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OIL SHALE OXIDATION AT SUBRETORTING TEMPERATURES

By
Irven A. Jacobson, Jr.

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Laramie Energy Technology Center
Laramie, WY 82071

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REPORT OF INVESTIGATIONS

OIL SHALE OXIDATION AT SUBRETORTING TEMPERATURES

By Irven A. Jacobson, Jr.

June 1980

U. S. Department of Energy
Laramie Energy Technology Center
Laramie, Wyoming

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by

Irven A. Jacobson, Jr.¹

ABSTRACT

Green River oil shale was air oxidized at subretorting temperatures. Off gases consisting of nitrogen, oxygen, carbon monoxide, carbon dioxide, and water were monitored and quantitatively determined. A mathematical model of the oxidation reactions based on a shrinking core model has been developed. This model incorporates the chemical reaction of oxygen and the organic material in the oil shale as well as the diffusivity of the oxygen into the shale particle. Diffusivity appears to be rate limiting for the oxidation. Arrhenius type equations, which include a term for oil shale grade, have been derived for both the chemical reaction and the diffusivity.

INTRODUCTION

Most oil-shale retorting processes currently in use preheat the shale with hot gases. If there is any oxygen present in these gases there is a possibility of oxidation of the raw shale. While heat is necessary to retort the shale, low temperature oxidation appears to decrease the potential oil yield of the shale (1, 6)².

Robinson, et al. (6) subjected raw oil shale to various oxidizing agents, including oxygen. They air-oxidized Green River oil shale of approximately $3.34 \times 10^{-4} \text{ m}^3/\text{kg}$ (80 gpt) Fischer Assay (3, 7) and less than 100 mesh particle size at 170°C for 14 weeks. Total weight loss of the shale was reported as 48.5 wt. pct. and the shale's hydrogen-to-carbon ratio decrease from 1.59 to 0.63.

Coomes and Sommer (1) studied the air oxidation of Green River oil shale in the 70 to 180°C range. They used three mesh sizes for the study: -1/4-inch to +8 mesh, -8 to +20 mesh, and -65 mesh. They found that 25 days of air oxidation at 120°C decreased Fischer Assay oil potential by 34 vol. pct. while gas and water production during retorting increased by 217 vol. pct. They also found that the oxidation decreased the organic carbon content of the shale, but not to the degree that oil yield was decreased.

¹Chemical Engineer

²Underlined numbers in parentheses refer to references at the end of this report.

While these authors agree about the decrease in oil potential during air oxidation neither the types nor quantities of gaseous materials released during oxidation are mentioned. As a further refinement to the Laramie Energy Technology Center mathematical model (2) of oil-shale retorting it was desirable to quantify the oxidation process. To obtain the necessary data for this modification of the model a low temperature air oxidation study was performed at LETC. The study was designed to determine the types and quantities of gaseous products produced during oxidation as well as providing rate data on which to base a mathematical oxidation model.

EXPERIMENTAL PROCEDURE

Samples of Green River oil shale were obtained for the study from the DOE Anvil Points mine located on the Naval Oil Shale Reserve near Rifle, CO. Three grades of oil shale were used. These samples had Fischer Assays of approximately 4.17×10^{-5} , 1.08×10^{-4} , and 1.96×10^{-4} m³/kg (10, 26, and 47 gpt). Each of these shale samples was crushed to less than 3.75×10^{-3} m (1/8 in.) in a jaw crusher and then to the final size in a gyratory crusher. The oil shale, after final crushing, was separated, using Tyler standard screens, into three size fractions for the study: -10 to +14 mesh, -14 to +20 mesh, and -20 to +28 mesh. Each of these fractions was mixed and riffled for Fischer Assay and elemental analyses.

