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# The Sedimentary Rock Program: A Summary of the Geochemical Characteristics of Shale Important to Waste Isolation

Gary K. Jacobs

Environmental Sciences Division
Publication No. 3217

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ENVIRONMENTAL SCIENCES DIVISION

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## ABSTRACT

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The geochemical characteristics of shales were investigated to evaluate their potential to serve as host media for the isolation of radioactive wastes. Four end-member shales for investigation were selected to represent smectite-rich, illite-rich, carbonate-rich, and organic-rich shales. The mineralogical differences between these shales were characterized and used to assess the potential behavior of these types of shales. The compositions of groundwaters associated with various shale terrains were obtained through a search of the literature and data bases. The ranges in groundwater composition can be summarized as follows: pH = 5.9-10.9, Na = 1.8-73,025 mg/L, Ca = 0.7-2000 mg/L, Mg = 0.2-559 mg/L, K = 0.2-349 mg/L, Cl = 0.5-120,008 mg/L, $SO_4$ = 0.2-5395 mg/L, and $SiO_2$ = 0.2-43 mg/L. Rock-water experiments and reaction path modeling were used to help interpret these results and perform sensitivity calculations. Sorption tests using Cs, Sr, U, Np, and Tc indicate that the shales have moderate to high affinity for ion-exchangeable cations. The behavior of redox-sensitive elements was somewhat more complicated, but mild sorption is suggested and may be related to the organic matter present in the shales, although the data do not support firm conclusions.

# 1. INTRODUCTION

Significant quantities of high-level radioactive wastes (HLW) exist now and will continue to be produced through the operation of commercial nuclear reactors and defense programs in the United States. The safe disposal of these wastes has been mentioned frequently as one of the most critical tasks facing geoscientists today. The problem is not a new one, however. In 1955 a meeting of prominent scientists and engineers was held at Princeton University to discuss the problem. They concluded that these wastes should be disposed of in deep geologic formations. Since then several studies comparing alternatives to deep geologic disposal have reached the same conclusion (DOE 1980). Although the specific geologic formations investigated have changed over the years, the U.S. Department of Energy (DOE), as well as its predecessors, has followed this directive in its search for a final disposal site for nuclear wastes.

A geologic repository will consist of a series of mined cavities at a depth greater than ≈300 m in stable rock formations. The wastes are to be encapsulated in corrosion-resistant metallic canisters, placed into the cavities, and surrounded (in some cases) by a clay packing material to help slow the migration of water to the canisters and reduce the mobility of contaminants released when the canisters fail. Current regulations (EPA 1985, NRC 1983) stipulate (1) that the canisters last from 300 to 1000 years, (2) that the groundwater flowing through the repository take at least 1000 years to reach the accessible environment (defined as 5 km from the repository or land surfaces/waters), and (3) that the total release of radioactive material from the repository to the accessible environment remain below specified levels for 10,000 years. The most likely scenario for the release of contaminants involves the infiltration of water into the repository accompanied by corrosion of the canisters, dissolution of the waste form (spent fuel rods or glass cylinders), and the subsequent migration of dissolved contaminants in the groundwater. Therefore, a site should have the following characteristics: (1) little groundwater; (2) slow groundwater movement; (3) long groundwater flow paths to the accessible environment; (4) geochemical properties of the groundwater that inhibit corrosion,

waste form dissolution, and radionuclide mobility; and (5) the presence of highly sorbent minerals along groundwater flow paths to act as scavengers for the radionuclides.

Until December 1987 three rock types were being considered for the first repository in the U.S., as directed by the Nuclear Waste Policy Act (NWPA 1982): basalt (Hanford Site, Washington), salt (Deaf Smith County, Texas), and tuff (Yucca Mountain Site, Nevada Test Site). Results from environmental assessments (DOE 1986a, 1986b, 1986c) suggested that all three sites would have acceptable performance characteristics. In addition to considering these sites for the first repository, DOE was planning for the possibility of a second repository and was targeting crystalline rocks as likely hosts. Sedimentary rocks, although not a part of the program to site a second repository, also were considered as possible host rocks. In December of 1987 the U.S. Congress (NWPAA 1987) directed DOE to concentrate on the characterization of only one site, the tuff formations at Yucca Mountain on the Nevada Test Site. Other programs for both the first and second sites were discontinued within 90 days of the amendments.

The Sedimentary Rock Program (SERP) at the Oak Ridge National Laboratory (ORNL) conducted investigations to assess the potential for shale to serve as a host medium for the isolation of high-level radioactive wastes. The emphasis on shale was the result of screening the major sedimentary rock types other than salt (shale, sandstone, carbonate, anhydrite, and chalk) for a variety of attributes that affect the performance of repositories. Results using a ranking methodology that considered the technical aspects of geology, geochemistry, hydrology, thermal performance, rock mechanics, natural resources, waste package degradation, costs, and total-systems studies suggested that, of the sedimentary rocks considered, shale offers the best potential for the safe isolation of wastes (Croff et al. 1986).

The geologic characteristics of shales constitute a rather broad spectrum. Therefore, more detailed studies on the hydrologic, geochemical, and thermomechanical properties of various shales were undertaken to identify relationships that may be present between the

geologic characteristics of shales and the performance aspects of a repository. Although the U.S. program investigating shale as a medium for the isolation of HLW has been discontinued, shales and clay-rich strata are still being actively pursued by other countries (e.g., Belgium, Italy, Switzerland). In addition, some of the characteristics that make shale desirable for a HLW repository also make it attractive as a medium for the disposal of both low-level radioactive and hazardous chemical wastes (Jefferies and Wisbey in press, Lee and Tank 1985).

