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Chemistry Division

Organic Geochemistry: Effects of Organic Components of Shales on Adsorption

Progress Report

Patience C. Ho

Nuclear and Chemical Waste Programs
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ABSTRACT

The Sedimentary Rock Program at the Oak Ridge National Laboratory is investigating shale to determine its potential suitability as a host rock for the disposal of high-level radioactive wastes (HLW). The selected shales are Upper Dowelltown, Pierre, Green River Formation, and two Conasauga (Nolichucky and Pumpkin Valley) Shales, which represent mineralogical and compositional extremes of shales in the United States. According to mineralogical studies, the first three shales contain 5 to 13 wt% of organic matter, and the two Conasauga Shales only contain trace amounts (2 wt%) of organic matter. Soxhlet extraction with chloroform and a mixture of chloroform and methanol can remove 0.07 to 5.9 wt% of the total organic matter from these shales. Preliminary analysis of these organic extracts reveals the existence of organic carboxylic acids and hydrocarbons in these samples. Adsorption of elements such as Cs(I), Sr(II) and Tc(VII) on the organic-extracted Upper Dowelltown, Pierre, Green River Formation and Pumpkin Valley Shales in synthetic groundwaters (simulating groundwaters in the Conasauga Shales) and in 0.03-M $NaHCO_3$ solution indicates interaction between each of the three elements and the organic-extractable bitumen.

EXECUTIVE SUMMARY

The Sedimentary Rock Program (SERP) at the Oak Ridge National Laboratory (ORNL) is investigating shales in the United States for their potential suitability as host rocks for the disposal of high-level radioactive wastes (HLW). Geochemical conditions (e.g., temperature, pressure, pH, redox conditions, rock composition, complexing agents and microflora) and the interaction of radionuclides, groundwaters and host rocks provide the dominant controls for limiting the mobility and transport of radionuclides which may be released when the waste packages ultimately fail. The geochemical conditions associated with the various shales being evaluated are quite different; the shales may have varying capabilities for the retention of radionuclides. One of the important factors that has not received much attention is the interaction of the nuclides with the organic content of the shales.

Shales of all geological ages contain at least some organic matter. The organic matter that was deposited and preserved in shales was synthesized by living organisms. The most important contributors of organic matter in sediments are phytoplankton, zooplankton, higher plants and bacteria. The organic material that is found in shale has been subjected to extensive physical, biological and chemical alteration. As a result of this process, much of the material became insoluble in common organic solvents or aqueous alkaline solvents; this insoluble portion of the organic material is referred to as kerogen. The relatively small fraction of the organic material which is mostly soluble in organic solvents is known as bitumen. According to the mineralogical study of the five chosen shales (Upper Dowelltown, Pierre, Green River Formation and two Conasauga Shales (Nolichucky and Pumpkin Valley Shales)) used in the SERP program done by Lee et al., the five shales contain organic matter ranging from less than 2 wt% (the two Conasauga Shales) to 13

wt% (the Green River Formation Shale). The Upper Dowelltown and Pierre Shale contain 11 and 5 wt%, respectively.

Because of the relatively high percentage of organic matter in shale, if shale formations are to be used as hosts for a HLW repository, the relationships between radionuclides and the organic matter should be studied. The objective of this study is to investigate and characterize the properties of organic matter in the five chosen shales and the possibility of interaction between the organic matter and nuclides.

Since shales contain mostly inorganic matter which hinders the analysis of organic matter, the organic and inorganic matter must first be separated. The first step of the approach was to isolate organic-soluble bitumen by organic extraction. After Soxhlet extraction with chloroform and a mixture of chloroform/methanol, 0.07 to 5.9 wt% of the total organic content was removed from these five shales. Elemental analyses of these organic extracts show that the H/C atomic ratio ranges from 1.48 (Upper Dowelltown Shale) to 2.49 (Pumpkin Valley Shale, one of the Conasauga Shales), which implies that the organic extracts from the Upper Dowelltown (1.48), Pierre (1.64) and Green River Formation (1.69) Shales contain more unsaturated compounds than the extracts from the two Conasauga Shales (Nolichucky and Pumpkin Valles Shales; 1.92 and 2.49 respectively). UV-VIS scans of these extracts in cyclohexane show that absorption mostly appears below 400 nm. Significant absorption occurs below 360 nm and increases rapidly as the wavelength decreases. This suggests that in these extracts the existence of large molecular-weight compounds such as poly-condensed aromatics is minimal. Infrared spectroscopy of the five extracts in carbon tetrachloride reveal the presence of carbonyl groups besides methyl and methylene groups (aliphatic, cyclic and aromatic), amides and hydroxide groups. Compounds containing carbonyl groups (other than from carboxylic acids), when oxidized, tend to form organic acids. Evidence from the

literature indicates that organic acids form complexes with nuclides, which may be important for radionuclide transport. In order to identify the carboxylic acid content in the organic-extractable bitumens, the extracts from Upper Dowelltown, Pierre and Green River Formation Shales were separated into acid and non-acid fractions. Preliminary characterization of the three acid fractions by gas chromatography/mass spectrometry (GC/MS) shows that carboxylic acids (saturated and unsaturated aliphatic, cyclic and aromatic) of C_8 to C_{20} exist in the Upper Dowelltown Shale, C_{15} to C_{19} exist in the Pierre Shale, and C_{17} to C_{23} exist in the Green River Formation Shale.

Although interactions between the identified organic compounds and nuclides have not been studied, preliminary results of adsorption of Cs(I), Sr(II) & Tc(VII) on the organic-extracted Upper Dowelltown, Pierre, Green River Formation and Pumpkin Valley Shales in synthetic groundwaters and in 0.03-M $NaHCO_3$ solution indicate interactions between each of these three elements and the organic-extractable bitumen.

1. Introduction

The Sedimentary Rock Program (SERP) at the Oak Ridge National Laboratory has been investigating shales in the United States for their potential suitability as host rocks for the disposal of high-level radioactive wastes (HLW). Shales are one of the most common and widespread rock types in the United States (1). Thick deposits of shale can be found in almost every state of the United States, and these deposits cover a wide variety of geological times from the Precambrian (0.6 - 3.0 x 10^9 years) through the Tertiary (1.3 - 2.5 x 10^7 years) period. It is well known that shales and other sediments of all ages contain at least some organic matter. The organic matter that was deposited and preserved in sediments was synthesized by living organisms. The most important contributors of organic matter in sediments are phytoplankton, zooplankton, higher plants and bacteria. The organic material that entered a sediment was subjected to extensive physical, biological and chemical alteration. As a result of this process, much of the material became insoluble in common organic solvents or aqueous alkaline solvents; this insoluble portion of the organic material is referred to as kerogen. The relatively small fraction of the organic material which is mostly soluble in organic solvents is known as bitumen. In ancient sedimentary rocks (such as shale) kerogen represents more than 80% of the organic matter (2,3). As reported in a previous review (4), some of the low molecular-weight compounds present in bitumen, particulary those in Green River Formation Shale and Chattanooga Shale, have been identified in recent years by the petroleum industry simply because organic matter in shales is considered as one of the principal sources of petroleum. Only general structural information is known about the insoluble kerogen, even though kerogen is the most abundant form of organic carbon on earth (2). The identified organic matter in shales covers many classes of organic compounds, which include hydrocarbons (aliphatic, cyclic and aromatic), acids, alcohols, steroids, terpenoids, carbohydrates and porphyrins (4).

In recent years, some studies have shown that organic materials such as acids form complex species with radionuclides (5-9) around radioactive waste disposal sites. In some cases, the organic matter did not come from the geological formations, but rather was produced by microbial activity in the pits and decay of organic material at the sites under such physical conditions as temperature, pressure, and radiation after radionuclide burial. However, the organic matter involved in most of the studies was either humic/fulvic acids or other humic material, and very few of them showed the possibility of interaction between radionuclides and lower-molecular-weight organic compounds.

If shale formations are to be used as hosts for high level radioactive waste repositories, the possibility of interaction between nuclides and the organic matter, especially those lower-molecular-weight organic compounds in shales that can be isolated from the shales by organic extraction and have proved to be slightly soluble in groundwater, must be considered. This would be especially important if the shales contained a high percentage of organic matter. It is the interactions between radionuclides, groundwaters and rocks that provide the dominant controls for limiting the mobility of radionuclides which are released from the waste packages of a HLW repository. The extent of the interactions are determined by the geochemical conditions of the repository environment which include chemical, physico-chemical and biological factors (e.g., temperature, pressure, pH, redox conditions, sedimentary rock composition, complexing agents and microflora).

The objective of this research is to identify and characterize organic matter in selected shales and at the same time to study the possibility of interaction between radionuclides and the organic matter. The selection of shales used in this study represented the end-members of shales (based on their composition for comprehensive mineralogical characterization) in the United States. They are the Chattanooga Shale (Upper Dowelltown Member; representing a carbonaceous shale), the Pierre Shale (a smectitic shale), the Green River Formation Shale (a carbonate-rich shale) and the Nolichucky and Pumpkin Valley Shales (illitic shales) (10). This report presents the isolation and identification of some members of the organic-solvent-soluble organic matter (organic-extractable bitumen) from these shales and evidences of interaction between these extractable organic matter and elements, such as Cs, Sr and Tc.

2. Experimental Section

2.1 Materials and Sample Preparations:

Five core samples of the shales (Upper Dowelltown, Pierre, Green River Formation, Nolichucky and Pumpkin Valley Shales) were characterzed by Lee et al. (10); they are described below.