Oxidation studies were performed in small tubular units operated in a vertical position with metered downward gas flow. A manifold of four reactors as shown schematically in figure 1 was assembled so each particle size group of each grade of shale could be studied at four temperatures, simultaneously. The reactors were made from 9.525×10^{-3} m (3/8 in.) O.D. by 8.89×10^{-4} m (.035 in.) wall stainless steel tubing .1778 m (7 in.) long. The ends of the reactors were fitted with swagelok fittings to facilitate insertion and removal from the manifold. Each reactor was equipped with a 1.5875×10^{-3} m (1/16 in.) stainless steel-sheathed type K thermocouple in the center on the longitudinal axis and a similar thermocouple on the outside wall. A thermistor temperature sensor was also located on the outside wall of the reactor and the full length of the reactor tube was wrapped with heating tape and ceramic fiber insulation. The thermistors on the outside of the reactors were used for temperature input to electronic controllers for temperature control of the reactors. A temperature variation of $\pm 1.1^{\circ}\text{C}$ (2°F) was observed for the outside, controlled, temperatures of the reactors. There was a temperature differential across the reactor, outside to center, of 11.1°C (20°F) at the highest temperature studied and 2.8°C (5°F) at the lowest temperature studied. Temperatures reported in this study are the averages of the inside and outside temperatures.

Figure 1. - Schematic of the Oxidation Equipment

Cylinders of nitrogen and air were used for the gas supplies. Pressure into the reactors was maintained at about 41 kPa (6 psig). Gas flow rate into the reactors was monitored with rotameters. Outlet gas flow was directed to either the atmosphere or a gas chromatograph (gc) with timer controlled solenoid valves. The atmospheric vents had restrictors installed to offer the same amount of back pressures as the gc gas sample system.

The off gas from each reactor was automatically sampled once an hour for gc analyses. It was possible to do an analysis in 15 minutes, therefore, each of the four reactors was sampled and analyzed in sequential order once an hour. A Fisher model 1200 Gas Partitioner³ was used for the gc gas analyses. The only gaseous compounds detected were nitrogen, oxygen, carbon monoxide, carbon dioxide, and water. Relative detector response factors were determined for all of the compounds in the products using appropriate standards and were used to correct the integrated peak areas. Molar gas quantities were further corrected to maintain a nitrogen balance between injection and production.

The four reactors were operated at 193, 203, 211, and 229°C (380, 397, 411, 444°F), respectively. Gas flow rate through the reactor tubes was maintained at $1 \times 10^{-5} \text{ m}^3/\text{min}$ which corresponds to $0.372 \text{ m}^3/\text{min}/\text{m}^2$ ($1.22 \text{ scfm}/\text{ft}^2$).

To perform an oxidation test the reactor tubes were each filled with a weighed amount of oil shale of the desired grade and particle size. The reactor tubes were attached to the manifold, and the thermocouples, thermistors, and heaters were connected to the temperature recorder and heater controllers. Air flow was established at room temperature and set to the desired rate. After setting the air flow, the air was turned off and nitrogen gas flow begun and the gc started. Reactor heaters were turned on. As the reactors heated to operating temperature carbon dioxide and water were evolved. After this initial evolution of surface adsorbed material was removed and a stable temperature reached, nitrogen flow was stopped and air flow begun. The switch in gases was made fifteen minutes before that reactor was to be sampled by the gc, therefore, each succeeding reactor had air flow established fifteen minutes after the previous reactor. Air flow was maintained for a minimum of twenty-five hours and then stopped at fifteen minute intervals in the same sequence as it was established. Nitrogen flow through the reactors was restarted when the air flow was turned off. After air flow to all reactors had been stopped, the heaters were turned off. Nitrogen flow was continued until the reactor temperatures had returned to room temperature. The reactors were then removed from the manifold and the oxidized shale weighed and ground for elemental analyses and the determination of potential oil recovery. No oil was found on the oxidized shale or in the collection system after an oxidation run.

³Reference to specific equipment is for identification only and does not imply endorsement by the U. S. Department of Energy.

Potential oil recovery determinations of the oxidized shale were made with a Chromalytics MP-2 Thermal Chromatograph which had been calibrated by analyzing oil shale samples of known oil yield potential.

RESULTS AND DISCUSSION

Table 1 lists the oxidation conditions, oil shale grade, oxidation times and recoveries for the tests made in the study. As can be seen, material balances were generally better than 95%.

Also included in the table are percent decrease in organic carbon content in the oxidized oil shale and the percent decrease in Fischer Assay oil potential. These values support the conclusions of previous workers concerning the decrease of potential oil yield with oxidation.

Several tests were also conducted with air diluted with nitrogen to give an oxygen content of less than 21%. Conditions and recoveries for these tests are listed in table 2. In general the same material and carbon balances are observed when less than 21% oxygen is available.

