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Geochemical Analysis of Leachates from Cement/ Low-Level Radioactive Waste/Soil Systems

L. J. Criscenti
R. J. Serne

September 1988

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
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GEOCHEMICAL ANALYSIS OF LEACHATES FROM CEMENT/LOW-LEVEL RADIOACTIVE WASTE/SOIL SYSTEMS

L. J. Criscenti
R. J. Serne

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Pacific Northwest Laboratory
Richland, Washington 99352

EXECUTIVE SUMMARY

Laboratory experiments were conducted by Pacific Northwest Laboratory (PNL) as part of the Special Waste Form Lysimeters - Arid Program. These experiments were conducted to investigate the performance of solidified low-level nuclear waste in a typical arid, near-surface disposal site, and to evaluate the ability of laboratory tests to predict leaching in actual field conditions. Batch leaching, soil adsorption column, and soil/waste form column experiments were conducted using Portland III cement waste forms containing boiling-water reactor evaporator concentrate and ion-exchange resin waste. In order to understand the reaction chemistry of the cement waste form/soil/ground-water system, the compositions of the leachates from the laboratory experiments were studied with the aid of the MINTEQ ion speciation/solubility and mass transfer computer code. The purpose of this report is to describe the changes in leachate composition that occur during the course of the experiments, to discuss the geochemical modeling results, and to explore the factors controlling the major element chemistry of these leachates.

Compositional analyses for leachates from the following experiments were available: 1) batch leaching experiments, in which either Portland III cement or Portland III cement mixed with the waste stream was placed in contact with ground water; 2) soil adsorption column experiments, in which either ground water or leachate from the batch experiments contacted soil; and 3) soil/waste form column experiments, in which either a blank or a real waste form was buried in soil and exposed to ground water as it passed through the columns. MINTEQ calculations were performed on the leachate compositions to examine the ion speciation of Ca, Mg, Si, B, CO_3, SO_4, and PO_4 in solution, and to evaluate potential solubility controls for these components.

This study indicates that interaction with either Portland III cement or a cement waste form alters the ground-water composition. The effects of the waste on the leachate composition are significant during the initial contact period but decrease with continued waste form/ground-water interaction. These initial effects include an increase in pH from approximately 8.00 to between 10 and 12, an increase in alkalinity, and increases in concentrations of Na, K,

SO_4, PO_4, and organic carbon. These effects are observed in both the batch leaching and soil/waste form column experiments. They are not observed in the soil adsorption column experiments, probably because the leachates from the batch experiments were mixed together before being added to the soil. The major changes in component speciation that result from the presence of the waste are an increase in phosphate- and sodium-bearing species. Minerals which are likely to precipitate to form a reaction rim around the waste form include calcite, dolomite, sepiolite, and quartz. The precipitation of these minerals would maintain the low concentrations of Ca, Mg, and Si observed in the leachates. A similar examination of the leachates from the field lysimeters, which are currently being monitored as part of the Special Waste Form Lysimeters - Arid Program, should indicate whether their major element concentrations are controlled by the same geochemical processes as those of the leachates obtained in the laboratory tests.

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1.0 INTRODUCTION

Laboratory and field leaching experiments are being conducted by Pacific Northwest Laboratory (PNL) to investigate the performance of solidified low-level nuclear waste in a typical, arid, near-surface disposal site. Batch leaching, soil column adsorption, and soil/waste form column experiments are being conducted in the laboratory using small-scale waste forms and Hanford Site ground water and sediment (from the U.S. Department of Energy's Hanford Site in southeastern Washington State). To date, these experiments have been done only with Portland III cement waste forms containing boiling-water reactor (BWR) evaporator concentrate and ion-exchange resin waste. Chemical analyses of all leachates sampled during these experiments are reported in the appendices of Walter et al. (1986).

In addition to the leachates from the laboratory experiments, drainage effluent from 10 field lysimeters containing liquid radioactive wastes solidified in either cement, vinyl ester-styrene, or bitumen has been sampled on a quarterly basis since October 1984. Chemical analyses for these leachates are also reported in Walter et al. (1986) and Jones et al. (1988). The lysimeter leachates are solutions that have contacted solid waste forms and then percolated through 1 m or less of sediment. Together, the compositional data gathered from the laboratory and field lysimeter experiments provide a substantial data set for geochemical analysis of the interaction of low-level radioactive waste forms with Hanford ground water and sediment which are typical of many semi-arid areas.

A geochemical code, MINTEQ, which can be used to calculate ion speciation/solubility, adsorption, oxidation-reduction, gas phase equilibria, and precipitation/dissolution of solid phases, has been selected to assist in evaluating the geochemical properties of the leachates. The selection of MINTEQ over other available geochemical codes (e.g., EQ3/EQ6) for the study of the interaction of solidified, low-level wastes with ground water is discussed in Peterson et al. (1987).

The objectives of this report are to examine the ion speciation/solubility results from MINTEQ to determine potential solubility controls for both the major and minor elements present in the leachates from the laboratory experiments, and to examine how the elements of interest are speciated in solution.

2.0 LABORATORY EXPERIMENTS

The laboratory experiments and the lysimeter studies are both described in detail in Walter et al. (1986). Table 2.1 lists the waste forms obtained for the Special Waste Form Lysimeters - Arid Program. Each of the five waste forms is represented in two lysimeters: 1) boric acid concentrate waste + masonry cement, 2) boric acid concentrate waste + bitumen, 3) evaporator-concentrate waste + Portland III cement, 4) evaporator-concentrate waste and ion-exchange resin + Portland III cement, and 5) evaporator-concentrate waste and ion-exchange resin + Dow® polymer. The waste form that consists of Portland III cement with evaporator concentrate and ion-exchange resin was chosen from the waste forms available for the laboratory experiments because it is

TABLE 2.1. Waste Forms Obtained for the Special Waste Form Lysimeters - Arid Program

Waste Stream	Reactor	Solidifying Agent
Boric acid concentrate waste	PWR(a)	Masonry cement
Boric acid concentrate waste	PWR	Bitumen
Evaporator-concentrate (Na_2SO_4) waste	BWR(b)	Portland Type III cement
Evaporator-concentrate (Na_2SO_4) waste and ion-exchange resin	BWR	Portland Type III cement
Evaporator-concentrate (Na_2SO_4) waste and ion-exchange resin	BWR	Dow® polymer (vinyl ester-styrene)

(a) PWR, pressurized-water reactor.
(b) BWR, boiling-water reactor.

® Dow is a registered tradename of the Dow Chemical Company, Midland, MI 48640.

characterized by the highest radioactivity and contains organic chelating agents that may increase the mobility of some radionuclides.

2.1 DESCRIPTION OF EXPERIMENTS

Three types of laboratory experiments are reported in Walter et al. (1986) 1) batch leaching of the solidified waste form, 2) soil column adsorption of the leachate produced in the first experiment, and 3) simultaneous leaching and adsorption of solidified waste forms in soil columns. The three types of experiments are illustrated in Figure 2.1. For each type, three replicate experiments were done: two that used either the waste form or the leachate from the waste form, and one that used either Portland III cement (referred to as a blank waste form) or Hanford ground water. In this way, changes in the geochemical character of the leachates caused by the waste itself and not the reaction of Hanford ground water with cement could be observed.

The batch leaching test was developed by the American Nuclear Society (ANS) working group 16.1. (ANSI/ANS 1986). Cylinders of both waste forms, 5 cm in height and 2.5 cm in diameter, were suspended in 600 ml of Hanford ground water contained in a 1-L wide-mouth polyethylene jar. At designated intervals, the leachates were removed and replaced with fresh ground water. In both experiments with the waste form, the rate of release of radionuclides was greatest during the first 5 days and slower for the remainder of the experiment.

In the soil column adsorption test, Hanford Site sediment was packed to an average dry bulk density of 1.9 g/cm^3 into three columns (length 8.7 cm; inner diameter 2.1 cm). Two columns were contacted with waste solution, and one was contacted with Hanford ground water. All three were pumped at a constant flow rate of 7 ml/h or 15 pore volumes (PV) per day.(a) This is much faster than in the lysimeter studies, where 2 to 3 PV have passed through the lysimeters in 2 to 3 years of monitoring.

(a) A pore volume is calculated to be the geometric volume of the column x (1 - bulk density/particle density).

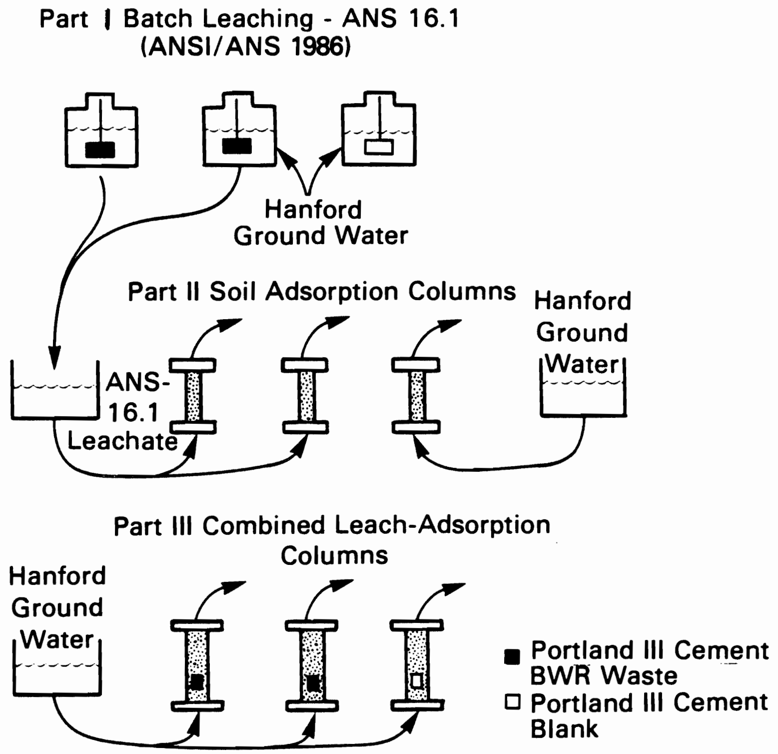

FIGURE 2.1. Laboratory Column Experiments Conducted for the Special Waste Form Lysimeters - Arid Program (BWR = boiling-water reactor) (from Walter et al. 1986)

In the combined leach/adsorption test, the waste forms were placed vertically into each column (length, 15.24 cm; inner diameter, 3.81 cm) at the inlet end and centered on top of 1.27 cm of Hanford Site lysimeter soil. The remaining space was packed with the same soil to a dry bulk density of 1.54 g/cm^3. The columns were saturated with Hanford ground water and allowed to sit for 16 h. Ground water was then pumped up through the columns at a flow rate of 3 ml/h (0.8 PV/day) for 115 days.

2.2 DISCUSSION

To interpret experimental data correctly and to develop geochemical models that describe the experiments, it is important to fully understand the experimental designs and their limitations.

Two important points about the batch leaching experiments must be mentioned before the information provided by the leachate compositions can be evaluated. First, the experiments are not static. The waste form and Hanford ground water are not placed in a jar and allowed to react to equilibrium; instead, the ground water is replenished periodically. Second, although the ground water is replaced, the waste form is not. Hence, it is inappropriate to discuss each leachate removed from the experiment on the basis of the time during which it has been in contact with the waste form. The leachate removed from the polyethylene jar after the fourth day of the experiment has never been in contact with a pristine waste form; rather, it has reacted with an already altered waste form that has been modified through previous reaction with Hanford ground water. Each new batch of Hanford ground water is reacting with a different solid assemblage. It is assumed that the ground water is changed frequently enough that the waste form/solution reactions are essentially the same as those between the waste form and fresh ground water. However, the waste-form-to-solution volume ratio is roughly 1:5, which means that the waste form is not in contact with an infinite supply of ground water. Between each sampling interval, therefore, fresh ground water reacts with the waste form, and both the waste form and the solution compositions change. Before a steady-state condition is achieved, the leachate is removed and replaced with fresh ground water.

In both the soil adsorption column and combined soil/waste form column experiments, fresh influent solution is continuously added to the columns. Theoretically, if the reactions that occur in the combined soil/waste form column experiment are either between the waste form and ground water or between the soil and leachates produced, then the results from the combined soil/waste form experiments should be comparable to the results from the batch leaching experiments combined with results from the soil adsorption column experiments. However, solutions collected from the batch experiments were mixed to make the influent solution for the soil adsorption experiments. To better simulate the combined soil/waste form column experiments, leachates from the batch experiments could have been added to the soil column consecutively. In addition, the two sets of column experiments were conducted at different flow rates; the pore water velocity in the soil adsorption columns was 10 times faster than through the combined soil/waste form columns, and therefore did not allow the same chance for equilibrium adsorption steady-state conditions to be achieved.

Interpretation of the leachate compositions is difficult because of these experimental limitations. Because steady-state or equilibrium conditions may never be achieved during the course of these experiments, solubility controls may never be established for the leachates analyzed.

3.0 MATERIALS

Geochemical modeling of a natural system requires complete data on the mineralogical and chemical composition of the starting materials. This section describes the materials involved in the experiments reviewed in Section 2.0: Portland III cement, Hanford sediment, and Hanford ground water.

3.1 WASTE STREAM

Each waste form is composed of a waste stream and a solidifying agent. The chemical analyses of the liquid waste streams are presented in Jones et al. (1988). Table 3.1 lists the chemical analysis determined for the waste stream in the waste form used in the experiments. This waste stream, the evaporator concentrate with ion-exchange resin, was sampled from a commercial boiling-water reactor site and consisted of a thick dark-brown sludge, visible resin beads, crystallized salts, and an almost colorless liquid. The suspended solids content of the slurry was 38.4% by weight. The supernatant solution had pH and Eh values of 10.36 ± 0.02 and 260 mV, respectively. The waste stream is predominantly sodium sulfate, but there are also considerable concentrations of phosphate, iron, calcium, chloride, aluminum, potassium, magnesium, and organic matter.

3.2 SOLIDIFYING AGENT

The solidifying agent used in the waste forms for the experiments is Portland III cement. A simplified analysis of Portland III cement(Neilson and Colombo 1982) is given in Table 3.2. Portland III cement is composed primarily of silica, lime, alumina, and ferric oxide. On wetting, the minerals in the cement hydrate, forming mostly amorphous calcium silicates, crystalline aluminoferrites and aluminates, and portlandite ($Ca(OH)_2$). When other components are present in the wastes, such as sulfate or bicarbonate, other reactions occur, forming compounds such as monosulfoaluminate ($3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$), ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$), gypsum ($CaSO_4 \cdot 2H_2O$), calcite ($CaCO_3$), and carbonated calcium aluminates and ferrites.

TABLE 3.1. Chemical Composition of Evaporator Concentrate Plus Ion-Exchange Resin

Constituent	mg/L	Constituent	mg/L
Al	1,072	Si	104
B	82	Sr	9.8
Ba	18.7	Ti	19.0
Ca	1,958	Zn	79.5
Cr	38.6	Zr	6.9
Fe	497.6	Cl	1,397
K	841	NO_3	<127
Mg	706	PO_4	10,668
Mn	61.3	SO_4	83,820
Na	58,040	TOM(a)	116
Ni	40.9	TOC(b)	87

(a) TOM, total organic matter.
(b) TOC, total organic carbon.

TABLE 3.2. Principal Compounds Present in Portland III Cement(a)

Compound	Formula	Composition (wt%)
Tricalcium silicate	$3CaO \cdot SiO_2$	53
Dicalcium silicate	$2CaO \cdot SiO_2$	19
Tricalcium aluminate	$3CaO \cdot Al_2O_3$	10
Tetracalcium alumino ferrite	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	7

(a) Taken from Neilson and Columbo (1982).

3.3 WASTE FORM

For the laboratory experiments, the Portland III cement powder was mixed with the evaporite + resin beads waste stream in a waste-to-binder ratio of

1:4. This ratio was provided by the power utility as an estimate of the waste-to-binder ratio used in the solidification of the full-scale waste forms (Walter et al. 1986).

3.4 HANFORD SEDIMENT

The soil used in the experiments comes from sediment remaining after refilling the lysimeters. The soil used in the lysimeter studies is a composite of material found in the top 8 m of the site before construction of the lysimeters began. The topsoil (30 cm) consisted of fine sand that is thought to belong to either the Winchester or Quincy sand soil series. Coarse sands and gravels underlie this topsoil. No chemical characterization data have been collected to date on this sediment. However, x-ray diffraction studies of similar sediments from the Hanford Site suggest that these sediments contain smectite, mica, and kaolinite.(a)

3.5 HANFORD GROUND WATER

An analysis of ground water at the Hanford Site, presumably free of contamination and representative of natural waters in the unconfined aquifer, is reported in Serne et al. (1987) for well 6-S3-25 of the Hanford Ground Water Monitoring Program (see Table 3.3).

From a MINTEQ ion speciation/solubility calculation, it appears that the Hanford ground water is close to equilibrium with calcite ($CaCO_3$), magnesite ($MgCO_3$), barite ($BaSO_4$), sepiolite $[(Mg_2(OH)(H_2O)Si_3O_{7.5} \cdot 2H_2O)]$, otavite ($CdCO_3$), and $MnHPO_4$. The speciation data from this analysis are illustrated in Figure 3.1.

This analysis of Hanford ground water provides a basis for discussion of the chemical composition of the leachates from both the experiments and the lysimeters. It will be used continuously throughout this report to compare how contact with the different waste forms affects the water composition.