The Upper Dowelltown Shale samples were from the Upper Dowelltown Member of Chattanooga Shale in Fentress County, Tennessee, at a depth of 141-142 m. This unit may be described as interbedded medium light gray claystone and dark gray shale beds, varying in thickness, but only 3-12 cm thick.

The Pierre Shale samples were representative of the Mobridge Member of Pierre Shale in Gregory County, South Dakota and were retrieved from a drill hole at a depth of 88.2 to 88.9 m. The core was described to be claystone that was thickly bedded, massive, nonfissle, slightly to moderately calcareous, soft, moist, medium gray with slight olive tinge, dense, solid, bedded at a low angle, and nonweathered.

The samples from the Green River Formation Shale originated in Garfield County, Colorado, and were drilled from the roof of the Colony mine. The samples were described as thinly bedded calcarious marl, very hard and compact.

Samples of Nolichucky and Pumpkin Valley Shales were from the Joy 2 well in Oak Ridge, Tennessee, at depths of 181 to 182 and 604 to 605 m, respectively. Both shales are part of the Conasauga Group, a complex sequence of Middle to Upper Cambrian clastic and carbonate strata. The Nolichucky section is described as a gray to brown shale-like limestone with discontinuous parallel bedding. The Pumpkin Valley section is maroon to gray, glauconitic, laminated silty mudstone.

The approximate mineralogical composition of the five whole-rock samples is reproduced from Ref. 10 and is given in Table 2.1. All of the shales contain organic matter; the Green River Formation Shale appears to have the most, while the representatives of the Conasauga Group, Nolichucky and Pumpkin Valley Shales, appear to have the least. The samples were pulverized in a mechanical "shatterbox" and sieved through 0.18 mm mesh for analysis and adsorption experiments.

Organic solvents such as chloroform, benzene, toluene, cyclohexane and acetic acid (to ACS specifications, EM Science Co.) and methanol (HPLC grade, Fisher), were used as received without further purification. Anion-exchange resins Dowex 1-4x (50 - 100 mesh, chloride form; Bio-Rad) and AG 1 - x2 (100-200 mesh, formate form; Bio-Rad) were washed four times with 10% HCl in methanol (by volume) and then were rinsed with distilled water until the washings were neutral to pH paper. The resins were activated with 10% potassium hydroxide in methanol (by weight), followed by rinsing with distilled water until the solution showed neutral to pH paper (11). After the removal of most of the aqueous solution by decantation, the resins were repeatedly washed with methanol first and then with cyclohexane, until the washing solution appeared as one phase. The resins then were extracted via Soxhlet extraction using cyclohexane over an overnight period and then stored in cyclohexane for later use.

Table 2.1. Mineralogical Composition of End-Member Shales[a]

Component	Upper Dowelltown Shale	Pierre Shale	Green River Formation Shale	Nolichucky Shale	Pumpkin Valley Shale
	Percent by Weight[b]				
Organic Matter	11	5	13	t	t
Chlorite/Kaolinite	4	t	t	14	15
Illite	49	t	10	43	57
Micas	t	4	t	t	t
Smectite	nd	59	nd	nd	nd
Carbonates	t	15	42	11	t
Quartz/Feldspars	25	11	28	29	22
Pyrite	6	2	t	t	t
Weight Loss (105°C)	1	4	2	2	2

[a] Lee et al. (1987) (Ref. 10).

b = observed from thin section and electron micrographs;

nd = not detectable.

t = trace (≤ 2%)

Adsorption experiments in this study were carried out in simulated saline groundwater (and its 100-fold dilution) with a composition similar to that in Ref. 12 and in a 0.03-M $NaHCO_3$ solution. The composition of the synthetic groundwater was reproduced from Ref. 12 and is given in Table 2.2. The groundwater has a density of ca 1.13 g/mL and can be characterized as acidic, highly saline and containing considerable quantities of alkaline earth ions. The ionic strength of this synthetic groundwater is 3.30 mol/L or about 3.42 mol/kg H_2O. The pH of the groundwater and its dilution were adjusted initially to pH 5. The aqueous solutions were prepared with doubly-distilled, deionized water. The tracers ^{137}Cs, ^{90}Sr and ^{95m}Tc used to determine the distribution of the nuclides in this study are the same as in Ref. 12 and are listed in Table 2.3.

2.2 Isolation of Organic Matter from Shale Samples

In this report, only the organic-solvent-extractable fractions of the organic matter in shales were isolated. The separation scheme is shown in Fig. 1. The isolation was done by Soxhlet extraction with chloroform and a mixture of chloroform and methanol (volume ratio 5 to 1). Each sample was extracted three times with each solvent, and each extraction lasted about seven days. The ratio of solids to solvent was 1 to 4 by weight. After extraction the chloroform and chloroform/methanol solutions were combined and solvents were removed under vacuum at ca 40°C. The dark brown, sticky residues from Upper Dowelltown, Pierre and Green River Formation Shales then were subjected to anion exchange resins for further separation into acid and non-acid fractions. The procedures for the ion-exchange chromatography were carried out as follows: the treated resins were packed into a glass column (0.8- x 22-cm), and the organic residues in cyclohexane were loaded onto the column and eluted with cyclohexane. Organic solutions which came out of the columns were labeled the non-acid fractions. The acid fractions which bonded with the resins were recovered by Soxhlet extraction with a solvent mixture of 5% acetic acid in benzene or

Table 2.2. Composition of Synthetic Brine Groundwater[a]

Component	Concentration (eq/L)	Concentration (g/L)
Na	2.00	46.00
K	0.0089	0.348
Mg	0.230	2.79
Ca	0.599	12.0
Sr[b]	0.027	1.20
Cl	2.86	101.29
Br	0.009	0.71

pH adjusted to 5 with HCl

[a] From Ref. 12.

[b] In some of the experiments to measure strontium sorption, the strontium was eliminated from the synthetic groundwater so that trace levels of strontium could be studied.

Table 2.3. Half-Lives, Decay Modes, and Radiations Emitted by Tracers used in this Study[a]

Nuclide	Half-Life	Principal Decay Mode	Radiations Detected
^{85}Sr	64.84 d	Electron Capture	514.0-keV gamma ray
^{137}Cs	30.17 y	Beta Decay	661.6-keV gamma ray (in decay of ^{137m}Ba)
^{95m}Tc	61 d	Electron Capture	204.1-keV gamma ray

[a] Data from Ref. 12.

toluene (11). After the removal of solvents, the acid and non-acid fractions were dried at ca 40°C under nitrogen before any further analysis. Due to the very small amounts of extractable organic matter (extracts) from the Nolichucky and Pumpkin Valley Shales, the extracts were not separated into acid and non-acid fractions. Further separations of the non-acid fractions of the three shale samples with higher organic content were not performed in this study due to time limitations.

The shale samples after extraction by organic solvents were labeled the organic-extracted shale samples. A small portion of the organic-extracted shales were also heated at 250°C for seventeen days in air and then extracted again with a mixture of chloroform and methanol. These twice organic-extracted and heated shale samples were labeled the organic-heated shale samples.

2.3 Analytical Methods

The organic-soluble residues from the shales were subjected to IR (infrared) and UV-VIS scans prior to fractionation into acid and non-acid fractions. IR scans were also performed on the solid shale samples. The solid shale samples were incorporated into KBr (infrared quality; Harshaw) pellets with a Wilks Model 36 Die (Foxboro). The organic residues were dissolved in either carbon tetrachloride (infrared quality; Fluka) or chloroform (infrared quality; Fluka). The IR spectra were obtained from a Bio-Rad FT-Infrared Spectrometer, Model FTS-60. UV-VIS scans of the residues were performed with a Perkin Elmer 559 UV-VIS spectrophotometer with cyclohexane (uv-cutoff at 198 nm; Burdick & Jackson) as solvent.

The acid fractions of the extracts from Upper Dowelltown, Pierre, and Green River Formation Shales and the non-fractionated organic extracts from Nolichucky and Pumpkin Valley Shales were alkylated with Methyl-8 reagent (Pierce) in order to convert the acids in these samples into methyl esters for GC/MS characterization. The GC/MS measurements were obtained by using Hewlett-Packard HP 5995A gas chromatograph/mass spectrometer system, fitted with a 30-m Durabond I narrow-bond, fused silica column (J. W. Scientific). The column temperature was programmed from 60°C (3-min hold) to 275°C with an increase of 10°C/min.

2.4 Adsorption Experiments

Adsorption of elements such as cesium, strontium and technetium on the organic-extracted and organic-heated shale samples was determined by a batch method similar to that used in Ref. 12 and the procedures are summarized as follows.

Adsorption of the elements was measured by determining the adsorption ratio (similar to a distribution coefficient) after exposure of the adsorbent (shale sample) to traced groundwaters. The adsorption ratio, which is here designated as R_s, is defined as the concentration of the nuclide in the adsorbent divided by the concentration of the nuclide in the groundwater, each being determined after the test. In this study as well as in the previous report (12), the unit for concentration in the adsorbent is moles/kg, and the unit in the solution is moles/L. Thus, the unit of R_s is L/kg. The amount adsorbed is determined by comparison of the concentrations of the adsorbate (adsorbing nuclide) in the solution before and after the test. It is then assumed that any reduction in concentration in the solution is a result of adsorption onto the adsorbent. Control experiments are carried out simultaneously with solutions that do not contain the solid phase to see whether there are other processes such as adsorption on the container or precipitation that could remove the adsorbate (nuclide) from the solution. The adsorption ratios (distribution coefficients) are calculated from the equation

$$R = \frac{(C_i - C_f) \times V}{C_f \times W} \quad (1)$$

where C_i is the initial concentration of the adsorbate (nuclide) in the solution, C_f is the final concentration in the solution, V is the initial volume of groundwater, and W is the weight of the adsorbent (shale).

