EG 137
HWRIC RR 054

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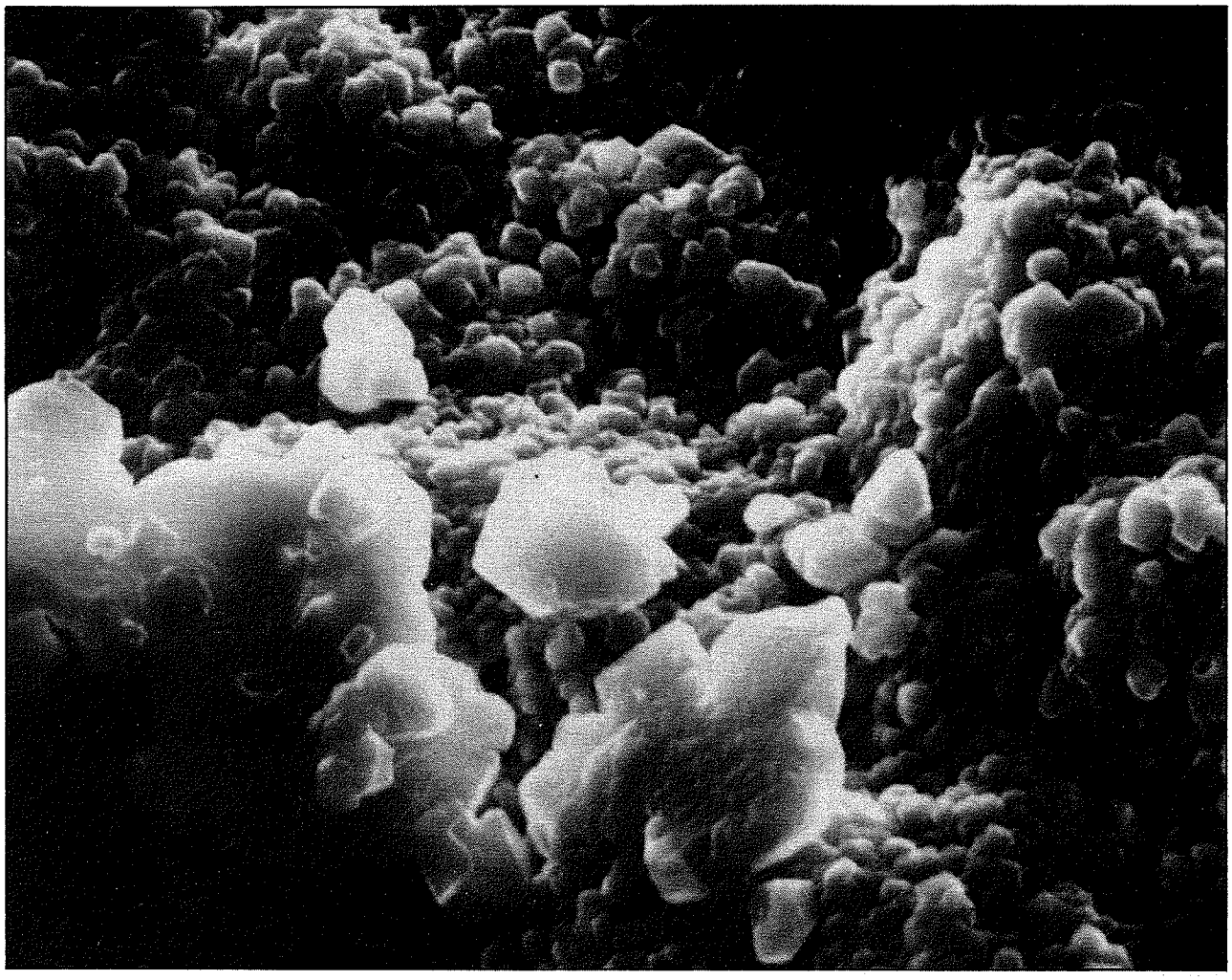

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ENVIRONMENTAL GEOLOGY 137
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Department of Energy and Natural Resources
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Prepared for
Hazardous Waste Research and Information Center
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HWRIC Project 88-066

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Printed by authority of the State of Illinois/1991/1200

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ABSTRACT

Two liquid hazardous wastes, an alkaline brinelike solution and a dilute acidic waste, were mixed with finely ground (<250 μm) rock samples of three injection-related lithologies, sandstone, dolomite, and siltstone. The batch experiments were conducted for 155 to 230 days at 325°K and 10.8 MPa pressure. The pH and inorganic chemical composition of the alkaline waste were not significantly altered after 230 days of mixing. The acidic waste was neutralized by carbonate dissolution and transformed into a nonhazardous waste.

Mixing the alkaline waste with the solid phases yielded several reaction products: brucite ($Mg(OH)_2$), calcite ($CaCO_3$), and possibly a sodium metasilicate. Claylike minerals formed in the sandstone; trace levels of hydrotalcite ($Mg_6Al_2CO_3(OH)_{16}\cdot 4H_2O$) may have formed in the siltstone. Mixing the alkaline waste with a synthetic brine yielded brucite, calcite, and whewellite ($CaC_2O_4\cdot H_2O$). The thermodynamic model PHRQPITZ predicted that brucite and calcite would precipitate from solution in the dolomite and siltstone mixtures and in the alkaline waste-brine system.

After 155 days of solid-liquid contact, the dilute acidic waste had not significantly altered the mineralogical composition of any of the three rock types. The model PHREEQE indicated that calcite was thermodynamically stable in the dolomite and siltstone mixtures, and it was detected in small quantities in the aged-solid samples. The sandstone-waste system appeared to equilibrate with amorphous silica, whereas silica equilibria may not have been attained in the dolomite and siltstone systems.

Computer models like PHRQPITZ and PHREEQE may be useful tools for estimating mineral equilibria in deep-well scenarios, but there is a need to expand the database used in these kinds of calculations. The predicted equilibria must be interpreted with caution.

ACKNOWLEDGMENTS

Partial support of this project was provided by the Hazardous Waste Research and Information Center of Illinois, a division of the Illinois Department of Energy and Natural Resources (ENR). Jacqueline M. Peden was the project officer of ENR Grant No. HWR 88066.

