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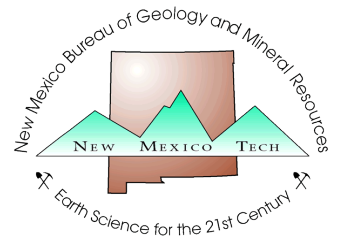
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The role of clay minerals in disposal and storage of hazardous materials

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Introduction

Hazardous materials in New Mexico, both stored and disposed of, are far too numerous to list here. However, it is certain that greater care of these materials must be taken in the near future. Most of New Mexico's population live in areas with a relatively shallow ground-water table (within 200 ft of the surface; Fig. 1) and in areas adjacent to major streams. With this concentration of people and the relative scarcity of water, significant contamination is possible from landfills, lagoons, spills, leakage from storage tanks, and other sources. Even in regions of low precipitation such as New Mexico, some leachate from landfills is formed, usually related to intense precipitation events (Flawn, 1970; Houghton, 1972; Stone, 1984). Appeals for updating siting regulations for storage and disposal of hazardous materials that might contaminate ground water (Longmire et al., 1981; Wilson, 1981; Hawley, 1983; Stone, 1984) have largely gone unnoticed, especially outside the Albuquerque metropolitan area.

The U.S. Environmental Protection Agency (EPA) has listed 129 priority pollutants (Keith and Telliard, 1979) and is currently considering banning land burial for 37 organic solvents (Table 1) because of their potential detrimental effects on ground water. The maximum permissible concentration of these solvents in ground water (which is being determined currently by the EPA) may be less than one part per billion, and some are not only toxic, but known carcinogens as well (George et al., 1985). Thus, the design of disposal sites and even holding tanks for hazardous materials, particularly for these solvents, is crucial to the protection of ground water.

The ability of soil materials as primary or secondary agents to retard movement of various kinds of hazardous materials, including these organic solvents, must be considered. Clayey materials are widely used as liners in landfills, the primary means of containment. As one of the most active parts of soil and rock units, clay minerals also serve as the secondary line of defense in the attenuation of hazardous substances. The purpose of this report is to explore current knowledge of the effect of clay minerals on the more mobile hazardous materials, particularly in regard to ground-water pollution.

Discussion

The preferred containment media for solid wastes in New Mexico have been thick clay-rich rocks with low permeability and high chemical-sorption properties (Longmire et al., 1981). If engineered disposal sites are developed, they commonly are constructed principally of locally occurring smectitic clay-bearing rocks or artificially emplaced clay barriers of Wyoming bentonite containing sodium smectite. However, these clay minerals expand in water and can undergo relative expansion or collapse due to replacement of water by other solvents, cation exchange, or increasing ionic strength at the clay-solvent interface (Griffin et al., 1985). If relative collapse and flocculation of the clay structures occur, the result will be cracks and much higher permeability.

Physical containment

Clay material in containment structures for hazardous materials offers several advantages over many other materials. Clay linings can be relatively inexpensive to construct, yet they are relatively thick and have low permeability to fluids, particularly over longer periods of time. However, even if clay material is not the barrier or one of the primary barriers to movement of pollutants, soils and bedrock containing clay minerals can provide attenuation for additional protection.

Liquid hazardous materials, whether stored or occurring as waste or leachate, can escape containment as a result of several natural and manmade factors. The more mobile liquids can move along joints, desiccation cracks, freeze-thaw cracks, root traces, animal burrows, permeable zones, faults or similar tectonic cracks, as well as through mine subsidence features or existing wells and mine shafts. These avenues of movement can be plugged with relative ease, at least for fairly short periods of time, by adequate packing or repacking of the site.