(a) Memo to S. J. Phillips, August 25, 1977, from R. J. Serne, D. Rai, M. A. Parkhurst, and J. F. Relyea, Pacific Northwest Laboratory, Richland, Washington.

TABLE 3.3. Hanford Ground-Water Analysis (November 1, 1985)[(a)]

Constituent	mg/L	Constituent	mg/L
Al	<0.01	Zn	0.084
Ba	0.051	F	<0.05
Ca	55.4	Cl	22
Cd	<0.005	NO_2	<0.03
Cr	<0.015	NO_3	0.1
Cu	<0.005	SO_4(c)	86
Fe	<0.01	HCO_3	171.83
K	7.351	CO_3	1.89
Mg	14.487	OH	0
Mn	<0.01	B(a)	0.0158
Na	26.130	B as H_3BO_3	0.09
P(b)	<0.10	PO_4(c)	<1
P as PO_4	<0.3	TOC	0.27
Pb	<0.04	Total alkalinity (as CO_3)	86.40
S(b)	28.994		
S as SO_4	87.0	IC	35.20
Si	15.30	Cations (meq/L)	5.30
Sr	0.25	Anions (meq/L)	5.34

(a) pH, 8.18 units; Eh, 310 mv.
(b) Measured on ICP.
(c) Measured on IC.

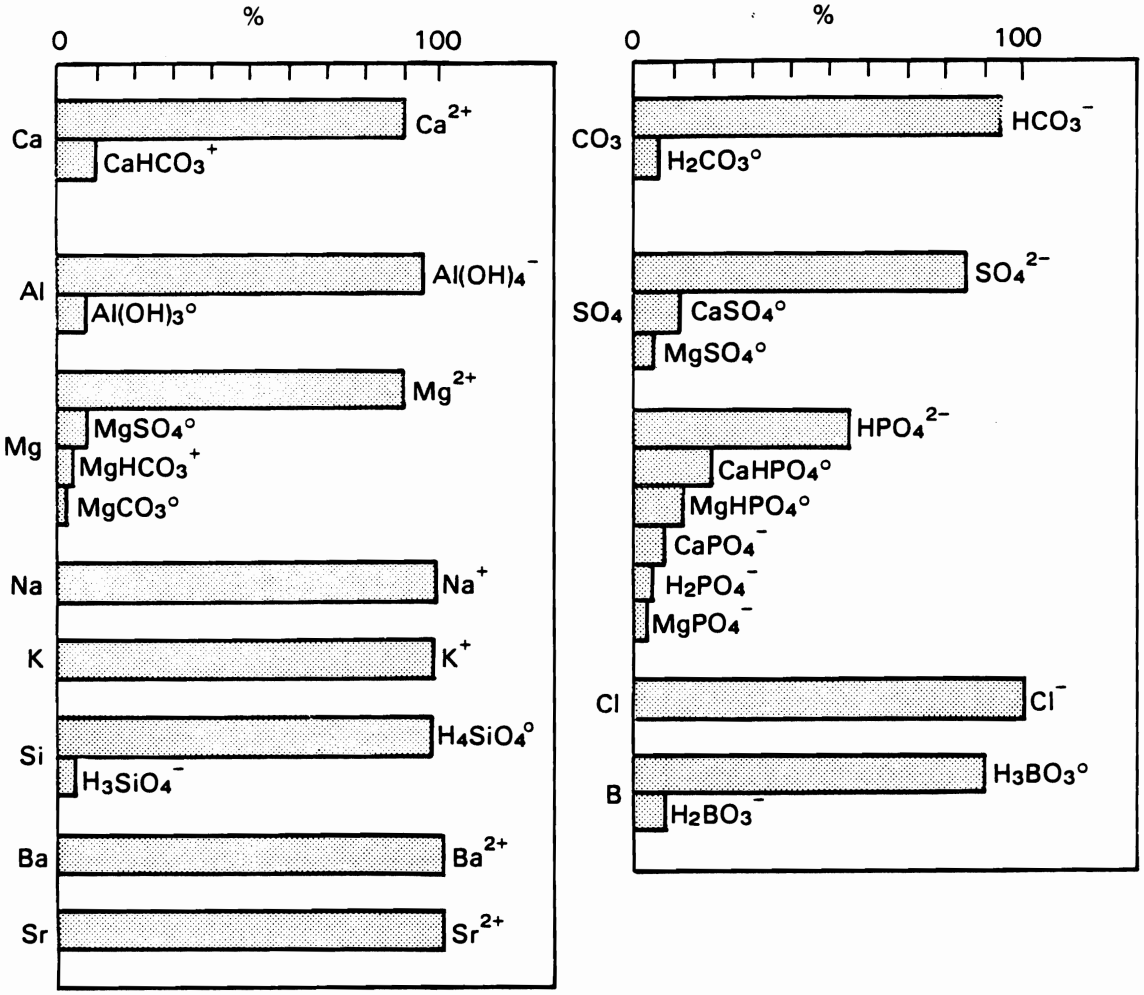

FIGURE 3.1. Speciation of Components in Hanford Ground Water (% is percentage of component found in species)

4.0 SUMMARY OF THE MINTEQ CODE

An overview of the MINTEQ geochemical code is presented in Peterson et al. (1987). This geochemical code was used in two different modes in this study: 1) ion speciation/solubility and 2) simple mass transfer. These modes incorporate three of the MINTEQ submodels discussed in Peterson et al. (1987). In the speciation submodel, the activities of complexed and uncomplexed cationic and anionic species, neutral ion pairs, and the cationic and anionic redox species are calculated from basic thermodynamic data.

These activities are then used in the solubility submodel to calculate ion activity products for the minerals in the data base. The calculated activity products (Q) are compared to the solubility products (K_{sp}) for the minerals through a saturation index [log (Q/K_{sp})]. This saturation index indicates the degree of undersaturation or oversaturation of a solution with respect to the mineral in question. If a solution is oversaturated with respect to a particular solid phase, the value of the saturation index [log (Q/K_{sp})] is greater than zero. Oversaturated conditions suggest that kinetic factors prevent the solid phase from precipitating at a rate that is sufficient to control the concentrations of its dissolved components. If the saturation index reflects undersaturation [log (Q/K_{sp}) is less than zero], it is concluded that either 1) a less soluble (thermodynamically more stable) solid is controlling the dissolved constituent concentrations, 2) another mechanism, such as adsorption, is controlling the concentrations of the component species below their solubility products, or 3) the constituent concentrations in the source are low.

Because of inaccuracies in the MINTEQ thermodynamic data base and in the measured solution compositions, it is unlikely that any saturation index calculated by MINTEQ will be exactly zero. Jenne et al. (1980) suggested an empirical rule that allows users to evaluate how close a particular mineral saturation index must be to zero to conclude that the solution is in equilibrium with that mineral. This rule states that the logarithm of the saturation index [log (SI)] must be within ±5% of the log (K_{sp}) for the mineral to be in equilibrium with the solution.

The ion speciation/solubility calculations are used to study the behavior of both major and minor elements in the leachates from both the laboratory experiments and lysimeters. The mass transfer submodel, which allows for the precipitation and dissolution of solid phases, is used in a preliminary manner to determine what minerals might precipitate from the leachates if they were allowed to react to an equilibrium assemblage.

Table 4.1 lists the components used for each MINTEQ calculation. Fluorine was ignored, and zinc was not always analyzed. Because Walter et al. (1986) could not obtain rapid measurements of inorganic carbon but did obtain total alkalinity measurements, the amount of carbon in the solution was determined by trial and error. Different values of inorganic carbon were chosen until the speciated solution was charge balanced and the calculated solution alkalinity agreed with the measured alkalinity. Modifications were made to MINTEQ to calculate both noncarbonate and carbonate alkalinity. Originally, MINTEQ considered the contribution of only a few aqueous species to the total alkalinity.

TABLE 4.1. Components Used in MINTEQ Calculations

Constituents		Redox Couples
Al	Mg	Fe^{2+}/Fe^{3+}
H_3BO_3	Mn	$Cr(OH)_2^+/CrO_4^{2-}$
Ba	Na	Co^{2+}/Co^{3+}
CO_3	PO_4	
Ca	SO_4	
Cl	H_4SiO_4	
Cd	Sr	
Cu	Zn(a)	
F(a)	MoO_4	
K	Pb	
NO_3	V	

(a) Fluorine and/or zinc are not always included in the chemical analysis.

Morrey[a] determined how each aqueous species contributes to the alkalinity, where the alkalinity is defined as the number of equivalents of H^+ consumed per mole of solution if that solution is titrated to a pH of 4.6. The alkalinity factors that Morrey[a] (1987) determined will vary with the specific solution composition, but the use of these factors provides a good initial guess for the alkalinity of an aqueous solution. The carbonate species that are now considered in the MINTEQ code to contribute to the alkalinity are listed in Table 4.2. The noncarbonate species that can contribute to the alkalinity are listed in Table 4.3.

TABLE 4.2. Carbonate Species That Contribute to Total Alkalinity

$CaHCO_3^+$
$CaCO_3^0$

$Cd(CO_3)_3^{4-}$
$CdHCO_3^+$
$CdCO_3^0$

$CoCO_3^0$
$CoHCO_3^+$

$CuCO_3^0$
$Cu(CO_3)_2^{2-}$
$CuHCO_3^+$

HCO_3^-
$H_2CO_3^0$

$MgCO_3^0$
$MgHCO_3^+$

$NaCO_3^-$
$NaHCO_3^0$

$NiHCO_3^+$
$NiCO_3^0$
$Ni(CO_3)_2^{2-}$

$MnHCO_3^+$

$Pb(CO_3)_2^{2-}$
$PbCO_3^0$
$PbHCO_3^+$

$UO_2CO_3^0$
$UO_2(CO_3)_2^{2-}$
$UO_2(CO_3)_3^{4-}$

$ZnHCO_3^+$
$ZnCO_3^0$
$Zn(CO_3)_2^{2-}$

(a) J. Morrey of the Pacific Northwest Laboratory, Richland, Washington, is preparing a report on acidic factors for computer use in calculating alkalinity aqueous equilibria.

TABLE 4.3. Noncarbonate Species That Contribute to Total Alkalinity

Al^{3+}
$Al(OH)_2^+$
$Al(OH)_4^-$
$Al(SO_4)_2^-$
AlF^{2+}
AlF_3 (aq)
$AlOH^{2+}$

$As(OH)_3$
$AsO(OH)_3$

$BaOH^+$

$BF(OH)_3^-$
$BF_2(OH)_2^-$
BF_3OH^-

CaF^+
$CaH_2PO_4^+$
$CaHPO_4$
$CaOH^+$
$CaPO_4^-$
$CaSO_4$ (aq)

$Cd(OH)_2$ (aq)
$Cd(OH)_3^-$
$Cd(OH)_4^{2-}$
$Cd(SO_4)_2^{2-}$
Cd_2OH^{3+}
$CdCl^+$
$CdCl_2$ (aq)
$CdNO_3^+$
$CdOH^+$
$CdSO_4$ (aq)

Cr^{2+}
$Cr(OH)_2^+$

CrO_4^{2-}
$Cr(OH)^{2+}$
$Cr(OH)_4^-$
Cr^{3+}
$CrO_3H_2PO_4^-$
$Cr_2O_7^{2-}$
$Cr_2(OH)_2(SO_4)S_{+2}$
$Cr_2(OH)_2(SO_4)$
$Cr_2(OH)_2(SO_4)_2$
$CrCl^{2+}$
$CrCl_2^+$
CrF^{2+}
$CrH_2PO_4^{2+}$
$CrNO_3^{2+}$
CrO_3Cl^-
$CrO_3HPO_4^{2-}$
$CrOHCl_2$ (aq)
$CrOHSO_4$ (aq)
$CrSO_4^+$

F^-

Fe^{3+}
FeF^{2+}
$Fe(SO_4)_2^-$
$Fe_2(OH)_2^{4+}$
$Fe_3(OH)_4^{5+}$
$FeCl^{2+}$
$FeCl_2^+$
$FeCl_3$ (aq)
FeF_3 (aq)
$FeH_2PO_4^+$
$FeH_2PO_4^{2+}$
$FeHPO_4^+$
$FeHPO_4$ (aq)

$FeOH^+$
$FeOH^{2+}$
$Fe(OH)_2^+$
$Fe(OH)_2$ (aq)
$Fe(OH)_3^-$
$Fe(OH)_3$ (aq)
$Fe(OH)_4^-$
$FeSO_4^+$
$FeSO_4$ (aq)

Fulv

HS
H_2CrO_4 (aq)
$HCrO_4^-$
$H_2BO_3^-$
HPO_4^{2-}
$H_2PO_4^-$
$H_2SiO_4^{2-}$
$H_3SiO_4^-$
HF (aq)
HF_2^-
HSO_4^-

Hum

KSO_4^-

MgF^+
$MgH_2PO_4^+$
$MgHPO_4$ (aq)
$MgOH^+$
$MgPO_4^-$
$MgSO_4$ (aq)

TABLE 4.3. (contd)

$Mn(NO_3)_2$ (aq)
$Mn(OH)_3^-$
$MnCl^+$
$MnCl_2$ (aq)
$MnCl_3^-$
MnF^+
MnO_4^-
MnO_4^{2-}
$MnOH^+$
$MnSO_4$ (aq)
MoO_4^{2-}

NaF (aq)
$NaHPO_4^-$
$NaSO_4^-$

NH_3 (aq)

$Ni(OH)_2$ (aq)
$Ni(SO_4)_2^{2-}$
$NiCl^+$
$NiCl_2$ (aq)
NiF^+
$NiOH^+$
$NiSO_4$ (aq)

OH^-

PO_4^{3-}

$Pb(OH)_2$ (aq)
$Pb(OH)_3^-$
$Pb(OH)_4^{2-}$
$Pb(SO_4)_2^{2-}$

Pb_2OH^{3+}
$Pb_3(OH)_4^{2+}$
$PbCl^+$
$PbCl_2$ (aq)
$PbCl_3^-$
$PbCl_4^{2-}$
$PbNO_3^+$
$PbOH^+$
$PbSO_4$ (aq)
S^{2-}

SiF_6^{2-}

SO_4^{2-}

$SrOH^+$

U^{4+}
UO_2^{2+}
$U(HPO_4)_2$ (aq)
$U(HPO_4)_3^{2-}$
$U(HPO_4)_4^{4-}$
$U(OH)_2^{2+}$
$U(OH)_3^{1+}$
$U(OH)_4$ (aq)
$U(OH)_5^-$
$U(SO_4)_2$ (aq)
$U_6(OH)_{15}^{9+}$
UCl^{3+}
UF^{3+}
UF_2^{2+}
UF_3^{1+}
UF_4 (aq)

UF_5^-
UF_6^{2-}
$UHPO_4^{2+}$
$(UO_2)_3(OH)_5^+$
UO_2Cl^+
UO_2F^+
UO_2F_2 (aq)
$UO_2F_3^-$
$UO_2F_4^{2-}$
$(UO_2)(H_2PO_4)_3^-$
$UO_2(H_2PO_4)_2$
$UO_2H_2PO_4^+$
$UO_2H_3SiO_4$
UO_2HPO_4 (aq)
$UO_2(HPO_4)_2$
$(UO_2)_2(OH)_2^{2+}$
UO_2OH^+
UO_2SO_4 (aq)
$UO_2(SO_4)_2^{2-}$
$UOHB^+$
USO_4^{2+}

V^{2+}
V^{3+}
VO^{2+}
VO_2^+

$Zn(OH)_2$ (aq)
$Zn(OH)_3^-$
$Zn(OH)_4^{2-}$
$Zn(SO_4)_2^{2-}$
$ZnOH^+$
$ZnSO_4$ (aq)

5.0 POTENTIAL SOLUBILITY CONTROLS

The solid phases considered as potential solubility controls in this report had to meet two criteria. First, geochemical evidence that the phase was of importance in the systems considered (waste form + ground water, leachate + soil, and waste form + ground water + soil) was required, and second, the thermodynamic data for the solid had to be present in the MINTEQ data base.

From Section 3.0, it is apparent that many of the compositional data that might prove useful to a geochemical modeling task are not currently available. For example, the solid phases present in the waste form and the solid phases present in the soil are unknown. However, an initial list of solids that might act as solubility controls on the systems considered can be compiled.

First, the solids that might play a role in cement/ground-water interactions are considered. Dry Portland III cement is primarily composed of tricalcium silicate, dicalcium silicate, tricalcium aluminate and tetracalcium alumino ferrite. On wetting, amorphous calcium silicates, crystalline aluminoferrites and aluminates, and portlandite form. Other minerals, such as monosulfoaluminate, ettringite, gypsum, and calcite, can also form (Bye 1983). Portland cement is frequently mixed with lime to form other types of cement. The MINTEQ thermodynamic database contains the equilibrium constants for lime, portlandite, monosulfate, ettringite, gypsum, and calcite.

On contact between a hardened cement waste form and ground water, a reaction rim of carbonate minerals tends to form on the waste form (Serne et al. 1987). The following carbonate minerals, in addition to calcite, were considered as potential solubility controls in the experiments: dolomite, magnesite, otavite, rhodochrosite, strontianite, and cerrusite.

Because the waste stream is characterized by high SO_4 and PO_4 concentrations, the following sulfate and phosphate solids, which have been observed to form at 25°C in soil environments and are in the MINTEQ thermodynamic data base, are considered: barite, celestite, $MnHPO_4$, strengite, and hydroxyapatite.