We thank Randy Bergonson of the Cabot Corporation, Tuscola, Illinois, for providing the acidic waste sample. At the Illinois State Geological Survey, Keith M. Mitchell provided valuable technical assistance, Dr. Randall E. Hughes performed the essential mineralogical analyses, and Dr. Jonathan H. Goodwin contributed helpful discussions on zeolites.

INTRODUCTION

Underground injection is a waste management technique whereby liquid wastes are placed into geological formations through specially designed and monitored wells. Geochemical reactions between the wastes and the receiving formation may determine whether injection at a specific site can be considered as waste *storage* or waste *treatment*.

Such interactions have not been extensively studied (Brower et al. 1989). There have been few detailed, laboratory studies of geochemical interactions (Fink et al. 1989, Crocker and Madden 1989, U.S. EPA 1990). The U.S. Environmental Protection Agency critically evaluated the environmental suitability of Class I well injection of hazardous wastes and proposed that untreated wastes be banned from injection (U.S. EPA, 1987, 1988). However, the U.S. EPA has proposed two circumstances whereby operators may petition to obtain a permit to inject waste liquids:

- Using hydrogeologic flow and transport models, the applicant could demonstrate that injected fluids would not migrate upward out of the injection zone or migrate within the injection zone to a point of discharge for 10,000 years. The EPA has interpreted "no migration" as containment for 10,000 years.

- The applicant could demonstrate that a hazardous waste would be transformed into a nonhazardous waste within the injection zone by neutralization (e.g., mixing acids with carbonates), adsorption (e.g., immobilization of hazardous constituents by clay minerals) degradation, and/or other mechanisms.

The second provision was the impetus for this study in deep-well geochemistry.

Because of the inherent complexity of reactions between liquid wastes and subsurface environments, some investigators are using models based on chemical thermodynamics to predict the fate of chemical constituents in injection scenarios. Scrivner et al. (1986) concluded that the fate of injected wastes could be determined by models that use "standard chemical engineering techniques." Opinions differ: Apps (1988) concluded that geochemical modeling of injected wastes has not been adequately tested in the field and the laboratory. He observed that many geochemical models currently available have not been adequately verified under ambient conditions, let alone those associated with deep-well injection.

To contribute to the general understanding of waste transformation in deep-well scenarios was the purpose of the study, which has continued the work of Roy et al. (1989). In the earlier, short-term (15 day) study, dissaggregated core samples were mixed in batch experiments with two liquid hazardous wastes. These experiments included the three common rock types (sandstone, dolomite, and siltstone) that are used in deep-well injection. Sandstone and carbonate represented typical injection formations in Illinois, whereas the siltstone was chosen to represent a confining layer. In the current study, the same rock samples and waste streams were used in long-term (5 to 7 month) batch studies. The liquid phases were then modeled using one of two thermodynamic equilibrium models to predict potential reaction products. Emphasis was given to verifying the predicted reaction products in order to evaluate how well model predictions compared to laboratory observations.

METHODS AND MATERIALS

Interaction studies were conducted in the laboratory. Teflon-lined Parr 600-mL stirred-pressure vessels were used and the procedures given in Roy et al. (Appendix B, 1989) were followed. Finely ground core samples of three injection-related rocks were mixed individually with two different liquid waste samples. A 1:10 solid:liquid ratio (wt/vol) was arbitrarily chosen for this study.

The three rock samples were finely ground to pass a 250-μm sieve to increase the surface area and therefore the potential reactivity of the solids within the time frame of the experiments. The pressure vessels were simultaneously heated to 325°K (52°C) and pressurized to 10.8 MPa (1566 psig) with nitrogen. This temperature and pressure corresponds to an injection depth of approximately 900 meters (2,953 feet). The disposal zones in Illinois range in depth from 469 to 1,684 meters (Brower et al. 1989).

The three types of rock used in this study were the same as those used in the short-term studies: the Mt. Simon Sandstone, the Potosi Dolomite, and the Proviso Siltstone Member of the Eau Claire Formation. Both the Mt. Simon and Potosi are used as injection formations in Illinois, and the Eau Claire Formation is the upper confining zone at two wells (Brower et al. 1989). Stratigraphic descriptions of the cores and the techniques used to prepare them are given in Roy et al. (1989).

The two liquid wastes included an alkaline, brinelike process water from pesticide manufacturing and an acidic (HCl) liquid that was a by-product from the production of a high-purity amorphous silica. The alkaline waste, collected from the injection wells at the Velsicol Chemical Corporation near Marshall, Illinois, was the same sample used in the short-term studies. This waste stream was hazardous, according to Illinois Environmental Protection Agency (IEPA) regulations (1984), because of its high pH and pesticide content. The alkaline waste sample was also mixed 1:1 (vol/vol) with a synthetic brine that had a chemical composition similar to brine samples collected near the injection wells (Meents et al. 1952). The acidic waste, collected from the injection wells at the Cabot Corporation plant near Tuscola, Illinois, was considered hazardous under IEPA regulations (1984) because of its low pH.

When the batch experiments were terminated, each pressure vessel was opened in a nitrogen-glove box, and the pH and oxidation-reduction potential (Eh) of the liquid phase were measured by electrode using standard methods (American Public Health Association 1985). The pH measurements were checked against Environmental Resources Associates (ERA) standards. Instrument calibration was performed in the nitrogen glove box with solutions at 52°C (the temperature of the pressure vessels). The potassium ferric-ferrocyanide solution described by ZoBell (1946) was used as an Eh reference solution (also Wood 1976).

Liquid samples were then collected for chemical characterization. The solution concentrations of Al, As, B, Ba, Be, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Pb, Si, and Zn were determined using a Model 1100 ThermoJarrell Ash Inductively Coupled Argon Plasma Spectrometer (ICAP). Instrument control, automatic background correction, and spectral interference correction were performed using a DEC Micro PDP 11/23 computer. U.S. EPA Method 6010 (1986) was used in quantification. A summary of QA/QC statistics is given in table 1. The detection limits for the ICAP were estimated as three times the standard deviation for each constituent at zero concentration. ICAP detection limits vary with operating conditions, and are particularly sensitive to argon-gas flow rates. Common or typical limits are given in table 1. The QA/QC standards used to verify results included an Interference Check Solution and several other reference samples obtained from the U.S. EPA and Environmental Resource Associates (ERA).