The characteristics of shales and clay-rich materials that make them desirable for waste management practices have been discussed previously (Hustrulid 1982; Isherwood 1981; Jefferies and Wisbey in press; Krauskopf 1986, 1988; Lee and Tank 1985). The two characteristics listed most often as being favorable are (1) the combination of low permeability and high porosity and (2) the high affinity of the clays for adsorbing contaminants. The hydraulic properties of shales and clays prevent the flow of substantial quantities of fluids through the fine-grained matrix. The sorption properties of shales and clay-rich strata further retard the transport of many contaminants (especially ion-exchangeable cations). Generally, the predominant pathway for transport in media such as these is through discrete fractures or fracture zones because of the low permeability of the matrix (d'Alessandro and Gera 1986, Fyfe et al. 1984). There are also two features that are commonly suggested as undesirable characteristics: (1) relatively weak strength, making mined openings unstable, and (2) temperature-induced mineralogical changes that could decrease the effectiveness of sorption and unfavorably alter the hydrologic nature of such geologic materials. The weak strength is mostly a concern for HLW repositories which must be constructed at depth, although engineering practices can be used to alleviate many potential problems. For wastes that can be disposed of in near-surface facilities, the strength of the geologic formation is much less of an issue. The most common problem discussed with respect to mineralogical alteration is the transformation of smectite to illite. This alteration can result in a reduction of sorption potential and less desirable

hydraulic properties (i.e., illites do not generate high swelling pressures as do smectites). Previous studies have investigated this issue (Eberl 1980, Eberl and Hower 1976, Yau et al. 1987), and the data suggest that this transformation is quite slow except under specific conditions. Both smectite- and illite-rich shales were included for study to address differences in performance between the two types of shales.

Because the mineralogic characteristics of shales span a rather broad spectrum, four end-member types were defined were study (Brookins and Stow 1986). These four types were selected to bracket possible ranges in organic content, relative quantities of illite vs smectite, and the presence of carbonate minerals (Fig. 1). The four shales

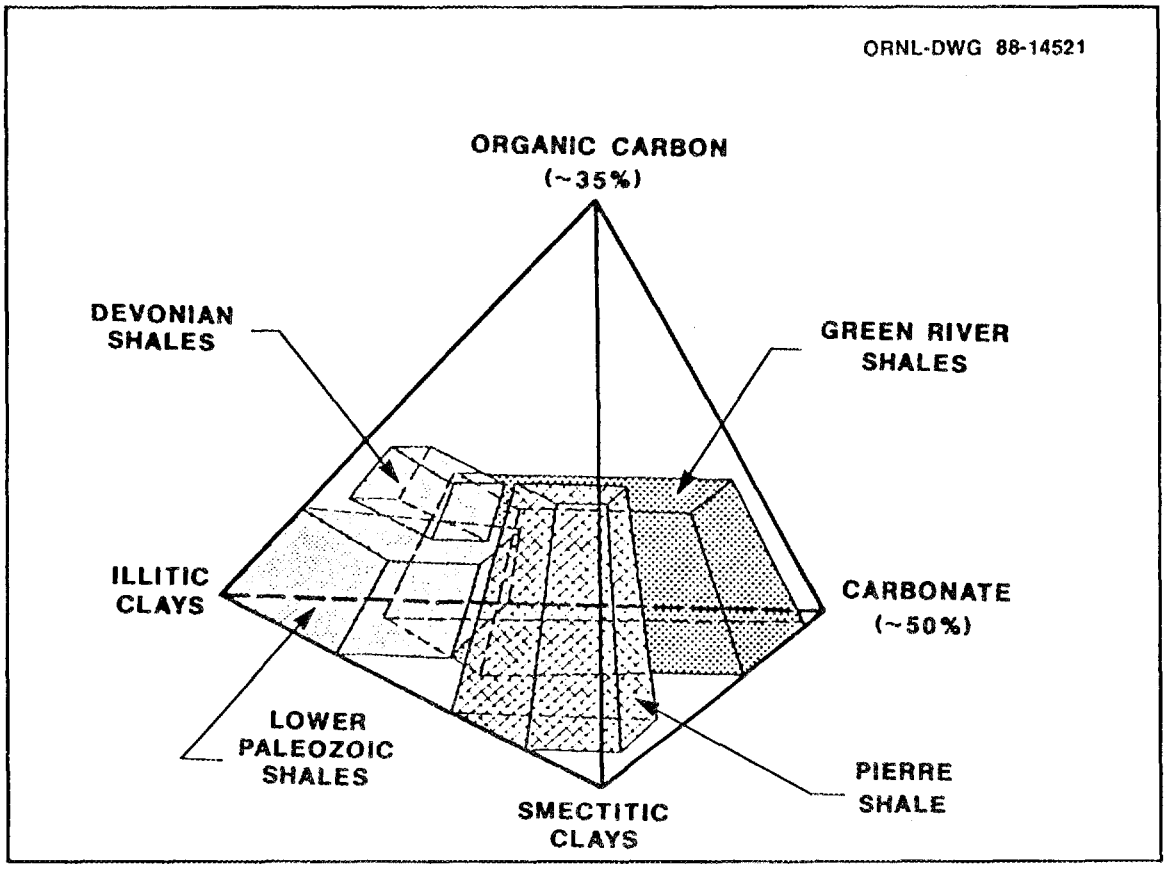


Fig. 1. Generalized representation of end-member shales in the illite-smectite-carbonate-organic carbon tetrahedron (after Brookins and Stow 1986).

selected for detailed study were the Pierre Shale (smectitic), Chattanooga Shale (organic rich), Green River Formation shales (carbonate rich), and the Nolichucky and Pumpkin Valley Shales (illitic).

