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Irradiation Studies on Coal and Its By-Products

I. Effect of Radiation and Oxygen at Ambient Temperatures on the Subsequent Plasticity of Bituminous Coals

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INTRODUCTION

The effect of radiation on materials is a subject which currently is receiving much attention. Such studies are important because of the changes induced in most materials when they are exposed to radiation. Changes may occur by many mechanisms, such as displacement of atoms caused by energy absorption from incident particles, ionization followed by bond breaking, and formation of free radicals. Studies of the radiation effects in solids indicate that the use of radiation can be a powerful tool for increasing the understanding of the nature of solids.

Organic-type materials, owing to a predominance of convalent bonds or weak van der Waals forces, are more severely changed or degraded than other solids. Changes that may take place in materials are hydrogenation, dehydrogenation, polymerization, cracking, decomposition, and cross-linking, with the degree of change depending upon the type of radiation, incident rate of radiation, extent of radiation time, chemical composition of material, initial state of material, and environment.

Since it is known that gamma radiation can either upgrade or degrade organic materials, a study of the possible effects of gamma radiation on changing the fluidity of bituminous coal is a logical step. For example, a decrease in fluidity for coals high in fluidity would be advantageous, probably resulting in an increase in coke yield and coke strength. On the other hand, an increase in fluidity for coals low in fluidity could result in their becoming satisfactory sources of coke.

EXPERIMENTAL

Coal Samples Used - Eight Pennsylvania bituminous coals were selected for study. Proximate and ultimate analyses of the coals are presented in Tables I and II.

Coal Preparation - The coals were ground to -40 mesh and stored under a nitrogen atmosphere until required for radiation studies. Approximately 50 grams of each coal were placed in quartz or Pyrex containers (4 in. long x 1-1/4 in. inside diameter) and sealed under each of the following conditions:

1. Vacuum - the samples were evacuated until the pressure was less than 10μ Hg and then sealed. The amount of oxygen available to the coal was ca. 2×10^{-6} cc./g.

2. Air - the samples were sealed immediately; these containers held air initially at atmospheric pressure. The amount of oxygen available to the coal was ca. 0.2 cc./g.

3. Oxygen - the samples were evacuated until the pressure was less than 10μ Hg. Oxygen was dosed into the container until the final oxygen pressure was approximately 700 mm. Hg, with the amount of oxygen adsorbed by the coal measured. The containers were then sealed. The amount of oxygen available to the coal was ca. 1.1 cc./g.

Radiation Studies - For radiation studies, the sealed samples were placed in a 40 mil thick cadmium container. Cadmium was used to decrease the slow neutron flux to a relatively low level, since it was desired to irradiate the coals primarily with gamma radiation. The cadmium container with 5 coal samples was lowered down a 3 in. diameter aluminum tube and positioned in the University nuclear reactor. The reactor, which can be classified as a light water cooled, light water moderated heterogeneous type, had its fuel elements located approximately 20 feet under water. Irradiation to a total dosage of 3.8×10^8 rads (requiring about 17 hours) was then carried out at ambient temperatures*. Approximately 90 per cent of the energy absorbed by the coal came from gamma rays and 10 per cent came from fast neutrons.

Gas Analysis - Analysis of the gas in the container following irradiation of the coals was made using gas chromatography. After releasing the gas from the container to the gas analysis system of the chromatographic unit, the gas was dried and its volume measured. The gas analysis was performed using either a 15-ft. #5A molecular sieve column with argon as a carrier gas or a 6-ft. silica gel column using helium as a carrier gas.

Plasticity Measurements - The conventional Gieseler apparatus, modified with auxiliary equipment for better temperature control and more accurate measurement of high fluidity values, was used to determine plastic properties of the coals. The tests essentially were made using the A.S.T.M. Proposed Method of Test (1). However, contrary to recommended procedures, the brake was not applied when the dial divisions exceeded 5 divisions per minute. Instead, the stirrer was allowed to move continuously until it travelled at least 600 dial divisions. For those coals where the stirrer moved more than 600 dial divisions, the brake was then used according to the Proposed Method of Test (1). This procedure was adopted in an attempt to break up the frothy coal mass which formed (and which would go up into the barrel of the Gieseler apparatus and cause sticking) when testing a highly fluid and highly swelling coal.