Table 1 Detection limits, percent bias, and coefficients of variation (CV) for each constituent (from QA/QC standards), and the relative percent differences (RPD) associated with samples by ICAP, unless otherwise noted.

Constituent	Common detection limits (µg/L)	QA/QC samples			Sample RPD[c]
		% Bias[a]	%CV[b]	No. of determinations	
Al (aluminum)	27	7.4	4	6	2.80
As (arsenic)	156	4.8	3	5	22.2
B (boron)	15	4.2	4	4	1.60
Ba (barium)	1	3.4	4	6	11.0
Be (beryllium)	1	6.0	7	6	15.6
Ca (calcium)	29	3.4	3	6	2.80
Cd (cadmium)	10	6.0	1	6	[d]
Cl(IC) (chlorine)	200	3.2	1	35	1.75
Cr (chromium)	5	4.7	3	6	6.60
Cu (copper)	2	3.5	3	6	12.9
F(IC) (fluorine)	200	9.1	3	27	7.28
Fe (iron)	1	7.5	8	6	9.50
K (potassium)	792	12.7	17	5	4.60
Mg (magnesium)	16	4.4	5	5	11.4
Mn (manganese)	1	2.7	3	6	1.70
Mo (molybdenum)	16	9.0	6	4	3.70
Na (sodium)	19	6.8	10	5	7.60
Ni (nickel)	30	6.7	7	6	11.0
NO_3(IC) (nitrate)	300	2.8	4	37	4.53
Pb (lead)	45	5.3	3	6	[d]
Si (silicon)	16	6.9	2	4	1.80
SO_4(IC) (sulfate)	300	5.5	2	34	12.6
Zn (zinc)	8	7.3	7	6	3.40

[a] % bias = ((|Measured conc - accepted conc|)/accepted conc) x 100.
[b] % CV = (|Standard deviation|/mean)x 100.
[c] RPD = $(|X_1-X_2|/((X_1+X_2)/2)$ x 100 where X_1 and X_2 are duplicate analyses of the same sample. The values here are the averages of two sets of duplicates.
[d] Concentrations in samples less than detection limit.

The solution concentrations of Cl^-, F^-, NO_3^- and SO_4^{2-} were determined using a Dionex 2110i ion chromatograph, following U.S. EPA Method 300.0 (O'Dell et al. 1984). A summary of relevant QA/QC statistics for these analyses is also given in table 1. The QA/QC standards used included the EPA solutions MINERAL, Nitrate/Fluoride, and the ERA Minerals WasteWater. The detection limits for the four anions were estimated empirically.

After all the free liquid was removed from the reaction vessel and filtered through a 0.45-µm Millipore membrane, the solid phases were dried slowly for 30 to 40 days by placing the pressure-vessel cylinder into a capped glass jar. The caps were periodically removed to facilitate the drying of the residual moisture. The selection of the aging interval was based on preliminary studies that indicated a slow dehydration period was helpful in developing crystalline

solid phases (also Hem and Lind 1983, Lind 1983). The solid phases were characterized (before and after the liquid wastes were added) using X-ray diffractometry (XRD) and a scanning electron microscope equipped with an energy dispersive system (SEM-EDS). The mineral equilibria of the solution phases were estimated using one of two computer-assisted thermodynamic models. This approach (laboratory studies coupled with modeling) was used to identify potential reaction products, and to evaluate how well model predictions compared with laboratory observations.

An Amray 1830 Scanning Electron Microscope (SEM) coupled with a Tracor Northern Energy Dispersive system was used to determine the morphology and composition of the solid phases. The SEM-EDS units were maintained by service contracts with Amray and Tracor Northern. The Amray 1830 was cleaned every 6 months and recalibrated by Amray. The resolution, checked using photographic techniques, was guaranteed (by AMRAY) to be 6 nm.

The Tracor Northern EDS unit operated in concert with the SEM. An area on a sample was excited by an electron beam, causing the emission of X-rays that were collected by the EDS collector and converted from a charge pulse to an amplified voltage pulse. The EDS system then counted, tabulated, stored, and graphically presented spectral data and X-ray map data. These data were used in semiquantitative calculations by software that uses either ZAF (atomic number, absorption, and fluorescence) or Bence-Albee correction factors. The software in the EDS system was calibrated with a copper standard to ensure that all peaks were identified correctly. The samples were sputter-coated with carbon because gold and palladium create spectral interferences. Sputter-coating is a preparatory process in which samples are coated with particulate carbon so that they will conduct an electrical charge. Carbon cannot be detected by the EDS.

The mineralogical composition of the solid phases was determined using a Phillips Norelco diffractometer with copper Kα radiation and a graphite monochromometer at 40 kV and 20 mA. The methods of Hughes and Warren (1989) were followed. Scans were conducted on the whole samples as collected from the pressure vessels, and depending on the composition of the specific sample, on randomly oriented powders (where the arrangement of the particles is random), water-insoluble residues, and oriented aggregates of the less than 2μm-size fraction of the whole sample and acid-insoluble residues. The oriented aggregates (oriented in the sense that the clay-sized flakes tend to be parallel to the substrate) were initially air-dried, then treated with ethylene glycol and heated to 375°C. The mineral phases were identified by comparisons with the data files of the American Society for Testing and Materials Joint Committee for Powder Diffraction, and with the library of standard X-ray diffraction patterns at the Illinois State Geological Survey.

RESULTS

Rock-Alkaline Waste Interactions

The short-term (15 day) studies of Roy et al. (1989) indicated that the major element composition of the alkaline, brinelike waste did not significantly change when mixed with samples of the Mt. Simon Sandstone, Potosi Dolomite, and Proviso Siltstone at 328°K and 11.7 MPa pressure. After 230 days of solid-liquid contact under similar conditions (325°K and 10.8 MPa pressure), the brinelike character of the waste was unchanged (table 2). The apparent increases in sodium and chloride may have been the result of chemical instability of the waste sample during the project and were accentuated by analytical error. However, the solution concentrations of some minor constituents (potassium, silica, sulfate, and nitrate) increased, in some cases by two orders of magnitude.