The purpose of this report is to summarize the geochemical information obtained through SERP over the last 3 years on the mineralogy (Sect. 2), groundwater chemistry (Sect. 3), and sorption (Sect. 4) characteristics of selected shales. The implications of the results of these various studies are discussed in Sect. 5. Details on the mineralogy may be found in Lee et al. (1987, 1988); on the sorption, in Meyer et al. (1987, 1988); and on the groundwater chemistry, in Von Damm (1987), Von Damm and Johnson (1987), and Von Damm and VandenBrook (1988).

## 2. MINERALOGY

The mineralogical characteristics of shales are important to the performance of a waste disposal system in two fundamental ways. First, the chemistry of groundwaters in shales can be at least partially controlled by the mineralogy of the host formation (Von Damm 1987, Von Damm and Johnson 1987). Second, the migration of radionuclides through shale formations is affected by the mineralogical properties of the host rock. One of the main reasons for the favorable ranking of shales among sedimentary rocks is the large affinity of clay minerals, the predominant mineral phase in shales, for sorbing radioelements (Croff et al. 1986). Therefore, information on the mineralogy of shales is basic to any study evaluating their potential for a waste disposal system.

Lee et al. (1987) describe the details of the methods and results of the mineralogical characterization of the four end-member shales. Tables 1-4 list the mineralogical, bulk chemical, and particle-size distribution and surface area properties of the shales.

Table 1. Mineralogical composition (wt %) of the Chattanooga Shale, Pierre Shale, Green River Formation, Nolichucky Shale, and Pumpkin Valley Shale[a]

| Constituent | Chattanooga | Pierre | Green River | Nolichucky | Pumpkin Valley |
|---|---|---|---|---|---|
| Organic matter | 11 | 5 | 13 | t | t |
| Chlorite + kaolinite | 4 | t | t | 141 | 15 |
| Illite | 49 | t | 10 | 43 | 57 |
| Mica | 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]t = trace (<2 wt %); nd = not detected.
Source: Lee et al. 1987.

Table 2. Bulk chemical composition of the Chattanooga Shale, Pierre Shale, Green River Formation, Nolichucky Shale, and Pumpkin Valley Shale

| | Chattanooga Shale | Pierre Shale | Green River Formation | Nolichucky Shale | Pumpkin Valley Shale |
|---|---|---|---|---|---|
| | | | Weight percent | | |
| $SiO_2$ | 57.78 | 49.22 | 34.24 | 40.66 | 62.06 |
| $Al_2O_3$ | 13.61 | 13.99 | 7.56 | 13.04 | 20.79 |
| $K_2O$ | 3.95 | 2.27 | 3.25 | 3.41 | 5.37 |
| $Na_2O$ | 0.38 | 0.66 | 0.70 | 0.34 | 0.66 |
| FeO | 5.79 | 5.40 | 2.70 | 3.99 | 6.69 |
| $TiO_2$ | 0.77 | 0.48 | 0.27 | 0.48 | 0.8 |
| MgO | 1.35 | 2.17 | 6.35 | 2.34 | 2.00 |
| CaO | 0.27 | 8.58 | 13.16 | 6.02 | 0.29 |
| $CO_3$ | <0.50 | 10.50 | 26.40 | 9.60 | <0.50 |
| $\Sigma S$ | 4.32 | 0.98 | 0.34 | 0.18 | 0.30 |
| $SO_4$ | 0.32 | 0.26 | 0.12 | 0.18 | 0.10 |
| Sulfide | 4.22 | 0.89 | 0.30 | 0.12 | 0.26 |
| | | | Parts per million | | |
| Ba | 1400 | 510 | 500 | 150 | 550 |
| Sr | 230 | 350 | 630 | 140 | 150 |
| P | 450 | 1600 | 320 | <290 | <290 |
| Mn | 150 | 640 | 400 | 320 | 320 |
| Ni | 210 | 72 | <55 | 61 | 62 |
| Co | 44 | 22 | 10 | 19 | 31 |
| Cu | 81 | 36 | 20 | <18 | <20 |
| Cr | 140 | 140 | 83 | 130 | 190 |
| Zn | 80 | 46 | <18 | 24 | 160 |
| V | 410 | 190 | 77 | 47 | 86 |
| U | 61 | 3 | 3 | 2 | 3 |

Source: Lee et al. 1987.

Table 3. Summary of particle-size distributions and surface areas of the four end-member shales[a]

| | Size distribution (wt %) | | | BET surface area ($m^2/g$) |
|---|---|---|---|---|
| | 180-53 μm | 53-2.8 μm | <2.8 μm | |
| Chattanooga Shale | | | | |
| a | 24 | 66 | 10 | 4.78 |
| b | 27 | 64 | 9 | 4.40 |
| Pierre Shale | | | | |
| a | 0 | 81 | 19 | 21.87 |
| b | 1 | 81 | 18 | 23.79 |
| Green River Formation | | | | |
| a | 13 | 74 | 13 | 1.92 |
| b | 20 | 68 | 12 | 2.03 |
| Nolichucky Shale | | | | |
| a | 18 | 67 | 15 | 17.11 |
| b | 20 | 72 | 26 | 13.33 |
| Pumpkin Valley Shale | | | | |
| a | 18 | 69 | 13 | 2.92 |
| b | 28 | 61 | 11 | 12.43 |

[a]The letters a and b indicate analyses on two batches of shale prepared independently. Particle sizes were determined by the Microtrac method so that aggregates of primary particles are registered as single particles.