Hydroxides such as diaspore, brucite, and ferrihydrite are readily precipitated from solution in soil environments. Although the solid phases present in the Hanford soil have not been completely documented, it is generally known to contain a silica phase and several clay minerals. The most likely silica phases are SiO_2 (amorphous), chalcedony, cristobalite, and quartz. The only clay mineral present in the MINTEQ thermodynamic database was kaolinite, which did not appear to be a solubility control for any of the leachates. Sepiolite has been observed to form in alkaline environments (Isphording 1973).

Several solid phases were considered only after the MINTEQ calculations were completed. If the saturation indices for a solid phase were $-1 < SI < 1$, the solid phase was considered as a possible solubility control. References that were used to investigate the environmental conditions in which various solid phases are found included <u>Chemical Equilibria in Soils</u> (Lindsay 1979), <u>An Introduction to the Rock Forming Minerals</u> (Deer, Howie and Zussman 1966), and <u>Minerals in Soil Environments</u> (Dixon and Weed 1977). A final list of the minerals considered and their chemical formulas is given in Table 5.1.

TABLE 5.1. Minerals Considered as Potential Solubility Controls

Minerals	Formula
Calcite	$CaCO_3$
Dolomite	$CaMg(CO_3)_2$
Magnesite	$MgCO_3$
Otavite	$CdCO_3$
Rhodochrosite	$MnCO_3$
Strontianite	$SrCO_3$
Cerussite	$PbCO_3$
Barite	$BaSO_4$
Gypsum	$CaSO_4 \cdot 2H_2O$
Celestite	$SrSO_4$
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$
Monosulfate	$Ca_4Al_2(SO_4)(OH)_{12} \cdot 6H_2O$
--	$MnHPO_4$
Strengite	$FePO_4 \cdot 2H_2O$
Hydroxyapatite	$Ca_5(PO_4)_3OH$
Brucite	$Mg(OH)_2$
Gibbsite	$Al(OH)_3$
Diaspore	$AlOOH$
Portlandite	$Ca(OH)_2$
Lime	CaO
Chromium hydroxide	$Cr(OH)_3$
Maghemite	γ-FeO_3
Ferrihydrite	$Fe(OH)_3$
Wulfenite	$PbMoO_4$
Amorphous silica	$SiO_2(A)$
Chalcedony	SiO_2
Cristobalite	SiO_2
Quartz	SiO_2
Sepiolite	$Mg_4(OH)_2(H_2O)_2Si_6O_{15} \cdot 4H_2O$
Willemite	$ZnSiO_4$

6.0 BATCH LEACHING EXPERIMENTS

This section discusses the results of the ANS 16.1 batch leaching experiments and the results of the MINTEQ ion speciation/solubility and mass transfer calculations on the leachates from these experiments.

6.1 CHEMICAL ANALYSES

Three sets of ANS 16.1 batch leaching experiments were performed: one on a blank waste form (Portland III cement only), and two on the mixture of Portland cement and evaporator concentrate + resin beads (waste forms 1 and 2). The results from Walter et al. (1986) suggest that the duplicate experiments using waste forms 1 and 2 produced similar results. Because of these similarities, and in order to limit the number of MINTEQ calculations required, the blank waste form experiment has been compared to the waste form 1 experiment.

Figures 6.1 through 6.15 illustrate the changes in solution composition that occurred through time for both ANS 16.1 experiments.(a) The reader should recall from Section 2.0 that at each sampling time, which corresponds to each point marked on the figures, all of the leachate is removed from the polyethylene jar and replaced with fresh ground water. Figure 6.1 illustrates that the pH of the leachates from both experiments rose to a peak after 1 day and then descended to a low point after 4 days of waste form/ground-water contact. The peak for waste form 1 was 11.59, and the peak for the blank waste form was 10.46. The pH of waste form 1 dropped to 10.69 and that of the blank waste form dropped to 8.73 between 1 and 4 days of waste form/ground-water contact. After 4 days of contact, the pH of the leachates from the blank waste form experiment appeared to stabilize near that of Hanford ground water, varying between 8.75 and 8.50. The pH for the leachates from waste form 1 continued to rise, reaching a maximum of 12.13 after 21 days of contact.

Figure 6.2 illustrates that the alkalinity of the leachates from waste form 1 increases to values much higher than that of Hanford ground water. The

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(a) HGW, Hanford ground water, for these and subsequent figures.

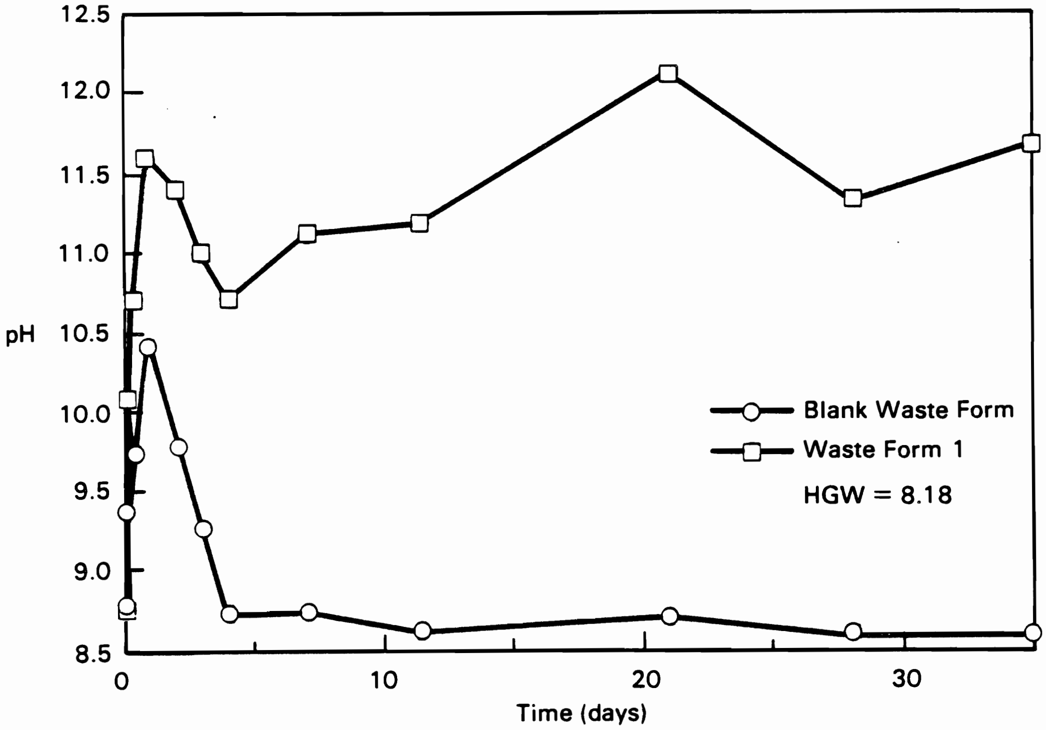


FIGURE 6.1. pH Values for the ANS 16.1 Leachates

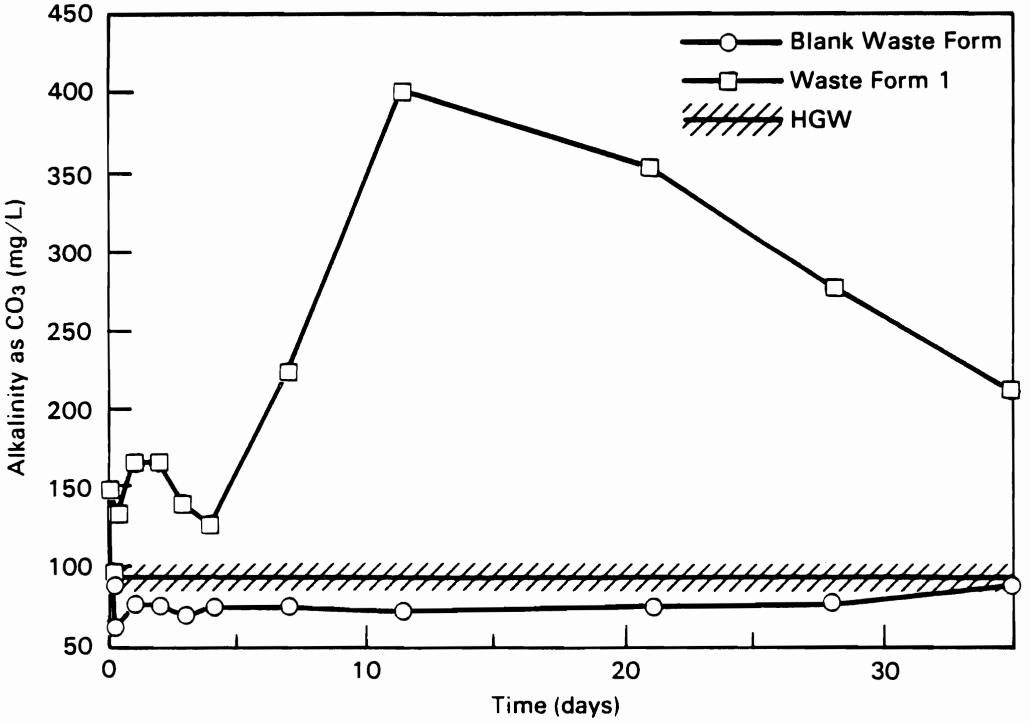


FIGURE 6.2. Alkalinity Values for the ANS 16.1 Leachates

maximum alkalinity (401.76 mg/L as CO_3^{2-}) is reached after 11 days of contact. The alkalinity of the leachates from the blank waste form decreases slightly, and after 35 days of contact returns to the Hanford ground-water alkalinity of 86.4 mg/L as CO_3^{2-}.

As mentioned in the discussion of MINTEQ, the alkalinity values could not be used directly for the ion speciation/solubility calculations. Instead, carbonate values were approximated by selecting values that brought the solution compositions into charge balance. It was observed that the carbonate content and the total alkalinity were both extremely sensitive to charge balance. Carbonate values were chosen such that the aqueous solution was within 1% of being charge balanced. Figure 6.3 illustrates the values for total carbonate that were used in the MINTEQ calculations. Table 6.1 provides a comparison between the measured alkalinity and the calculated alkalinity. The calculated noncarbonate and carbonate contributions to the alkalinity are also listed.

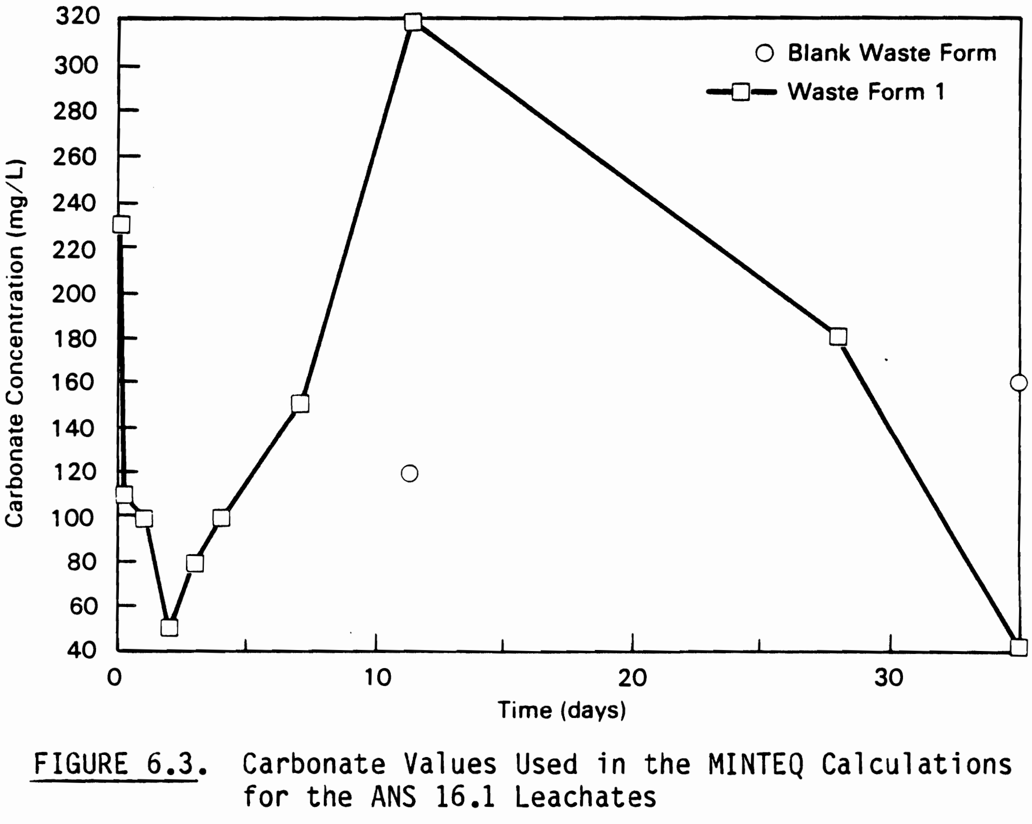


FIGURE 6.3. Carbonate Values Used in the MINTEQ Calculations for the ANS 16.1 Leachates

TABLE 6.1. Measured Versus Calculated Alkalinity for Batch Leaching Experiments

Sample	Total Alkalinity as CO_3^{2-} (mg/L) Measured	Total Alkalinity as CO_3^{2-} (mg/L) Calculated	Noncarbonate Alkalinity Calculated (%)	Carbonate Alkalinity Calculated (%)
BWF[a]: 11.4 days	71.28	62.40	2.14	97.86
BWF: 35 days	88.20	83.10	1.58	98.42
WF1[b]: 2 hours	142.56	143.10	5.16	94.84
WF1: 6 hours	132.84	135.60	26.55	73.45
WF1: 1 day	165.24	166.80	94.06	5.94
WF1: 2 days	165.24	156.60	69.08	30.92
WF1: 3 days	139.32	126.96	41.02	58.98
WF1: 4 days	126.36	124.17	28.00	72.00
WF1: 7 days	223.56	203.28	30.15	69.85
WF1: 11.4 days	401.76	381.00	19.35	80.65
WF1: 28 days	217.20	260.10	33.56	66.44
WF1: 35 days	207.90	218.10	82.12	17.88

(a) BWF, blank waste form.
(b) WF1, waste form 1.

The measured and calculated alkalinity compare reasonably well: in the poorest agreement, the values are different by 16.5%. The alkalinity of the leachates from the blank waste form is predominantly (>95%) the result of carbonate species in solution; for the waste form 1 leachates, the proportions of carbonate and noncarbonate alkalinity vary considerably. For example, after 1 day of contact, 94% of the alkalinity can be attributed to noncarbonate species; after 11 days only 19% of the alkalinity is noncarbonate, and after 35 days most of the alkalinity of the leachate is once again noncarbonate in nature.

Calcium concentrations in the leachates from both experiments are below the concentrations found in Hanford ground water (see Figure 6.4). Again the blank waste form appears to be reequilibrating with the ground water more quickly than waste form 1. During the first day of contact, Ca concentrations decrease from more than 55 mg/L to less than 20 mg/L in the leachates from both experiments as the pH increases from less than 9 to more than 10. The Ca concentrations in the leachates in contact with the blank waste form then increase through time toward the Hanford ground-water concentration of 55.4 mg/L. This trend suggests that the Portland III cement reacts with the ground water on initial contact, precipitating a calcium-rich solid, possibly calcite ($CaCO_3$). On further contact, this reaction slows. The decrease in Ca concentration associated with an increase in pH is consistent with the precipitation of either calcite or portlandite [$Ca(OH)_2$]. For the waste form 1 leachates, Ca concentrations continue to decrease to less than 10 mg/L after 1 month of contact; calcium-bearing minerals must continue to precipitate from the alkaline solutions, removing Ca from the ground water.