Table 2 Inorganic chemical composition of the alkaline waste sample before reaction and after contact with the injection-rock samples and a synthetic brine.

	Unreacted waste liquid	Waste +			
		Sandstone	Dolomite	Siltstone	Syn. brine
pH	12.6	12.6	11.6	12.5	12.1
Eh(mV)[a]	+606	+61	+118	+65	+61
Pheno. alk[b]	17,920	19,610	11,030	18,060	12,840
Total alk[b]	21,550	23,120	22,460	27,280	15,456
Al (aluminum)[c]	2.90	3.50	1.40	3.10	1.70
As (arsenic)	<0.05[d]	1.60	2.10	2.40	1.20
B (boron)	7.36	7.50	5.20	10.5	5.92
Ba (barium)	<0.06	0.006	0.010	0.055	0.188
Be (beryllium)	<0.01	0.019	0.031	0.030	0.029
Ca (calcium)	1.00	0.07	0.49	0.50	422
Cd (cadmium)	<0.03	<0.03	<0.03	<0.03	<0.03
Cl (chlorine)	105,000	123,700	116,700	147,700	118,000
Co (cobalt)	<0.04	<0.03	<0.03	<0.03	<0.03
Cu (copper)	<0.05	0.15	0.14	0.16	0.22
F (fluorine)	156	169	193	200	1.67
Fe (iron)	0.47	0.53	0.09	0.19	0.72
K (potassium)	34.1	282	237	1,230	37.0
Mg (magnesium)	<0.07	1.70	0.09	2.40	<0.005
Mn (manganese)	<0.01	0.061	0.024	0.037	0.050
Na (sodium)	84,000	113,500	108,800	138,400	102,100
Ni (nickel)	<0.03	<0.09	<0.09	<0.09	<0.09
NO_3 (nitrate)	242	397	401	531	142
Pb (lead)	<0.03	<0.09	<0.20	0.12	<0.02
Si (silicon)	10.8	2,760	2.40	2,260	0.62
SO_4 (sulfate)	89.9	257	228	501	42.0
Zn (zinc)	<0.05	0.15	<0.01	0.10	0.48

[a] Referenced to a ZoBell solution.
[b] Reported as mg/L calcium carbonate.
[c] Reported as total mg/L.
[d] Note that the detection limits reported in this table may differ from those in table 1. The limits here, determined when the sample was analyzed, are specific to the operating conditions on that day.

The thermodynamic model PHRQPITZ (Plummer et al. 1988) was used to describe the mineral equilibria of the rock-alkaline waste systems. This program is a smaller version of PHREEQE (Parkhurst et al. 1980), which contains the Pitzer virial coefficient equations for calculating activity coefficients in high-ionic strength solutions (Pitzer 1973). The addition of the Pitzer equations to thermodynamic models has been acknowledged as a major improvement for calculating mineral equilibria in deep-well systems (Apps 1988). The thermodynamic models WATEQ2 (Ball and Jenne 1979) and SOLMNEQF (Kharaka and Barnes 1973) were used to model the short-term (15 day) rock-alkaline waste solutions. Only limited interpretations were possible with WATEQ2 and SOLMNEQF because the ionic strength of the solutions was too concentrated for these models to accurately estimate activity coefficients. The computer model PHRQPITZ also has limitations. The database of Pitzer interaction parameters is applicable to only 18 constituents: Ba, Br, Ca, Cl, CO_2, CO_3, Fe, H, H_2O, HCO_3, K, Li, Mg, Mn, Na, OH, SO_4,

and Sr. Data for other constituents such as silica are either incomplete or nonexistent (L. N. Plummer, personal communication, 1989).

Research is ongoing in this area. Models such as PHRQPITZ are limited by the availability of studies used to derive the interaction parameters. Reduction-oxidation equilibria are not considered by the program, and Plummer et al. (1988) cautioned that the model should not be used at temperatures greater than 60°C without a more extensive investigation of the temperature dependence of most interaction parameters. The data in table 2 were used as input, and the MacInnes convention was used as the activity-coefficient scale (Plummer et al. 1988).

PHRQPITZ also does not contain pressure equilibria. The output from PHRQPITZ was corrected manually using the regression of Lown et al. (1968):

$$\ln(K^p/K^a) = -\Delta VP/RT + 0.5\ \Delta KP^2/RT$$

where K^p is the solubility constant at pressure P
K^a is the solubility constant at 1 atm.
ΔV is the change in molar volume of the components (cm^3/mole)
ΔK is the change in compressibility of the components (cm^3/mole-atm)
R is the gas constant (82.06 cm^3-atm/mole-°K)
T is temperature (°K)

The molar volume and compressibility data of Millero (1982) were used for the corrections.

The results of the application of PHRQPITZ to the sandstone-alkaline waste system after 230 days of contact are summarized in table 3. The computer model indicated that brucite ($Mg(OH)_2$) and magnesite ($MgCO_3$) were thermodynamically stable, and hence could nucleate and precipitate from solution. Neither phase was detected by XRD in the postreaction solid phases, possibly because the total mass of magnesium in solution was very low. Moreover, magnesite does not readily precipitate from solution at low (<100°C) temperatures because of kinetic limitations (Sayles and Fyfe 1973).

