

Ozonization of Chattanooga Uraniferous Black Shale

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CHATTANOOGA (Topblack) shale contains less than 0.01% of uranium, but the extensive lateral deposit constitutes a large uranium reserve. The shale contains about 60% silicate minerals (quartz, feldspar, muscovite, and clays), 20% organic matter, 15% pyrite, and 5% miscellaneous minerals (1). All of these components are finely divided, thoroughly intermingled, and cemented together by the organic matter, making mechanical separation extremely difficult. No crystalline uranium compounds were identified. From alpha tracks observed in film placed in contact with thin sections of the shale, the uranium seems to be randomly distributed throughout the matrix of the rock. This is believed to indicate that the uranium was precipitated from sea water under reducing conditions (1), and no doubt the organic matter of the shale was responsible for the reduction.

Efficient recovery of the uranium obviously must involve some kind of concentration, of which leaching seems to be the most promising. Since the shale is essentially a mudstone, in which the mineral particles are cemented together by the organic matter, any reaction which would remove the organic matter and cause the rock to revert to a mud would improve the contact between the extractant and the mineral particles. Moist ozone is such a reagent. Organic double bonds are oxidized to carboxylic and ketonic groups, depending on the degree of substitution, and yield water-soluble degradation products. Consequently when the ozonized shale is treated with water, it yields a pulp which is easily extracted by aqueous solutions.

The pyrite in the shale is also attacked by moist ozone, producing sulfuric acid and ferrous sulfate. Sulfuric acid leaching of the shale has recently been described (9), using acid prepared from the shale by pressure oxidation of the pyrite with molecular oxygen at elevated temperatures. Consequently only work on oxidation of pyrite and organic matter of the shale by moist ozone will be described. Information on the organic acids produced has been obtained for possible industrial application.

Ozone was produced by a laboratory-type, silent-discharge ozonizer used in previously work on coal (5). The concentration of ozone was 3.5% by volume at an oxygen flow rate of 9 liters per hour. The ozone stream was moistened before passing it over the samples by bubbling it through water.

OZONIZATION OF PYRITE

Pyrite was ozonized separately to establish its behavior uncomplicated by the presence of other constituents in the shale. A sample of pure crystalline pyrite ground to minus 140 mesh was treated to a stream of moist ozone in two stages of 43 and 48 hours. Following each exposure the sample was extracted first with water, then with ether, in a Soxhlet. Iron was extracted by the water as ferrous sulfate (Table I), but basic ferric sulfate slowly crystallized out in the boiling flask, because of oxidation by air. Extraction

with ether removed a small amount of elemental sulfur which crystallized in the monoclinic form on evaporating the ether. The production of elemental sulfur by the action of ozone is similar to the behavior of hydrogen peroxide on pyrite (8).

In addition to iron sulfate salts and elemental sulfur, a part of the sulfur of the pyrite was oxidized to sulfur trioxide and was carried out by the oxygen stream. The amount was determined by precipitating it as barium sulfate and weighing. The shale contained pyrite particles from 100 microns down to submicroscopic size, and consequently it reacted more rapidly than the minus 140-mesh pyrite.

OZONIZATION OF THE SHALE

When moist ozone was passed over the shale, both ozone and moisture were absorbed. Carbon dioxide was evolved, but no sulfur trioxide. Possibly sulfur trioxide was not evolved in the presence of the shale because it reacted with the organic matter. On extracting the treated shale with water, most of the iron was removed as ferrous sulfate; the sulfuric acid produced extracted calcium, magnesium, and other cations including uranium. Extraction of the shale residue with ether removed a small amount of elemental sulfur and dark-colored organic acids not soluble in water. Distillation of the water extract gave a small quantity of volatile acids, mainly acetic acid. After the water extract had been dried, ether extracted about half of the organic material in the form of carboxylic acids. A part of the remainder could be extracted by methanol and other polar solvents, but large amounts of inorganic salts were also extracted, making further separation difficult. To avoid this complication, samples of the mineral-free organic matter or kerogen were prepared and ozonized.