In the experiments, ca 4 mL of groundwater was used. The ratio of solids to groundwater was 1 to 20. The shale samples were added to tared tubes and the tubes were reweighed to determine the shale weight. The groundwater is then added and the tubes were again reweighed. The ground- water volume was calculated from the weight and density. All determinations of groundwater volume are based on weight. The tubes were weighed at the beginning and end of every equilibration to determine any solution loss.

The tubes containing the shale and groundwater were then gently shaken for a three-day pre-equilibration period. After the pre-equilibration, the solutions were centrifuged and the supernatant was decanted to avoid loss of adsorbent. The shales, which at this time are packed at the bottom of the tube, were resuspended in fresh groundwater and the pre-equilibration procedure was repeated twice. The pH of the supernatant was measured after decanting and the principal cations in the groundwaters were also analyzed in order to determine whether the pre-equilibration periods were sufficient to reach groundwater compositions within 5% of the initial composition. After the pre-equilibration periods, traced groundwater was added along with enough untraced groundwater to bring the volume to the desired level. The pre- equilibrated shale and the traced groundwater were then gently shaken for fifteen days. Test samples and controls (tubes containing traced groundwater but no adsorbent) were done in triplicate. After fifteen days of equilibration the samples were centrifuged and the tracer content of the final solutions was assayed. Values of R_s were calculated by using Eq. 1. All equilibrations were carried out at room temperature in the presence of air. No attempt was made to keep the pH of the solutions constant during the experiment, but the pH was allowed to shift to a value determined by the interactions between the shale and the groundwater.

SEPARATION SCHEME

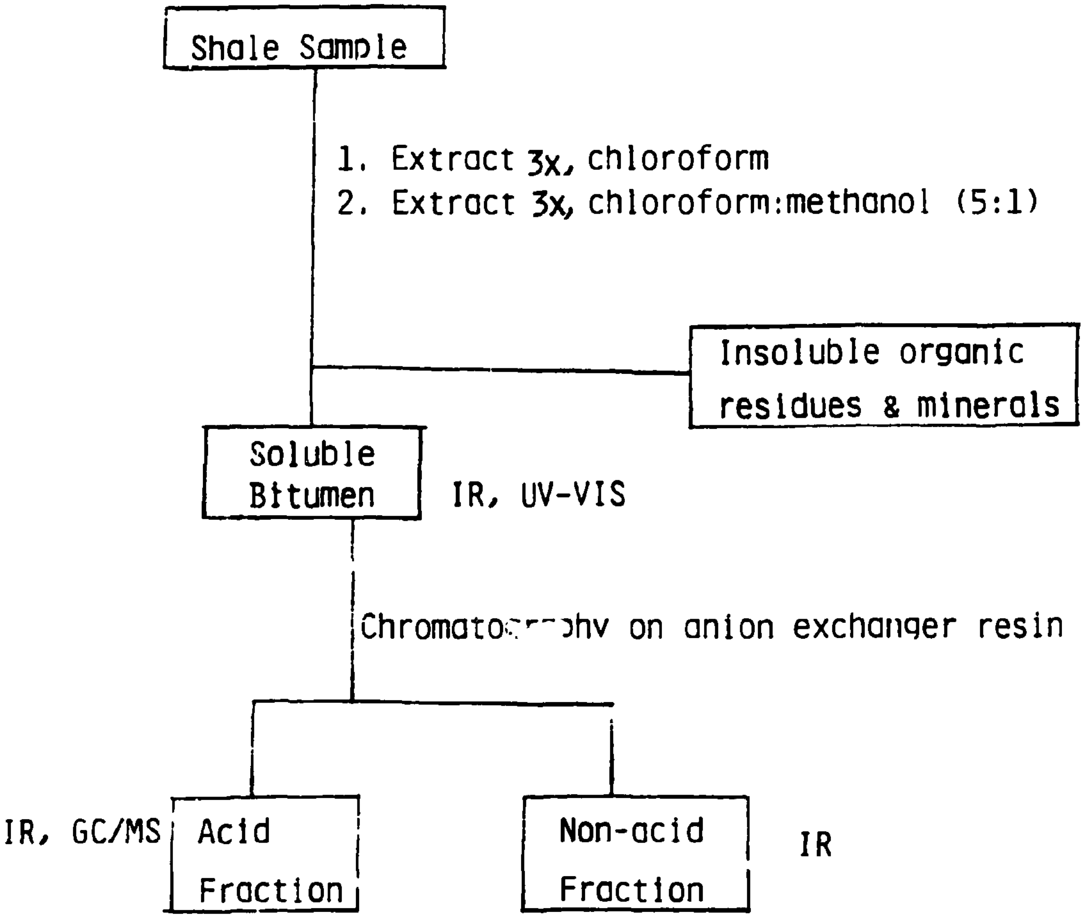


Figure 1

3. Results and Discussion

3.1 Isolation and Characterization of Organic-Soluble Bitumens from Shales

The shales in this study that were selected for their potential suitability as host rocks for the disposal of high-level radioactive wastes are Upper Dowelltown, Pierre, Green River Formation, Nolichucky and Pumpkin Valley Shales. The mineralogical compositions of these shales as shown in Table 2.1 (reproduced from Ref. 10) indicate that three of the five shales, the Upper Dowelltown Shale, the Pierre Shale and the Green River Formation Shale, contain higher percentages of organic matter than the two Conasauga Shales. The Green River Formation Shale contains the most organic matter (13 wt%), followed by the Upper Dowelltown Shale (11 wt%) and the Pierre Shale (5 wt%). Since shales contain mostly inorganic matter, which hinders the analysis of organic matter in shale, the organic and inorganic matter had to be separated first before analysis.

Before separation, the solid shale samples were scanned with FT-infrared (KBr). These IR-spectra of the solid samples were difficult to analyze, due to the overlapping of peaks from the large fractions of clay minerals, pyrite and other inorganic compounds.

In this study, an attempt was made to isolate only the organic-soluble bitumens from the various shale samples. The separation of organic-soluble bitumens from shales in this study was obtained by the method of organic solvent extraction. The solvents used were chloroform and a mixture of chloroform/methanol (volume ratio = 5:1). The amount of bitumens that could be removed from shales in this manner ranged from ca 0.07 wt% (Nolichucky and Pumpkin Valley Shales) to 5.9 wt% (Pierre and Green River Formation Shales) of the total organic matter. The results are given in Table 3.1. After extraction, parts of the extracted shale samples were heated at 250°C for seventeen days and then were extracted again with the mixture of chloroform/methanol.

Table 3.1. Amount of Organics Removed by Solvent Extraction From Shale and Heated Shale Samples

Shale	Total Organic Content[a] (Wt% of Shale)	Organic-Extractable Bitumen (Wt% of Total Org. Content)	Organic-Extractable Pyrolytic Residue (Wt% of total Org. Content)
Upper Dowelltown	11	5.1	5.5
Pierre	5	5.9	1.5
Green River Formation	13	5.9	1.1
Nolichucky	trace (2)	0.07[b]	nd
Pumpkin Valley	trace (2)	0.08[b]	nd

[a] Data from Ref. 10.

[b] Assume the total organic content in these shale is 2 wt%.

nd = not determined.

In this way, more organic matter was removed from the organic-extracted shale samples. Organics removed in this manner may not all be from the bitumen, but rather from a mixture of bitumen and decom- posed kerogen (13). The results are given in Table 3.1.

Elemental analysis of the organic extracts of bitumens of the shale samples are shown in Table 3.2. Data in Table 3.2 indicate that the H/C atomic ratio of these organic extracts ranges from 1.48 (Upper Dowelltown Shale) to 2.49 (Pumpkin Valley Shale) and suggest that the organic-extractable bitumens from the Upper Dowelltown (1.48), Pierre (1.64), and Green River Formation (1.69) Shales contain more unsaturated compounds than the extractable bitumens from Nolichucky and Pumpkin Valley Shales, which are 1.92 and 2.49, respectively.

The IR spectroscopy of the five extractable bitumen samples in carbon tetrachloride reveals the presence of $-CH_2$, $-CH_3$ bands (of aliphatic, aromatic and cyclic compounds) (2960-2850 cm^{-1}, 1450-1460 cm^{-1}, 1370-1380 cm^{-1} and 700 cm^{-1}), $-NH_2$ (amide) (and -OH) bands (1650 cm^{-1}, 1400-1040 cm^{-1}), carbonyl and carboxylic group (C=O bands; 1700-1730 cm^{-1}) (2,14,15). According to Tissot and Welte (2) the C=O band of the extractable bitumen fraction is more pronounced than in the kerogen fraction thus suggesting that carbonyl and carboxylic groups are more frequently related to aliphatic chains and small cyclic structures than to polycondensed aromatic and heterocyclic nuclei. The presence of carboxylic and carbonyl groups indicate that these organic extracts contain compounds such as acids, esters, amides, alcohols and ketones, etc. It is known that organic acids in geological media behave as ligands to form organometallic complexes with trace metals (5-9,16). The formation of these complexes may influence radionuclide transport. IR spectra of the organic extracts of the two Conasauga Shales and the acid and non-acid fractions of the other three shales are given in Figs. 2-5.