Figure 6.5 illustrates the distinct differences in the Mg leachate concentrations for the two experiments. Again, as for Ca, the Mg concentrations initially decrease during the first day of contact, then rise during the next 3 days of contact. The Mg concentration in the leachates in contact with the blank waste form decreases to 11.37 mg/L and then increases to concentrations representative of the Hanford ground water (14-15 mg/L). The leachate concentration of Mg for the waste form 1 experiment drops to 4.52 mg/L after 1 day of

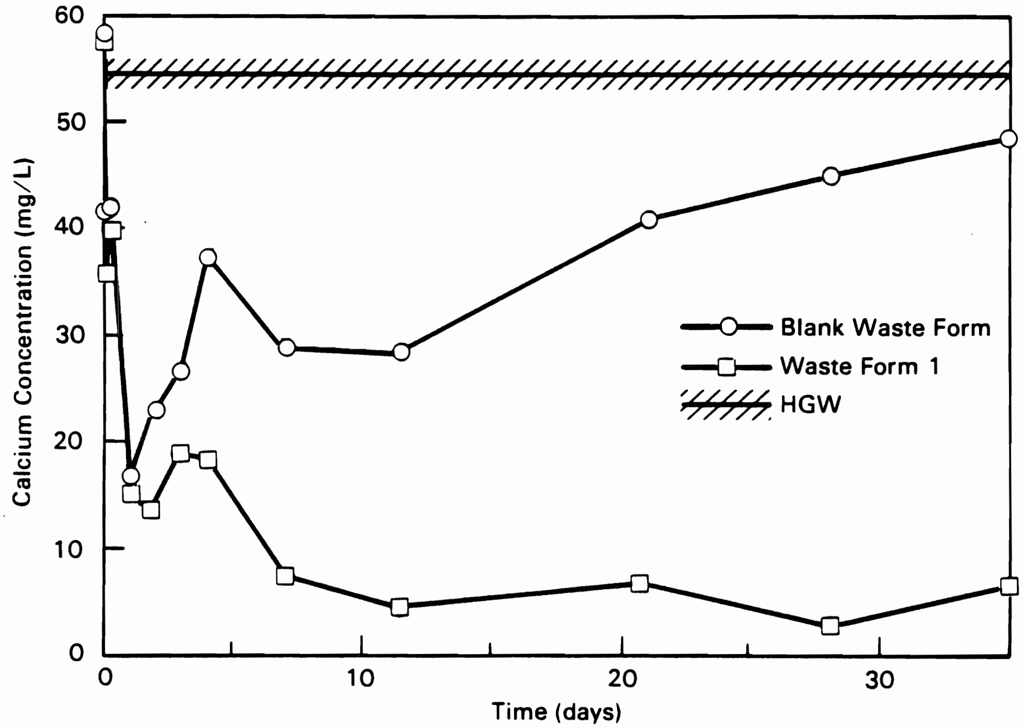


FIGURE 6.4. Calcium Concentrations in the ANS 16.1 Leachates

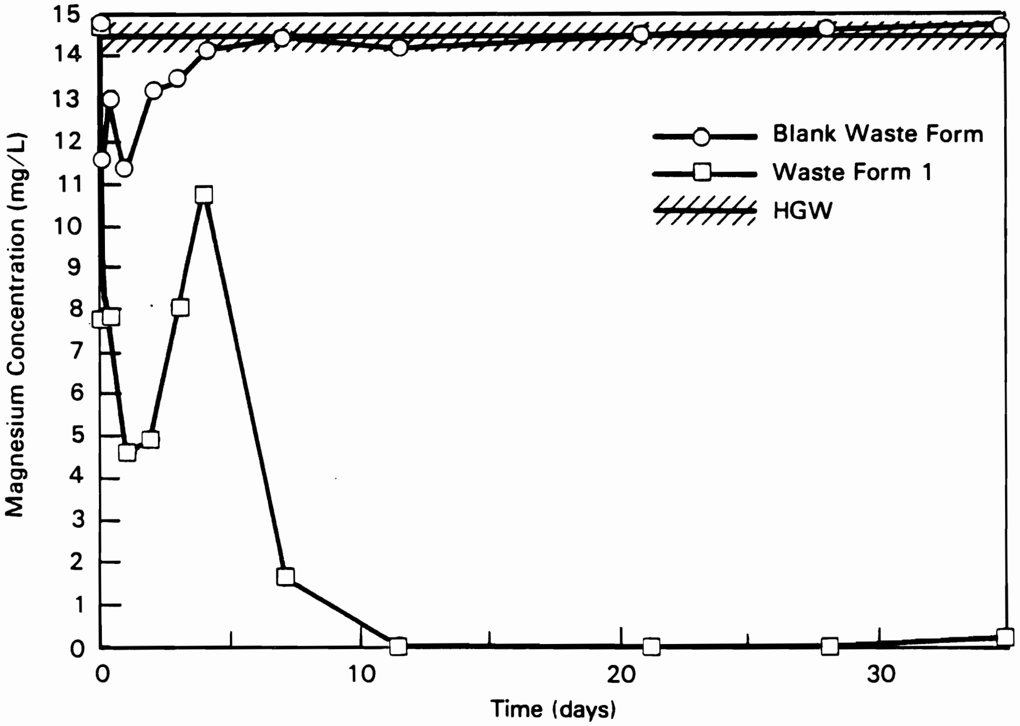


FIGURE 6.5. Magnesium Concentrations in the ANS 16.1 Leachates

contact, rises to 10.83 mg/L after 4 days of contact, and then drops nearly to zero for the duration of the experiment. This suggests a strong solubility control for Mg.

Figures 6.6 and 6.7 illustrate the variation in Na and SO_4 concentrations with time. In the leachates in contact with the blank waste form, both components (Na and SO_4) are near Hanford ground-water concentrations (26.13 mg/L and 86.86 mg/L, respectively). Because the waste stream is predominately Na_2SO_4, variations in Na and SO_4 concentrations in the leachates from the waste form 1 experiment should be parallel if both are leaching from the waste form at the same rate and if no precipitation occurs. Both components show an initial rise in concentration (from less than 50 mg/L to greater than 180 mg/L Na, and from less than 100 mg/L to greater than 170 mg/L SO_4) during the first day of contact, followed by a decrease in concentration through day 4, and reaching a maximum on day 11 of the experiment. The peak in Na and SO_4 concentrations after 1 day of contact is paralleled by a peak in leachate pH. The maximum Na and SO_4 concentrations are observed after 11 days of contact in the same leachate that has the maximum observed alkalinity. This suggests that after 11 days the waste stream, not the cement, is important in controlling the alkalinity as well as the Na and SO_4 concentrations. The maximum concentration of Na is 384.78 mg/L and the maximum concentration of SO_4 is approximately 238 mg/L. However, Figure 6.8 illustrates that, on a per mole basis, more Na than SO_4 is entering the ground water from waste form 1. This suggests that the precipitation of one or more sulfate-bearing minerals is removing sulfate from solution.

Phosphate concentrations (Figure 6.9) follow a similar pattern to sulfate concentrations. Contact between ground water and Portland III cement does not increase the phosphate concentration in solution, while contact between ground water and waste form 1 leads to increased phosphate concentrations in solution. Following the same pattern as Na, SO_4, and alkalinity, an initial peak in phosphate concentration is reached after 1 day of contact, a valley at 4 days of contact, and finally a maximum value of approximately 10.5 mg/L after 11 days of contact. Although Na, SO_4, and PO_4 concentrations increase with increasing alkalinity, they do not appear to contribute significantly to the

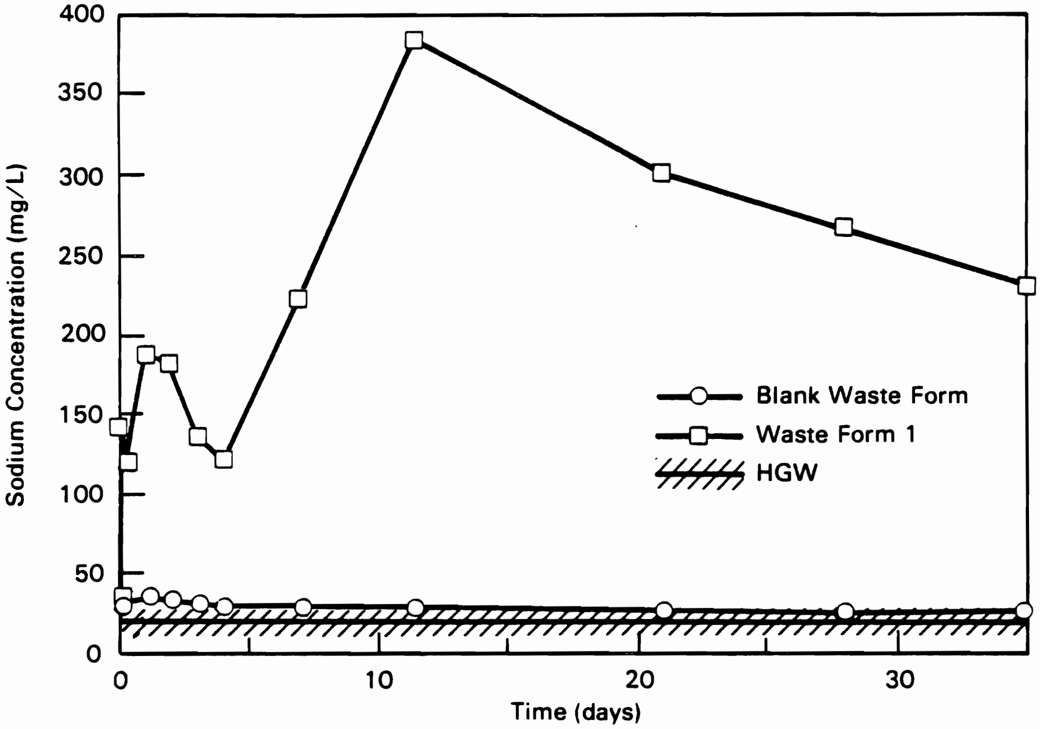


FIGURE 6.6. Sodium Concentrations in the ANS 16.1 Leachates

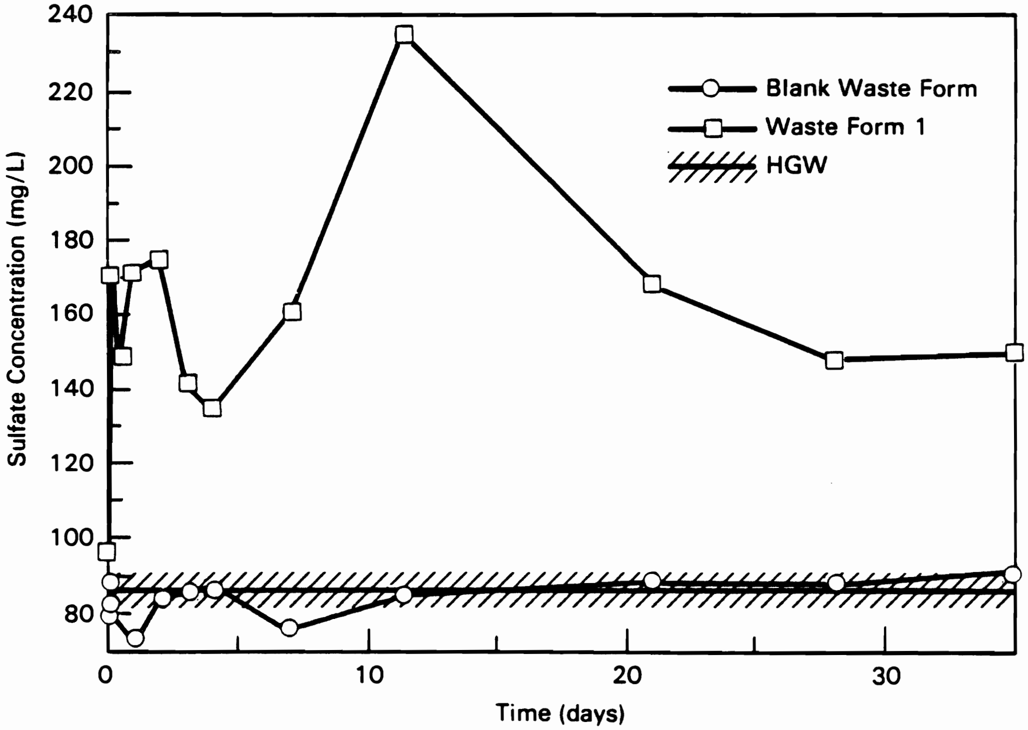


FIGURE 6.7. Sulfate Concentrations in the ANS 16.1 Leachates

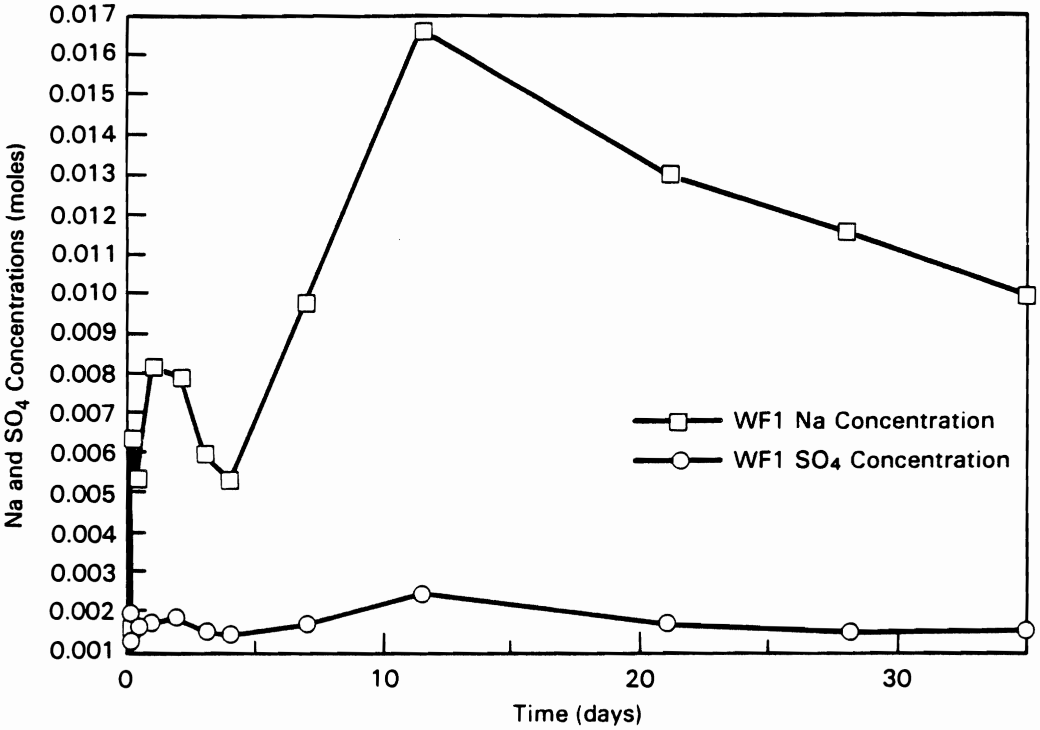


FIGURE 6.8. A Comparison of Sodium and Sulfate Concentrations in the ANS 16.1 Leachates

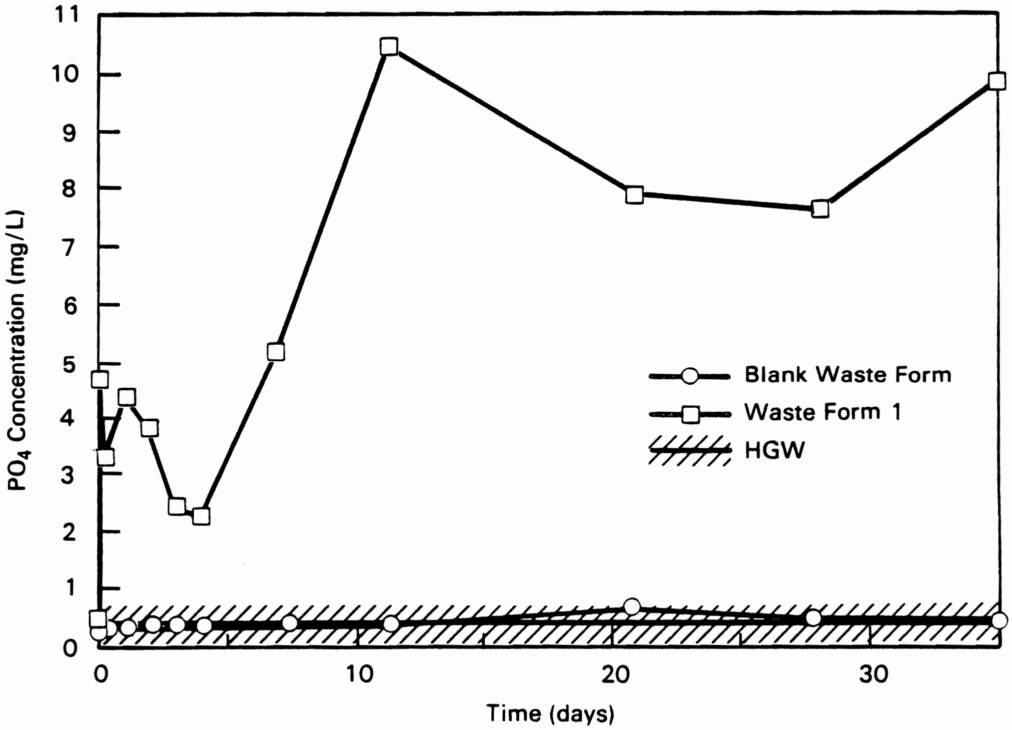


FIGURE 6.9. Phosphate Concentrations in the ANS 16.1 Leachates

total alkalinity. According to the MINTEQ calculations (Table 6.1), only 19% of the alkalinity results from noncarbonate species.

Although aluminum and silicon are both major components of Portland III cement, neither element is present in large concentrations in the leachates from the blank waste form or waste form 1. Aluminum concentrations are maintained below detection limit throughout both experiments, despite variations in pH. Silicon concentrations illustrated in Figure 6.10 range from 14 to 17 mg/L in the leachates in contact with the blank. Silicon concentrations decrease from almost 17 mg/L to less than 9 mg/L in the leachates from the waste form 1 experiment. Silicon and aluminum may never leach from the waste forms or they may be immediately incorporated into new solid phases. Silicon may be controlled by different silicate phases in the blank waste form and waste form 1 leachates.

Potassium concentrations (Figure 6.11) in the leachates from both experiments are higher than the Hanford ground-water concentration of 7.35 mg/L. For the blank waste form a maximum potassium concentration of about 50 mg/L occurs after 1 day of contact while roughly the same peak concentration is delayed for 11 days in the leachates from the waste form 1 experiment. Potassium in the waste form 1 leachates must come from both the cement and the waste stream.