The SEM-EDS investigations revealed the presence of claylike aluminosilicates that appeared to be forming as alteration products of the feldspars (fig. 1). Such reactions are not unlikely given the highly alkaline nature of the waste and the duration of the solid-liquid contact (Berner and Holdren 1977). Clay mineral equilibria could not be assessed because of a lack of accurate Pitzer interaction parameters for aluminum and silica. The SEM-EDS investigations also revealed the sporadic occurrence of fibrous crystals (fig. 2) that were composed of sodium and silicon in a mole ratio of 2:1 Na:Si. Aluminum appeared to be associated with the crystals, but in small quantities. Zeolites may form as authigenic (in situ) alteration products of feldspars in alkaline-brine environments (Hay 1966), but the stoichiometric relationship of Na, Si, and Al did not suggest that these sodium-rich crystals were any type of known sodium zeolite. Hence, the crystals were classified as hydrated sodium metasilicates. At the pH of the alkaline waste (12.6), the dominant form of silicon should have been anionic mononuclear or multimeric species, and there was an abundant supply of Na^+ to form a sodium silicate. It was not certain whether the sodium silicates formed during the 230-day mixing interval or during the drying-aging process that was necessary to prepare the solid phases for analysis. The consumption of Na^+ did not result in detectable decreases in solution concentration (table 2) because of analytical error in the determinations.

The model PHRQPITZ predicted that brucite and calcite ($CaCO_3$) would be thermodynamically stable in the dolomite-alkaline waste solution (table 3). The presence of both phases was verified by XRD, and silt-sized calcite crystals were located using SEM-EDS. The relative

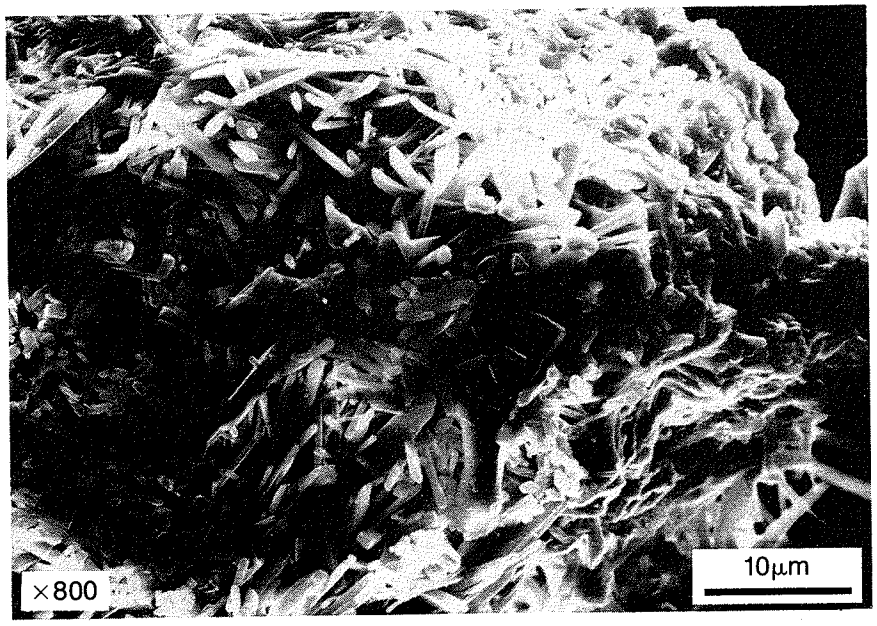

Figure 1 Claylike aluminosilicates (lighter colored masses and filaments) associated with feldspars (darker, blocky masses) in the sandstone-alkaline waste solid phase.

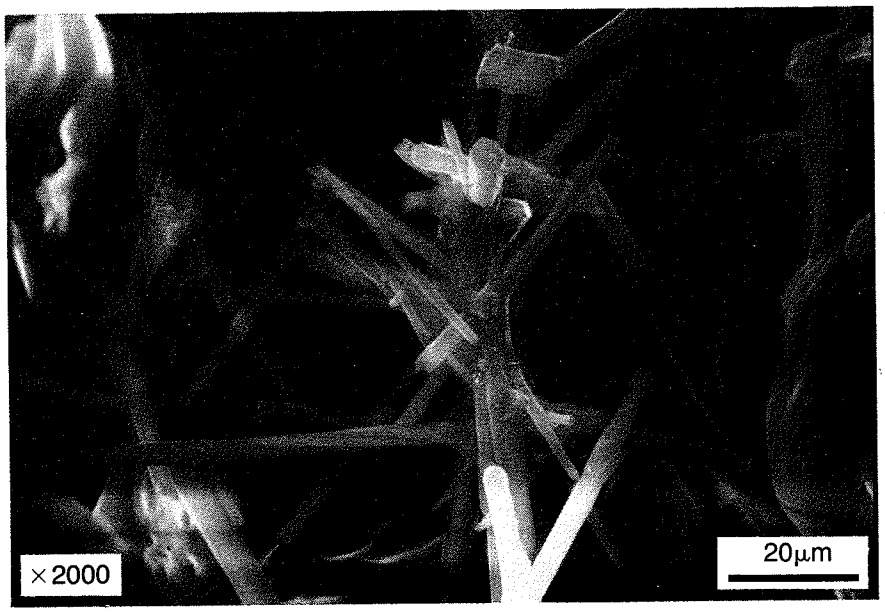

Figure 2 Probable hydrated sodium metasilicate crystals in the sandstone-alkaline waste solid phase.

Table 3 Summary of the mineral phases initially present in the Mt. Simon Sandstone, Potosi Dolomite, and Proviso Siltstone (P = present but not quantified), those predicted to be thermodynamically stable in the rock-alkaline waste suspension after 230 days at 325°K and 10.8 MPa pressure (X), and the mineral phases actually detected (D).