RESULTS AND DISCUSSION

Analyses of Gases Evolved From the Coals During Irradiation - Table III presents data on the total amount and analysis of the gas evolved from the coals following irradiation in vacuum and oxygen; values for the individual gases are accurate to ±5%. With the present chromatography apparatus, it was not possible to determine water vapor; the gas analyses, therefore, are reported on a dry basis. Other gases, such as ammonia and the oxides of nitrogen

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* During the irradiations, it is estimated that the temperature in the coal containers did not exceed 40°C.

which may be formed during the irradiation, were not analyzed for in the present work. Gas analyses have not been reported for the coals irradiated in an air atmosphere because the nitrogen formed following irradiation was a composite of that released from the coal and that added initially in the air. That is, it was not possible to put the results on a basis of gas released from the coal since there was some uncertainty as to the volume of the sample container upon sealing, and hence, uncertainty as to the amount of nitrogen added initially. On the other hand, on the basis of vacuum-irradiation results, no free oxygen was released from the coals. Hence, in the oxygen-irradiation runs (there was oxygen found in the gas following irradiation for three of the coals), the amount of gas released from the coal could be calculated by placing the analyses on an oxygen-free basis.

It is seen from Table III that the amount of gas released from the coals on irradiation at ambient temperatures was quite small in comparison to the total volatile matter content of the coals. More gas was released consistently from the coal upon oxygen irradiation than upon vacuum irradiation, with the ratio of the gas-release volumes ranging from 1.8 to 5.0.

The presence of an oxygen atmosphere during irradiation is seen to have a marked (but not consistent) effect on the analysis of the released gas. As expected, the amount of carbon dioxide and carbon monoxide produced was greatly increased upon oxygen irradiation. The following reactions can be responsible for the increase in the amount of these two gases:

$$O_2 \rightsquigarrow O + O$$

$$C_f + O \rightarrow C(O)$$

$$C(O) \rightarrow CO$$

$$CO + O + M \rightarrow CO_2 + M$$

$$O_2 + O + M \rightarrow O_3 + M$$

$$C_f + O_3 \rightarrow CO + O_2$$

It is noted that a significant amount of carbon dioxide was also released from the coal during vacuum irradiation. It is suggested that this carbon dioxide was a result of decarboxylation of peripheral carboxyl groups on the coal (2,3), release of occluded carbon dioxide from the fine pore system, and/or oxidation of methane (for oxygen irradiation). The second possibility will be considered in more detail shortly.

The effect of radiation and atmosphere on the release of hydrogen from the coals is complex. For coals 167 and 169, release of hydrogen upon vacuum irradiation was negligible. On the other hand, oxygen irradiation of these two coals resulted in a substantial release of hydrogen. For the remainder of the coals, except 166, there was still a somewhat greater amount of hydrogen released upon irradiation in oxygen than in vacuum. For the low volatile coal, 166, the amount of hydrogen released upon either irradiation in vacuum or oxygen was essentially identical.

The effect of radiation and atmosphere on the release of nitrogen from the coals is also complex. For coal 169, the amount of nitrogen released upon oxygen irradiation was appreciably less than that released upon vacuum irradiation. On the other hand, for the other seven coals, oxygen irradiation resulted in the release of considerably more nitrogen than did vacuum irradiation.

From Table III, it is seen that the quantities of methane and ethane produced upon irradiation are very small. Again the results are complex. For methane, oxygen irradiation resulted in increased yields for coals 167, 169, A, and B and decreased yields for the other four coals. For ethane, oxygen irradiation resulted in an increased yield for coal B and a decreased yield for coals 166, 168, 169, C, and D.

Only in the case of coals 166, 167, and 168 was there any residual oxygen present after oxygen irradiation. For these three coals, 37, 11, and 22%, respectively, of the oxygen initially present (approximately 1.2 cc./g. of coal at S.T.P.) was recovered as oxygen following irradiation. This suggests that these coals were especially resistant to oxygen attack (also suggested from plasticity data to be presented later). Considering the large decrease in oxygen pressure during irradiation, the oxygen appearing as carbon dioxide and carbon monoxide in the product gas was small.