Table 3.2. Elemental Analysis of Organic-Extractable Bitumens From Shales

	Weight Percent					Atomic Ratio
Shale	C	H	S	N	O	H/C
Chattanooga	81.59	10.09	3.51	0.96	3.38	1.48
Pierre	72.38	9.87	3.92	1.09	8.57	1.64
Green River Formation	78.14	11.00	1.29	0.81	3.79	1.69
Nolichucky	59.65	9.53	0.13	0.61	2.04	1.92
Pumpkin Valley	39.55	8.20	nd	nd	2.13	2.49

nd - not determined

UV-VIS scans (800 to 190 nm) of the five organic-extractable bitumens in cyclohexane are presented in Figs. 6 and 7 where it is shown that the absorption mostly appeared below 400 nm. Significant absorption occurred below 360 nm and increased rapidly as the wavelength decreased. This demonstrates that in these extracts the existence of larger-molecular compounds, such as poly-condensed aromatic rings and polycyclic structure, is minimal, which is in agreement with the results of Tissot and Welte (2).

Tables 3.3 and 3.4 give the preliminary identification of organic compounds in the acid fractions of Upper Dowelltown, Pierre and Green River Formation Shales and the extracts of the two Conasauga Shales by GC/MS. Because of the large numbers of compounds in these samples and the limited information on hand, only a small number of the compounds have been identified at present. The identifiable organic compounds listed in Tables 3.3 and 3.4 were confirmed by comparing mass spectra with authentic compounds (when possible) and published MS spectra of organic extracts of shales (17-22). Also attempts at interpreting the mass spectra were performed by following the ground rules of the mass spectral fragmentation path of substances (23-25).

Tests for the possibility of interaction between the identified individual organic compound and elements were not carried out in this study. However, studies of the interaction between three elements (cesium, strontium and technetium) and the extractable organic matter were performed, and the results are discussed below.

Table 3.3. Components Identified by GC-MS in the Acid Fraction of Organic-Extractable Bitumen from Shales

Shale	Non-Acids		Acids (as methyl ester)	
	Empirical Formula	Molecular Wt	Empirical Formula	Molecular Wt
Chattanooga	$C_{13}H_{26}$	182	$C_8H_8O_2$	136
	$C_{15}H_{32}$	212	$C_{12}H_{16}O_2$	192
	$C_{16}H_{34}$	226	$C_{17}H_{34}O_2$	270
	$C_{21}H_{40}$	292	$C_{18}H_{36}O_2$	284
			$C_{19}H_{38}O_2$	298
			$C_{20}H_{40}O_2$	312
Pierre			$C_{15}H_{30}O_2$	242
			$C_{17}H_{34}O_2$	270
			$C_{18}H_{36}O_2$	284
			$C_{19}H_{36}O_2$	296
			$C_{19}H_{38}O_2$	298
			$C_{18}H_{34}O_4$	314
Green River Formation	$C_{13}H_{26}$	182	$C_{17}H_{34}O_2$	270
	$C_8H_{15}ClO_2$	178	$C_{20}H_{40}O_2$	312
	$C_{21}H_{40}$	292	$C_{21}H_{42}O_2$	326*
			$C_{21}H_{42}O_2$	326*
			$C_{22}H_{44}O_2$	340
			$C_{23}H_{46}O_2$	354
			$C_{25}H_{50}O_2$	382

*Isomers

Table 3.4. Components Identified by GC-MS in the Organic-Extractable Bitumen from Shales

	Non-Acids		Acids (as methyl ester)	
Shale	Empirical Formula	Molecular Wt	Empirical Formula	Molecular Wt
Nolichucky	$C_8H_{13}ClO_2$	176	$C_{14}H_{28}O_4$	260
	$C_{20}H_{38}$	278	$C_{17}H_{34}O_2$	270
	$C_{22}H_{46}$	310	$C_{19}H_{38}O_2$	298
	$C_{23}H_{48}$	324		
	$C_{27}H_{56}$	380		
	$C_{29}H_{60}$	408		
	$C_{30}H_{62}$	422		
Pumpkin Valley	$C_8H_{15}ClO_2$	178	$C_{15}H_{27}O_4$	271
	$C_{22}H_{46}$	310	$C_{19}H_{38}O_2$	298
	$C_{25}H_{52}O$	368	$C_{23}H_{46}O_2$	354

3.2 Adsorption of Cesium, Strontium and Technetium on Organic-Extracted Shales Under Oxic Conditions

In a previous report (12), we presented the results of adsorption of cesium, strontium, technetium, neptunium and uranium on samples of clay minerals and samples of the untreated five end-member shales, under oxic conditions at room temperature. In this report, the adsorption of cesium, strontium and technetium onto the organic-extracted Upper Dowelltown, Pierre, Green River Formation and Pumpkin Valley Shales is presented. The adsorption of cesium on the organic-heated Pierre Shale and strontium on the organic-heated Upper Dowelltown Shale are also included. The results are compared with the adsorption data of these elements on the corresponding untreated shale samples to reveal any interaction between the nuclides and the organic-extractable bitumens. The results are given in Tables 3.5 to 3.7. All adsorption experiments were carried out in the synthetic groundwaters and in the 0.03-M $NaHCO_3$ solution which are used in Ref. 12. The pH of the concentrated brine and the diluted brine were adjusted initially to ca 5. Cesium and strontium are assumed to exist as singly- and doubly-charged aquo ions in the pH ranges of the synthetic groundwaters (12). Since the experiments were carried out under mildly oxidizing conditions, technetium is expected to be present as the pertechnetate ion, TcO_4^-. During the adsorption experiments, the pH was allowed to float to a final value without any control. In general, the pH of the concentrated brine increased to the value range of 6.5 - 7.5 and the pH of the diluted brine increased to the value range of 8 to 8.5 during the course of the experiments on the organic-extracted Pierre, Green River Formation and Pumpkin Valley Shales and the organic-heated Pierre Shale. These pH values are comparable to those of systems containing the corresponding untreated shales. However, the pH changes of the brine groundwaters which were in contact with the organic-extracted Upper Dowelltown Shales are quite different from those that were in contact with the untreated shale samples. The concentrated and the diluted brine groundwaters became quite acidic after three days of pre-equilibration. This was a very different pattern from that of the untreated Upper Dowelltown Shale sample when it was equilibrated with the brine groundwaters. The pH changes in systems containing untreated and organic-extracted Upper Dowelltown Shale samples are shown in Fig. 8. It can be seen that in systems containing untreated Upper Dowelltown Shale and brine groundwaters, the pH changed rather slowly; it took usually about thirty days to reach a pH value below 4. Actually this rapid drop in pH has been noticed before with one of these particular shales; when an Upper Dowelltown Shale sample was heated at 250°C in the air for six months and then was contacted with the brine groundwaters. For this case the pH also became very acidic after three days of pre-equilibration. From Table 2.1, it can be seen that Upper Dowelltown Shale contains the highest percentage of pyrite (FeS_2) among all five shale samples and contains only trace amount of carbonates. It is understandable that during equilibration in air, pyrite in shale will gradually oxidize to ferric sulfate (as shown in Eq. 2) and at the same time the pH of the equilibrating solution becomes acidic. Since heat enhances the process of oxidation, after six months of heating most of the pyrite in shale will have been converted to ferric sulfate (10,13,26). It is not surprising to find that the equilibrating solutions are acidic in systems containing heated Upper Dowelltown Shale and brine groundwaters. However, it is interesting to note that after removal of part of the organic matter from this shale, the oxidation process is also rapidly enhanced. Evidently the existence of the small amount of organic-extractable bitumen interferes with the oxidation of pyrite to ferric sulfate.

$$4\ FeS_2 + 15\ O_2 + 14\ H_2O \rightarrow 4\ Fe(OH)_3 + 16\ H^+ + 8\ SO_4^{2-} \qquad (2)$$

The pH of the 0.03-M $NaHCO_3$ solution remained above pH 8 for the tests with organic-treated Upper Dowelltown Shale, which are similar to other shale samples, due to the buffering action of the bicarbonate ion.

Concentrations of the three elements (Cs, Sr and Tc) used in this study are the same as in Ref. 12, e.g. at trace level ($5\text{x}10^{-11}$ to $1\text{x}10^{-8}$ M) in the linear adsorption region.

3.2.1 Cesium

The results of adsorption of cesium with initial concentrations of $5\text{x}10^{-11}$ and $1\text{x}10^{-8}$ mol/L onto the organic-extracted Upper Dowelltown, Pierre, Green River Formation and Pumpkin Valley Shales and onto the organic-heated Pierre Shales are given in Table 3.5, for the concentrated and diluted brine groundwater and in the 0.03-M $NaHCO_3$ solution. The adsorption ratios (distribution coefficients) are almost independent of loading. However, it can be seen that the adsorption ratios were reduced in every system containing the organic-extracted shale samples and the concentrated or diluted brine groundwater. Data from the systems containing corresponding untreated shale samples were reproduced from Ref. 12 for comparison. Values of adsorption ratios in the bicarbonate solution do not show a consistent pattern, especially when the concentration of cesium is $5 \text{ x } 10^{-11}$ mol/L. In most cases, adsorption ratios were reduced, but in a few cases the ratios increased. Most probably, this was partially due to the effect of pH. Usually adsorption tends to increase with pH, although for cesium, this effect is small (12). Besides, at low concentrations of cesium there is always a chance that adsorption onto walls of the container may occur.

The adsorption ratios of cesium for the organic-heated Pierre Shale samples are comparable with the ratios for the organic-extracted Pierre Shale. Although after heating, more organic matter was removed (see Table 3.1) from the shale sample (13), it seems that the effect of the latter removed organics on the adsorption of cesium was not as important as the effect from those organics removed before heating.

