _e	effective diffusivity	m ² /sec
E	energy of activation	cal/mole
ΔH _r	energy of reaction	joules/mole O ₂
k	reaction rate constant	m/sec
k _e	effective thermal conductivity	watts/m k
k _o	Arrhenius constant	m/sec
R _s	reaction rate (based on free stream condition)	moles/sec m ³
R _p	reaction rate within particle	moles/sec m ³
r	radius	m
r _p	pore radius in particles	m
S _g	specific surface of spent shale	m ² /kg
T	temperature	K
α	fraction of carbon consumed	dimensionless
β	dimensionless parameter $\left[\frac{-\Delta H_r C_s D_e}{k_e T} \right]$	dimensionless
γ	dimensionless parameter (E/RT)	dimensionless
Γ	correction factor	dimensionless
ε	porosity	dimensionless
η	catalyst effectiveness factor	dimensionless
Φ	Thiele Modulus $\left[r_s \sqrt{\frac{\rho S_g k}{D_e}} \right]$	
ρ	density	kg/m ³
Subscripts		
c	refers to boundary of unreacted carbon	
p	refers to particle (except r _p which is pore radius)	
s	refers to surface or free stream value	

APPENDIX A

CALCULATION OF PARAMETERS FOR OIL SHALE

Calculation of β

The parameter β is defined by the formula

$$\beta = \frac{(-\Delta H_r) (C_s D_e)}{k_e T_s} \quad A(1)$$

In order to evaluate β for the oxidation of carbon residues in oil shale, each of the terms in Equation A1 must be evaluated. The parameters were all evaluated (as functions of temperature where appropriate), by the methods outlined below.

a) $(-\Delta H_r)$ Heat of Reaction

The following constant values of the heats of reaction were employed:

For oxidation to CO 2.21×10^5 joules/mole O_2

For oxidation to CO_2 3.93×10^5 joules/mole O_2

b) C_s (oxygen concentration)

The oxygen concentration was calculated from the ideal gas law as follows:

$$C_s \left(\frac{\text{moles}}{\text{m}^3} \right) = \frac{P_{O_2} \text{ (atm)}}{8.2057 \times 10^{-5} T(K)} \quad A(2)$$

c) D_e (effective diffusivity)

The effective diffusivity was calculated from bulk diffusivity by employing the parallel pore model of Wheeler⁽¹⁰⁾ which reduces to the following expression if Knudsen diffusion is unimportant.

$$D_e = D_b \epsilon^2 \quad A(3)$$

Knudsen diffusion is not important for pore of radius larger than about 10^{-7} m at atmospheric pressure.⁽⁵⁾

The bulk diffusivity of oxygen in the gas mixture was estimated from the Equation⁽²⁾.

$$D_b = 0.18 \left(\frac{T}{298} \right)^{1.75} \quad A(4)$$

d) k_e (effective thermal conductivity)

The effective thermal conductivity for spent shale was calculated from the equations of Tihen, Carpenter, and Sohns,⁽⁶⁾ according to the equation

$$k_e = C_1 + C_2 F + C_3 T + C_4 F^2 + C_5 T^2 + C_6 F T \quad A(5)$$

where F is the Fischer Assay of the shale and T the temperatures. Values of the constants C_1 through C_6 are given in the work cited for both the direction parallel and the direction perpendicular to bedding planes.

Calculation of ϕ and γ

k (reaction rate constant)

The reaction rate constant employed was that taken from the work of Hottel, et al⁽⁷⁾ according to the equation

$$k = 6.53 \times 10^5 \sqrt{T} e^{\frac{-44000}{RT} \text{ cal/mole}} \quad \text{m/sec} \quad A(6)$$

γ (Arrhenius Parameter)

γ can be obtained by inspection from Equation A6 and was evaluated from A7

$$\gamma = E/RT = \frac{22143}{T} \quad A(7)$$

(ρS_g) (surface area/unit volume of particles)

The surface area was evaluated by assuming the porosity results from pores which are right circular cylinders of uniform radius

$$\rho S_g = \frac{2 \epsilon}{r_p} \quad A(8)$$

r_p (pore radius)

r_p was assigned a value of 10^{-6} m ⁽¹⁾

ϵ (porosity)

The following values of porosity were used ⁽³⁾

Grade	Porosity
15 gpt	0.22
25 gpt	0.33
35 gpt	0.42

Typical Values of Φ , η , and Γ are shown in Table AI for spherical particle 6 inches in diameter for oxidation of carbon to CO.

TABLE AI
(6" dia. particles)

Oil Shale Grade And Temperature		Φ	η	$\Gamma(\alpha = 0.2)$
15 gpt	500°F	.122	.999	0.8
	1000°F	.115	.026	.0025
	1400°F	.1857	.0016	1.1×10^{-5}
25 gpt	500°F	0.1	.999	0.8
	1000°F	93.7	.032	.0038
	1400°F	.1517	.0020	1.7×10^{-5}
35 gpt	500°F	.088	.999	0.8
	1000°F	83.1	.036	.0047
	1400°F	.1344	.0022	2.1×10^{-5}

APPENDIX B

RESULTS OF NUMERICAL SOLUTIONS OF

HEAT AND MATERIAL BALANCE EQUATIONS ⁽⁹⁾

The following figures from the work of Weisz and Hicks ⁽⁹⁾ show the relationship of η to ϕ for the important values of γ and β . The analytical solution (Equation 7) corresponds to the solution when $\beta = 0$.

FIG. 1. Relationship of utilization factor and dimensionless diffusion parameter.

FIG. 2. Relationship of utilization factor and dimensionless diffusion parameter.

FIG. 3. Relationship of utilization factor and dimensionless diffusion parameter.

FIG. 4. Relationship of utilization factor and dimensionless diffusion parameter.

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