Misunderstandings about the effectiveness of clay liners remain. Some researchers ☞
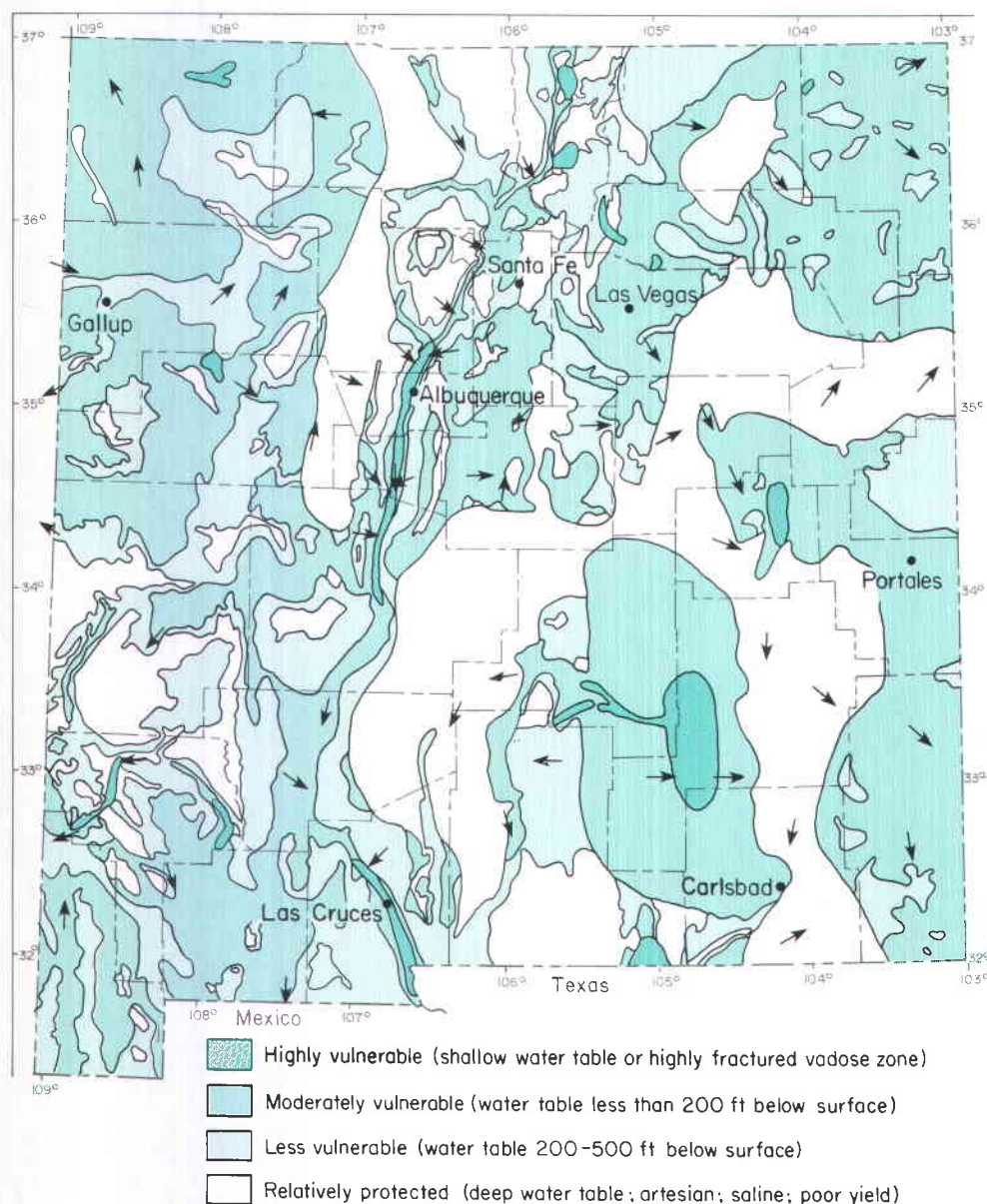

FIGURE 1—Relative vulnerability of New Mexico aquifers to contamination from various surface discharges (after Wilson, 1981).