Table 3.5. Cesium (I) Adsorption on Shale Samples[a]

Name Shale	Groundwater	Initial Conc. C_s (mol/L)	Untreated Shale		Organic-Extracted Shale		Organic-Heated Shale	
			Rs (L/Kg)	Final Avg pH	Rs (L/Kg)	Final Avg pH	Rs (L/Kg)	Final Avg pH
Upper Dowelltown	A	$1x10^{-8}$	152 ± 2	3.90	76.6 ± 2.0	2.85		
		$5x10^{-11}$	123 ± 3	3.81	79.2 ± 4.8	2.58		
	B	$1x10^{-8}$	18467 ± 1038	4.24	3807 ± 859	2.88		
		$5x10^{-11}$	17571 ± 1837	3.82	4606 ± 891	2.68		
	C	$1x10^{-8}$	14204 ± 5739	8.31	8673 ± 1175	7.95		
		$5x10^{-11}$	10904 ± 1459	8.22	14603 ± 1631	7.60		
Pierre	A	$1x10^{-8}$	107 ± 9	6.37	93.5 ± 0.3	6.62	88.9 ± 3.0	6.57
		$5x10^{-11}$	102 ± 4	6.12	96.8 ± 5.2	6.71	91.6 ± 1.3	6.57
	B	$1x10^{-8}$	11223 ± 553	7.86	5056 ± 478	8.16	6103 ± 571	7.96
		$5x10^{-11}$	13026 ± 1517	7.87	7726 ± 1455	8.08	5502 ± 752	7.96
	C	1.10^{-8}	9493 ± 993	8.00	7655 ± 592	9.21	7826 ± 1857	8.83
		$5x10^{-11}$	10220 ± 794	8.36	13493 ± 1474	8.39	8001 ± 1043	8.87
Green River Formation	A	$1x10^{-8}$	5.2 ± 2.4	6.93	0.36 ± 0.06	7.04		
		$5x10^{-11}$	12.1 ± 4.1	6.87	0.49 ± 0.15	7.06		
	B	$1x10^{-8}$	182 ± 5	8.31	143 ± 9	8.60		
		$5x10^{-11}$	413 ± 40	8.35	157 ± 13	8.51		
	C	$1x10^{-8}$	1317 ± 565	9.03	659 ± 26	9.33		
		$5x10^{-11}$	907 ± 82	9.05	798 ± 34	9.30		
Pumpkin Valley	A	$1x10^{-8}$	70.0 ± 14.6	6.55	52.3 ± 1.4	6.61		
		$5x10^{-11}$	79.1 ± 10.3	6.77	54.0 ± 5.3	6.66		
	B	$1x10^{-8}$	10698 ± 1564	6.79	6790 ± 415	8.32		
		$5x10^{-11}$	13741 ± 921	6.93	7947 ± 392	8.19		
	C	$1x10^{-8}$	10169 ± 2030	8.79	7832 ± 320	9.14		
		$5x10^{-11}$	12641 ± 1433	9.37	9222 ± 2402	9.03		

[a] Each sample contained ca 0.2g of shale and 4 ml of groundwater. The samples were preequilibrated 3 times for at least 3 days each, and the final equilibration was for 15 days at room temperature.

Groundwaters: A - concentrated brine; B - 100/1 dilution of A; C - 0.03-M $NaHCO_3$

3.2.2 Strontium

The adsorption of strontium on the organic-extracted Upper Dowelltown, Pierre, Green River Formation and Pumpkin Valley Shales is given in Table 3.6. Because of the low adsorption of strontium on the untreated shale samples in the concentrated brine groundwater (12), adsorption tests with the organic-extracted shale samples were performed only in the diluted brine groundwater and in the 0.03-M $NaHCO_3$ solution. The initial concentration of strontium was $1x10^{-8}$ mol/L. In Table 3.6, it is observed that except for the Pumpkin Valley shale, the adsorption ratios of strontium on these organic-extracted shale samples in the diluted brine groundwater are slightly lower than those of the corresponding untreated shale samples. Because the Pumpkin Valley Shale contains only trace amounts of organic matter and the adsorption of strontium on this shale is generally low, it is not surprising that the adsorption of strontium on the organic-extracted and the untreated Pumpkin Valley Shale samples is about the same. The results from adsorption of strontium on the organic-extracted shale samples in the carbonate solution are again not consistent This may be due to the effect of pH. The adsorption ratio of strontium on untreated shale samples increases with the increasing of pH (12). This may also be because of interference from precipitation. Precipitation of strontium species as carbonate and hydroxide often occurs and could be misinterpreted as adsorption. During the adsorption tests of this study and the previous study (12), it was found that the counting rate (gamma ray) of control samples (containing only solution but no adsorbent) containing ^{90}Sr in the bicarbonate solution was reduced to about 93% of the original counting rate after 15 days of equilibration. Evidently in these bicarbonate solutions, precipitation and on adsorption by the tubes occurred, and thus the results of adsorption in the bicarbonate solution are not as reliable as those in the brine groundwaters.

Table 3.6 Strontium (II) Adsorption on Shale Samples[a]
Initial Sr Conc: 1×10^{-8} mol/L

Name Shale	Ground-water[b]	Untreated shale		Organic-Extracted Shale		Organic-Heated Shale	
		Rs (L/Kg)	Final Avg.pH	Rs (L/Kg)	Final Avg.pH	Rs (L/Kg)	Final Avg.pH
Upper	B	3.5 ± 0.3	3.37	1.7 ± 0.1	2.68	3.4 ± 1.2	2.67
Dowelltown	C	146 ± 18	8.69	232 ± 77	8.31	742 ± 249	7.38
Pierre	B	36.6 ± 0.5	7.21	33.4 ± 0.7	8.05		
	C	534 ± 245	8.41	758 ± 115	8.88		
Green River	B	3.3 ± 1.4	7.52	2.2 ± 1.4	8.07		
Formation	C	138 ± 12	9.09	120 ± 5	9.15		
Pumpkin Valley	B	10.9 ± 0.8	7.65	11.6 ± 0.9	7.97		
	C	713 ± 117	9.45	249 ± 25	9.16		

[a] Each sample contained ca 0.2 g of shale and 4 ml of groundwater.
[b] The strontium normally present in the concentrated brine and the dilute brine was omitted in these tests.

B = 100/1 dilution of concentrated brine
C = 0.03 M-$NaHCO_3$

The adsorption ratio of strontium on the organic-heated Upper Dowelltown Shale is not significantly different from the untreated shale sample but is higher than on the organic-extracted shale samples in the diluted brine groundwater. This might be because the organic material released from the kerogen after heating (which could not be removed by further organic extraction) enhanced the adsorption. Additional tests are necessary to understand this increase in adsorption.

3.2.3 Technetium

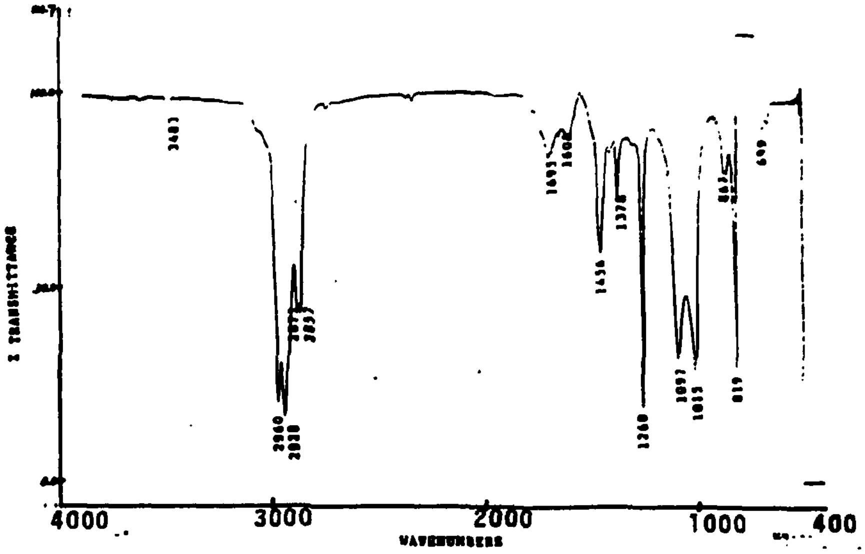
Table 3.7 shows the results of adsorption of technetium on the organic-extracted Upper Dowelltown, Pierre, Green River Formation and Pumpkin Valley Shales in concentrated and diluted brine groundwater and in the 0.03-M $NaHCO_3$ solution. The initial concentration of Tc was $1x10^{-8}$ mol/L. Results from the literature (27,28) have shown that adsorption of technetium can be greatly enhanced on adsorbents such as soil and sediment, which contain organic matter. As we have reported in the previous study (12), a significant amount of technetium can be adsorbed by the untreated shale samples. It is expected that after the partial removal of organic matter from the shale samples, the adsorption of Tc on these organic-extracted shale samples should decrease. As it can be seen, this is true in most of the systems shown in Table 3.7. In systems containing the organic-extracted Upper Dowelltown Shale sample, the adsorption did not decrease, but increased, especially in the system containing the dilute brine groundwater and the organic-extracted Upper Dowelltown Shale. This may be related to the low pH value of the pre-equilibrating and equilibrating solutions as shown in Fig. 8. The acidity of the equilibrating solutions definitely has an effect on the adsorption of technetium on the organic-extracted Upper Dowelltown Shale samples. It is known that adsorption of TcO_4^- on certain adsorbents increases with decreasing pH (28). Of course, the increase may involve other factors besides pH changes. Before the exact interaction between technetium and organic matter is found, a conclusion cannot be drawn.