At this stage, the effect of the combination of radiation and oxygen atmosphere on the amount of the different gases released from the various coals is not well understood. However, the nitrogen results perhaps permit some understanding. Essentially, the nitrogen could come from three sources - peripheral amino groups, cyclic structures, and occluded nitrogen (4). Radiation, perhaps, would detach peripheral amino groups from the coal structure (the abundance of these groups in coal is small), these groups then reacting with hydrogen atoms to produce ammonia (2). However, in other irradiation studies, as yet unpublished, the authors have found pure ammonia to be quite stable to the radiation used in this research. For example, for a dosage of 10^8 rads, only ca. 0.4 per cent of ammonia (at pressures between 0.1 and 1 atm.) decomposed to hydrogen and nitrogen. Numerous workers (5) have shown that nitrogen present in cyclic groups in coal is largely resistant to removal by oxidation. Therefore, it would appear that the large increase in nitrogen-release from seven of the coals upon oxygen irradiation, in comparison to vacuum irradiation, cannot be explained on the basis of nitrogen-release from cyclic structures.

It seems more reasonable to attribute the majority of the nitrogen coming from the coals to occluded nitrogen. That is, coal is known to be permeated with molecular sized pores (6) which can trap gases. Vacuum irradiation could result in the release of nitrogen from these pores by two mechanisms. First, radiation could produce a small steady-state concentration of nitrogen atoms, which because of their smaller size, could migrate through the molecular openings more rapidly. Second, radiation could increase the magnitude of oscillations of some of the atoms in the coal around the molecular openings, because of their collison with fast neutrons. This increase in magnitude of oscillation would permit a more rapid transport of gas through the molecular openings (7). Oxygen irradiation of coal could result in the release of more nitrogen than that released during vacuum irradiation, since slight oxidation of coal is known to significantly increase the size of the molecular openings (8).

It is of interest to report some results lending support to the suggestion that radiation did enhance the removal of occluded gas from the pores of the coal. Prior to the filling of the quartz containers with oxygen for irradiation studies, the free space of the containers (with coal present) was determined using helium at room temperature for seven of the coals. Following the determination of free space and before filling the containers with oxygen, the coals were outgassed at room temperature to a pressure of

less than 10μ Hg for 4 to 6 hours. Despite this outgassing, helium was found in the product gas following irradiation for three of the coals - the amount ranging from a trace for coal 168 to 0.05 cc./g. for coal B. In the case of coal B, the helium constituted ca. 16 per cent of the dry, product gas.

In the light of the conclusions for the source of most of the nitrogen, it is also probable that some of the carbon dioxide (in the vacuum irradiation) and hydrogen released from the coals was originally present as occluded gas.

Whether irradiation in oxygen, rather than in vacuum, is expected to decrease or increase the amount of methane and ethane released is difficult to predict. While enlargement of molecular sized openings during irradiation in oxygen could enhance the release of these hydrocarbons, their radiation-induced oxidation to carbon dioxide and water would decrease their concentration [illegible] the released gas. Both effects appear to be operative to varying [illegible] depending upon the coal, as judged from the data in Table III.

Plasticity of Heated Coals Following Irradiation - Gieseler plasticity data were determined on the unirradiated and irradiated coals. At least three plasticity runs were performed on each sample of coal, with the over-all precision being ca. ±15 per cent. The plasticity data are presented in Table IV and Figure 1. Where more than one result is presented for a coal, duplicate irradiations have been performed.

The results clearly show that irradiation in vacuum or in a substantial partial pressure of oxygen can have a marked effect on the subsequent maximum fluidity of heated bituminous coals. Irradiation in the presence of a substantial partial pressure of oxygen generally had more effect on plasticity than did irradiation in vacuum. For six of the coals, vacuum irradiation had a relatively small effect on fluidity. The exceptions were coals A and B, where irradiation reduced maximum fluidities by ca. 50 per cent.

For six of the coals, air irradiation resulted in a significant (and in some cases very large) increase in maximum fluidity. For two of the coals (a low volatile coal and one of the high volatile A coals which showed a significant decrease in fluidity after vacuum irradiation), air irradiation had a negligible effect on fluidity.

The effect of oxygen irradiation on the fluidity of the coals was more varied. For five of the six high volatile A coals, oxygen irradiation substantially lowered the fluidity below that of the corresponding unirradiated coals. For high volatile A coal 168 and the medium volatile coal, oxygen irradiation increased the maximum fluidity over that of the unirradiated coals. Oxygen irradiation had a negligible effect on the fluidity of the low volatile coal.

It is of interest that major changes in fluidity upon irradiation were not accompanied by large changes in the temperatures at which the maximum fluidity occurred. As a typical example, consider coal A. The unirradiated coal had a maximum fluidity of 397 d.d.p.m. at 422°C. The maximum fluidity of the sample irradiated in air was increased markedly to 3566 d.d.p.m., but the temperature of maximum fluidity remained at 422°C.