Highly vulnerable (shallow water table or highly fractured vadose zone)

Moderately vulnerable (water table less than 200 ft below surface)

Less vulnerable (water table 200–500 ft below surface)

Relatively protected (deep water table; artesian; saline; poor yield)

have stated that a "cake or impervious layer of lightly packed bentonite molecules . . . usually 3 mm thick . . . is an effective barrier to water movement since the permeability of the filter cake can be as low as 10^{-9} cm/sec" (Ressi and Cavalli, 1985, p. 336). However, even whether or not a clay liner is initially water saturated can have an effect on containment. Unsaturated clayey materials with a preferential orientation of the clay minerals may have linear voids that promote rapid movement of liquids in those directions. In addition, many landfill leachates, particularly the organic solvents, do not act on clay minerals in the same manner as water. Surface diffusion, phase transitions, and syneresis beneath the water table may cause unstable conditions or enhance the mobility of the ions in the solute-clay system (Lundgren and Soderblom, 1985). In syneresis (the shrinkage and dewatering of a colloidal sediment due to aggregation of particles by chemical attraction) the clay colloid becomes flocculated and develops cracks. These cracks are very common in nature as mineral fillings, slickensides, and "joints" in clay mineral-rich rocks; they are similar to, but distinct from, desiccation cracks. Expansion of the clay mineral structure also can disrupt clay liners and, after a change in pore-fluid chemistry, may be followed by a relative collapse of the clay structure, resulting in higher permeability.

Some disposal (or storage) sites using clay materials and designed with the best information available only a few years ago have proven unable to contain certain toxic materials. One of the best examples is the hazardous-waste-disposal facility near Wilsonville, Illinois. A disposal company began operating a 130-acre landfill in November 1976. The operation was a trench-and-fill procedure that relied on the indigenous glacial till containing illite and mixed-layer clay minerals for natural attenuation of the leachate. In February 1982 the Illinois Environmental Protection Agency discovered through routine monitoring of wells at the site that migration of organic pollutants as far as 50 ft from the trenches had occurred in a 3-year period; the migration rates were 100 to 1,000 times faster than predicted. In March 1982 a court ruled that all wastes must be exhumed and removed from the site. The removal began in September 1982 and continued until February 1986.

Reports by the Illinois State Geological Survey about the site from 1982 to the present point out that many of the problems were not fully realized until exhumation of the site began, which revealed changes in the soil, clay-rich glacial till, and bedrock (Griffin et al., 1985). The reports concluded that the higher-than-predicted migration rates could be accounted for by the differences between laboratory and field measurements of hydraulic conductivity. These differences appeared to be primarily due to the inability of small laboratory specimens, whether "undisturbed" or recompacted, to simulate field conditions, such as flow through relatively large joints or partings present in natural materials.

A two-layer concept of containment, which uses clays with other materials such as sheets of high-density polyethylene, has been developed to further seal some sites (Ressi and Cavalli, 1985). High-density polyethylene can have a permeability as low as 10^{-12} cm/sec (Ressi and Cavalli, 1985). However, the crucial point is that all containment barriers will leak eventually (Roy and Griffin, 1986), and a completely impermeable barrier to the movement of solutes from the sites cannot be built.

Chemical containment

Chemical activity between pollutants and the confining or surrounding materials is significant. Many reactions involve little or no interactions with clay minerals. Those non-clay reactions include oxidation-reduction, particularly in the vadose zone (Garrels and Christ, 1965; Griffin and Shimp, 1978); hydrolysis, when dissolved contaminants react with water (Hem, 1970); buffering of the ground-water pH, which generally ranges from 6.5 to 8.5 in New Mexico (Longmire et al., 1981); microbial degradation (Griffin et al., 1978; Griffin and Roy, 1986); dilution in ground water (Griffin and Roy, 1986); and volatilization of the more vaporizable organic contaminants in ground water. In the case of volatile pollutants, as in the loose valley fill of the Rio Grande, an upward movement toward the above-ground atmosphere has been noted (Marrin and Thompson, 1984).

The ion-exchange capacity of clay minerals for metal cations and anions and organic molecules is one of the best known attenuating reactions (Grim, 1968; Griffin and Shimp, 1978; Mortland, 1980). It is the reversible interchange between compounds, one of which commonly, but not exclusively, occurs in the aqueous environment. Cation exchange is the dominant ion exchange affecting clays as well as soils, sediments, and weathered rocks because of the net negative charge carried by these particles; however, anion exchange with particular clay minerals is also possible. The ion exchange capacities typical of New Mexico's clayey materials range up to 150 milliequivalents (meq) per 100 g

TABLE 1—The solubility of the 37 organic solvents proposed to be banned from land disposal, soil-water partition coefficients (K_{oc}), and their mobility classification (after Griffin and Roy, 1985). a = miscible in water; b = no n-octanol data known.