Figures 6.12 through 6.15 illustrate the variation in solution concentrations of Ba, B, Sr, and Cl for both ANS 16.1 experiments. Barium concentrations are low relative to Hanford ground water (0.05 mg/L) in the leachates in contact with waste form 1. They are initially low in the leachates in contact with the blank but increase through time, reaching the ambient ground-water value of roughly 0.058 mg/L. Boron concentrations range from greater than 0.05 mg/L to less than 0.16 mg/L. All leachate boron concentrations are higher than that in the Hanford ground water. Strontium concentrations in the waste form 1 leachates are low from 1 to 4 days of contact, then they increase to the Hanford ground-water concentration of 0.25 mg/L. In the blank waste form leachates, strontium is leached quickly during the first few hours of contact, and continues to leach more readily than from waste form 1. Chlorine shows almost identical concentration trends in both ANS 16.1 experiments. A peak of greater than 26 mg/L Cl^- is reached after 7 days of contact and a minimum of

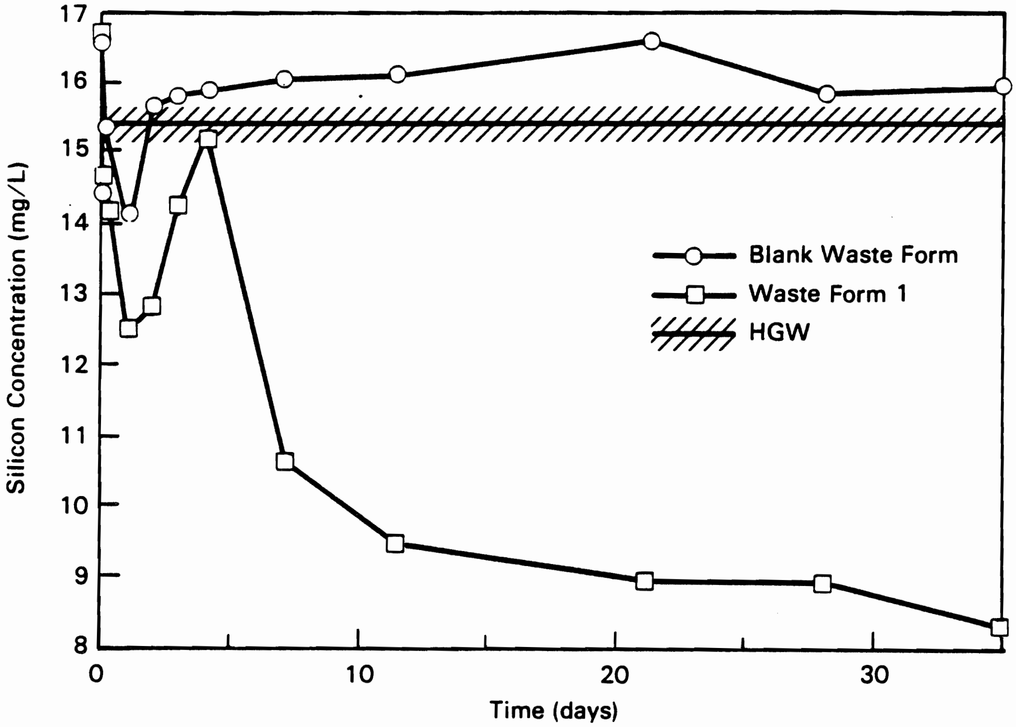


FIGURE 6.10. Silicon Concentrations in the ANS 16.1 Leachates

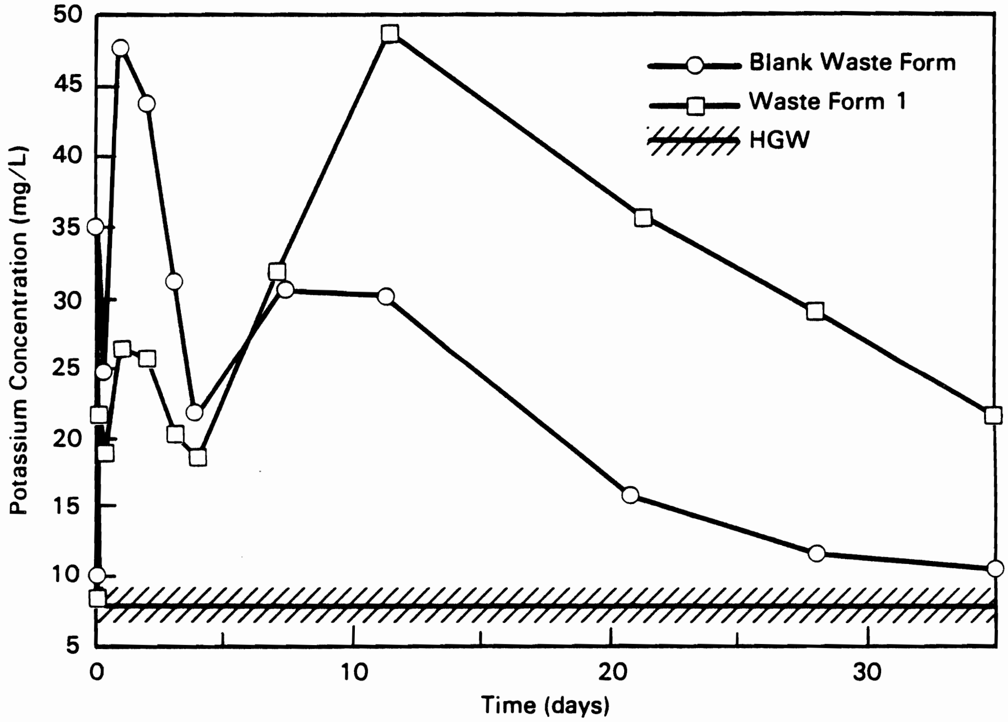


FIGURE 6.11. Potassium Concentrations in the ANS 16.1 Leachates

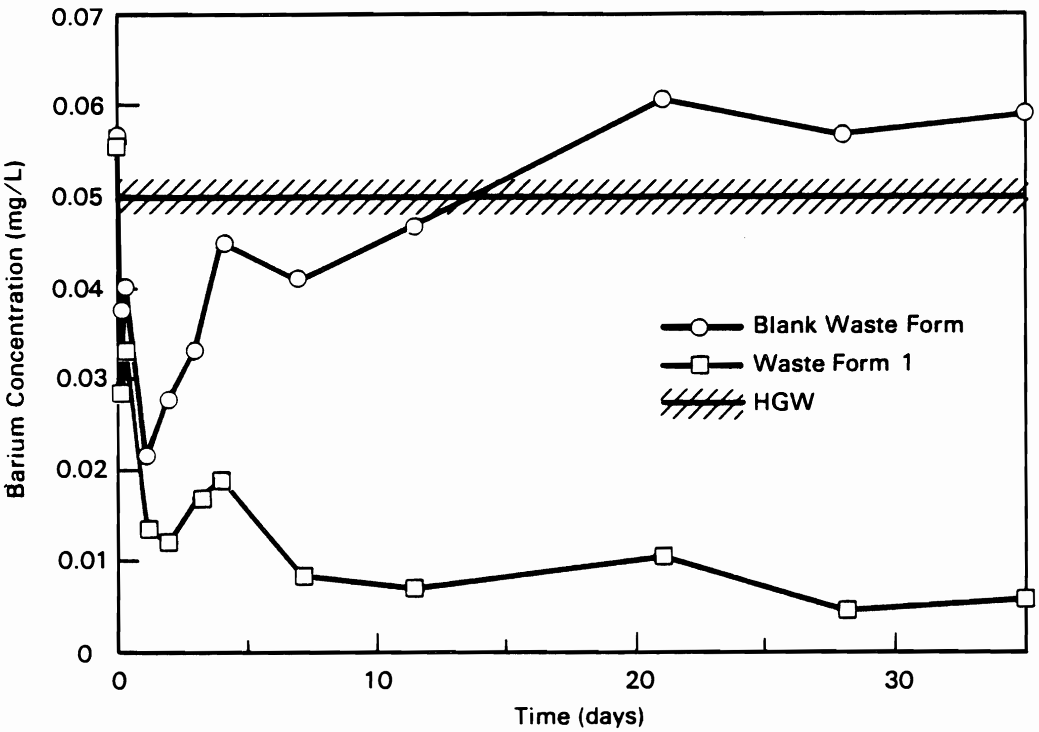


FIGURE 6.12. Barium Concentrations in the ANS 16.1 Leachates

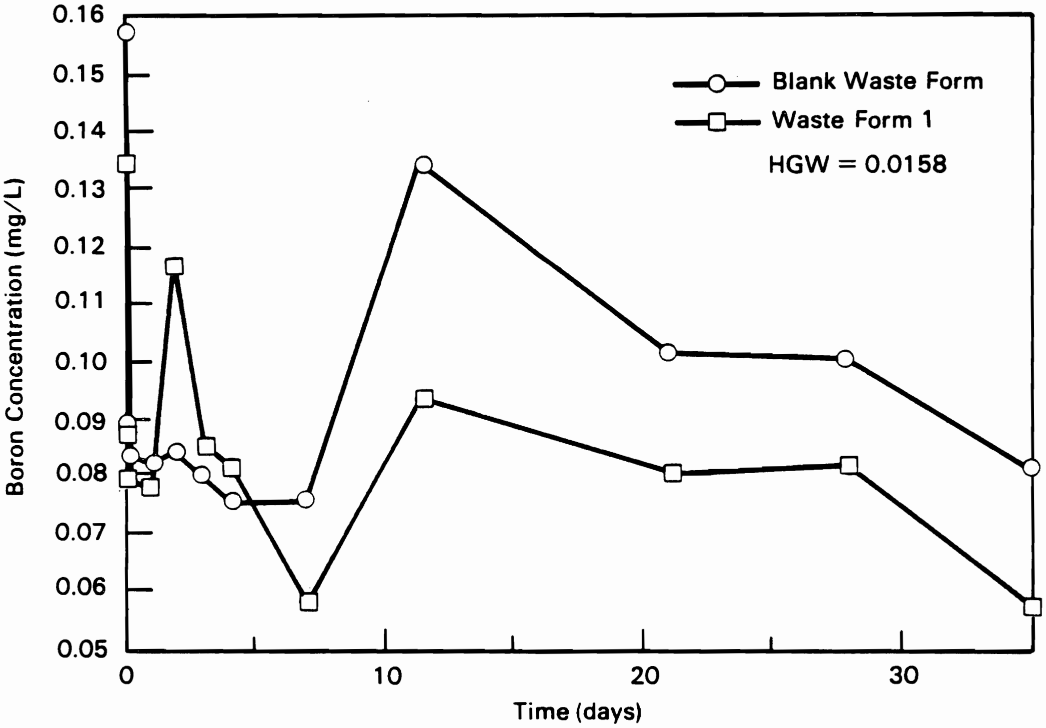


FIGURE 6.13. Boron Concentrations in the ANS 16.1 Leachates

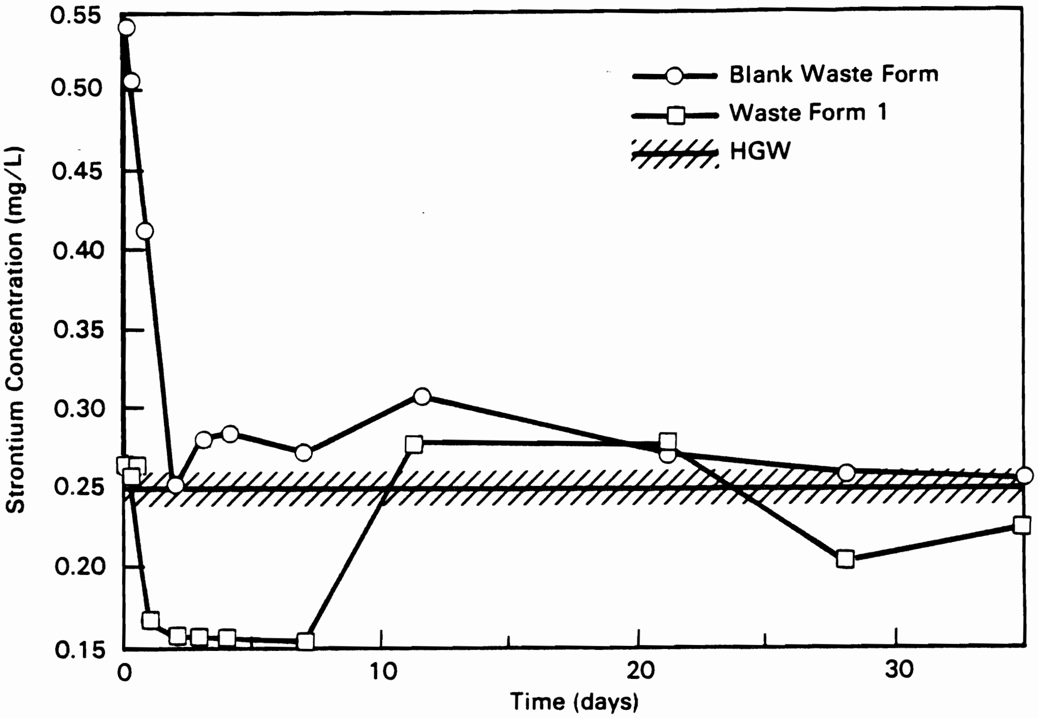


FIGURE 6.14. Strontium Concentrations in the ANS 16.1 Leachates

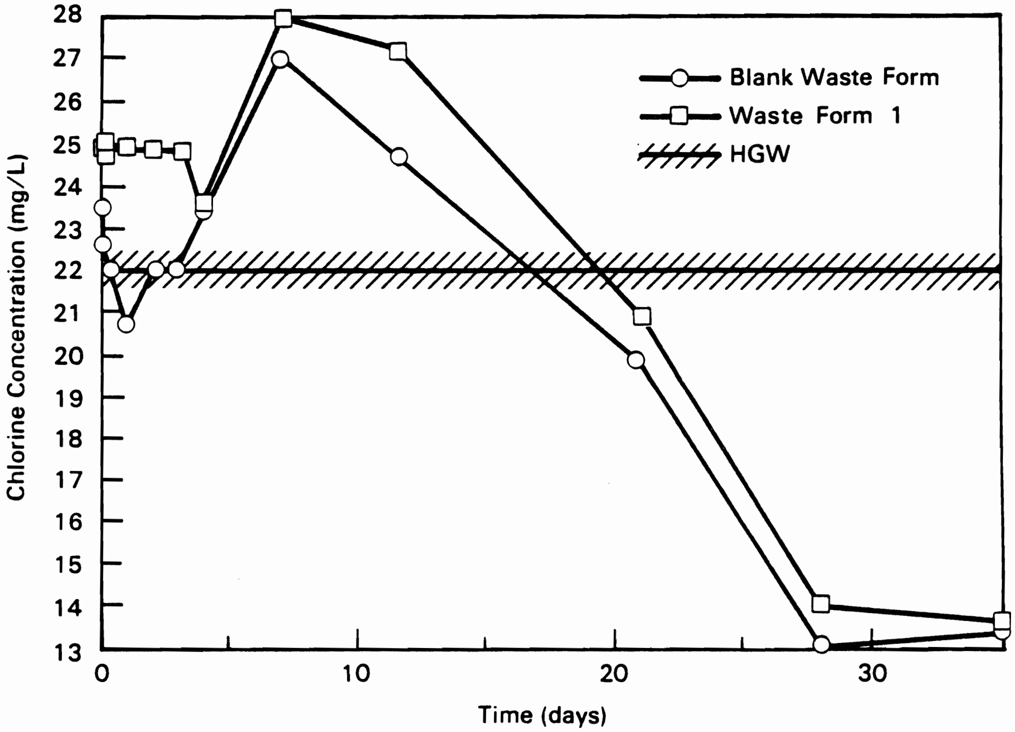


FIGURE 6.15. Chlorine Concentrations in the ANS 16.1 Leachates

less than 15 mg/L after 25 days of contact. Chlorine concentrations in the leachates are from cement leaching, not the waste stream.

In summary, it appears that the concentrations of most of the components in solution are initially pH dependent. In both the blank waste form and waste form 1 experiments, a maximum in pH after 1 day of contact corresponds to a minimum in Ca, Mg, Si, and Ba concentrations and a maximum in K concentrations. In fact, these variables (pH, K, Ca, Mg, Si, and Ba) display the same trends in the leachates from both experiments for the first 4 days of waste form/solution contact. These trends suggest that reactions between cement and ground water initially control the leachate concentrations in both experiments.

However, SO_4, PO_4, and Na concentrations in the leachates from the waste form 1 experiment increase with K during the first day of the experiment and decrease during the next 3 days of contact. These components in waste form 1 are predominately from the waste stream, not the cement. Initial reactions during the first 4 days of the experiments are probably between the surfaces of the waste forms and the ground water. Diffusion of components through the waste forms may become important later in the experiments, after the surfaces have been modified through precipitation/dissolution reactions and when the waste forms have remained in contact with the solution for longer periods of time.

6.2 ION SPECIATION

Figures 6.16 through 6.29 illustrate the species distribution for the major components in the leachates from both ANS 16.1 experiments. The first column in each figure represents the species distribution calculated for Hanford ground water using MINTEQ. Figures 6.16 through 6.22 show that there are no major differences in the species distribution for Ca, Mg, Si, B, CO_3, SO_4, and PO_4 for the Hanford ground water and the leachates in contact with the blank waste form. Calcium (Figure 6.16) is present in solution primarily (~90%) as the free ion Ca^{2+}. Approximately 10% of the calcium in solution is present as $CaSO_4^0$, $CaCO_3^0$, and $CaHCO_3^+$. Magnesium (Figure 6.17) is also present in solution in four forms (Mg^{2+}, $MgCO_3^0$, $MgHCO_3$, and $MgSO_4^0$), again primarily as the free ion Mg^{2+}.