Mineral phase	Sandstone			Dolomite			Siltstone		
	Initial	Predicted	Detected	Initial	Predicted	Detected	Initial	Predicted	Detected
Quartz	90%		D	5%		D	50%		D
Potassium feldspar	6%		D	P		D	25%		D
Dolomite	P	X	D	95%	X	D	5%	X	D
Illite	P		D	P		D	P		D
Kaolinite				P		D			
Chlorite	P			P		D	P		D
Smectite	P								
Brucite		X			X	D		X	D
Calcite					X	D		X	D
Claylike alumino-silicates			D						
Gaylussite ($Na_2Ca(CO_3)_2 \cdot 5H_2O$)					X			X	
Halite			D			D		X	D
Hydrotalcite ($Mg_6Al_2CO_3(OH)_{16} \cdot 4H_2O$)									D?
Magnesite ($MgCO_3$)		X						X	
Pirssonite ($Na_2Ca(CO_3)_2 \cdot 2H_2O$)					X			X	
Sodium metasilicate ($Na_2SiO_3 \cdot nH_2O$)			D						D
Sodium zeolite									D?

abundance and crystallinity of the calcite and brucite probably resulted from the drying-aging process as opposed to being solely precipitated in the presence of the waste solution; however, their presence was consistent with the modeling. The presence of two hydrated sodium-calcium carbonates was also predicted, but neither phase was detected by XRD. The model calculated that the solution was undersaturated with respect to halite. Halite (NaCl) was always present in the solid phases as a simple evaporitic artifact of sample preparation. PHRQPITZ also predicted magnesite and gypsum ($CaSO_4 \cdot 2H_2O$) would be unstable, and neither phase was detected. The sodium metasilicate crystals were not present in the dolomite. Note that the significant increase in solution silica associated with the siltstone and sandstone was absent with the dolomite (table 2).

The mineral equilibria of the siltstone-alkaline waste system (table 3) were similar to those of the dolomite; both brucite and calcite were predicted to be stable, and the presence of these reaction products was verified by XRD. One small peak in the diffractogram of the solid phases suggested the presence of hydrotalcite, a hydrated magnesium-aluminum-hydroxycarbonate. Hydrotalcite is a rare mineral that generally occurs in metamorphic rocks (Drits et al. 1987). Diffraction peaks suggestive of a sodium-rich zeolite were present, but they were barely above the background radiation and were present only at low diffraction angles. The sodium metasilicate crystals that were absent in the dolomite were present in the siltstone.

Reaction products predicted on the basis of short-term studies (Roy et al. 1989) were calcite and brucite. In addition, significant quantities of calcite and brucite were also identified in sidewall core samples collected from the dolomitic injection zone at the Velsicol facility at Marshall, Illinois (Mehnert et al. 1990). There has been some question whether the brucite in the zone formed as an alteration product of the dolomitic injection formation or whether it precipitated in the waste-groundwater mixing zone. The alkaline waste was mixed for 63 days as a 1:1 (vol/vol) dilution with a synthetic brine composed of 3 M NaCl, 0.1 M $CaCl_2$, and 0.1 M $MgCl_2$; the pH was adjusted to 7.0. PHRQPITZ predicted that both brucite and calcite would precipitate from solution, and both phases were detected (fig. 3C). These results indicated that the brucite at the field site could have formed when the waste initially mixed with groundwater, and later when the undiluted waste was in contact with the rock matrix.

The solid mass also contained a minor amount of whewellite, a calcium oxalate. This unusual crystalline phase was probably derived from the organic components present in the waste (Roy et al. 1989). A trace of illite was also detected. Apparently, a portion of the aluminum in the waste was removed to form this phase.

Confirmed and proposed reactions between the alkaline waste and brine and/or rocks were generalized:

$$Mg^{2+} + 2OH^- = \underset{\text{brucite}}{Mg(OH)_2\downarrow} \qquad [1]$$

$$Ca^{2+} + CO_3^{2-} = \underset{\text{calcite}}{CaCO_3\downarrow} \qquad [2]$$

$$SiO_2 + (n+1)H_2O + 2Na^+ = \underset{\text{sodium metasilicate}}{Na_2SiO_3 \cdot nH_2O\downarrow} + 2H^+ \qquad [3]$$

$$\text{Feldspar} \rightarrow \text{"claylike aluminosilicates"} \qquad [4]$$

It was evident that the formation of solid phases would lead to a decrease in the pH of the liquid, and thus might help render an alkaline waste less hazardous—if the pH was the only criterion. However, the actual changes in pH (table 2) in this study were generally not significant.

Rock-Acidic Waste Interactions

As the short-term interaction studies demonstrated, the acidic waste was neutralized within 15 days when mixed with any of the three rock types. The mechanism of neutralization was largely an acid-base reaction that occurred because all three core samples contained carbonates. Although the second waste sample collected at the same injection well was more acidic than the earlier sample (pH 1.2 versus 1.9), the pH of the liquid phase had increased after 155 days to greater than 5.0 (table 4) because of carbonate dissolution. The neutralization of the acidic waste by the sandstone may have been facilitated by the dissolution of clay minerals and ion exchange reactions. The molar quantity of Ca, relative to Mg, in the 155-day solution could not be attributed only to dolomite dissolution.

The thermodynamic model PHREEQE (Parkhurst et al. 1980) was used to describe the mineral equilibria of the rock-acidic waste systems. This model was used instead of PHRQPITZ because PHREEQE contains a more comprehensive database. The solutions were sufficiently dilute (≤0.23 M) to justify the use of this model. The Davies equation was used by PHREEQE to calculate single-ion activity coefficients; it is reasonably accurate to ionic strengths up to about 0.5 M (Sposito 1984). Like PHRQPITZ, PHREEQE does not contain pressure equilibria, and the output was corrected manually. The data in table 3 were used as the input.