Solvent	Solubility (mg/L)	log K_{oc} (from solubility) (eq. [1])	log K_{oc} (from K_{ow}) (eq. [5])	Mean K_{oc}	Mobility classification
1. Acetone	∞	—[a]	0.015	1	Very highly mobile
2. Benzene	1,780 (20°C)	1.93	2.01	97	Highly mobile
3. n-Butyl alcohol	70,800 (30°C)	0.94	1.02	10	Very highly mobile
4. Carbon disulfide	2,940 (20°C)	1.80	—[b]	63	Highly mobile
5. Carbon tetrachloride	800 (25°C)	2.15	2.44	232	Medium mobility
6. Chlorobenzene	448 (30°C)	2.31	2.57	318	Medium mobility
7. o-Dichlorobenzene	150 (20°C)	2.62	3.06	898	Low mobility
8. m-Cresol	21,800 (20°C)	1.26	1.55	27	Very highly mobile
9. o-Cresol	24,500 (20°C)	1.23	1.24	17	Very highly mobile
10. p-Cresol	19,400 (20°C)	1.29	1.27	19	Very highly mobile
11. Cyclohexanone	50,000 (30°C)	1.04	0.96	10	Very highly mobile
12. Ethyl acetate	85,300 (20°C)	0.89	0.91	8	Very highly mobile
13. Ethyl benzene	150 (20°C)	2.60	2.87	622	Low mobility
14. Diethyl ether	60,050 (25°C)	0.99	0.96	9	Very highly mobile
15. Isobutyl alcohol	87,000 (20°C)	0.89	0.92	8	Very highly mobile
16. Methanol	∞	—[a]	-0.23	<1	Very highly mobile
17. Methylene chloride	13,200 (20°C)	1.40	—[b]	25	Very highly mobile
18. Methyl ethyl ketone	270,000 (20°C)	0.58	0.55	4	Very highly mobile
19. Methyl isobutyl ketone	19,000 (20°C)	1.30	1.42	24	Very highly mobile
20. Nitrobenzene	2,000 (20°C)	1.90	1.79	67	Highly mobile
21. Pyridine	∞	—[a]	0.84	7	Very highly mobile
22. Tetrachloroethylene	150 (20°C)	2.60	2.41	303	Medium mobility
23. Trichloroethylene	1,000 (20°C)	2.09	2.22	152	Medium mobility
24. 1,1,1-Trichloroethane	700 (20°C)	2.19	—[b]	155	Medium mobility
25. Toluene	500 (20°C)	2.28	2.43	242	Medium mobility
26. m-Xylene	146.0 ± 1.6 (25°C)	2.61	2.91	610	Low mobility
27. o-Xylene	170.5 ± 2.5 (25°C)	2.57	2.55	363	Medium mobility
28. p-Xylene	156.0 ± 1.6 (25°C)	2.59	2.87	565	Low mobility
29. Trichlorofluoromethane (F–11)	110 (25°C)	2.68	—[b]	479	Medium mobility
30. 1,1,2-Trichloro-1,2,2-trifluoroethane (F–113)	170 (25°C)	2.57	—[b]	372	Medium mobility
31. Chlorodifluoromethane (F–22)	3,000 (25°C)	1.79	—[b]	62	Highly mobile
32. Dichlorofluoromethane (F–21)	9,500 (25°C)	1.48	—[b]	30	Very highly mobile
33. Dichlorodifluoromethane (F–12)	280 (25°C)	2.43	—[b]	269	Medium mobility
34. Chloropentafluoroethane (FC–115)	60 (25°C)	2.85	—[b]	708	Low mobility
35. 1,2-Dichlorotetrafluoroethane (F–114)	130 (25°C)	2.64	—[b]	437	Medium mobility
36. 1,1,1,2-Tetrachloro-2,2-difluoroethane (R–112a)	100 (25°C)	2.71	—[b]	513	Low mobility
37. 1,1,2,2-Tetrachloro-1,2-difluoroethane (F–112)	120 (25°C)	2.66	—[b]	457	Medium mobility

for cations and up to 31 meq/100 g for anions (Longmire et al., 1981).