Source: Lee et al. 1987.

Table 4. Summary of particle-size distributions after geochemical fractionation of pulverized shales[a].

| | Size distribution (wt %) | | | |
|---|---|---|---|---|
| | 180-53 μm | 53-2 μm | 2-0.2 μm | <0.2 μm |
| Chattanooga Shale | 1 | 64 | 26 | 9 |
| Pierre Shale | 1 | 31 | 19 | 50 |
| Green River Formation | 1 | 54 | 14 | 32 |
| Nolichucky Shale | 1 | 49 | 21 | 30 |
| Pumpkin Valley Shale | 7 | 63 | 18 | 12 |

[a]Treatment to disperse the shales assures that the distribution is of primary particles, not aggregates.

The Chattanooga Shale consists of thin beds rich in silt-size (0.02-0.04 mm) detrital quartz grains alternating with a clay- and organic-rich matrix to create laminae 0.01-0.03 mm thick. The Chattanooga Shale has a relatively low surface area (4.6 $m^2/g$) for its moderately high clay content (35 wt %, sum of 2-0.2 and <0.2 μm fractions, Table 4), suggesting that extensive compaction and cementation of the particles has occurred. Microscopic analyses support this hypothesis and also indicate that the micropores are filled with organic matter. Güven et al. (1988) found that the illite particles, the predominant clay in this shale, were coated with an iron oxide. Iron oxide increased in abundance upon heating in air at 600°C for 24 h, probably a result of the oxidation of pyrite. The implications of the presence of pyrite and organic matter are presented in Sect. 5.

The loosely packed nature of the Pierre Shale was indicated by the high surface area (23 $m^2/g$) and clay content (69 wt %). Micropores and fractures, commonly observed in intact samples, often have carbonates present in them. These openings would probably be closed under natural water-saturated conditions because of swelling of the smectite clay (59 wt %) in the sample.

The Green River Formation, selected as the carbonate end-member shale, also contains a substantial quantity of organic matter (13 wt %). The sample was structurally competent and had a low surface area (2 $m^2/g$) for the relatively high clay content (46 wt %). The organic matter, which appeared to be more liquid like than the solid macerals found in the Chattanooga Shale, was concentrated in laminae but also tended to fill the micropores and coat the mineral particles. This feature resulted in the hydrophobic behavior of the pulverized shale in aqueous suspensions.

The illitic shales (Nolichucky and Pumpkin Valley Formations) have moderate surface areas (15 $m^2/g$) and (13 $m^2/g$), respectively, for their clay contents. The carbonate in the Nolichucky Formation typically occurs as secondary calcite filling fractures, although some detrital dolomite and calcite were also observed. Many of the fractures have a stair-step configuration. The Pumpkin Valley Shale is somewhat more laminated with layers of detrital grains separated by organic- and clay-rich laminae.

## 3. GROUNDWATER CHEMISTRY

The chemistry of groundwaters is critical to the performance of a waste isolation system. The parameters pH, redox state, and concentrations of major and minor cations and anions will influence several performance features. For example, the corrosion of canisters for HLW or other containers for low-level waste (LLW) or hazardous wastes will be controlled by the groundwater chemistry (especially pH, salinity, and redox state). The dissolution rate of waste forms will also be at least partially controlled by groundwater chemistry. Once contaminants are dissolved, their mobility will be a strong function of the groundwater chemistry. Sorption reactions are strongly dependent on the pH, redox state, and anion composition of groundwaters. High concentrations of cations may compete for adsorption sites or complexing agents, thus affecting sorption behavior. It is important to address these issues by determining the potential range of groundwater compositions in a disposal site. With the elevated temperatures associated with HLW isolation, it is important to perform experiments and sensitivity modeling to estimate the changes that may occur in groundwater chemistry as a result of rock-water interactions. For low-temperature systems, where man-made materials such as concrete are used, large changes in pH, [Ca], [$\Sigma CO_3$], etc., can occur and should be investigated (Jefferies and Wisbey in press).

The characterization of groundwaters associated with shales was addressed in three ways. First, a literature survey of groundwaters in shale terrains was conducted (Von Damm 1987). Second, experiments to determine rock-water interactions were performed (Von Damm and Johnson 1987). Third, a geochemical model was used to perform sensitivity calculations (Von Damm and VandenBrook 1988).