Hourly and cumulative production of carbon dioxide and carbon monoxide are tabulated in table 3 for two runs. These runs, 5-4 and 9-3, are typical of the tests performed. Because of the carbon dioxide produced by degassing of the oil shale during heat up and the flushing of the gases out of the reactor after the oxygen was shut off, the cumulative totals in table 3 are less than the total recovery reported in table 1. As can be seen from the table, the gas production goes immediately to a high level and slowly decreases as the oxidation continues. This type of production is typical of reactions that are concentration dependent which includes all reactions except those which are zero order.

As might be expected, the disappearance of organic carbon from the oil shale by oxidation:

can be kinetically complex. Different functions of carbon concentration were plotted against oxidation time in attempts to determine reaction order. A first-order type plot produced the straightest lines but, as can be seen in figure 2, these lines show some curvature. The curvature appears both as an intersection of two straight lines as for test 5-4 or as a gently curving line as for test 9-3. Such a curvature, especially the type of plot as test 5-4 could be caused by two first-order reactions of different rates. The disappearance of organic carbon showing two different first-order reaction rates can be explained in the following manner: If the organic carbon is distributed uniformly throughout the shale particle, oxygen from the gas stream can readily react with carbon on or very near the surface of the particle. Oxygen will have to diffuse into the shale particle to react with the internal carbon. Because gas diffusion through the shale pieces is a slow process the more the oxidation has to rely on oxygen diffusion the slower the apparent reaction rate.

TABLE 1. Test conditions, product distribution and recoveries for oil shale oxidation tests.