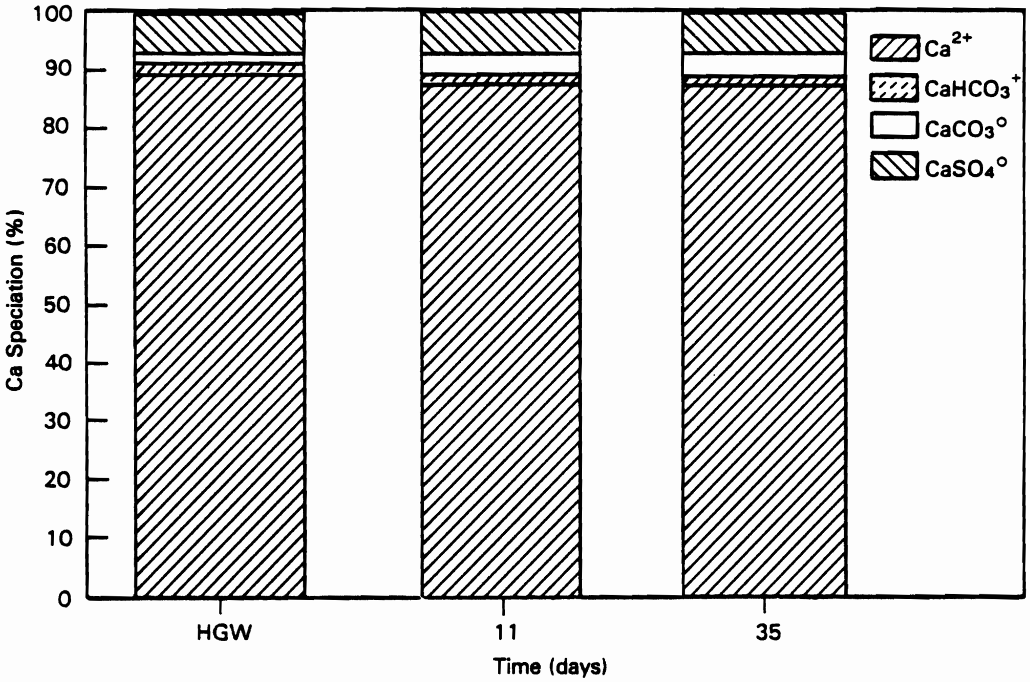


FIGURE 6.16. Calcium Species Present in the ANS 16.1 Blank Waste Form Leachates

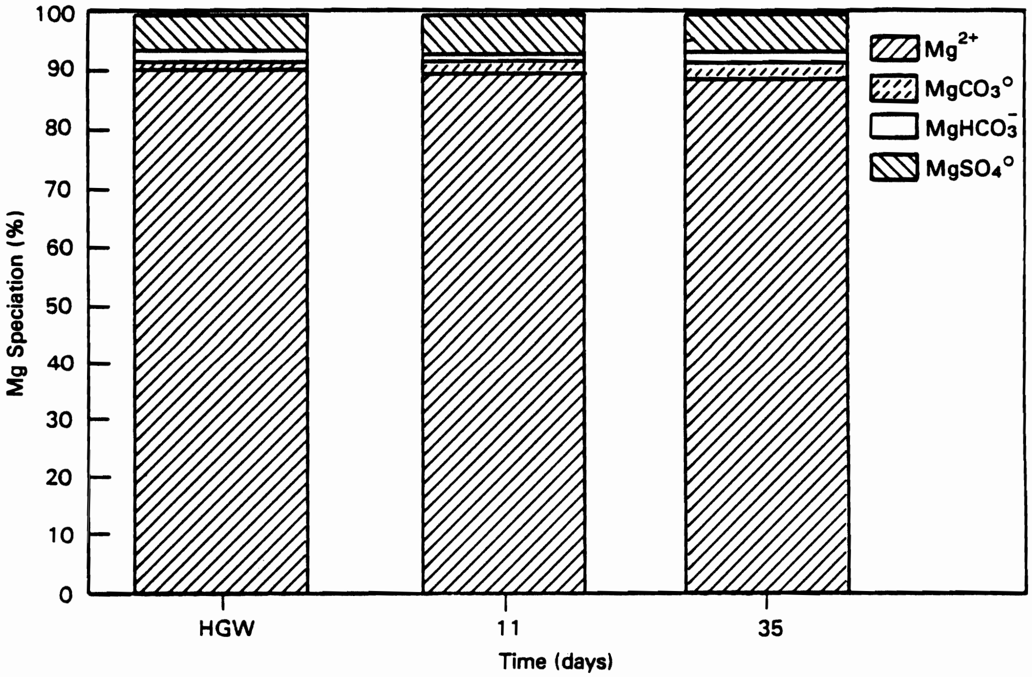


FIGURE 6.17. Magnesium Species Present in the ANS 16.1 Blank Waste Form Leachates

Silicon and boron (Figures 6.18 and 6.19) are each present in a neutral species ($H_4SiO_4^0$ and $H_3BO_3^0$, respectively) and a negative species ($H_3SiO_4^-$ and $H_2BO_3^-$, respectively). The majority (>95%) of silicon is present in solution as H_4SiO_4. More of the negative complex $H_3SiO_4^-$ (~5%) is present in the leachates from the blank waste form experiment than in the Hanford ground water (~2%). Roughly 20% of the boron present in the leachates is in the complex $H_2BO_3^-$, while only 10% of the boron in the Hanford ground water is present in this complex.

The carbonate species (Figure 6.20) present in the Hanford ground water are not the same as those present in the leachates from the blank waste form experiment. In both cases, HCO_3^- is the predominant carbonate species. However, a minor amount of $H_2CO_3^0$ is present in the ground water, while minor amounts of CO_3^{2-} and $CaCO_3^0$ are present in the leachates.

Sulfate is present as SO_4^{2-}, $MgSO_4^0$, and $CaSO_4^0$ in both the Hanford ground water and the leachates in contact with the blank waste form (Figure 6.21). Phosphate (Figure 6.22) is present in six species ($MgPO_4^-$, $MgHPO_4^0$, $CaHPO_4^0$, $CaPO_4^-$, HPO_4^{2-}, and $H_2PO_4^-$) in both the leachates and ground water. Approximately 50% of the phosphate in solution is present as HPO_4^{2-}. $H_2PO_4^-$ is present in only minor amounts (<5%), and the rest of the phosphate in solution is fairly evenly distributed among the other four species.

While there are no major variations in species distribution in the leachates in contact with the blank waste form, major changes in the distribution of major component species do occur during the batch leaching experiment with waste form 1. Figure 6.23 shows that while calcium is present in four species (Ca^{2+}, $CaHCO_3^+$, $CaCO_3^0$, and $CaSO_4^0$) in the Hanford ground water, it is present in six species in the leachates that were in contact with waste form 1. The additional calcium complexes present in solution are $CaPO_4^-$ and $CaOH^+$. Ca^{2+}, the predominant (~90%) calcium species in the ground water, becomes progressively less important as the experiment proceeds until, after 11 days of waste form/ground-water contact, only 15% of the calcium in solution is present as the free ion. $CaCO_3^0$ (aq) is a more important calcium complex in the leachates than in the ground water; on average, 25% of the calcium in the leachates is present

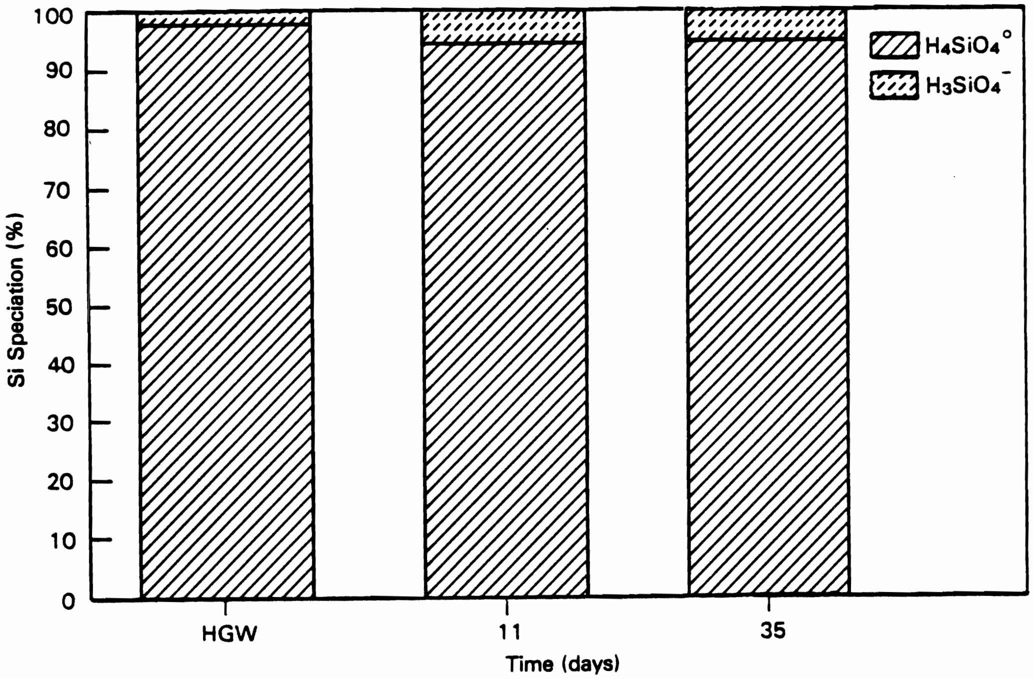


FIGURE 6.18. Silicon Species Present in the ANS 16.1 Blank Waste Form Leachates

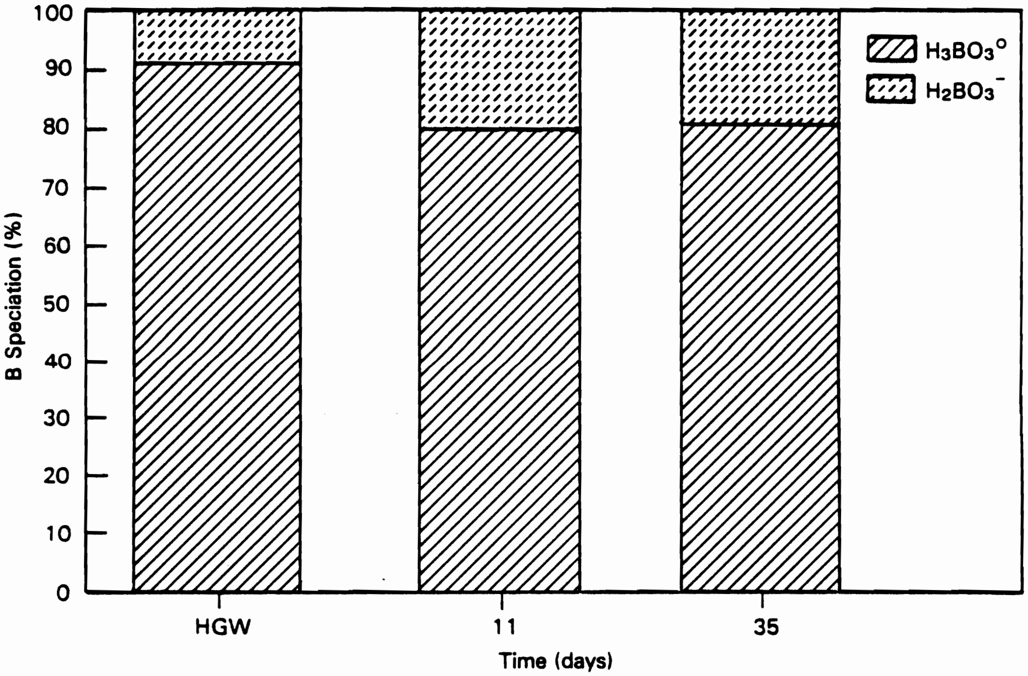


FIGURE 6.19. Boron Species Present in the ANS 16.1 Blank Waste Form Leachates

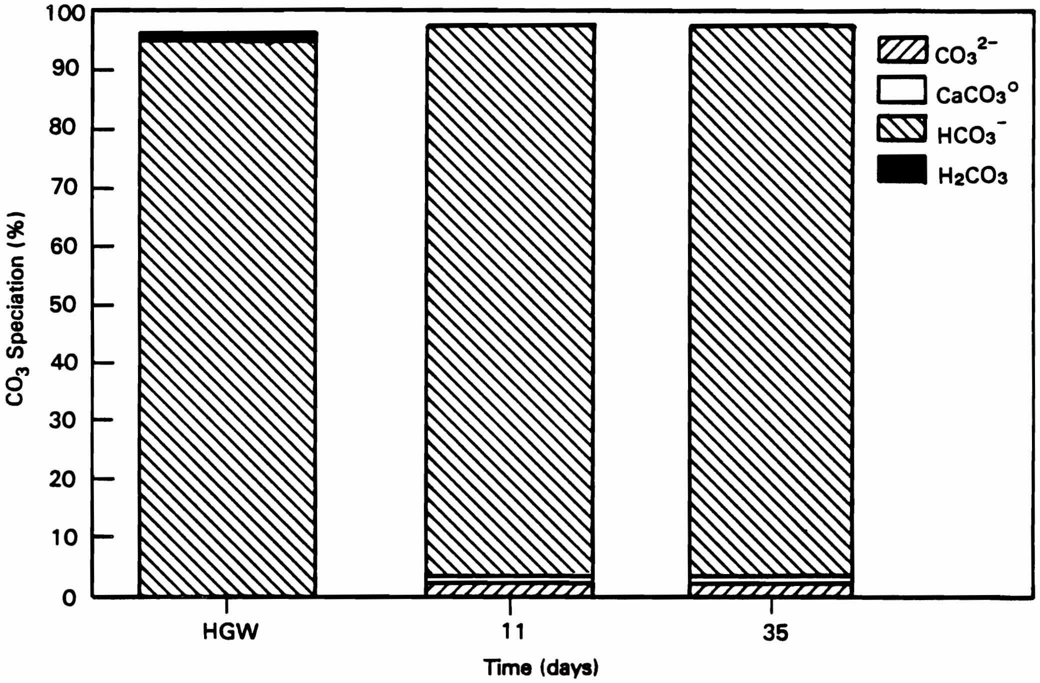


FIGURE 6.20. Carbonate Species Present in the ANS 16.1 Blank Waste Form Leachates

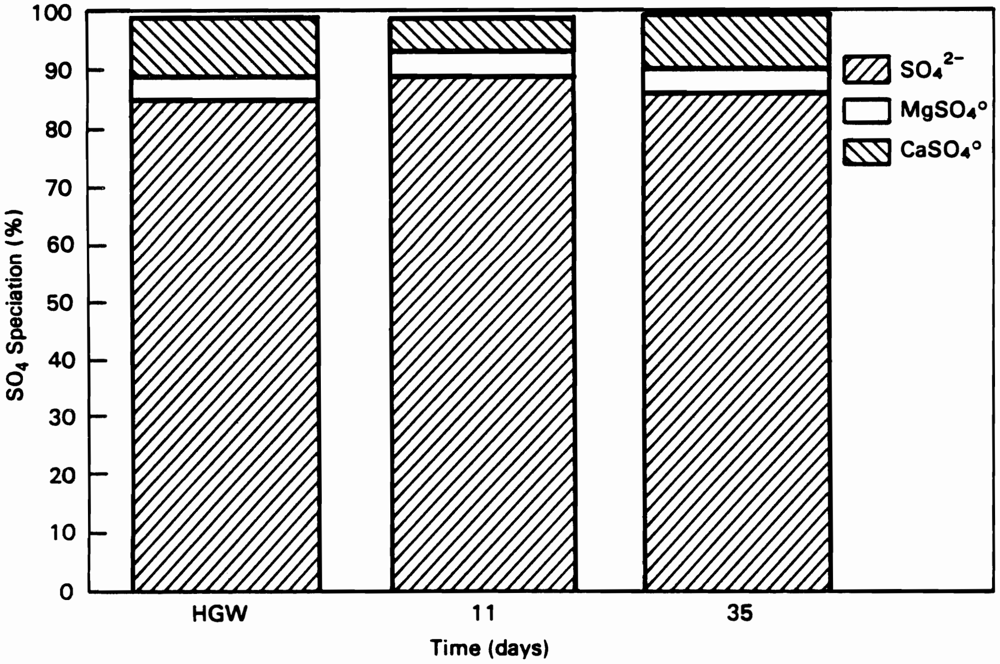


FIGURE 6.21. Sulfate Species Present in the ANS 16.1 Blank Waste Form Leachates

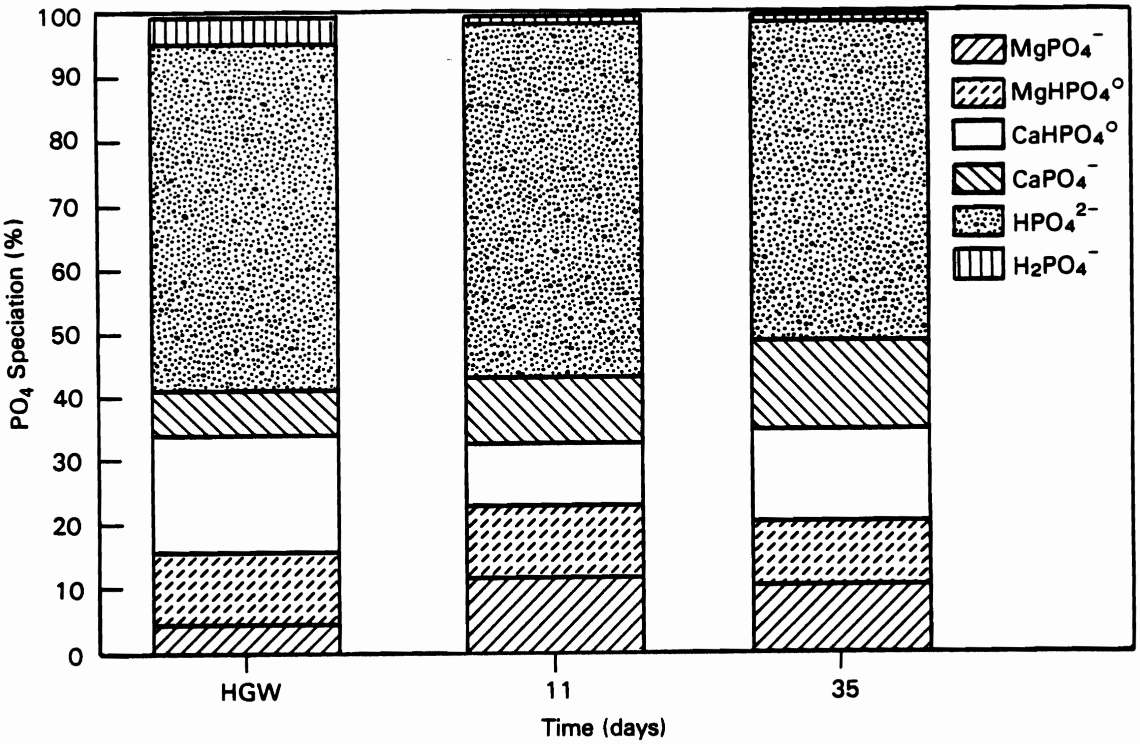


FIGURE 6.22. Phosphate Species Present in the ANS 16.1 Blank Waste Form Leachates