Von Damm (1987) obtained over 600 analyses of groundwaters from depths of 61 to 3627 m through a search of the literature and the U.S. Geological Survey WATSTORE data base. Analyses were screened for completeness and charge balance before being included in the final data set for analysis. The groundwaters were grouped into four broad

geographic types: (1) Gulf Coast, (2) Northern Great Plains (only waters from the Pierre and Bearpaw Formations were included), (3) Green River (only waters from the Green River Formation were included) and, (4) Midcontinent. Table 5 summarizes the chemical features of these

Table 5. Summary of groundwater compositions for selected shales

| | Gulf Coast | Pierre and Bearpaw | Green River | Mid-continent |
|---|---|---|---|---|
| Maximum depth (m) | 1834.9 | 701 | 3627.1 | 1895.9 |
| Number of formations | 9 | 2 | 1 | 11 |
| Number of samples | 114 | 54 | 249 | 169 |
| pH | 5.9-9.4 | 7.0-8.7 | 7.3-10.9 | 6.7-9.4 |
| Alkalinity (meq/L) | 0.03-23.6 | 5.89-20.0 | 2.88-304. | 2.20-21.6 |
| Constituent (mg/L) | | | | |
| Ca | 1-1996 | 3.9-688 | 0.7-1496 | 0.8-508 |
| Mg | 0.2-559 | 1.3-160 | 0.2-369 | 0.2-190 |
| Na | 1.8-73025 | 63-18009 | 78-20010 | 2.3-1800 |
| K | 0.2-259 | 2-220 | 0.3-349 | 0.2-62 |
| Cl | 0.7-120008 | 5.9-28008 | 1-33999 | 0.5-2599 |
| $SO_4$ | 0.2-2602 | 0.8-1997 | 3-5395 | 0.8-3101 |
| $SiO_2$ | 0.2-56 | 4-43 | 2-28 | 1-25 |

Source: Von Damm 1987.

waters. The compositions of the waters show a wide range and typically overlap for some constituents. Generally, the waters are Na-Cl dominated, although some exceptions do occur. No chemical trends with depth were identified, even when a single formation was considered. Constant molar ratios of Na:Cl (1:1) and Ca:Mg (≈2:1) over a range in total concentration suggest that halite and carbonate dissolution may have played a role in the development of the current chemical composition. Calculations with the geochemical model EQ3NR (Wolery 1983) indicate the waters are now undersaturated with respect to halite

and, in most cases, with respect to calcite and dolomite. The waters are calculated to be supersaturated with respect to silica phases. Limited data on aluminum concentrations and redox-sensitive elements prevented a detailed analysis of aluminosilicate saturation indices or redox state. Batch rock-water experiments were performed by using 12 shales in distilled water at 20°C and 100°C for a period of approximately 40 d (Von Damm and Johnson 1987). Mineralogical changes and solution compositions were determined at the end of the tests. The predominant anion in the final solutions was generally sulfate. Although the test vessels were purged with nitrogen, anoxic conditions could not be maintained throughout the tests, so the elevated sulfate concentrations are probably a result of the oxidation of pyrite in the shale samples. Sodium or calcium was usually the predominant cation in the reacted waters. Final pH values were acidic to neutral (6.5-8.2 for 20°C tests, 3.4-7.7 for 100°C tests) and apparently were controlled by the presence or absence of sufficient calcite or dolomite to offset the oxidation of pyrite. Mineral alterations identified included the loss of calcite and pyrite and the appearance of an Fe-oxide, consistent with the above hypothesis. Calculations using EQ3NR also support this result and suggest potential considerations for waste isolation performance (see Sect. 5).

To complement the experimental results and literature survey results, Von Damm and VandenBrook (1988) modeled the irreversible reaction of two shales with groundwaters representative of the shale formations. Illite- and smectite-rich shales were modeled from ambient temperatures (<15°C) up to 250°C with several different assumptions and constraints (see Von Damm and VandenBrook 1988 for details). The results are summarized in Tables 6 and 7. As expected with the assumption of equilibrium, the calculations illustrate that the presence of even small amounts of a reducing phase (organic matter, pyrite, etc.) caused the system to become reducing (compare initial and final values for Eh and log $f_{O_2}$. Generally, the illite-rich system evolved to more acid conditions than the smectite-rich system, although the final mineralogy was similar, especially at the higher temperatures.

Table 6. Summary of minerals calculated to be produced during reaction path modeling between selected shales and shale groundwaters at a water/rock ratio of ≈0.15

| Shale | T (°C) | Final equilibrium mineral assemblage[a] (listed in decreasing quantities) |
|---|---|---|
| Pumpkin Valley | 250 | Quartz, illite (muscovite), calcite, Ca-smectite, albite, pyrite, 14Å-daphnite, (trace of graphite, Rekjanes-smectite, strontianite) |
| Pierre | 250 | quartz, graphite, calcite, Ca-smectite, 14Å-daphnite, pyrite, illite (muscovite), dolomite, siderite, paragonite, (trace of Rekjanes-smectite) |

[a]See Table 1 for initial mineral assemblages.
Source: Von Damm and Vandenbrook 1988.

Table 7. Summary of solution characteristics calculated to occur during reaction path modeling between selected shales and shale groundwaters at a water/rock ratio of ≈0.15

| | Pumpkin Valley (initial) | Pumpkin Valley (final) | Pierre (initial) | Pierre (final) |
|---|---|---|---|---|
| T (°C) | 13.5 | 250. | 10.5 | 250. |
| P (bars) | 1. | 40. | 1. | 40. |
| pH | 5.6 | 5.5 | 7.9 | 6.1 |
| log $f_{O_2}$ | -1.3 | -39. | -74. | -38. |
| Eh (V) | 1.0 | -0.35 | -0.25 | -0.4 |
| log molal | | | | |
| $\Sigma CO_3^{2-}$ | -4.5 | -0.5 | -1.8 | -0.2 |
| $\Sigma C$ | -5.5 | -2.9 | -1.8 | -0.08 |
| $\Sigma SO_4^{2-}$ | -1.8 | -2.7 | -3.5 | -2.7 |
| $\Sigma S^{2-}$ | -142. | -4.6 | -5.0 | -4.2 |
| $\Sigma S$ | -1.8 | -2.7 | -3.5 | -2.7 |
| Na | -0.3 | -0.3 | -1.3 | -1.3 |
| K | -4.5 | -0.5 | -4.1 | -3.1 |
| Ca | -2.8 | -2.8 | -4.0 | -4.2 |
| Mg | -1.9 | -4.1 | -4.4 | -6.0 |
| Al | -3.4 | -4.1 | -7.6 | -5.4 |
| Fe | -3.0 | -3.0 | -13.4 | -5.4 |
| Mn | -4.8 | -150. | -6.4 | -66. |
| Si | -4.3 | -2.3 | -4.3 | -2.2 |

Source: Von Damm and Vandenbrook 1988.