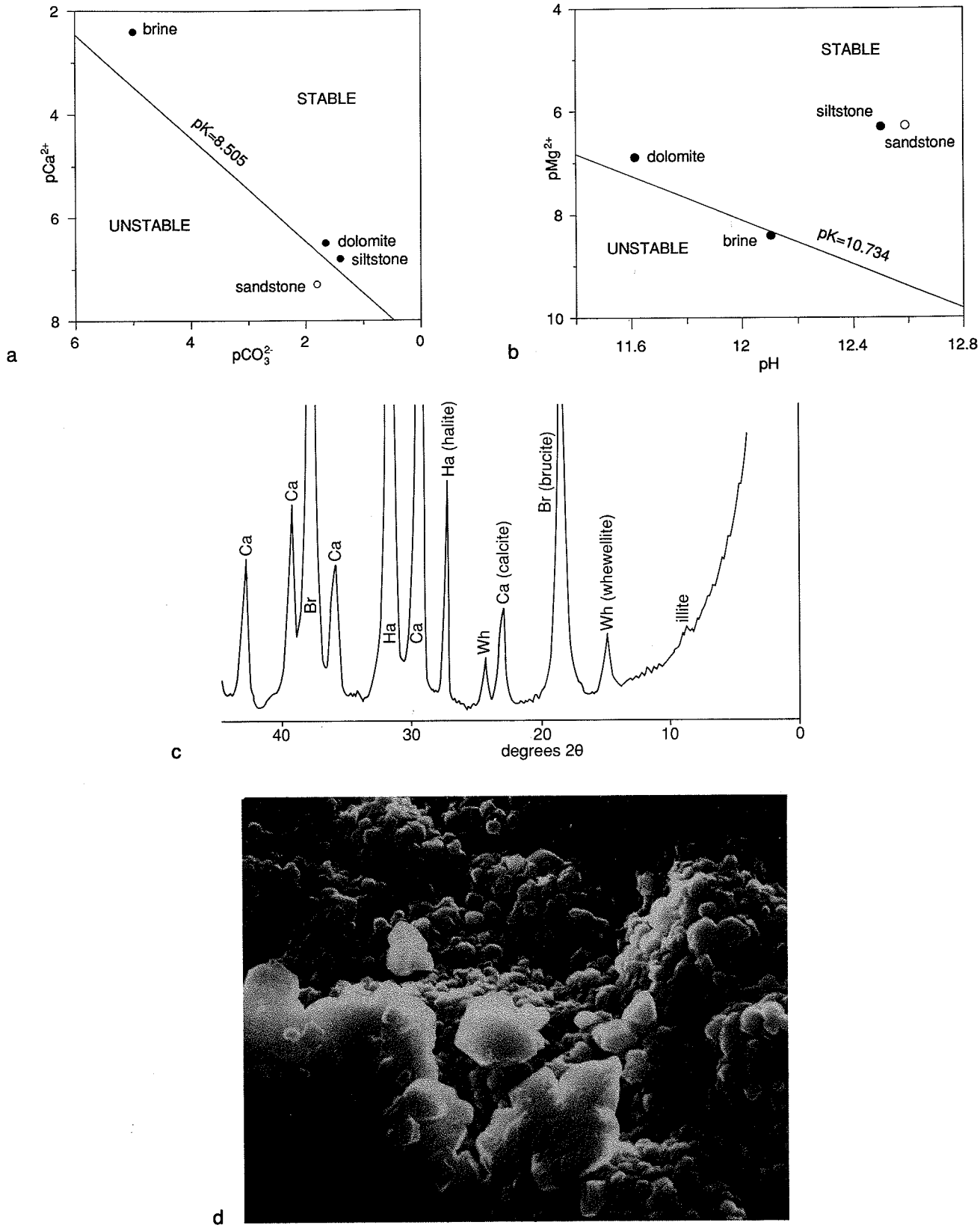

Figure 3 Reaction products generated by mixing the alkaline waste with the synthetic brine at 325°K and 10.8 MPa pressure: (a) calcite equilibria, (b) brucite equilibria, (c) XRD diffractogram of the solid phase, and (d) SEM photograph of calcite crystals in the aged solid phase.

Table 4 Inorganic chemical composition of the acidic waste sample before and after contact with the injection-rock samples.

	Waste[a] liquid	Waste[b] liquid	Waste +		
			Sandstone	Dolomite	Siltstone
pH	1.94	1.20	5.34	7.57	7.54
Eh(mV)[c]	+817	+823	-1	+14.5	+29
Total alk[d]			28.5	101	100
Al (aluminum)[e]	8.90	1.10	2.20	0.70	0.80
As (arsenic)	0.07	0.10	2.00	3.10	1.00
B (boron)	0.12	0.17	0.97	0.68	1.11
Ba (barium)	0.06	0.02	0.97	0.40	0.77
Be (beryllium)	<0.01	<0.0005	0.006	0.002	0.003
Ca (calcium)	92.9	52.4	3,540	729	1,560
Cd (cadmium)	<0.03	<0.01	<0.10	<0.10	0.02
Cl (chlorine)	878	4,000	7,710	4,155	4,580
Cr (chromium)	<0.02	0.04	0.54	0.32	0.41
Cu (copper)	<0.05	0.013	0.08	0.05	0.20
F (fluorine)	0.75	<0.20	2.16	1.49	1.64
Fe (iron)	24.9	5.19	263	0.32	1.01
K (potassium)	3.04	3.00	137	35.0	49.0
Mg (magnesium)	38.0	29.4	181	1,240	599
Mn (manganese)	1.51	0.26	8.92	0.12	7.03
Na (sodium)	14.1	34.1	105	84.9	902
NO_3 (nitrate)	<0.03	<0.03	3.70	1.76	5.16
Pb (lead)	<0.03	<0.02	0.15	<0.08	<0.08
Si (silicon)	7.23	5.40	54.9	5.20	19.5
SO_4 (sulfate)	119	163	192	99.0	115
Zn (zinc)	0.45	0.07	6.78	0.07	0.39

[a] June 1987 data from Roy et al. (1989) for comparisons.
[b] This project (March 1989).
[c] Referenced to a ZoBell solution.
[d] Reported as mg/L calcium carbonate.
[e] Reported as total mg/L.

The application of this computer model to the sandstone-waste mixture was not very informative, however. Chlorite and dolomite were predicted to be unstable, and the trace quantities that were initially present in the sandstone dissolved. Some type of aluminum hydroxide phase and barite were predicted to form but neither was detected by XRD. There was a slight indication in the XRD diffractograms that a vermiculitic phase formed as a reaction product, possibly as an alteration product of the 2:1 clays.