Sorption is one of the prominent containment reactions used in the attenuation of organic pollutants. Of most interest is the fixing of certain sorbed ions by clay minerals in those states that are nonexchangeable or exchangeable only with great difficulty. Although activated carbon and synthetic resins are used in wastewater treatment, coal char and clay minerals are also known to immobilize leachates (Griffin et al., 1978) and have been used for this purpose in landfills (Longmire et al., 1981) because of their cost effectiveness. Improvement of the adsorptive capacity of clays by treatment with several chloride salts of aliphatic amines has been explored with positive results by Wolfe et al. (1985).

Cation and dipole interactions in montmorillonite complexes with small polar compounds such as ethanol and acetone are also important (Theng, 1974). In fact, calcium-saturated montmorillonite, common in the clay-rich units in New Mexico, is more effective in adsorption of these solvents than the widely used sodium-saturated (Wyoming bentonite) variety. Similarly, the copper-montmorillonite system may be even more effective than other metal-bearing montmorillonites (Theng, 1974). Thus, it may be effective to "engineer" a clay to build the most efficient barrier to the movement of specific contaminants such as solvents, as suggested by Jarrett and Marwood (1985) and Wolfe et al. (1985).

Organic molecules emanating from hazardous waste sites may be altered and/or neutralized by the catalyic activity of clay minerals. Because of their small size and unusual intercalation properties, clay minerals afford an appreciable surface area for the adsorption of organic molecules and catalysis (Pinnavaia, 1983). The interlameller surface in smectites can be as much as 750 m^2/g, and the size of the exchanging ion is therefore the limiting factor in determining ion loading. Some recent studies on the intercalation of clay minerals with thermally stable, tightly bound cations show that these cations act as molecular props or pillars, keeping the silicate layers separated in the absence of a swelling solvent (Pinnavaia, 1983). In these cases pore sizes can be made larger than some currently used molecular sieves, such as faujasitic zeolites.

Time as a factor in attenuation

In addition to physical and chemical containment, the length of time of containment is important in the attenuation of hazardous materials. Griffin and Roy (1985) classified solvents (Table 1) from "low mobility" to "very highly mobile" (in time) based on the solubility of organic compounds (usually hydrophobic solutes) and soil-water partition coefficients, or the aqueous solubility of organic solutes and soil-water partition coefficients. Another method of determination is the n-octanol-water combination, which has been used for a number of years to estimate

bioaccumulation and has been adapted to predict the mobility of organic solvents in water-saturated soil materials (Briggs, 1973; Karickhoff et al., 1979; Kenaga, 1980; Means et al., 1980; Schwarzenbach and Westall, 1981; Hassett et al., 1983).

Roy and Griffin (1986) predicted how and when some solvents move from a disposal site through time. They approached the problem of predicting the capacity of a disposal site to attenuate potential pollutants by considering ground-water dilution, dispersion, adsorption, hydrolysis, and biodegradation, but they did not include the positive activity of clay minerals. They concluded that some of the solvents listed in Table 1 cannot be adequately removed from the environment but others can, provided that proper facilities are constructed and the movement of solutes from the site is adequately monitored. Griffin and Roy (1986) provide an understanding of some of the mechanisms by which pollutants are attenuated, but most importantly, they point out that the time frame must be considered. As has been shown above, clay minerals are an additional factor involved in that time frame.

Conclusions

The limitation of movement of leachates from landfills, pits, ponds, and lagoons, as well as solutes and solvents from leaking storage tanks, will be of increasing importance to the citizens of New Mexico. Hydrocarbons and brines connected with oil fields pose a pollution problem in large parts of the state. With the EPA promulgating the maximum allowable level of hazardous materials, such as organic solvents, in drinking water and the possible banning of some organic species from landfills, greater care must be taken to ensure adequate safeguards for ground water. Clearly, increased care must be taken in the siting of landfills, disposal facilities, storage tanks, and other possible sources of contamination, but the intelligent use of clay materials as either the primary or secondary attenuation media is also imperative.