Secondary zeolites were predicted to form only in the illitic system, while smectites and "illite" (muscovite was assumed to be an analog for illite because of a lack of thermodynamic data for true illite) formed in the smectitic systems. Rather than providing absolute predictions of the behavior of actual rock-water systems, these calculations illustrate the utility of geochemical models for evaluating geochemical conditions, especially when their use is complemented with data from field and experimental investigations.

# 4. RADIONUCLIDE SORPTION

The potential for the sorption of contaminants by the minerals and organic matter in shales is one of their most desirable features for waste management (Hustrulid 1982; Isherwood 1981; Krauskopf 1986, 1988; Lee and Tank 1985). Reactions that are important to the retardation of elements include ion exchange, precipitation, adsorption, complexation, and oxidation-reduction. In shales and clay-rich rocks, it is likely that ion exchange and adsorption will predominate, although oxidation-reduction with accompanying precipitation could also be an important retardation mechanism for redox-sensitive elements such as uranium and technetium.

A series of scoping tests was completed to begin to identify parameters that are important to the sorption behavior of shales. The parameters studied included water/rock ratio (W/R), pH, contact time, groundwater chemistry, and heat treatment of shales. The five shales (see Sect. 2) were used with three different synthetic groundwaters. The three solutions were designed to represent the compositional ranges found by Von Damm (1987): (1) a brine solution (46 g/L Na, 0.4 g/L K, 2.8 g/L Mg, 12 g/L Ca, 1.2 g/L Sr, 101 g/L Cl, 0.7 g/L Br, pH = 5); (2) a 100-fold dilution of the brine solution; and (3) 0.03 mol/L $NaHCO_3$ (representative of waters from the Green River Formation). The sorption ratios (Rs, mL/g) were highly dependent on the conditions of the experiments and details can be found in Meyer et al. (1987, 1988) and Ho (1988).

Figure 2 summarizes the results of the sorption tests for cesium. The sorption ratios (Rs, mL/g) were sorted from low-to-high values and plotted against an arbitrary sample number. The data include results from tests with varying pH, initial concentration of Cs, W/R ratio, contact time, and solution chemistry. The two plateau regions generally indicate Rs values from tests using the brine solution (lower Rs) vs tests with the more dilute solutions (higher Rs). The Chattanooga Shale was not tested under all conditions because of significant pH excursions during the tests. Cesium is generally highly sorbed by all the shales.