Table 3.7 Technetium (VII) Adsorption on Shale Samples[a]
Initial Tc Conc: 1×10^{-8} mol/L

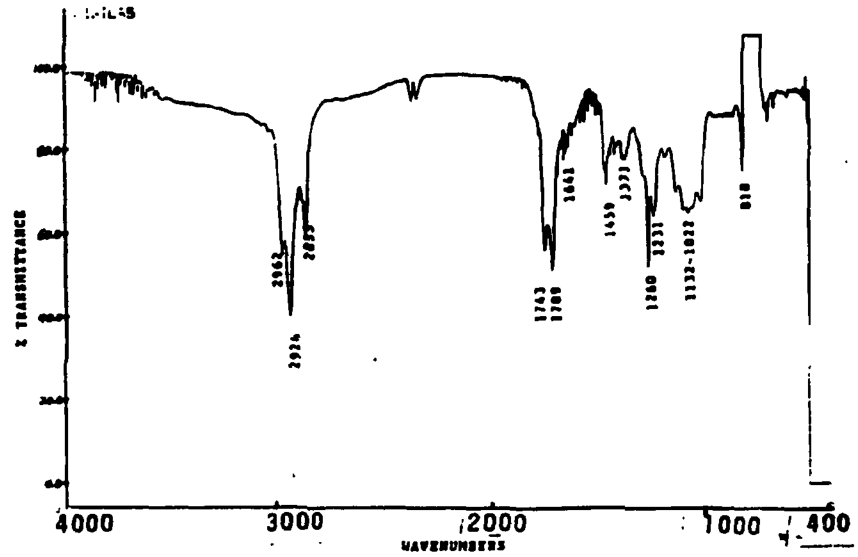
Name Shale	Groundwater	Untreated Shale		Organic-Extracted Shale	
		Rs (L/Kg)	Final Avg. pH	Rs (L/Kg)	Final Avg. pH
Upper	A	22.9 ± 3.1	3.68	65.6 ± 2.9	3.52
Dowelltown	B	266 ± 18	3.54	1185 ± 242	3.21
	C	14.8 ± 1.1	8.24	26.6 ± 6.1	8.49
Pierre	A	4.1 ± 1.8	6.58	3.0 ± 1.9	7.38
	B	3.0 ± 0.7	--	1.6 ± 0.2	8.47
	C	1.7 ± 0.4	8.52	0.27 ± 0.27	9.05
Green River	A	1.6 ± 0.6	6.98	0.33 ± 0.15	7.53
Formation	B	1.84 ± 0.04	--	1.1 ± 0.2	8.81
	C	0.26 ± 0.32	9.09	0.41 ± 0.16	9.37
Pumpkin Valley	A	1.1 ± 0.9	6.93	-0.21	7.35
	B	0.92 ± 0.52	--	0.52 ± 0.19	8.68
	C	1.0 ± 1.0	9.59	0.51 ± 0.23	9.26

[a] Each sample contained ca 0.2 g of shale and 4 ml of groundwater.

Groundwater: A - concentrated brine
B - 100/1 dilution of A
C - 0.03 M-$NaHCO_3$

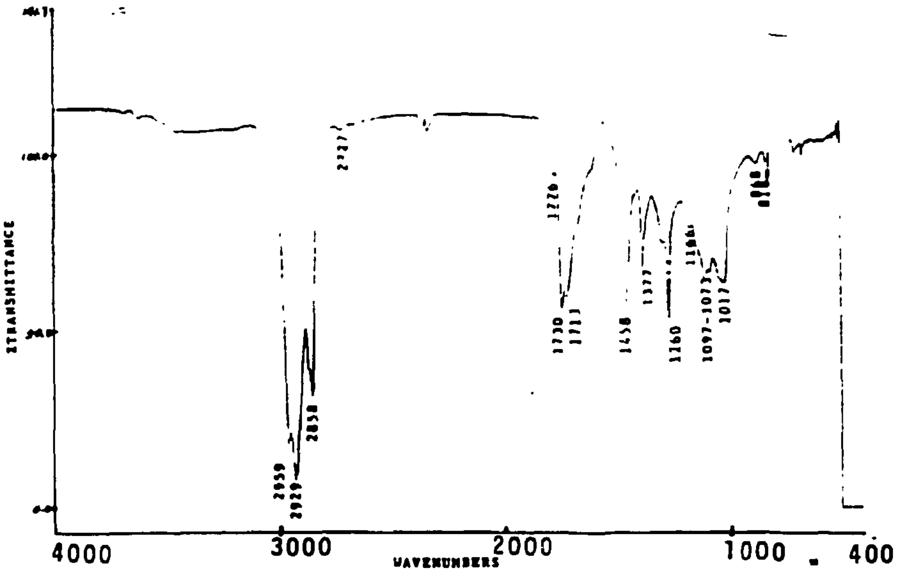


Chattanooga Shale: NON-ACID FRACTION
(in CCl_4)

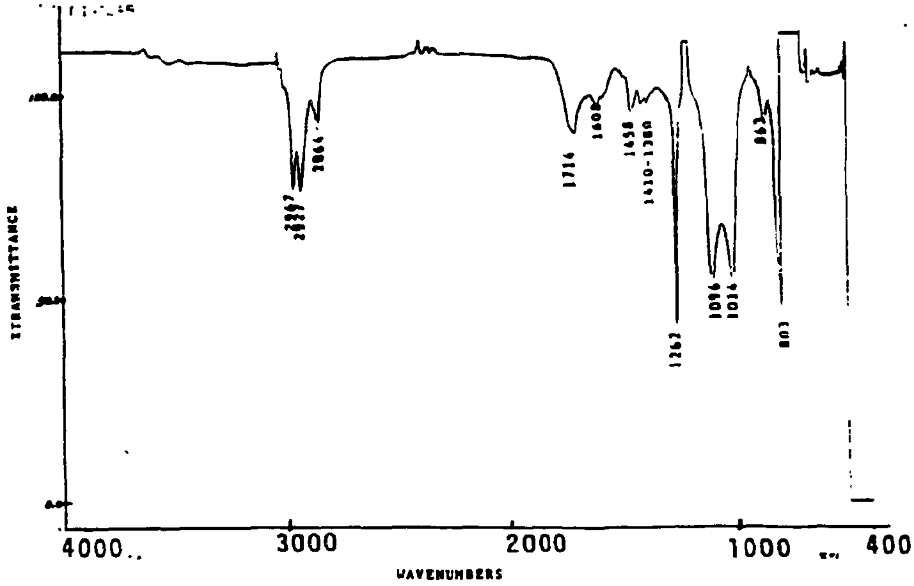


Chattanooga Shale: ACID FRACTION
(in CCl_4)

Fig. 2 IR Spectra of the Acid and Non-acid Fractions of the Organic-extractable Bitumen from Upper Dowelltown Shale

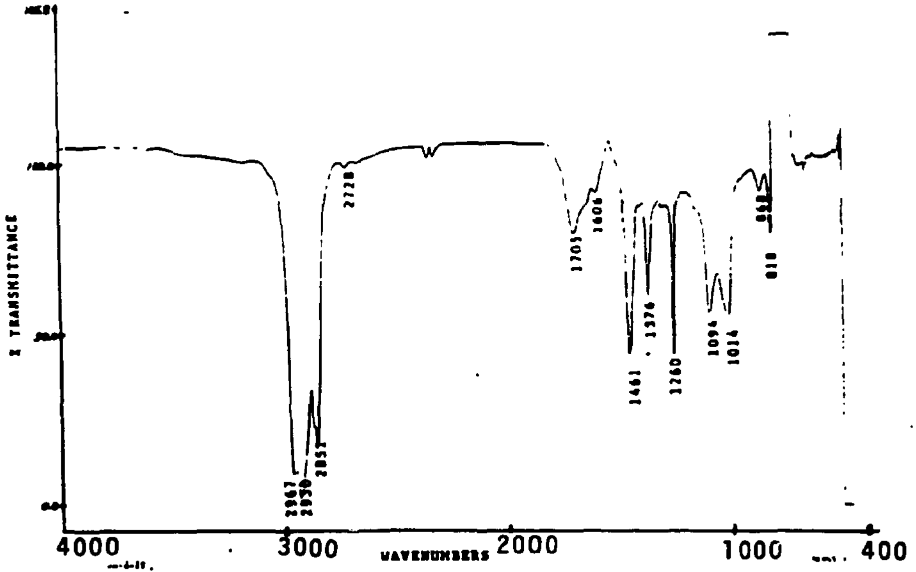


Pierre Shale: NON_ACID FRACTION
(in CCl_4)