Run	Oil Shale Grade, $\text{m}^3/\text{kg} \times 10^4$ (gpt)	Particle size, mesh	Oxidation Temperature, $^{\circ}\text{C}$	Oxidation Time, hour	Shale weight, $\text{kg} \times 10^3$		Organic Carbon, $\text{kg} \times 10^3$	Gaseous Products Out, $\text{kg} \times 10^3$			Material Balance, wt/pct	Carbon Balance, wt/pct	Decrease in Organic Carbon, pct	Decrease in Fischer Assay, pct
					In	Out		CO_2	CO	H_2O				
1-1	1.0766 (25.8)	-10+14	193.3	24	8.9093	8.8412	1.0085	0.11371	0.01895	0.1850	99.4	88.9	7.2	-
-2			202.5		9.3260	9.2294	1.0056	.17074	.03331	.2273	99.0	94.2	10.6	33.2
-3			210.8		9.2132	9.0992	1.0429	.16603	.03258	.1761	98.4	93.9	10.7	35.1
-4			229.1		8.8621	8.6636	1.0032	.62518	.14282	.3415	96.8	100.6	20.8	42.1
2-1	1.0849 (26.0)	-14+20	193.3	66	10.2236	9.0964	1.1675	.31115	.04227	.25643	115.5	93.1	17.5	28.8
-2			202.5		9.4851	9.3017	1.0832	.48937	.08554	.37504	106.0	103.6	13.5	45.7
-3			210.8		9.0031	8.8184	1.0282	.45845	.07691	.34179	106.3	94.3	14.5	40.1
-4			229.1		9.0569	8.6683	1.0343	1.02735	.21430	.40489	100.8	112.6	28.9	60.0
3-1	1.0849 (26.0)	-20+28	193.3	42	9.5086	9.3938	1.0840	.28755	.05524	.3774	101.4	88.6	13.4	38.5
-2			202.5		9.2679	9.1342	1.0565	.34783	.06994	.3575	98.1	84.5	20.1	38.2
-3			210.8		8.5938	8.4489	.9797	.50308	.10669	.4118	97.7	93.0	17.5	43.2
-4			229.1		8.5954	8.2938	.9799	1.02328	.22689	.4444	94.2	106.3	22.8	58.3
4-1	.42478 (10.2)	-10+14	193.3	43	9.5886	9.5146	.4842	.08663	.00965	.09156	98.3	103.0	2.0	23.0
-2			202.5		10.3187	10.2127	.5211	.14024	.01679	.13205	97.7	94.4	13.5	22.2
-3			210.8		10.0787	9.9627	.5090	.11954	.01386	.10668	97.8	92.1	14.5	27.5
-4			229.1		9.9548	9.8344	.5027	.18926	.03074	.15404	97.9	87.2	24.8	32.5
5-1	.38222 (9.2)	-14+20	193.3	47	9.9059	9.3696	.4596	.11283	.00769	.07936	93.1	97.7	4.5	14.8
-2			202.5		10.2967	10.2051	.4773	.16079	.01617	.12533	97.2	101.0	8.8	20.3
-3			210.8		9.8132	9.5156	.4553	.16972	.01873	.13104	95.5	98.0	11.2	20.9
-4			229.1		9.6144	9.4886	.4461	.29982	.05293	.20005	97.0	103.8	18.5	44.8
6-1	.39432 (9.5)	-20+28	193.3	40	9.6633	9.5928	.4600	.04922	.00931	.06235	97.4	86.6	16.6	23.9
-2			202.5		9.9057	9.8284	.4715	.09110	.01705	.15535	100.6	98.7	7.4	23.3
-3			210.8		9.5571	9.4598	.4549	.20113	.04849	.16339	97.2	102.7	13.0	37.1
-4			229.1		9.1935	9.0488	.4376	.13324	.02774	.22554	96.9	88.4	21.4	52.4
7-1	1.9678 (47.2)	-10+14	193.3	66	8.1524	7.9762	1.6223	.29123	.05366	.46071	95.9	96.6	7.7	31.7
-2			202.5		8.2139	8.0272	1.6396	.38906	.07467	.46132	94.8	88.0	18.6	45.0
-3			210.8		7.3787	7.1002	1.4684	.49083	.09855	.49806	93.3	102.5	7.3	41.3
-4			229.1		8.3033	7.8526	1.6524	.92261	.18844	.68598	92.6	95.0	20.9	54.1
8-1	2.0125 (48.2)	-14+20	193.3	46	7.6255	7.4596	1.5160	.31725	.08467	.54173	97.2	92.0	14.1	13.0
-2			202.5		7.9897	7.8099	1.5884	.39873	.10008	.52857	95.9	90.6	16.8	28.6
-3			210.8		7.7974	7.5351	1.5501	.52218	.12352	.53246	95.6	93.0	16.5	30.5
-4			229.1		7.9654	7.5578	1.5835	.85431	.18789	.60214	96.5	90.5	25.0	46.7
9-1	1.9658 (47.1)	-20+28	193.3	48	7.5955	7.4235	1.5442	.36060	.11605	.64557	98.1	92.1	15.8	29.7
-2			202.5		7.9104	7.7119	1.6082	.51813	.16101	.54370	94.8	93.5	17.9	27.1
-3			210.8		7.4435	7.2087	1.5133	.53415	.16373	.54274	98.7	89.8	22.4	46.7
-4			229.1		7.6895	7.1943	1.5633	.57215	.16510	.49974	94.7	76.6	34.0	62.8

TABLE 2. - Test conditions, product distribution and recoveries for oil shale oxidation tests with less than 21% oxygen.

Run	Oil Shale Grade, m ³ /kg x 10 ⁴ (gpt)	Particle size, mesh	Oxygen in injection Gas, vol%	Oxidation Temperature, °C	Oxidation Time, hour	Shale weight, kg x 10 ³		Organic Carbon, kg x 10 ³	Gaseous Products Out, kg x 10 ³			Material Balance, wt/pct	Carbon Balance, wt/pct	Decrease in Organic Carbon, pct
						In	Out		CO ₂	CO	H ₂ O			
10-1	1.0766 (25.8)	-10+14	15.8	193.3	45	9.3874	9.2984	1.0627	.20409	.02654	.25130	98.9	100.0	5.4
-2			16.2	202.5		9.2921	9.1764	1.0519	.27670	.04791	.30260	99.2	100.0	8.0
-3			8.1	210.8		9.5897	9.5161	1.0856	.13613	.01398	.10120	98.6	100.7	2.6
-4			.01	229.1		9.3562	9.2572	1.0591	.02461	.00019	.08380	100.1	97.3	2.3
11-1	1.9678 (47.2)	-10+14	5.0	193.3	42	7.5036	7.3880	1.4932	.10152	.02155	.10562	98.9	100.4	.5
-2			5.0	202.5		7.7753	7.6364	1.5473	.13960	.02999	.13829	98.6	95.6	6.0
-3			5.0	210.8		7.4549	7.3244	1.4835	.16221	.03126	.17628	98.6	96.0	6.2
-4			5.0	229.1		7.3210	7.1071	1.4567	.32848	.07774	.30793	98.1	102.1	5.7
12-1	1.9678 (47.2)	-10+14	11.0	193.3	49	8.2277	8.1248	1.6373	.14549	.02843	.13901	94.0	90.7	11.4
-2			11.0	202.5		7.9438	7.8393	1.5808	.18798	.04491	.15222	93.7	104.1	3.2
-3			11.0	210.8		7.7260	7.5967	1.5375	.25970	.05297	.17576	93.6	97.0	7.5
-4			11.0	229.1		8.2797	8.0107	1.6477	.46906	.24459	.23107	93.0	101.1	10.2