The effect of pre-oxidation of coal at elevated temperatures and in the absence of radiation on the subsequent coking qualities of coal has

been widely discussed. Many workers (9-14) report that the fluidity of coal, as measured by the Gieseler plastometer, decreases following pre-oxidation. To the authors' knowledge, no published results are available which report that pre-oxidation in the absence of radiation increases the fluidity of coal. However, on the basis of the present results, mild oxidation (that is, with a limited amount of oxygen available to react with coal) promoted by radiation can increase markedly the maximum fluidity of some coals. Whether the same effects can be achieved (and as precisely) by mild oxidation in the absence of radiation will be investigated on the same coals as used in this work.

Work is also being continued in this area directed toward studying the effect of prior irradiation of coal on the nature of the coke and by-products produced upon carbonization. In addition, it is desired to understand the relationships between the chemical and physical properties of coals and the effect of radiation and atmosphere on their subsequent carbonization behavior. As expected, it is not possible on the basis of simple proximate or ultimate analyses to predict these effects.

CONCLUSIONS

The effect of radiation on evolved gas composition and plastic properties of coal is found to vary with the coal being investigated and irradiation atmosphere. Lower rank coals appear to be more affected by the combination of radiation and oxygen atmosphere than do higher rank coals.

By proper selection of atmosphere, together with radiation, the fluidity of coals can be altered to marked extents.

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TABLE I

PROXIMATE ANALYSES (AIR-DRY BASIS) OF COALS USED

Coal	% Moisture	% V.M.	% C.	% Ash	A.S.T.M. Rank
166	0.9	16.2	73.6	9.3	Low Volatile
167	1.0	26.9	62.1	10.0	Medium Volatile
168	0.6	28.9	61.2	9.3	High Volatile A
169	1.9	38.4	51.9	7.8	High Volatile A
A	2.3	38.1	53.1	6.5	High Volatile A
B	1.8	36.7	55.6	5.9	High Volatile A
C	1.8	36.8	55.2	6.2	High Volatile A
D	1.3	38.2	53.4	5.7	High Volatile A

TABLE II

ULTIMATE ANALYSES OF COALS USED*

Coal	% N	% S	% H	% C	% O	% Ash
166	1.06	1.33	3.80	80.59	5.20	8.02
167	0.92	2.30	4.73	77.86	4.81	9.38
168	0.90	1.73	4.83	78.72	4.50	9.32
169	1.45	1.64	5.07	75.98	7.69	8.17

* Ultimate analyses of Coals A, B, C, and D are not available, as yet.

TABLE III

ANALYSES OF GAS EVOLVED FROM COAL (DRY BASIS) UPON IRRADIATION TO 3.8×10^8 RADS IN VACUUM AND OXYGEN

Coal	Volume of Gas Released cc./g. of coal, S.T.P.	Gas Composition - Per Cent					
		H_2	N_2	CO_2	CO	CH_4	C_2H_6
166-Vacuum	0.048	36.2	7.2	54.8	T	1.5	0.3
166-Oxygen	0.192	8.9	53.2	31.3	6.3	0.3	T
167-V	0.034	0.2	68.9	30.2	T	0.7	0.0
167-O	0.168	26.9	43.5	24.9	4.3	0.5	T
168-V	0.036	50.4	25.7	19.0	T	3.6	1.4
168-O	0.132	26.1	47.0	20.9	5.5	0.6	T
169-V	0.050	0.1	47.0	45.4	1.4	1.0	5.1
169-O	0.148	66.0	3.9	22.3	6.4	1.4	0.2
A-V	0.144	71.4	9.1	16.4	1.8	1.4	T
A-O	0.264	56.5	13.2	24.2	5.0	1.1	T
B-V	0.112	71.4	10.7	14.5	1.3	1.6	0.5
B-O	0.236	53.8	17.2	21.7	5.7	1.2	0.5
C-V	0.064	67.3	11.8	9.0	0.6	10.5	0.8
C-O	0.164	39.3	29.9	22.5	7.6	0.7	0.0
D-V	0.114	76.8	1.9	11.5	1.0	5.6	3.2
D-O	0.314	48.1	29.6	16.3	4.8	0.9	0.3

TABLE IV

EFFECT OF A RADIATION DOSAGE OF 3.8 x 10^8 RADS AND OXYGEN AT AMBIENT TEMPERATURES ON THE SUBSEQUENT MAXIMUM FLUIDITY OF BITUMINOUS COALS AS DETERMINED BY THE GIESELER APPARATUS