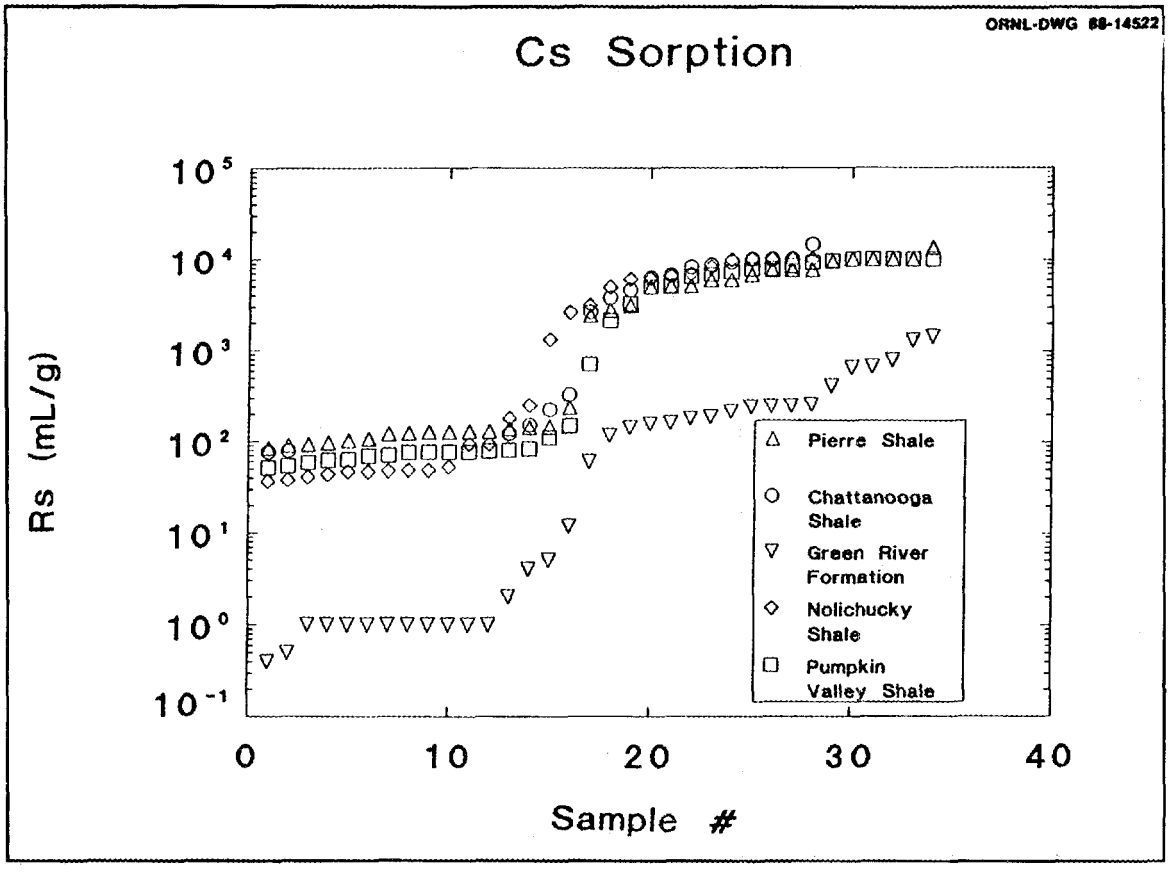


Fig. 2. Sorption data (Rs, mL/g) for cesium on selected shales. Source: Meyer et al. 1987, 1988; Ho 1988.

Sorption is reduced in the brine solution compared to that in the more dilute solutions, a behavior consistent with an ion-exchange mechanism. The Green River Formation gave the lowest Rs values, while values for the other shales were approximately the same.

Figure 3 illustrates the data for the sorption of strontium onto the various shales. The data are presented in the same manner as in Figure 2. For Sr, little to no sorption occurred in tests with the brine solution. The Rs values are generally lower by a factor of approximately 10 than those for cesium. As with cesium, the Green River Formation has the lowest Rs values. The Pierre Shale, with its higher smectite content, tended to have higher Rs values than the more illitic shales.

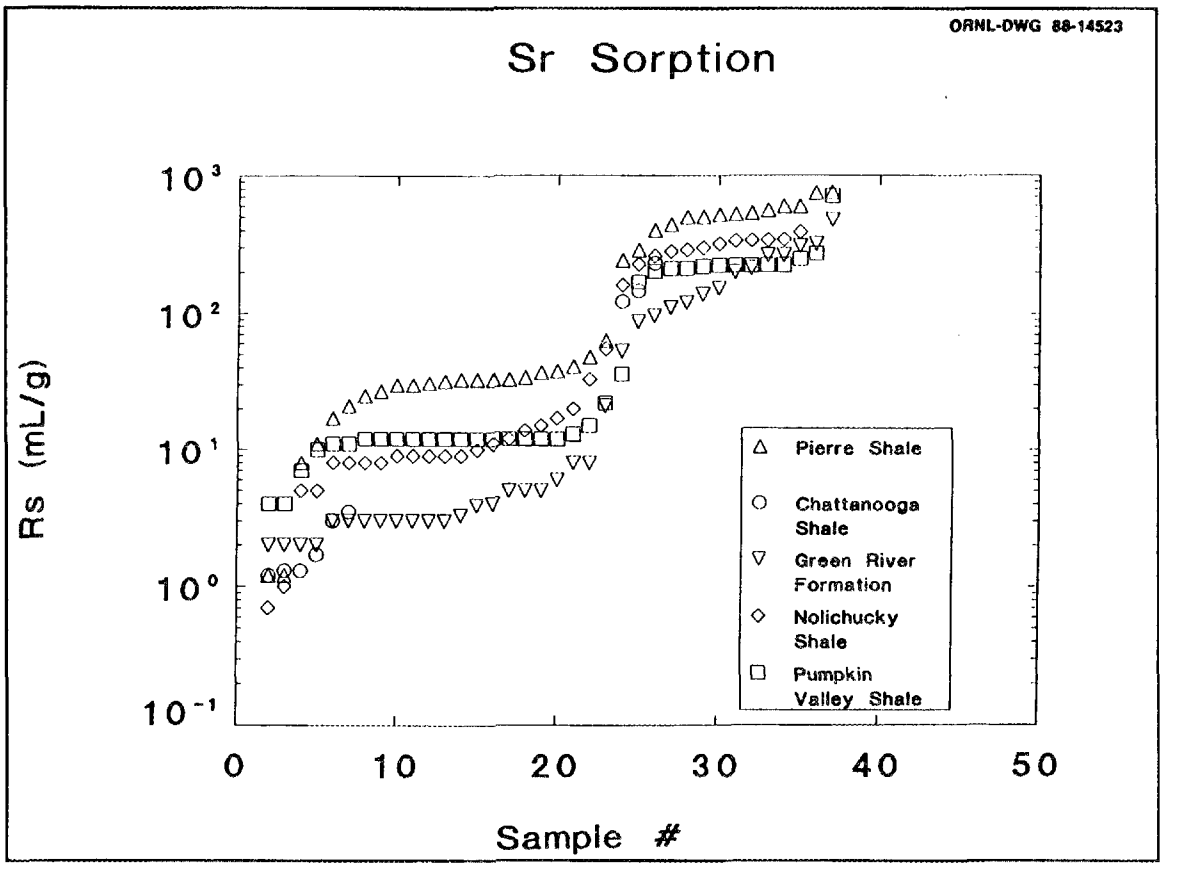


Fig. 3. Sorption data (Rs, mL/g) for strontium on selected shales. Source: Meyer et al. 1987, 1988; Ho 1988.