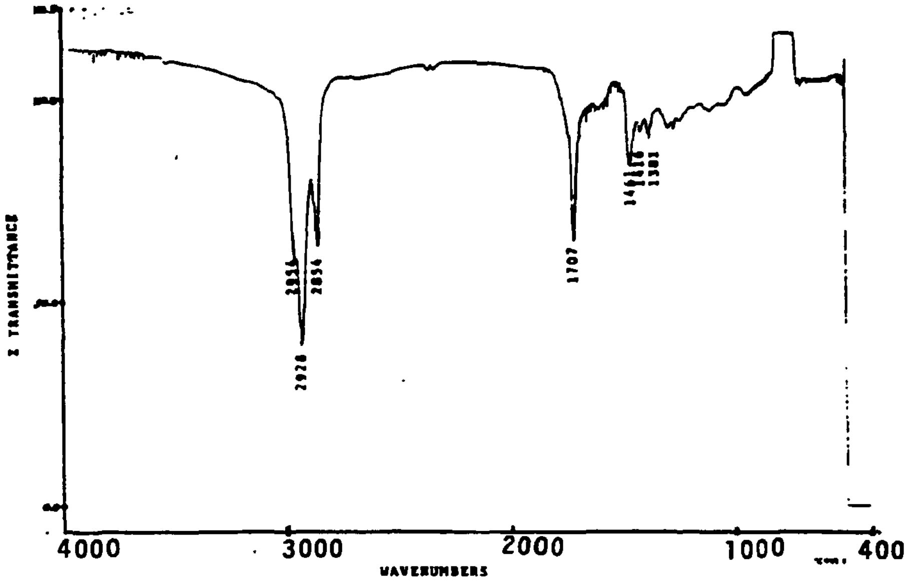


Pierre Shale: ACID FRACTION
(in $CHCl_3$)

Fig. 3 IR Spectra of the Acid and Non-acid Fractions of the Organic-extractable Bitumen from Pierre Shale

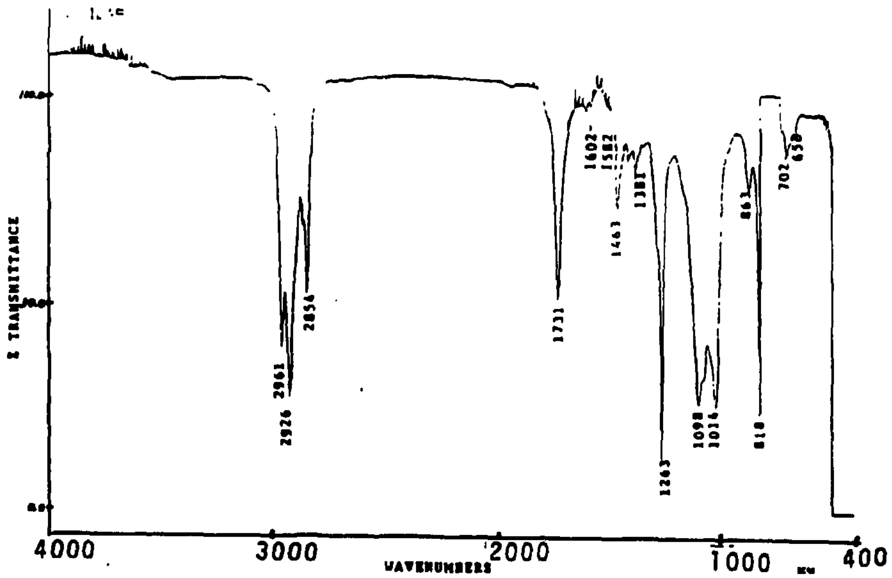


Green River Formation: NON-ACID FRACTION

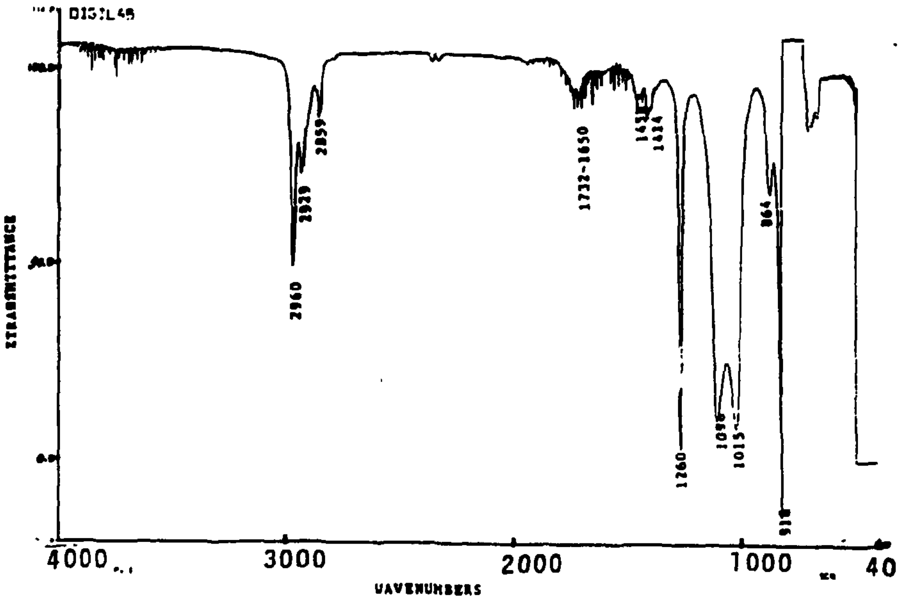


Green River Formation: ACID FRACTION
(in CCl_4)

Fig. 4 IR Spectra of the Acid and Non-acid Fractions of the Organic-extractable Bitumen from Green River Formation Shale



Nolichucky Shale: ORGANIC EXTRACT
(in CCl_4)



Pumpkin Valley Shale: ORG. EXTRACT
(in CCl_4)

Fig 5 IR Spectra of the Organic-extractable Bitumen from Nolichucky and Pumpkin Valley Shales

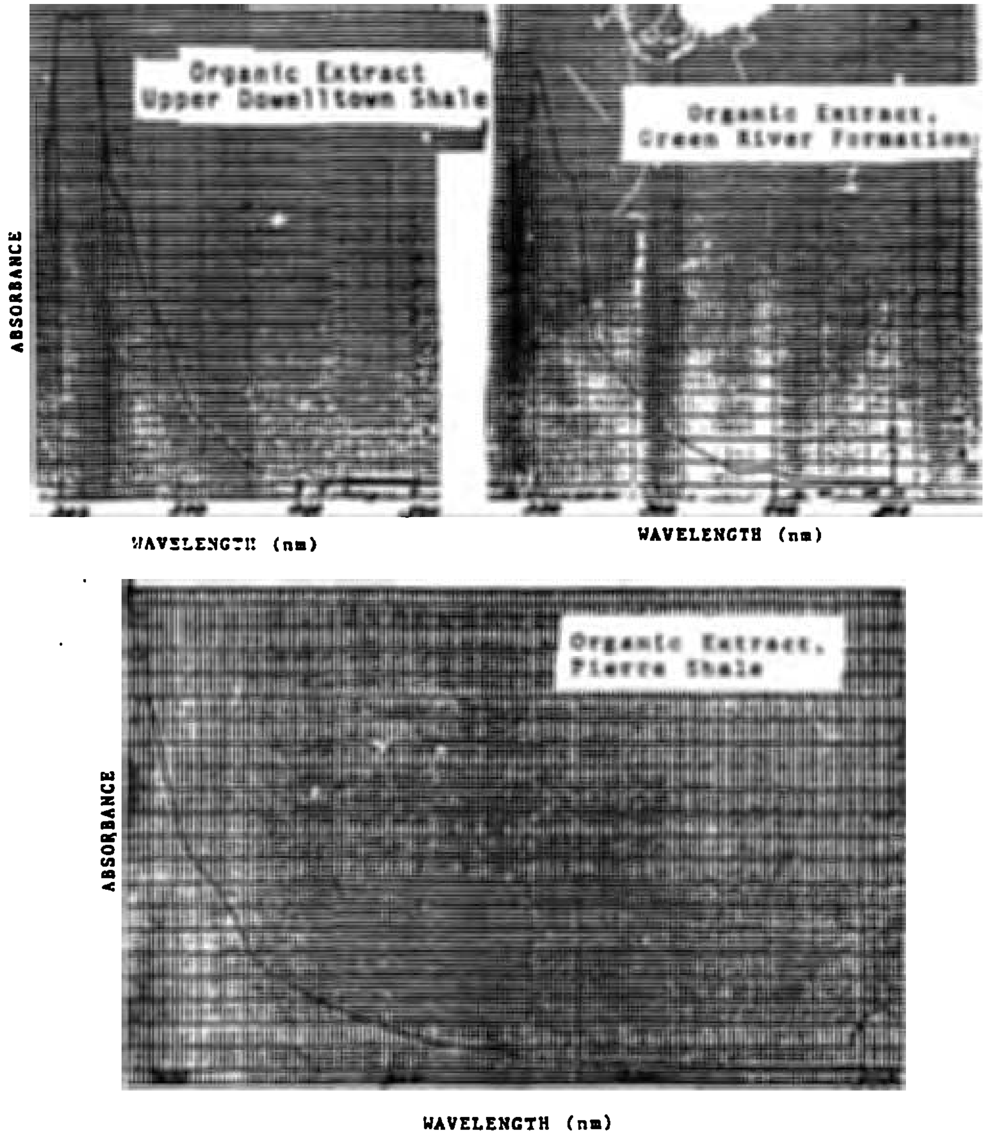


Fig. 6 Ultra-violet Spectra of Organic-extractable Bitumen from Upper Dowelltown, Pierre, Green River Formation Shales