The sandstone-acidic waste system appeared to equilibrate with chalcedony, a fibrous habit of low quartz in the short-term studies. The presence of chalcedony was not confirmed, and it was proposed by Roy et al. (1989) as a "model mineral" to generalize the temperature-dependent distribution of silica in solution in the short-term studies. However, the kinetics of silicate dissolution and precipitation are slow. The attainment of silica equilibrium in strong bases at high temperatures may require weeks to months (van Lier et al. 1960), and in aqueous solution

at ambient temperatures, months to years (Krauskopf 1956). Morey et al. (1962) found that quartz equilibrium in aqueous solution was attained in a few days at temperatures above 100°C, whereas about 390 days were required to precipitate quartz at 25°C. Because of the conditions of these experiments (52°C, 155 days), the attainment of silica equilibrium could not be ruled out or assumed. The model PHREEQE suggested that the sandstone-waste solution was near equilibrium with amorphous silica. Amorphous silica often exerts a metastable equilibrium control on silica concentrations because of the slow rate of inversion to quartz (Siever 1962). Weres and Apps (1982) pointed out that amorphous silica is one of the more common solid phases that form during reinjection of geothermal brines.

Other than carbonate dissolution, the neutralization of the acidic waste by both the dolomite and siltstone did not significantly alter the mineralogical composition of either rock (table 4). PHREEQE predicted that calcite could form in the neutralized solution, and a trace quantity of calcite was detected by XRD in both reacted samples. Other reaction products were predicted to be present (gibbsite, magnesite, $ZnSiO_3$, and amorphous iron hydroxide), but they were not detected by either SEM-EDS or XRD. The dolomite-waste system was undersaturated with respect to quartz, whereas the siltstone liquid was closer to equilibrium with chalcedony than any other silica phase. Because it is not known whether the solutions reached silica equilibrium, the significance of these observations could not be addressed without further research.

CONCLUSIONS

In general, the long-term (155 to 230 days) batch studies of the two liquid hazardous wastes with the three common injection-related rock types yielded results that were comparable to those obtained from short-term (15 days) studies. The pH and the major element composition of an alkaline, brinelike hazardous waste were not significantly altered when mixed with samples of sandstone, dolomite, or siltstone for 230 days. The solution concentrations of potassium, silica, sulfate, and nitrate increased. Under these specific laboratory conditions, there were no geochemical mechanisms that significantly transformed the chemical composition of the waste. These results suggested that chemical transformation may be minimal after the waste has been injected. As observed in the short-term studies, the dilute acidic waste was neutralized as a consequence of carbonate dissolution, ion exchange, or clay-mineral dissolution, and hence was transformed into a nonhazardous waste. These results indicate that the injection of this specific waste stream into carbonate formations is environmentally acceptable.

Rock-Alkaline Waste Interactions

Mixing the alkaline waste with the solid phases yielded several solid-phase reaction products. Brucite ($Mg(OH)_2$), calcite ($CaCO_3$), and some type of sodium metasilicate were present in some of the aged solid phases. Also, claylike minerals formed in the sandstone, and trace levels of hydrotalcite ($Mg_6Al_2CO_3(OH)_{16}\cdot 4H_2O$) may have been present in the siltstone.

The thermodynamic model PHRQPITZ predicted that both brucite and calcite would form in the dolomite, siltstone, and waste-brine systems. Because neither phase was detected in the rock samples before the experiments, it was concluded that PHRQPITZ correctly calculated their thermodynamic stabilities in the high-ionic strength (5.8 to 8.2 M) matrix. Some reaction products would be formed in amounts too small to be detected by XRD because the initial amount of a given reactant in the rock or in the liquid phase was low.

The computer model PHRQPITZ may be a useful tool for estimating mineral equilibria in deep-well-injection scenarios. Because of a lack of thermodynamic data, however, this specific model cannot describe silicate equilibria. The formation of a sodium silicate, for example, could not be

evaluated. It was not certain whether it formed as a result of the drying-aging process used to prepare the samples, or if the solid phase precipitated during the 230-day contact period. This example highlights the need for further basic research in order to expand the database needed for these kinds of calculations.

Rock-Acidic Waste Interactions

The mineralogical composition of each of the three rock types was not significantly altered when reacted with the dilute acidic waste. The model PHREEQE indicated that calcite could precipitate from the neutralized-waste solution of the 155-day dolomite and siltstone mixtures. Calcite was detected in small quantities in the aged samples, whereas it was not detected in the rock samples before the acid was added.

Because the reaction kinetics of silica at low temperatures are extremely slow, conclusive evidence about the mineral equilibria of silica was difficult to obtain. The sandstone-waste system appeared to equilibrate with amorphous silica, whereas equilibrium may not have been attained in the dolomite and siltstone systems. The available data base (such as that used by PHREEQE) may be useful at least for simple applications in deep-well injection, but the predicted equilibria must be interpreted with caution.

FUTURE RESEARCH

Using batch experiments, we examined the geochemical reactions of finely ground rock samples with two liquid wastes. The rock samples were ground to ensure that the chemical reactions would take place within a reasonable time.

A potential drawback to this experimental approach is the implicit assumption that the mineralogical composition of pore surfaces and intergrain voids that come in contact with injected fluids are the same as those of the bulk mass. This assumption is commonly not valid, particularly with sandstone and siltstone clastics, where the composition of the cementing materials or mineral coatings differs from that of the bulk mass (Wilson and Pittman 1977, Scholle 1979). Diagenetic clays such as chlorite, illite, or kaolinite may coat sand grains and pore spaces or fractures. Such clays may represent a small fraction of the bulk mineralogy of the rock, yet they may be the primary surfaces reacting with injected fluids. Some petroleum reservoirs, for example, were treated with acids to increase permeability, but reactions with clay minerals within pore voids resulted in such damage to the reservoir that petroleum production ceased (Almon and Davies 1981, Eslinger and Pevear 1988). Similar reactions can occur in sandstone and siltstone injection units.

Future research on the fate of deep-well injected wastes should include detailed petrographic characterization of rock samples. Scanning electron microscopy coupled with energy dispersive analyses, X-ray diffractometry, and thin-section analyses could be used to determine whether the pore mineralogy differed significantly from the average composition of the rock under study. If there were significant differences, then core-flow experiments might be required for predicting the extent of waste transformation or the formation of reaction products.

Core-flow experiments, in which the liquid waste is passed through whole-rock core samples, could be designed to simulate subsurface temperatures and pressures. Such experiments could also be used to measure changes in rock permeability produced by pore plugging (e.g., the formation of inorganic precipitates or organic emulsions) or by dissolution.

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