Technetium Rs values ranged from 0 to 10 mL/g on all shales except for the Chattanooga Shale, which had a few values from 10-100 mL/g and two determinations with Rs values greater than 100 mL/g. The sorption may have occurred on either the pyrite or organic matter in this shale, or perhaps on the clay minerals, because of the low pH values generated during some of these tests (as low as ≈3-4). Heat treating the Chattanooga Shale to decompose the organic matter decreased Rs values, while extracting the organic matter with solvents prior to the sorption tests generally increased Rs values. The explanation for this behavior is unknown at this time and additional experiments will be necessary to draw any firm conclusions on the behavior of Tc in shales.

Experiments with uranium (added as $UO_2^{2+}$) were complicated by apparent precipitation as a result of pH effects and interactions with

the shales. In general, Rs values were similar for the various shales, and most were 100 mL/g or less. A few determinations were made for neptunium (as $NpO_2^+$). The behavior was similar to that of cesium in that sorption was significantly less (by a factor of ≈10) in the brine solution. Rs values for the dilute solutions were generally 100-2000 mL/g, although the Pumpkin Valley Shale had values less than 100 mL/g.

## 5. DISCUSSION

The data obtained thus far on the mineralogy, groundwater chemistry, and sorption behavior of shales do not allow quantitative comparisons between the various shales investigated. Rather, the analyses to date suggest areas of research that require further elucidation prior to detailed assessments.

More work is needed on the mineralogical aspects because of the broad range of compositions found in shales. In addition to basic characterization, it would be useful to investigate the nature of trace elements found in shales. For example, the Chattanooga Shale is rich in uranium (Bell 1978) and some preliminary work (Lee et al., ORNL, personal communication) suggests that the uranium is located within specific phases (detrital silicates, fossiliferous phosphates, etc.) rather than being in association with clays and organic matter. Additional work such as this, as well as other studies on the behavior of uranium in argillaceous rocks, would be beneficial (see, for example, Goldhaber et al. 1987, Hoeve and Quirt 1987, Meunier et al. 1987, Robbins 1978, Shirvington 1983). The stability of smectite remains an issue although much work has already been done (Eberl 1970, Eberl and Hower 1976, Yau et al. 1987). It appears that the transformation will be quite slow at low temperatures and will be an issue only in the vicinity of waste packages in an HLW repository with high waste loadings. Again, natural analog studies may provide significant insight into clay stability under geologic conditions and over time periods not possible through experimentation (Leoni et al. 1984). Additional work on the characterization of organic matter is also critical. Güven et al. (1988) and Ho (1988) describe the nature of organic material in some of the end-member shales studied. Some of the organic compounds identified in the kerogen of shale are known to form carboxylic acids through rock-water interactions (Eglington et al. 1985, Kawamura and Kaplan 1987). These acids could increase the solubility and mobility of some metals (Drummond and Palmer 1986). The organic matter also may provide a sink for redox-sensitive elements such as

uranium (Nakashima et al. 1987), and additional work would be desirable. Clay-organic interactions have also been described that could impact the behavior of these systems (Gibbons and Soundararajan 1988).

The range of groundwater compositions in shales is large and commonly overlaps between various shales. The presence of pyrite in shales could be deleterious if oxidizing conditions were to prevail. Acidic waters could be generated that would tend to enhance the corrosion of metallic containers and the solubility of elements that tend to hydrolyze. However, if sufficient carbonate is present, the trend toward acidic conditions would be mitigated. Also, if conditions remain anoxic enough to stabilize the pyrite, the tendency toward oxidation-driven acid formation would not occur. Cleveland et al. (1983a, 1983b) and Rees et al. (1985) investigated the behavior of Pu, Np, and Am in various groundwaters and found that a shale groundwater from the Pierre Formation consistently resulted in the lowest steady-state concentrations of these elements. They attributed this behavior to the high concentration of sulfate in this water. It is not clear if the high sulfate in the Pierre Formation results from the oxidation of pyrite as found in the experiments of Von Damm and Johnson (1987) or if some other mechanism is responsible. Fisher (1987) has shown that substantial concentrations of organic acids occur in many deep subsurface waters. Measurable quantities of organic acids also were generated in the rock-water tests (100°C only) of Von Damm and Johnson (1987). Further attention should be directed toward shale terrains because of the potential for these organic acids (e.g., acetate) to increase the solubility and mobility of certain metals. The results of these studies indicate that further work on the ranges of groundwater compositions likely to be encountered in shales is necessary and that possible controls on the solution chemistry need to be elucidated.

Available data indicate that the sorption of ion-exchangeable cations will be quite strong, except in groundwaters of high ionic strength. Other elements (Tc, U, and Np) will have sorption behavior highly dependent on both the mineralogy of the particular shale and the chemistry of the associated groundwaters. Parameters such as contact

time, W/R ratio, and thermal alteration may play a significant role in the sorption behavior. As discussed above, the role of organic matter needs to be investigated further. Ho (1988) found that extracting organic matter from the shales and then performing sorption tests resulted in substantial changes in Rs values. Without tests designed to establish the sorption mechanisms in these complex systems, quantitative comparisons between various shales will be difficult.

The information obtained through SERP suggests that shales have geochemical attributes favorable for the isolation of HLW in a repository. However, significant additional work would be required to begin to quantify these attributes for use in more specific assessments. The data can also be used to support analyses of waste management systems for LLW and perhaps hazardous chemical waste, as the hydrologic and geochemical parameters of interest are similar.

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