Coal	Initial Softening[1] Temp. °C.	Maximum Fluidity D.D.P.M.[2]	Maximum Fluidity °C.[3]	Solidification Temp.[4] °C.
166	433	1.4	472	494
166-Vacuum	423	1.2	454	488
166-Air	425	1.3	450	472
166-Oxygen	435	0.6	464	499
167	365	451	425	457
167-V	353	610	432	472
167-A	350	822	426	450
167-A	364	935	429	463
167-O	367	1117	440	490
168	347	2767	432	479
168-V	338	2530	427	452
168-V	354	1911	428	481
168-A	339	3936	428	458
168-A	345	3860	428	472
168-O	356	3651	439	489
169	342	1139	424	458
169-V	357	1016	431	468
169-V	337	900	426	460
169-A	337	3193	429	462
169-A	344	3029	427	465
169-O	370	222	436	467
A	348	397	422	457
A-V	347	177	424	458
A-V	350	190	428	458
A-A	344	3566	422	454
A-O	373	124	430	450
B	347	1583	430	462
B-V	351	853	429	461
B-A	349	1484	434	464
B-O	372	701	434	459
C	345	5098	434	470
C-V	347	5207	426	468
C-A	342	6878	423	465
C-O	356	2788	438	475

TABLE IV. (Contd)

Coal	Initial Softening[1] Temp. °C.	Maximum Fluidity D.D.P.M.[2]	Maximum Fluidity °C.[3]	Solidification Temp.[4] °C.
B	345	1778	421	460
D-V	340	1850	422	451
D-A	344	3461	423	456
D-O	356	1083	430	467

1 Temperature of first detectable continuous movement of pointer

2 Dial divisions per minute on the Gieseler scale

3 Temperature of maximum fluidity corresponding to maximum rate of pointer movement

4 Temperature at which pointer shows no further movement

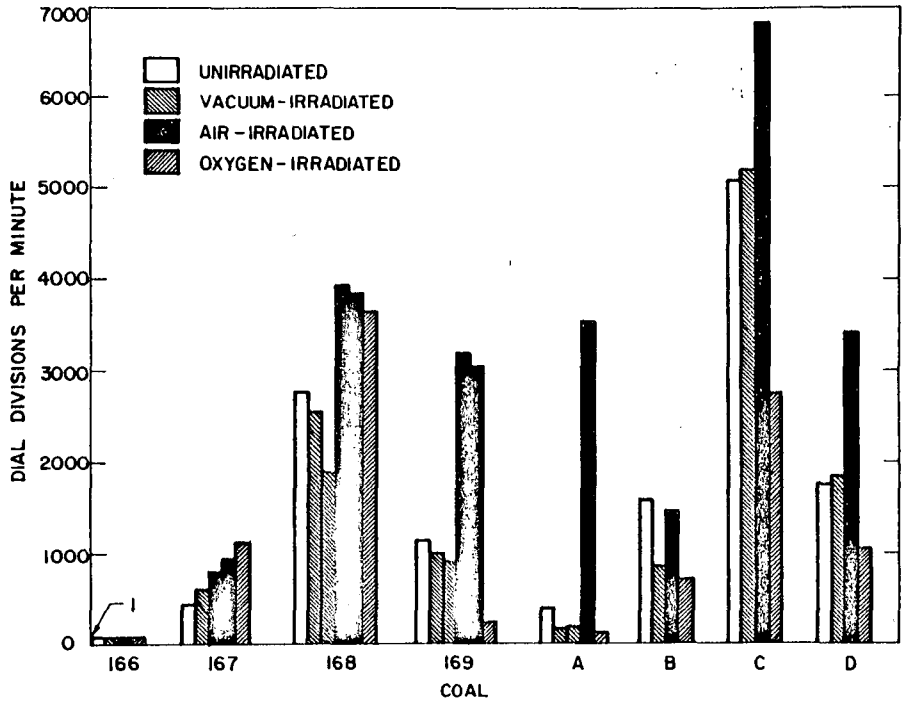

FIGURE 1 - EFFECT OF A RADIATION DOSAGE OF 3.8×10^8 RADS AND OXYGEN AT AMBIENT TEMPERATURES ON THE SUBSEQUENT MAXIMUM FLUIDITY OF BITUMINOUS COALS AS DETERMINED BY THE GIESELER APPARATUS.