TABLE 3. - Carbon Oxide Production For Oxidation Runs 5-4 and 9-3

Time, hours	Run 5-4				Run 9-3			
	CO ₂ Production, kg		CO Production, kg		CO ₂ Production, kg		CO Production, kg	
	Hourly x10 ⁶	Cumulative x10 ⁵	Hourly x10 ⁷	Cumulative x10 ⁶	Hourly x10 ⁶	Cumulative x10 ⁵	Hourly x10 ⁶	Cumulative x10 ⁵
.25	3.3571	.3357	9.8870	.9887	5.6178	.5618	1.7004	.1700
1.25	11.5424	1.4900	30.9281	4.0815	25.1068	3.0725	7.8315	.9532
2.25	10.6464	2.5546	27.3815	6.8197	22.4855	5.3210	7.0224	1.6554
3.25	10.1456	3.5692	24.7211	9.2918	20.5490	7.3759	6.4243	2.2979
4.25	9.8292	4.5521	22.8642	11.5782	19.5663	9.3325	6.1805	2.9159
5.25	9.3604	5.4881	21.4378	13.7220	18.1632	11.1488	5.7744	3.4934
6.25	9.2588	6.4140	20.2546	15.7474	16.6245	12.8113	5.3532	4.0287
7.25	8.9859	7.3126	18.8871	17.6362	15.5996	14.3712	5.0982	4.5385
8.25	8.5813	8.1707	17.7948	19.4156	14.7480	15.8460	4.7874	5.0172
9.25	8.4721	9.0179	16.8991	21.1055	13.8324	17.2293	4.4808	5.4653
10.25	8.2827	9.8462	16.6497	22.7705	13.3759	18.5669	4.3365	5.8990
11.25	8.0976	10.6560	15.8565	24.3562	14.4896	20.0158	4.5632	6.3553
12.25	7.9202	11.4480	15.1808	25.8742	14.2489	21.4407	4.6218	6.8175
13.25	7.6892	12.2169	14.4477	27.3190	13.5588	22.7966	4.3439	7.2519
14.25	7.5753	12.9744	14.1624	28.7352	12.9069	24.0873	4.1950	7.6714
15.25	7.1022	13.6846	13.0222	30.0375	12.5015	25.3374	3.9991	8.0713
16.25	7.0730	14.3919	12.7854	31.3160	12.0281	26.5403	3.8917	8.4604
17.25	6.8328	15.0752	12.3023	32.5462	11.5104	27.6913	3.8279	8.8432
18.25	6.7477	15.7500	11.6822	33.7144	11.4747	28.8388	3.7840	9.2216
19.25	6.6265	16.4126	11.4515	34.8596	10.4879	29.8876	3.5112	9.5727
20.25	4.8060	16.8932	7.1920	35.5788	9.6764	30.8552	3.2966	9.9024
21.25	5.1147	17.4047	6.8753	36.2663	9.6394	31.8191	3.2888	10.2313
22.25	4.7963	17.8843	6.6540	36.9317	9.2196	32.7411	3.1492	10.5462
23.25	4.6906	18.3534	6.5191	37.5836	9.8371	33.7248	3.2988	10.8761
24.25	4.5402	18.8074	6.3840	38.2226	8.6727	34.5921	2.9704	11.1731
25.25	4.7120	19.2786	6.4119	38.8632	8.4637	35.4384	2.9293	11.4660
26.25	4.6255	19.7412	6.3379	39.4970	8.1424	36.2527	2.7785	11.7439
27.25	4.6467	20.2058	6.0045	40.0975	8.2814	37.0808	2.8442	12.0283
28.25	4.5347	20.6593	6.2402	40.7215	7.7300	37.8538	2.6392	12.2922
29.25	4.3302	21.0923	6.0279	41.3243	8.2219	38.6760	2.8540	12.5776
30.25	4.4440	21.5367	5.2255	41.8468	8.3884	39.5148	2.7881	12.8564
31.25	4.2816	21.9649	5.4710	42.3939	7.8520	40.3000	2.6287	13.1193
32.25	4.0976	22.3746	5.2571	42.9196	7.5920	41.0592	2.5790	13.3772
33.25	4.2630	22.8010	5.5328	43.4729	7.5544	41.8147	2.5637	13.6336
34.25	4.1959	23.2205	5.1969	43.9926	7.1544	42.5301	2.3875	13.8723
35.25	4.1574	23.6363	4.9823	44.4908	7.1059	43.2407	2.4857	14.1209
36.25	4.1231	24.0486	4.6084	44.9517	6.8727	43.9280	1.2627	14.2472
37.25	4.0977	24.4584	4.7205	45.4237	6.6928	44.5973	1.2269	14.3699
38.25	4.0458	24.8629	4.6205	45.8858	6.6995	45.2672	2.3691	14.6068
39.25	3.9145	25.2544	4.2915	46.3149	6.6988	45.9371	2.2582	14.8326
40.25	3.8924	25.6436	4.6671	46.7816	6.3887	46.5760	1.5378	14.9864
41.25	3.7212	26.0157	4.2966	47.2113	6.1349	47.1895	1.0967	15.0960
42.25	3.8977	26.4055	4.4499	47.6563	6.4993	47.8394	1.1631	15.2123
43.25	4.0336	26.8089	4.8888	48.1452	5.9704	48.4364	1.0685	15.3192
44.25	4.0250	27.2114	4.6909	48.6143	6.1220	49.0486	1.1071	15.4299
45.25	4.0830	27.6197	4.5959	49.0739	6.2198	49.6706	1.1431	15.5442
46.25	4.0134	28.0210	4.4962	49.5235	5.7759	50.2482	1.0390	15.6481
47.25	3.8711	28.4081	4.4085	49.9643	5.8116	50.8294	1.0550	15.7536
48.25					5.8939	51.4187	1.0929	15.8629