PREPARATION AND PROPERTIES OF THE ORGANIC MATTER

Separation and purification of the organic matter were difficult. No solvent, either high or low boiling, was found that would completely dissolve the kerogen (11). Neither

Table I. Percentage Distribution of Iron and Sulfur in Ozonization Products of Pyrite

Products	Time of Ozonization, Hours					
	43		48		Total (91)	
	Fe	S	Fe	S	Fe	S
Fe SO ₄ ·4 H ₂ O	14.4	8.2	7.4	4.3	21.8	12.5
Fe ₃ (SO ₄) ₂ (OH) ₅ ·2H ₂ O	0.6	0.2	1.4	0.5	2.0	0.7
Elemental	...	0.4	...	0.2	...	0.6
SO ₃	10.0
Total	15.0		8.8		23.8	23.8
Pyrite reacted (100%- residue)	30.5		15.7		46.2	

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have physical methods based on differences in density (7) been successful. The best method was to remove the inorganic constituents by means of acids, hot hydrochloric and hydrofluoric, to remove silicate minerals and cold 1 to 4 nitric acid to remove pyrite (10). After these treatments the ash content was reduced to 1.0%, but the nitrogen content was increased from 1.8% to 4.0% on an ash-free basis (Table II). The introduction of nitrogen into the structure was unfortunate, but a better method of removing pyrite could not be found. Zinc and hydrochloric acid have been suggested (4) but were ineffective for this shale.

The composition of the purified kerogen (Table II), indicates an empirical formula of approximately $C_{11}H_{11}O_3$, if nitrogen and sulfur are neglected. Thus the kerogen has an oxygenated structure which contains some type of unsaturation based on its H to C ratio of one. The kerogen after hydrofluoric acid treatment but before nitric acid treatment gives the infrared spectrum shown at the top of Figure 1. Strong bands at 3.44, 3.54, and 6.90 microns suggest considerable aliphatic character, and the strong band at 6.22 microns is believed to be due to conjugated olefinic and/or aromatic structures which react with ozone.

On treatment of the kerogen with cold dilute nitric acid the second spectrum in Figure 1 was obtained. All spectra shown in Figure 1 were made at 0.4% concentration in potassium bromide pellets, and may be compared on that basis. The generally increased intensity of the bands following nitric acid treatment is due to the removal of pyrite. Oxidation of the carbon structure is indicated by the absorption at 5.85 microns, which is probably due to carbonyl groups. Of particular importance, however, is the introduction of pairs of bands at 6.45 and 6.55, and at 7.50 and 7.62 microns. Known nitro compounds absorb characteristically at these wave lengths and it seems very probable that nitro groups are introduced into the kerogen by the cold dilute nitric acid. Increased absorption is also observed at 9.5 to 10 microns and this may be due to the introduction of nitroso groups.

OZONIZATION OF THE PURIFIED KEROGEN

The purified kerogen reacted readily with moist ozone with the evolution of carbon dioxide. After 48 hours of treatment, the sample was extracted successively with ether, water, and sodium hydroxide. The amount of oxalic acid in the ether extract was determined by precipitating its calcium salt from an aqueous solution and titrating the

oxalate ion with standard permanganate (5). From these results a yield of 9.2% of oxalic acid was calculated, 34.0% of other ether-extracted acids, and 37.5% of water-extracted acids (Table III). The sodium hydroxide extract was strongly acidified with hydrochloric acid, and the precipitated humic acid-like product filtered out, giving a 10.5% yield of these acids. The acid filtrate was evaporated to dryness and extracted with acetone. The yield of these water-soluble acids, 14.5%, is taken as the difference in weight between the total material extracted by sodium hydroxide and the humic acids precipitated. The residue insoluble in sodium hydroxide amounted to only 3.0%. It is of interest to compare these results with those obtained by air oxidation at 200° C. (6).

Analyses of the products isolated, and the distribution of the carbon of the kerogen in products are also given in Table III. The per cent of carbon oxidized to carbon dioxide was determined separately on a small analytical sample. Carbon dioxide is not considered to be a primary product of ozonization, but to result from secondary reactions, particularly oxidations caused by the production of hydrogen peroxide which results from the reaction of ozonides with water, and which is known to oxidize carbonaceous matter to carbon dioxide. The main products then are ether-soluble acids and water-soluble acids. It is believed that further ozonization of the humic acids and the residue, accounting for 12.5% of the carbon, would result in soluble acids also.