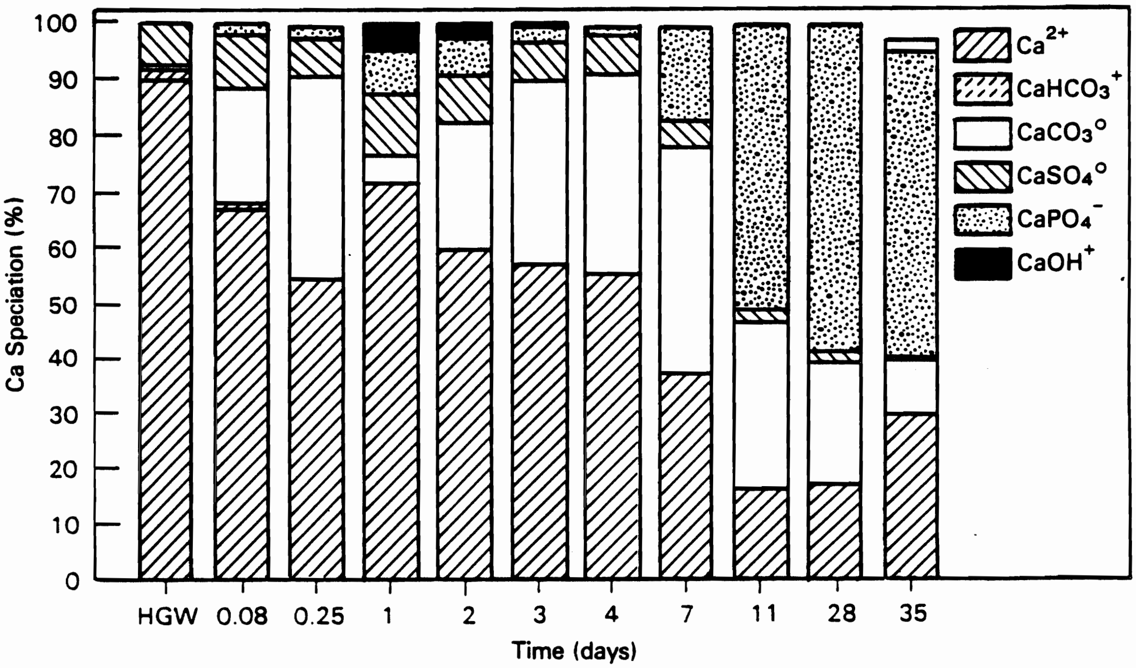


FIGURE 6.23. Calcium Species Present in the ANS 16.1 Waste Form 1 Leachates

as $CaCO_3^0$ (aq). $CaPO_4^-$ becomes the predominant calcium species in solution after 11 days of contact with waste form 1. $CaOH^+$ is only present in minor amounts (<5%) in some of the leachates.

The species distribution for magnesium is illustrated in Figure 6.24. Again, magnesium is present in the leachates in six forms: Mg^{2+}, $MgCO_3^0$, $MgHCO_3^-$, $MgSO_4^0$, $MgPO_4^-$, and $MgOH^+$. Mg^{2+}, the predominant magnesium ion in the Hanford ground water, becomes less significant as the experiment proceeds. After 35 days, the three predominant magnesium species are $MgPO_4^-$, Mg^{2+}, and $MgOH^+$, in that order. The magnesium hydroxide species, $MgOH^+$, can account for up to 25% of the magnesium in solution; it is more prevalent than the equivalent calcium hydroxide species, $CaOH^+$.

It is worth noting that, although the pH of the leachate after 1 day and the pH after 28 days are both about 11.5, the solution compositions are sufficiently different that the speciation of Ca and Mg is not the same. After 1 day of contact, Ca^{2+} is the predominant calcium species; after 28 days, $CaPO_4^-$ is the predominant calcium species. Magnesium is present as Mg^{2+}, $MgOH^+$, and $MgPO_4^-$ after 1 day of contact between waste form 1 and the Hanford ground water. The same species are present after 28 days of contact, but their order of significance has changed to $MgPO_4^-$, Mg^{2+}, and $MgOH^+$.

The majority of the silicon in the ground water is present as $H_4SiO_4^0$, while $H_3SiO_4^-$ and $H_2SiO_4^{2-}$ are the major silicon species in the leachates from the waste form 1 experiment (Figure 6.25). Boron, present mainly as H_3BO_3 in Hanford ground water, is present mainly as $H_2BO_3^-$ in the waste form 1 leachates (Figure 6.26).

Carbonate species (Figure 6.27) in Hanford ground water include HCO_3^- and $H_2CO_3^0$. Carbonate is present in five species in the leachates from the waste form 1 experiment: these species are CO_3^{2-}, $MgCO_3^0$, $CaCO_3^0$, HCO_3^-, and $NaCO_3^-$. CO_3^{2-} replaces HCO_3^- as the predominate species in the leachates after 6 h (0.25 day) of contact. $CaCO_3^0$ and HCO_3^- are significant species in the leachates analyzed after 6 h (0.25 day), 3 days, and 4 days of contact. $NaCO_3^-$ becomes a more significant species after 11 days of contact between waste form 1 and ground water.

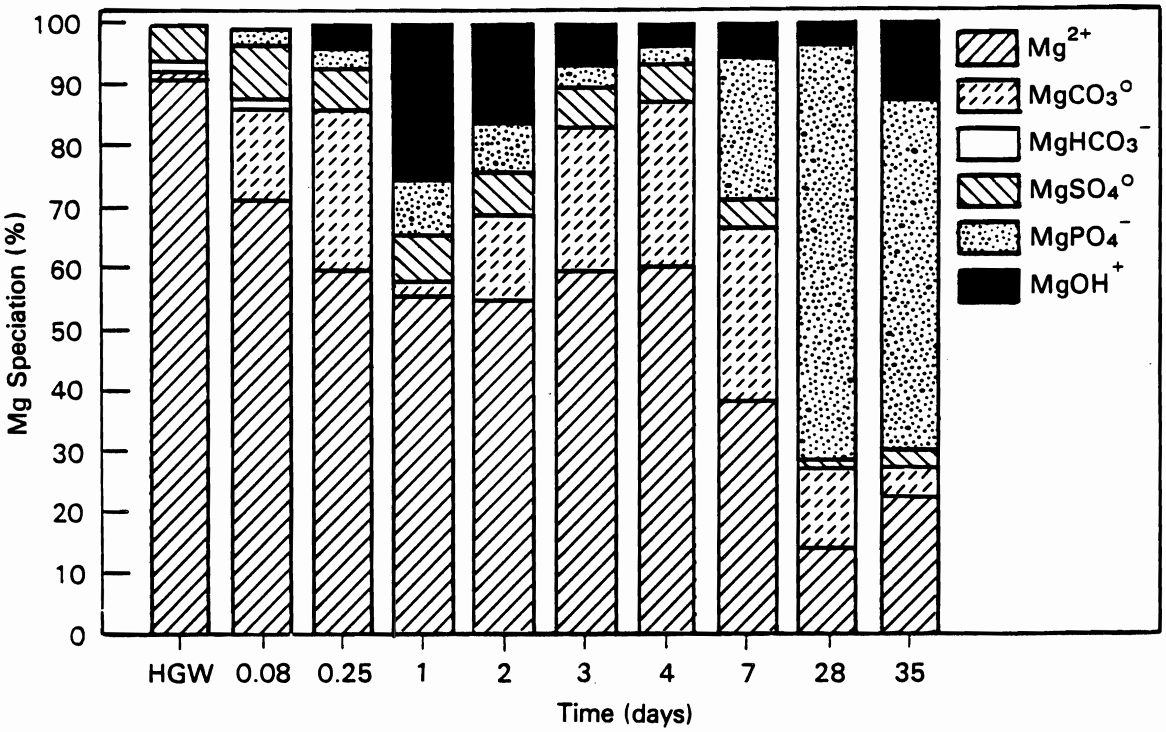


FIGURE 6.24. Magnesium Species Present in the ANS 16.1 Waste Form 1 Leachates

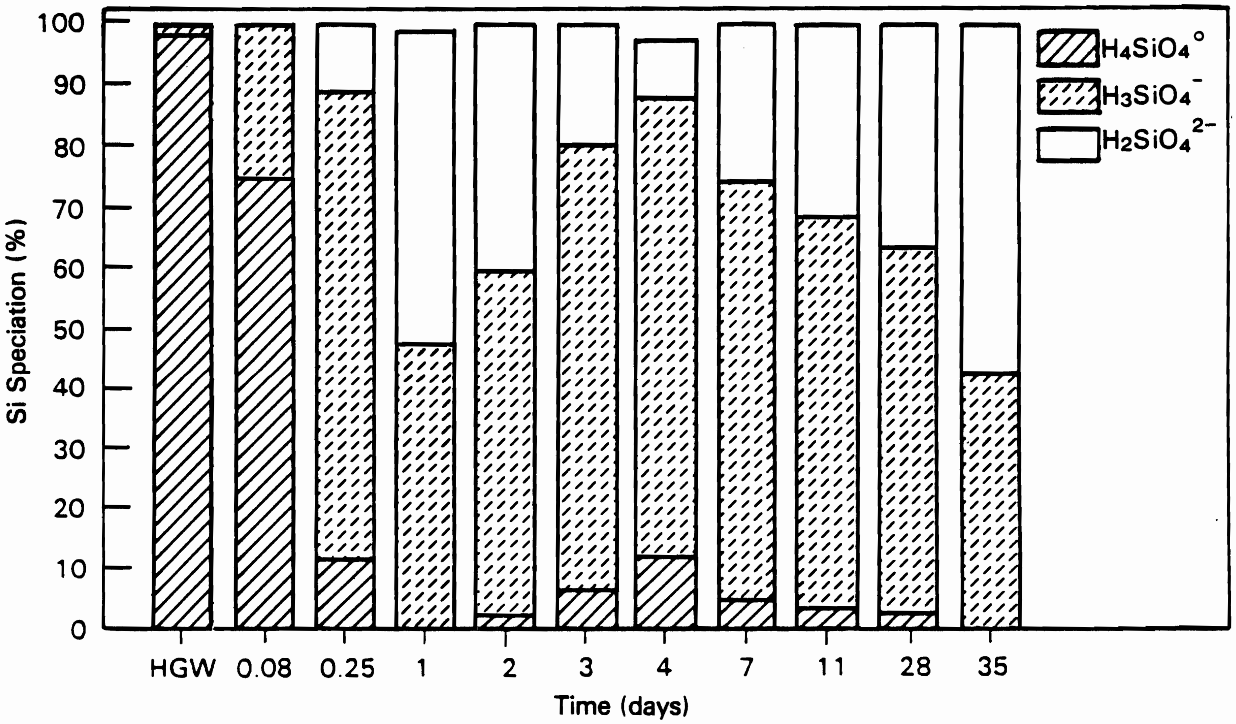


FIGURE 6.25. Silicon Species Present in the ANS 16.1 Waste Form 1 Leachates

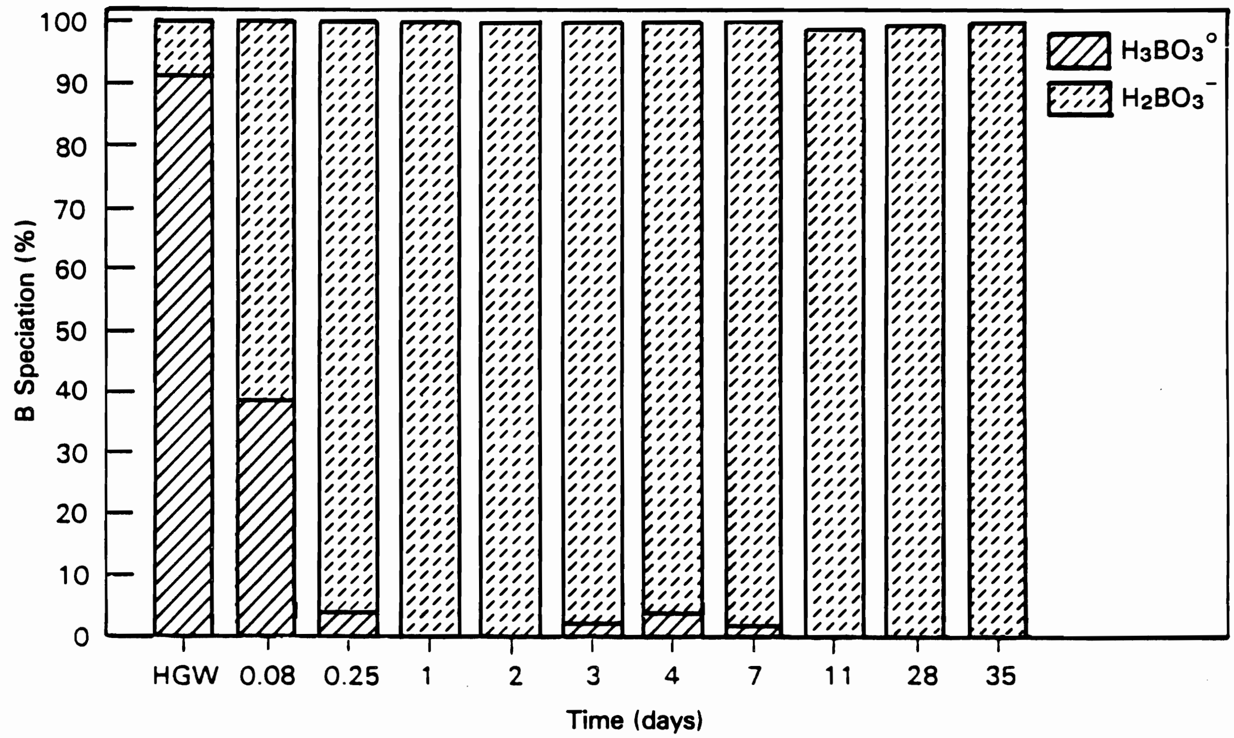


FIGURE 6.26. Boron Species Present in the ANS 16.1 Waste Form 1 Leachates

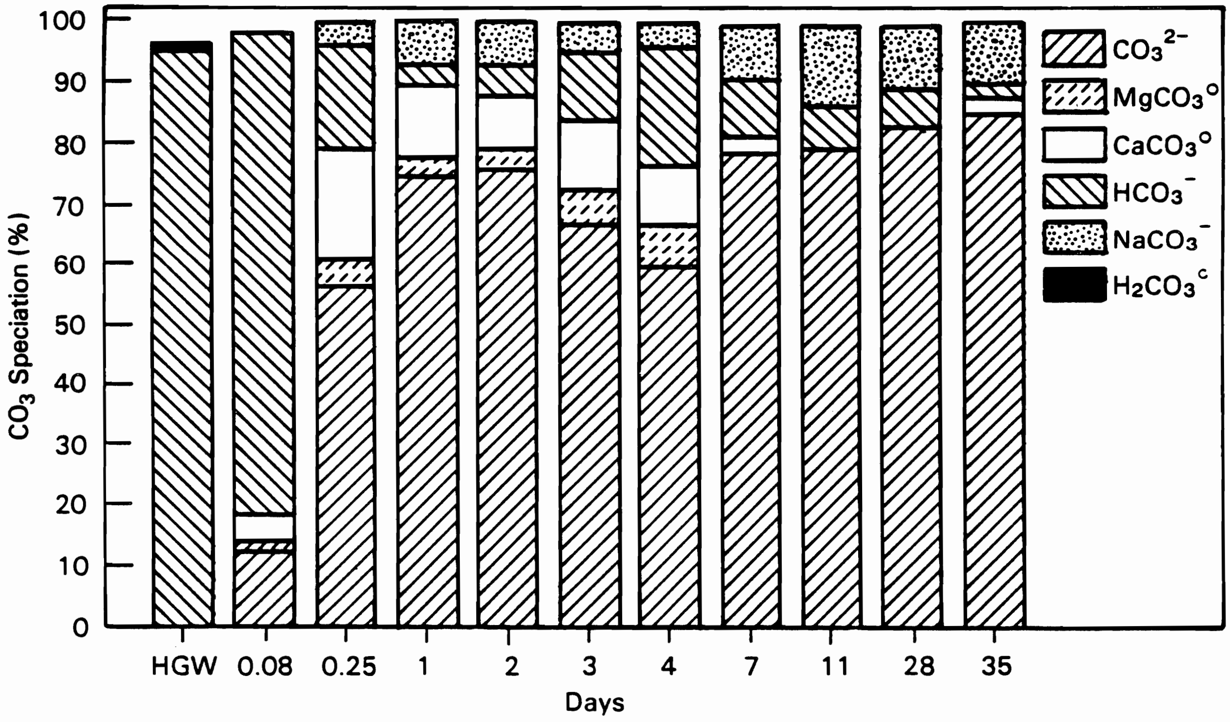


FIGURE 6.27. Carbonate Species Present in the ANS 16.1 Waste Form 1 Leachates

Sulfate (Figure 6.28) is present mainly as SO_4^{2-}, $CaSO_4^0$, and $MgSO_4^0$ in Hanford ground water. SO_4^{2-} remains the predominant sulfate species throughout the experiment. $NaSO_4^-$ appears as a new species after 2 h of contact between the ground water and waste form 1. The other species ($CaSO_4^0$ and $MgSO_4^0$) become negligible in concentration after 7 days of waste form/water contact.