Figure 2. - Organic Carbon Disappearance vs. Time Plot for Low Temperature Oxidation of Oil Shale

The crushed oil shale particles are odd shaped platelets. For the mathematical modeling of the oxidation reaction a cylindrical shape was chosen as the closest approximation. Particle diameters were determined from the average size openings of the sieves used to prepare the samples and are shown in table 4.

TABLE 4. - Mesh Size and Particle Diameter

Mesh Tyler Range	Average Particle Diameter m x 10 ⁴
-10 +14	14.1
-14 +20	10.0
-20 +28	7.1

The shape factor or length to diameter ratio was determined to be 1.47 by averaging microscopic measurements.

Three factors affect a heterogeneous reaction such as is considered here: (1) Diffusion through the stagnant gas layer next to the solid, (2) gaseous diffusion into and out of the solid, and (3) the chemical reaction (4). It was felt that the conditions used during the oxidation study would tend to eliminate the effects of the diffusion through the stagnant gas. This leaves diffusion through the solid and chemical reaction to be considered. If the diffusion through the stagnant gas layer actually does have some effect on the reaction, it is incorporated into the effects of gas diffusion through the solid.

A shrinking core model fits the process because the inorganic material remains constant and the organic material dispersed throughout the particle undergoes reaction. Levenspiel (4) presents the necessary equations for gaseous diffusion through the solid and chemical reaction for a shrinking core model. These equations, which were derived for spherical particles, were modified for cylindrical particles. The two new equations are:

Gas diffusion through the solid

$$t_1 = \frac{1}{4} \frac{\rho \lambda R^2}{(1+\lambda)bDC} \left[1 - 3\left(\frac{\bar{r}}{R}\right)^2 + 2\left(\frac{\bar{r}}{R}\right)^3 \right] \quad (1)$$

and chemical reaction

$$t_2 = \frac{3}{2} \frac{\rho \lambda (R-\bar{r})}{2(1+\lambda)bkC} \quad (2)$$

where

- t = time, hours
- ρ = molar density of carbon in the shale, mol/cm^3
- λ = shape factor = 1.47
- R = original radius of the shale particle, cm
- $\bar{r}$ = radius of unreacted core at time t , cm
- b = stoichiometric amount of oxygen consumed for carbon reacted = 3.088
- C = molar concentration of oxygen in the gas stream, for air = $9.369 \times 10^{-6} \text{ mole/cm}^3$
- D = effective diffusion coefficient for the gases in the oil shale particle, cm/hour
- k = first order reaction rate constant for the carbon-oxygen reactions, cm/hour

Stoichiometric oxygen consumption, b , was determined by averaging the oxygen consumed per carbon oxidized for all of the tests. This was necessary because oxygen was also consumed in oxidizing hydrogen and possible other unknown oxidation reactions. Another useful relationship for the modeling calculations is

$$X = 1 - \left(\frac{\bar{r}}{R}\right)^3 \quad (3)$$

where X = fraction of organic carbon reacted (evolved as oxides of carbon) by time t .

Oxidation time reported in this study is the sum of the times for diffusion, t_1 , and the time for chemical reaction, t_2 . Therefore, equations 1 and 2 are added together to give the measured time of oxidation

$$t = \frac{\rho\lambda}{2(1+\lambda)bC} \left[\frac{R^2 M}{2D} + \frac{3(R-\bar{r})}{k} \right] \quad (4)$$

where

$$M = 1 - 3\left(\frac{\bar{r}}{R}\right)^2 + 2\left(\frac{\bar{r}}{R}\right)^3$$

which on rearrangement gives

$$\frac{3(R-\bar{r})}{R^2 M} = \frac{t}{NMR^2} k - \frac{k}{2D} \quad (5)$$

where

$$N = \frac{\rho\lambda}{2(1+\lambda)bc}$$

Equation 5 is convenient to solve by graphical methods. When $3(R-\bar{r})/R^2M$ is plotted against t/NMR^2 the slope of the resulting line is the first order reaction rate constant, k , for the disappearance of the organic carbon. The intercept of the line is $k/2D$ from which the effective diffusion coefficient can be derived.

A least squares method was used to evaluate equation 5 for k and D for each of the oxidation tests. First, the total fraction of organic carbon reacted and removed as oxides of carbon, X in equation 3, was determined for each hour of the test. Equation 3 was used to calculate the unreaction particle radius, $\bar{r}$, which was then used in equation 5. Figure 3 is a plot of equation 5 for tests 5-4 and 9-3. As can be seen, the plotted data appears linear. The first order reaction rate constants, the slope of the line, for all of the tests had an r^2 of greater than 0.90.

In determining the Arrhenius parameters for the specific reaction rate constant with the standard equation:

$$\ln k = \ln A - E/RT \quad (6)$$

where

E = activation energy, kcal/mole

A = constant

R = gas constant

T = temperature, $^{\circ}K$

it was found that plotting $\ln k$ versus $1/T$ produced different lines for each of the oil shale grades tested. This is due in part to the difference in natural porosity exhibited by the oil shale as the potential oil yield increases. To simplify future work, oil shale grade was incorporated into the Arrhenius equation in the following manner:

$$\ln k = \ln A_1 + B_1G - E_1/RT \quad (7)$$

where

G = oil shale grade

B_1 = constant

Figure 3. - Plot of $3(R-\bar{r})/R^2M$ vs. t/NMR^2 for Determination of k and D

A similar equation can also be used to relate the apparent diffusion constant, D , to temperature and oil shale grade. An Arrhenius type equation can be used for the gas diffusion because of the relatively small temperature range being covered. The Arrhenius type equations for the chemical reaction rate constant and gas diffusion were evaluated by least squares calculations using the method of McBride and Villars (5). These equations have been evaluated to be:

$$\begin{aligned} \ln k &= -5.8333 + 6285.7G - 2360.0/T & (a) \\ \ln D &= 6.1542 + 114.44G - 10757.3/T & (b) \end{aligned} \quad (8)$$

where

$$\begin{aligned} G &= \text{oil shale grade, m}^3/\text{kg} \\ T &= \text{temperature, } ^\circ\text{K} \end{aligned}$$

Diffusivity, as calculated by equation 8b, is about 500 times smaller than the reaction rate calculated by equation 8a. This shows that the oxidation rate is limited by the diffusion rate of oxygen into the shale particle. Lack of natural permeability in the raw shale accounts for the relatively low diffusivity.