The composition of the ether- and water-extracted acids shows that they are highly oxygenated. This together with their relatively small equivalent and molecular weights (Table IV), shows that the macromolecular kerogen has been extensively cleaved. The distribution of the oxygen in these acids is similar. About 50% is in carboxyl groups, 10 to 15% in carbonyl (12) and hydroxyl groups (2), and the remainder in unreactive groups, possible such as cyclic ethers and nitro and nitroso groups. Both types of acids give ammonia when warmed with sodium hydroxide. In the case of the ether-soluble acids, 19.6% of the 2.4% of nitrogen they contained is evolved as ammonia, while 42.9% of the 3.4% in the water-extracted acids is so evolved. This behavior is similar to that observed when nitric acid-oxidized coal humic acids or certain pure compounds are refluxed with alkali (3), and suggests that the source of the nitrogen is the nitric acid used to remove pyrite from the kerogen rather than the original nitrogen.

INFRARED SPECTRA

The infrared spectrum of the ether-soluble acids shows all of the absorptions of carboxylic acids, including bands at about 3.2, 5.79, 7.1, 8, and 11 microns (Figure 1). Absorptions of ketonic carbonyl and hydroxyl groups identified chemically can likewise be observed. Aliphatic carbon-hydrogen absorption at 3.4 and 3.5, and at 6.9 microns are visible, but the nitro bands are very much reduced. Ammonium ion bands at 3.25 and 7.1 microns fit into the spectrum very well, which could account for the

Table II. Analysis of Kerogen

Element	Shale Treated with HCl, HF		Residue Treated with Cold 1:4 HNO ₃	
	As recd.	Ash-free	As recd.	Ash-free
Carbon	52.6	65.9	65.7	66.3
Hydrogen	4.3	5.4	5.3	5.3
Nitrogen	1.4	1.8	4.0	4.0
O + S (by diff.)	21.5	26.9	24.0	24.4
Ash	20.2	...	1.0	...

Table III. Yields and Analyses of Products Obtained by Ozonizing Kerogen for 48 Hours

	% Yield	% C	% H	% N	% S	% O ^a	% Ash	% of C of Kerogen
Oxalic acid	9.2	26.6	2.2	71.6	...	3.7
Other ether-sol. acids	34.0	44.3	4.7	2.4	0.7	46.1	1.8	22.9
Water-extracted acids	37.5	38.2	4.5	3.4	1.7	50.4	1.8	21.8
NaOH-sol. humic acids	10.5	60.7	4.8	2.6	1.8	29.1	1.0	9.8
Water-sol. acids ^b	14.9 ^c	12.7 ^c
NaOH-insol. residue	3.0	58.9	5.4	2.8	2.0	15.0	15.9	2.7
Carbon dioxide	26.4 ^c

^a By difference. ^b These acids remained in solution when sodium hydroxide extract was acidified. ^c Includes acetic acid and losses.