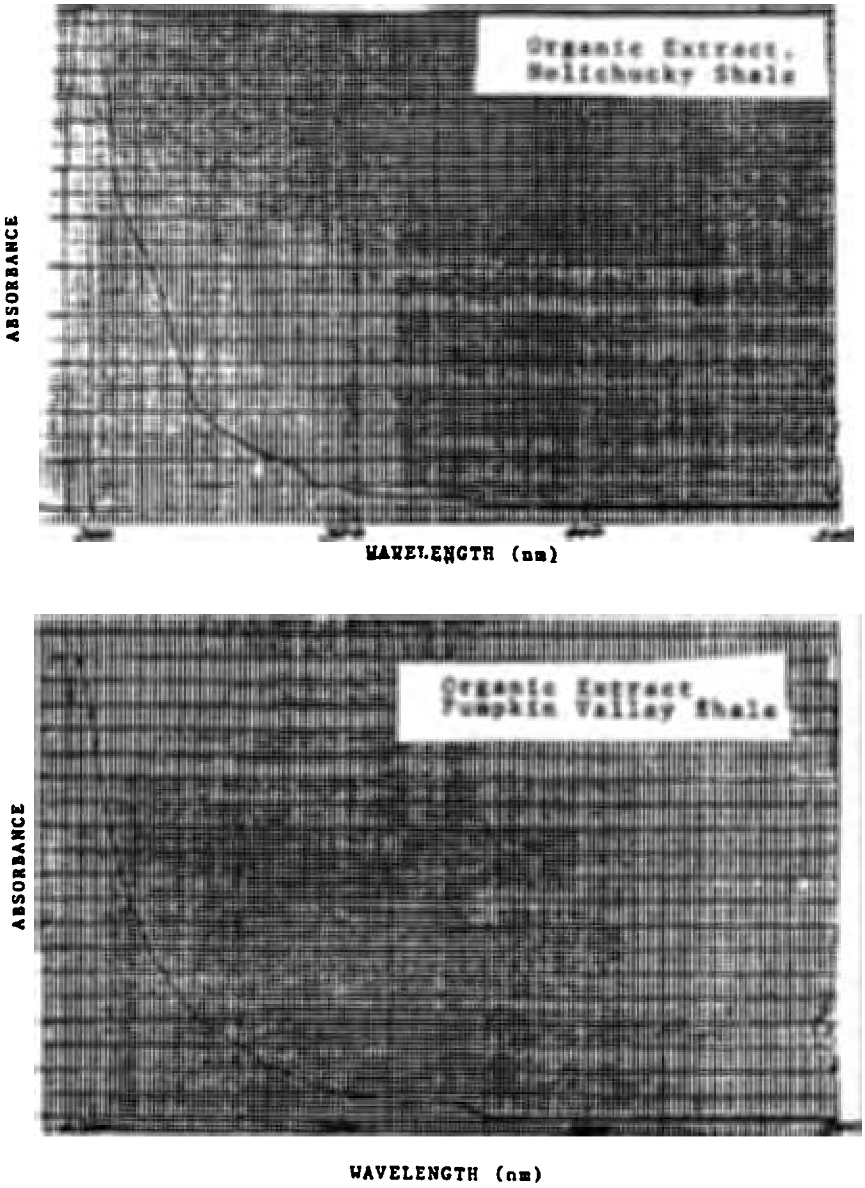


Fig. 7 Ultra-violet Spectra of Organic-extractable Bitumen from Nolichucky and Pumpkin Valley Shales

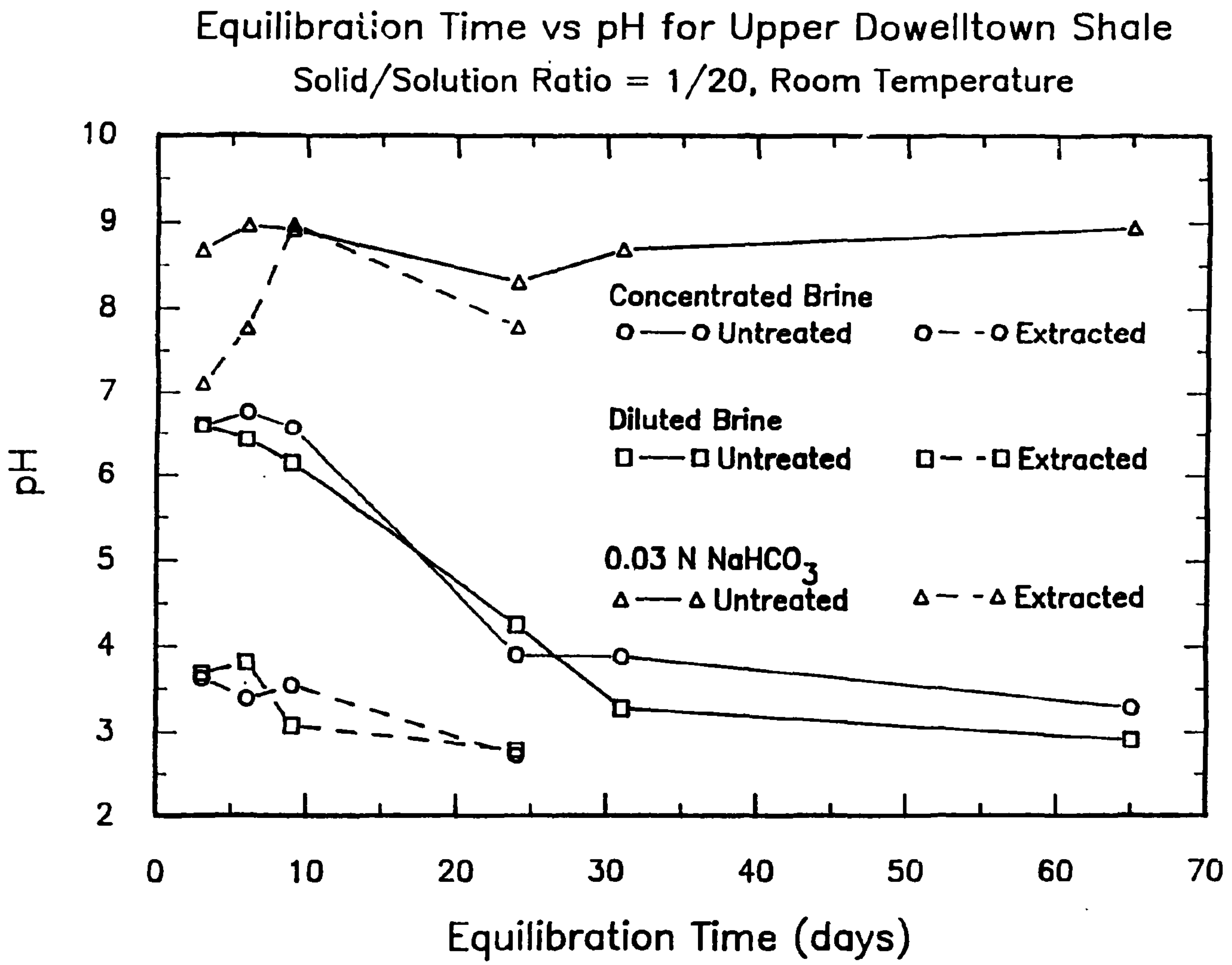

Equilibration Time vs pH for Upper Dowelltown Shale
Solid/Solution Ratio = 1/20, Room Temperature
Concentrated Brine
○—○ Untreated
○- -○ Extracted
Diluted Brine
□—□ Untreated
□- -□ Extracted
0.03 N $NaHCO_3$
△—△ Untreated
△- -△ Extracted
pH
2
3
4
5
6
7
8
9
10
0
10
20
30
40
50
60
70
Equilibration Time (days)

Figure 8

4. Conclusion

Soxhlet extraction with chloroform and a mixture of chloroform/methanol removed 0.07 to 5.9 wt% of total organic matter from five selected shale samples. The organic materials removed in this manner are portions of the bitumens in these shales.

UV-VIS spectroscopy indicates that organic components contained in these extracts were mostly lower-molecular-weight organic compounds; the existence of higher-molecular-weight compounds such as polycondensed aromatics is minimal. IR spectroscopy reveals that sharp and strong absorption bands of carboxylic and carbonyl groups appear in spectra of the extracts of Upper Dowelltown, Pierre, Green River Formation and Nolichucky Shales but there are only moderately strong absorption bands in the spectrum of the extract of Pumpkin Valley Shale. The existence of carboxylic groups indicates the presence of carboxylic acids in these extracts. Carboxylic acids behave as ligands which form organometallic complexes with trace metals. This fact may be important in mobilization, transportation, and accumulation of radio-active nuclides.

Extracts of the Upper Dowelltown, Pierre, and Green River Formation Shales were further fractionated into acid and non-acid fractions. Carboxylic acids as methyl esters (aliphatic, cyclic, and aromatic) which could be identified at present from GC/MS spectra of the acid fractions of the extractable bitumens from Upper Dowelltown, Pierre, and Green Formation Shales and of the extractable bitumens from Nolichucky and Pumpkin Valley Shales are:

C_8 - C_{20} in Upper Dowelltown Shale
C_{15} - C_{19} in Pierre Shale
C_{17} - C_{23} in Green River Formation Shale
C_{14} - C_{19} in Nolichucky Shale
and C_{15} - C_{23} in Pumpkin Valley Shale.

Adsorption results of Cs(I), Sr(II), and Tc(VII) on the organic-extracted Upper Dowelltown, Pierre, Green River Formation, and Pumpkin Valley Shales in synthetic groundwaters, when compared with the results of systems containing corresponding untreated shale samples, showed that interactions did occur between these three nuclides and the extractable organic components as a whole. The pH of the synthetic groundwater solutions in systems containing the Upper Dowelltown Shale were also affected by the extractable organic matter. This evidence proves that the small amounts of the extractable bitumens from these specific shales are large enough to play a role in the transport of nuclides.

It is evident that considerable study is needed on the nature of the organic matter in shales and in other surrounding materials near nuclear burial sites and the relationships between the organic matter and radio- nuclides present in nuclear waste.

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