To show how well the rate constants calculated by equations 8 predict the oxidation process, figure 4 was drawn. In this figure the individual points represent the actual production of carbon dioxide and carbon monoxide as determined on an hourly basis. The solid line is predicted production using the constants from equations 8 in equation 4. This figure is representative of the results obtained in looking at all of the test data. This mismatch between the actual and calculated lines is partly due to the accumulation of all of the errors into the final two equations.

It is of interest to note that shale particle size is accounted for in the original rate equations by R and $\bar{r}$. Inclusion of oil shale grade in the final equation is necessary because the permeability of raw shale changes as the amount of organic material changes.

With the equations and constants developed it is possible to determine the amount of organic carbon removed from oil shale by low temperature oxidation. It is also possible to calculate the quantity of oxygen needed for any specified amount of oxidation.

No attempt was made to obtain specific reaction rate constants for the formation of either carbon dioxide or carbon monoxide during oxidation. For most of the oxidation tests performed, the molar ratio of carbon dioxide to carbon monoxide is 3.01. There appears to be enough random variation that it would not be possible to determine any effects on this ratio from temperature or oil shale grade.

Figure 4. - Actual and Calculated Organic Carbon Disappearance vs. Time Plot for Low Temperature Oxidation of Oil Shale

As has been previously reported (1, 6) potential oil yield, as determined by Fischer Assay, decreases more rapidly with oxidation than the organic carbon content of the oil shale. This is possibly due to the formation of oxidation products in the organic material of the oil shale which inhibits or decreases oil formation from part of the organic carbon. While equations 5 and 8 can be used to determine the quantity of organic carbon remaining in the oil shale after oxidation they do not give much of an indication of the remaining oil potential. Equation 9 was derived to correlate the percent decrease in Fischer Assay oil potential per unit time with temperature and particle size.

$$P = 7.5211 + 1.8975 \times 10^{-2}/R - 3475.6/T \quad (9)$$

where P = percent decrease in Fischer Assay oil potential per hour

R = particle radius in cm
T = temperature, °K.

This correlation has a goodness of fit (r^2) of 0.83. Fischer Assay oil potential can be calculated for Green River oil shale from percent organic carbon in the raw shale by empirical equation 10 derived from published data (8)

$$G = 1.0393 \times 10^{-5}L - 1.0019 \times 10^{-5} \quad (10)$$

$$G^1 = 2.4907L - 2.4011$$

where

G = Fischer Assay oil potential, m³/kg
G¹ = Fischer Assay oil potential, gpt

and

L = weight percent organic carbon in the oil shale.

If organic carbon analysis is available for the oxidized shale the decrease in potential oil yield can be determined by equation 11.

$$P_1 = 2.6318 + 1.0292 \times 10^{-2}/R - 1346.3/T + 1.6753F \quad (11)$$

where

P₁ = percent decrease in Fischer Assay oil potential per hour
from that calculated from equation 10

and

F = volume percent of oxygen in the inlet gas

Fischer Assay type analyses were not performed on the shale samples which were oxidized with less than 21% oxygen. It is assumed that equation 10 could be modified to include oxygen if the data were available.

SUMMARY

Oil shale from the Green River formation was ground to less than 10 mesh and air oxidized under controlled conditions. Gaseous products evolved during the oxidation were monitored. The oxidation process can be described by a shrinking core heterogeneous reaction process involving gas diffusion through the solid particle and a first order carbon oxidation reaction. Gas diffusion is the rate controlling step in the process. Arrhenius type equations which include oil shale grade were derived for both the gas diffusion and reaction rate constants.

Fischer Assay oil potential of the oil shale on oxidation decreases at a faster rate than predicted by the decrease in organic carbon in the shale. This is possibly due to oxygen being bound into the organic matter and inhibiting its thermal conversion to liquid products. Equations are presented to predict the decrease in oil yield per hour based on particle size and oxidation temperature.

The derived equations which are presented will add much improvement to the current mathematical oil shale retorting models.

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