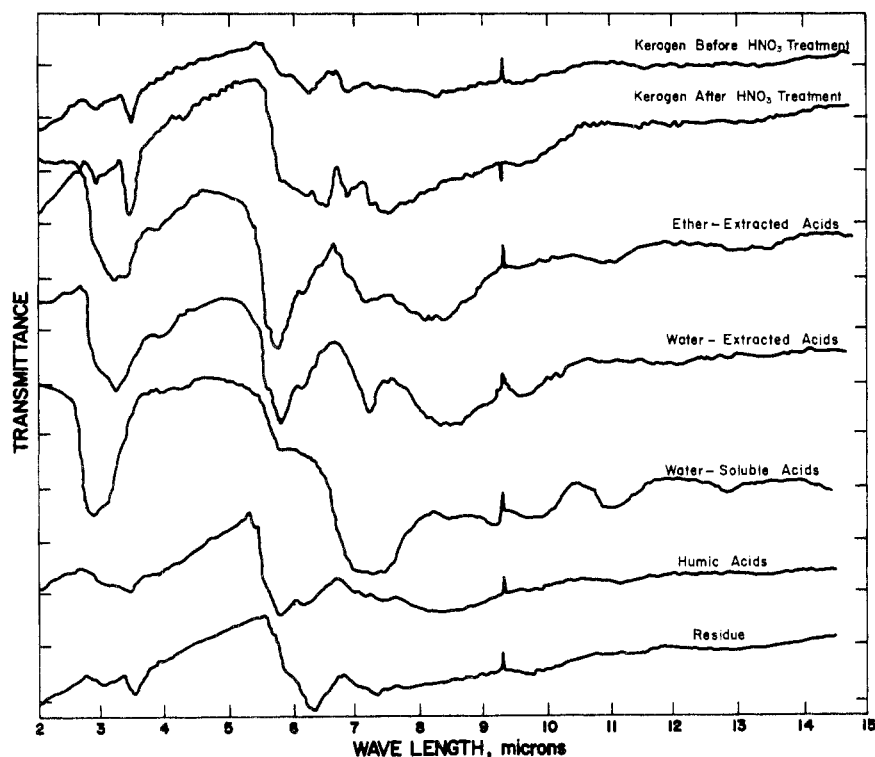


Figure 1. Infrared spectra

Table IV. Equivalent and Molecular Weights and Oxygen Distribution of Ether- and Water-Extracted Acids

	Acids	
	Ether-extd.	Water-extd.
Equiv. Wt.	117	126
Mol. Wt.	200	390
Total Oxygen, %		
Carboxyl	59.2	50.5
Carbonyl	6.0	5.6
Hydroxyl	4.5	8.4
Unidentified	30.3	35.5

liberation of ammonia when the extract is treated with sodium hydroxide. The 6.24-micron band is still present, which suggests that this band is caused by aromatic structures resistant to ozone. Shoulder bands at 5.4 and 5.6 microns suggest a tendency for acid anhydride or lactone formation under conditions of preparing the potassium bromide windows.

The spectrum of the water-extracted acids (Figure 1), is very similar to that of the ether-extracted acids. Carboxylic, ketonic, and hydroxylic absorption bands can all be observed. The aliphatic carbon-hydrogen bands seem to be weaker, as well as the nitro absorptions. On the other hand, the band at 7.14 microns is more intense than the same band in the ether-soluble acids, consequently it seems that this fraction contains more ammonium salts than the ether-extracted fraction.

Another feature of the spectrum of the water-extracted acids is a band at 9.54 to 9.64 microns. Since nitroso groups absorb in this region, it seems probable that this band is due to this group, introduced into the kerogen directly, or indirectly by the reduction of the nitro groups introduced originally.

Spectra were also made of the humic acids, the accompanying water-soluble acids which were not precipitated with the humic acids, and the alkali-insoluble residue (Figure 1). The spectrum of the water-soluble acids is different from that of the water-extracted acids shown above it. The carbonyl band at about 5.8 microns is very small for a carboxylic acid, as is the hydroxyl absorption above 3 microns. On the other hand, there are strong absorptions at about 7 and 11 microns, which suggest the presence of carboxylate salts. To account for the isolation of sodium salts, as well as free acids, it is believed that, when the acidified filtrate was evaporated to dryness, nonvolatile organic acids displaced a part of the volatile hydrochloric acid, forming sodium salts which were extracted by acetone during extraction in a Soxhlet. No further study of this fraction was made because of the relatively small quantity.

The spectrum of the humic acids in Figure 1 is generally similar to those of the ether- and water-extracted acids. The carboxylic acid absorptions are less intense, but this is probably due to fewer carboxyl groups and a larger molecu-

lar weight. The residue insoluble in sodium hydroxide gave the last spectrum in Figure 1. It is similar to that of the original kerogen before treatment with dilute acid, except that the 6.2-micron band is more intense. Possibly this can be accounted for by the presence of a larger proportion of aromatic structures, which are less reactive to ozone, than in the original kerogen.

These results show that ozonolysis of the kerogen of the Chattanooga shale converts over 60% of its carbon to water-soluble acids. These have molecular weights in the range of 200 to 400 and equivalent weights of about 120. The polyfunctional nature of these acids suggests the possibility of their use in industrial applications.

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