Many of the special properties of clay minerals discussed above assist in the attenuation of ground-water contaminants. The use of "engineered" clay materials specially altered to be more effective as barriers to the movement of specific hazardous materials is possible. In order to predict the effectiveness, adequate testing of the indigenous clay-bearing units and any clay materials used as liners is required. These tests should be designed to examine the effects of all hazardous materials, stored or disposed of, as well as leachates that could move from the site into the surrounding area. Also, the materials used for containment must be effective for the length of time necessary to attenuate the hazardous materials to environmentally safe levels; in some cases, this could be hundreds of years. In all phases of disposal or storage of hazardous materials clay minerals can be of great value.

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MINING REGISTRATIONS

(May 1, 1986, through August 19, 1986)

Bureau of Mine Inspection   Energy & Minerals Dept.   2825–E Broadbent Pkwy. NE   Albuquerque, NM 87107

Date and operation	Operators and owners	Location
5-1-86 gold, silver	Operator—Midnight Mine, Goldfields Consolidated Mines Co., P.O. Box 1670, T or C, NM 87901; Gen. Mgr.—Patrick Freeman, 1006 Kopra, T or C, NM 87901, phone: 894–7739; Gen. Supt.—James Ray Nation, General Delivery, Winston, NM, phone: 894–7495. Property owner—Goldfield Consolidated Mines Co.	Sierra County; private land; sec. 1, T12S, R9W; directions to mine: about 4 mi southwest of Chloride up Byers Run; go about 1 mi west of St. Cloud Mill up S. Fork Creek, turn south up Byers Run and go about 2 mi south; the mine is about 0.25 mi west up a small arroyo off Byers Run.
5-1-86 storage vault	Operator—CST Project, P.O. Box 2534, Las Vegas, NM; Gen. Mgr.—Russ Bellin, P.O. Box 8775, Santa Fe, NM 87502–8725, phone: 641–5340; person in charge—F. E. Valencia, same address and phone; Gen. Supt.—Richard Ung, same address and phone. Property owner—Church of Spiritual Technology, 5299 Countain Ave., Ste. 285, Hollywood, CA 90029, phone: (213) 669–8465.	San Miguel County; private land; directions to vault: go 50 mi east of Las Vegas, NM, on NM–65/104 to Trementina School; go past school on NM–65; turn left at cattle crossing on county road 56A and go 13 mi.
5-19-86 gold	Operator—LaPaz Bear Creek Placer, LaPaz Bear Creek, Inc., P.O. Box 17, Pinos Altos, NM 88053; Gen. Mgr.—Joy Merz, same address, phone: 538–9611; person in charge—Leslie Billingsley, same address and phone; Pres.—Dan E. Lewis, LaPaz Mining, Inc., 1803 W. Grant Rd., Tucson, AZ 85745. Property owner—Ruth Ann and Jim E. Rodgers, P.O. Box 111, Silver City, NM 88061.	Grant County; sec. 24, T16S, R14W; directions to mine: turn left at mile 9.4 of Hwy. 15; go 1.1 mi to plant site.
6-27-86 gold, silver	Operator—Big G., Dynapac, Fairway Dr., T or C, NM 87901; Gen. Mgr.—Harold Smith, same address, phone: 894–2593; person in charge—Dene Pierce, 310 Vetter, T or C, NM 87901, phone: 894–7589. Property owner—Harold Smith.	Socorro County; federal land; sec. 13, T9S, R6W; directions to mine: Springtime Campground Rd., between Luna Park and Springtime.
6-27-86	Operator—WIPP Site, U.S. Dept. of Energy, P.O. Box 3090, Carlsbad, NM 88220; Const. Mgr.—U.S. Army Engr. Dist., Albuquerque District Engr., P.O. Box 1580, Albuquerque, NM 87103, phone 766–2732; person in charge—Area Engr., P.O. Box 2346, Carlsbad, NM 88220, phone: 887–0586; Const. Contractor—Brinderson Corp., 19700 Fairchild, Irvine, CA 92715, phone: 885–2197; Const. Contractor—Foley Co., 7501 Front Street, Kansas City, Missouri 64120. Property owner—U.S. Dept. of Energy, P.O. Box 3090, Carlsbad, NM 88220.	Eddy County; federal land; directions to mine: 34 mi south of Carlsbad, NM on NM–285.