Phosphate is present in six aqueous complexes in the Hanford ground water: $H_2PO_4^-$, $MgPO_4^-$, $MgHPO_4^0$, $CaHPO_4^0$, $CaPO_4^-$, and HPO_4^{2-} (see Figure 6.29). HPO_4^{2-} is the most important phosphate species present in the ground water. With the exception of $H_2PO_4^-$, these same complexes are found in the leachates. PO_4^{3-} is also present in minor amounts in the leachates after 7 days of contact. $MgPO_4^-$ and $CaPO_4^-$ are the predominant phosphate species through 7 days of contact; the concentration of $MgPO_4^-$ then becomes negligible, and $CaPO_4^-$ and HPO_4^{2-} are the major phosphate species in solution after 11 and 28 days of waste form/ground-water contact. In the final leachate sampled, after 35 days of contact, phosphate is present primarily (90%) as $CaPO_4^-$, and in minor quantities as $MgPO_4^-$, HPO_4^{2-}, and PO_4^{3-}.

6.3 SATURATION INDICES FOR MINERALS

The nature of the ANS 16.1 batch leaching experiment is such that an equilibrium state between the waste form and leachate may never be attained. The waste form is placed in contact with Hanford ground water for a period of time during which reaction can occur, then the leachate is completely replaced by fresh ground water. This experiment is an attempt to mimic a flow-through experiment in which the waste form is continuously in contact with fresh ground water. From the concentration and speciation data for the waste form 1 leachates, it can readily be observed that the waste form has not come to equilibrium with Hanford ground water: Reactions between the two are still occurring. The leachates from the blank waste form experiment are very similar in composition to Hanford ground water. It is unclear whether the blank waste form is in equilibrium with the ground water or not.

Table 6.2, which presents the saturation indices for minerals that might participate in reactions that occurred during these experiments, shows that Hanford ground water and the leachates from the blank waste form experiment are

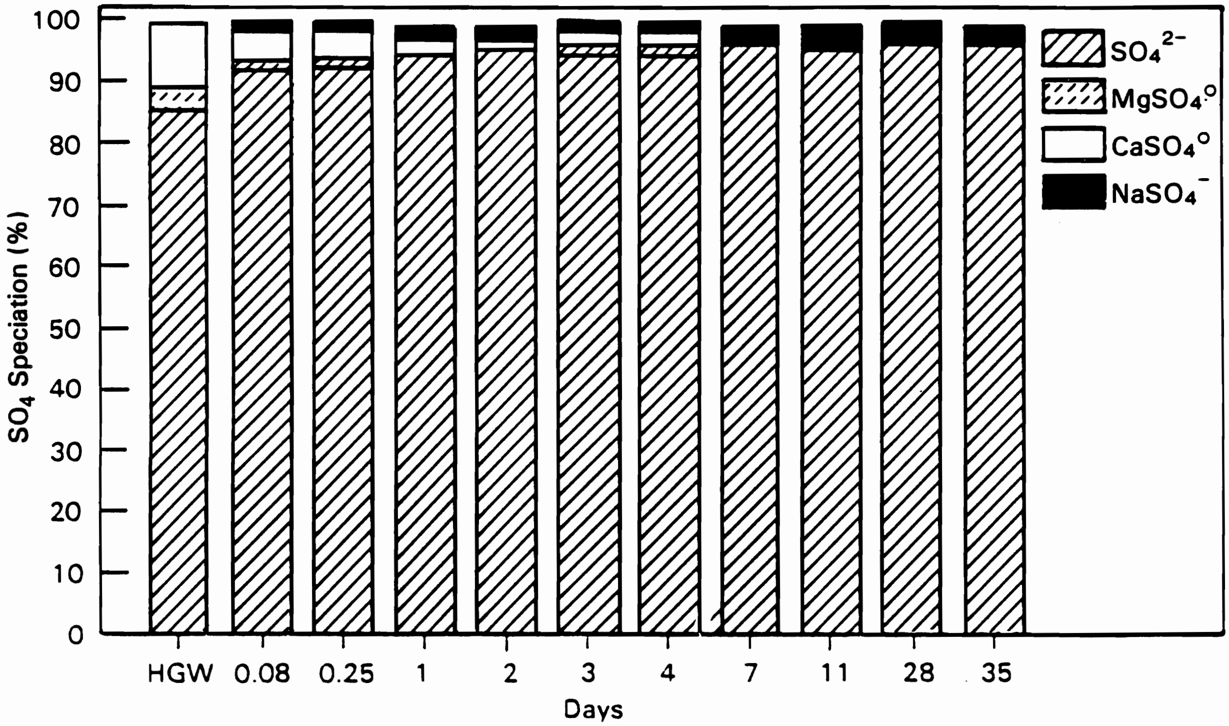


FIGURE 6.28. Sulfate Species Present in the ANS 16.1 Waste Form 1 Leachates

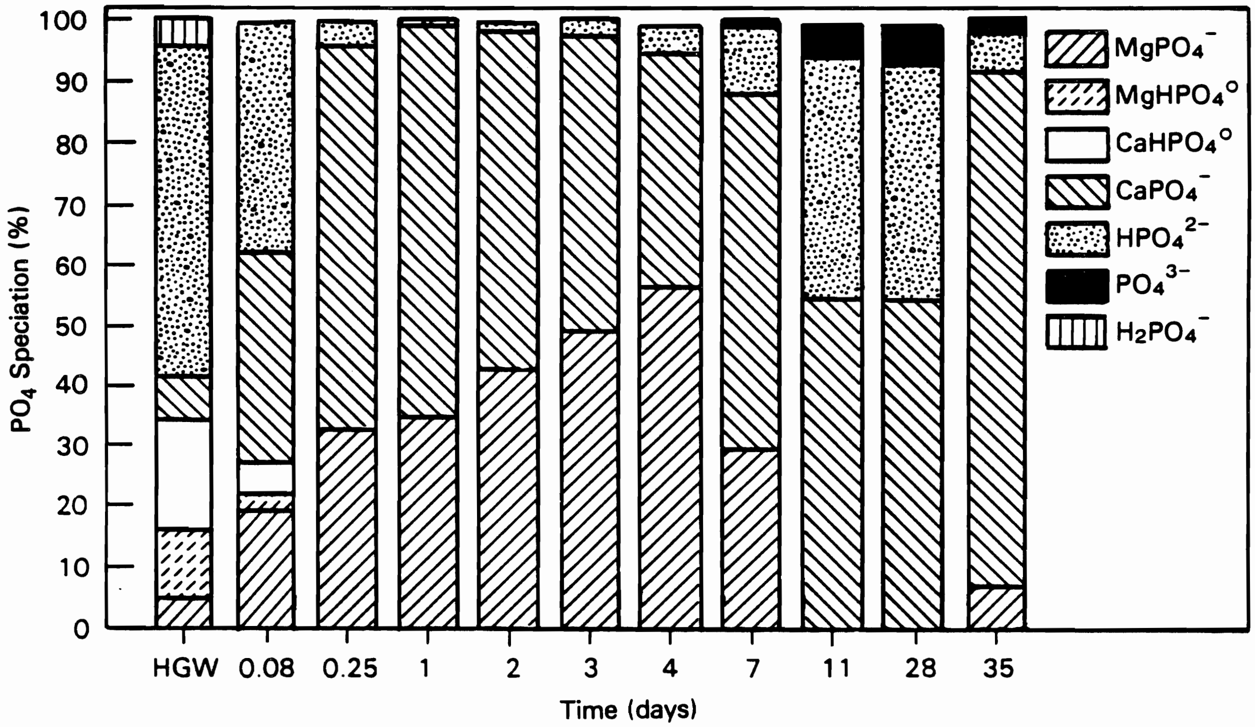


FIGURE 6.29. Phosphate Species Present in the ANS 16.1 Waste Form 1 Leachates

TABLE 6.2. Saturation Indices for Potential Solubility Controls in Batch Leaching Experiments

Sample	HGW(a)	Blank(b) (11.4)	Blank (35)	WF1(c) (4)	WF1 (7)	WF1 (11.4)	WF1 (28)	WF1 (35)
Carbonates								
Calcite	0.663	0.644	0.965	1.538	1.219	0.875	0.535	0.523
Dolomite	1.017	1.262	1.688	3.156	2.045	--	-0.991	-0.190
Magnesite	-0.142	-.122	0.227	1.122	0.331	--	-2.022	-1.208
Otavite	0.828	0.899	0.914	1.945	1.876	1.906	1.797	0.879
Rhodochrosite	-1.282	-1.304	-1.215	-0.286	-0.283	-0.077	-0.342	-1.302
Strontianite	-1.205	-0.835	-0.825	-0.852	0.374	0.874	0.579	0.013
Cerrusite	-0.860	-0.782	-0.793	-1.526	-2.142	-2.211	-2.589	-4.356
Sulfates								
Barite	0.118	0.111	0.215	-0.110	-0.459	-0.467	-0.768	-0.635
Gypsum	-1.482	-1.747	-1.517	-1.977	-2.504	-3.025	-3.328	-2.692
Celestite	-2.508	-2.384	-2.465	-3.524	-2.507	-2.442	-2.442	-2.359
Ettringite	-21.495	-20.480	-19.211	-14.065	-15.733	-18.892	-19.744	-14.551
Monosulfate	-23.593	-22.047	-21.237	-15.173	-15.785	-17.902	-18.148	-14.227
Phosphates								
$MnHPO_4$	0.200	-0.064	0.022	-0.590	-0.150	0.575	0.395	-0.591
Strengite	-1.885	-3.23	-3.08	-9.629	-10.196	-9.778	-10.099	-10.471
Hydroxyapatite	2.026	2.353	3.669	7.922	8.788	8.289	7.796	9.936
Hydroxides/Oxides								
Brucite	-0.446	-0.370	-0.352	0.854	0.639	-2.978	-1.408	-3.443
Gibbsite	-0.254	-0.178	-0.160	-2.458	-2.885	-2.786	-3.088	-3.251
Diaspore								
Portlandite	-9.372	-8.818	-8.637	-5.059	-4.802	-5.272	-5.179	-3.848
Lime	-19.494	-18.940	-18.759	-15.181	14.923	-15.394	-15.301	-13.97
$Cr(OH)_3$								
Maghemite ($\gamma Fe0_3$)	6.292	5.230	5.256	1.252	0.398	0.215	-0.007	-0.425
Ferrihydrite	1.448	0.917	0.930	-1.072	-1.499	-1.591	-1.702	-1.911
Wulfenite	--	0.166	-0.413	-1.660	-3.403	-3.615	-3.978	-5.119
Silicates								
SiO_2 (A)(d)	-0.561	-0.553	-0.557	-1.472	-2.099	-2.272	-2.438	-2.980
Chalcedony	0.252	0.260	0.256	-0.659	-1.286	-1.459	-1.625	-2.167
Cristobalite	0.316	0.324	0.320	-0.595	-1.222	-1.395	-1.561	-2.103
Quartz	0.735	0.743	0.739	-0.176	-0.803	-0.976	-1.142	-1.684
Sepiolite (C)(e)	0.163	1.861	1.781	6.833	4.521	--	-0.587	2.101
Willemite	0.562	-0.887	-1.211	-0.156	-0.838	-1.223	-1.420	--

(a) HGW, Hanford ground water.
(b) Numbers in parenthesis are days experiment has been under way.
(c) WF1, waste form 1.
(d) A, amorphous.
(e) C, crystalline.

oversaturated and undersaturated with respect to the same minerals. For the carbonate minerals, these solutions are all slightly oversaturated with respect to calcite, dolomite, and otavite; in equilibrium with magnesite; and undersaturated with respect to rhodochrosite, strontianite, and cerrusite. The sulfate minerals considered include barite, gypsum, ettringite, and monosulfate. The leachates and the ground water appear to be in equilibrium with barite and undersaturated with respect to the other three minerals. These solutions also appear to be in equilibrium with $MnHPO_4$ and oversaturated with respect to hydroxyapatite. The leachates and the ground water are oversaturated in quartz and undersaturated with respect to amorphous SiO_2. The only noticeable difference between the Hanford ground water and the leachates is that the ground water appears to be in equilibrium with sepiolite, while the leachates are oversaturated with respect to sepiolite.

The leachates are extremely undersaturated with respect to any of the possible cement minerals considered (portlandite, lime, ettringite, and monosulfate; saturation indices of -9, -19, -21, and -23, respectively). These results suggest that either 1) the reactions between the cement and Hanford ground water are extremely slow, and therefore do not strongly affect the leachate compositions over the course of the experiment, 2) mixing between the fluid trapped in the pores of the cement block and the bulk solution outside the block is extremely slow, or 3) a reaction rim that forms on the cement block is removing the cement from contact with the ground water. A reaction rim would most likely consist primarily of one or more of the oversaturated minerals. A preliminary mass transfer calculation, using MINTEQ, suggests that calcite, dolomite, and quartz would precipitate from the leachate.

The mineral saturation indices are different for the leachates from the waste form 1 experiment. Calcite, dolomite, and magnesite become more oversaturated after 4 days of contact with the ground water, and then become less saturated as the experiment progresses. This suggests that conditions are favorable for the precipitation of these carbonate phases. Barite is in equilibrium with the early leachates and undersaturated in the later leachates. Gypsum is undersaturated throughout the experiment. The leachates are extremely oversaturated with respect to hydroxyapatite. This observation is consistent with the increase in phosphate concentration in the leachate and the increased importance of calcium phosphate species in solution. The rate of precipitation for hydroxyapatite must be very slow in comparison to the rate at which phosphate is leaching from the waste form. The leachates are also extremely oversaturated with respect to sepiolite, and slightly oversaturated with respect to brucite.

The cement minerals are all closer to equilibrium with the leachates in contact with waste form 1, than with the leachates in contact with the blank waste form or with Hanford ground water. For example, the saturation index for portlandite in the solution in contact with cement only is approximately -9, while the same index is approximately -3 for the solution in contact with waste form 1. This observation suggests that waste form 1 and the ground water are reacting more quickly than the blank waste form in contact with the ground water. The cement in this waste form may be hydrating more quickly, forming ettringite or monosulfate within the block. Because the waste stream contains high calcium and sulfate concentrations, it is possible that the activities of these components in the pore fluid within the block are more suitable for ettringite or monosulfate precipitation to occur. If this reaction is occurring inside the block, it would serve to explain why more sodium than sulfate is leaching from waste form 1. The increased Ca concentration in the waste stream could also increase the activity of calcium in the leachates, bringing portlandite and lime closer to equilibrium with the leachates. A preliminary mass transfer calculation suggests that if a reaction rim is forming around waste form 1, it would consist primarily of sepiolite, dolomite, and calcite.

7.0 SOIL ADSORPTION EXPERIMENTS

This section describes both the results for the soil adsorption column experiments and the results of the ion speciation/solubility calculations for the leachates from these experiments.

7.1 CHEMICAL ANALYSES

Three sets of soil adsorption experiments were performed: Hanford sediment and ground water were used in one set, and Hanford sediment and a mixed leachate from the ANS 16.1 batch leaching of waste form 1 were used in two. All 24 available ANS 16.1 leachates (Walter et al. 1986) were mixed together to create a solution of sufficient volume. The composition of this mixed leachate was not determined analytically; however, an average composition was calculated for the major elements (Table 7.1). Because the results of both experiments with the leachate from the batch experiments [referred to as Soil Adsorption Column - Waste Form 1 in Walter et al. (1986)] were similar, only one of these experiments will be compared to the experiment using Hanford sediment and ground water.

Figures 7.1 through 7.15 illustrate the changes in solution composition as a function of pore volumes of fluid that have traveled through the soil adsorption columns. As shown in Figure 7.1, the pH for the blank soil column leachates increases slightly from 8.45 to 8.7 with continued contact between the soil and the Hanford ground water. The pH for the leachates from the waste form 1 soil column fluctuates between 8.5 and 10, reaching a maximum after 110 pore volumes of fluid have passed through the column. No trend in pH values is apparent in this experiment.

Figure 7.2 illustrates changes in alkalinity throughout the course of the experiments. The alkalinity for the blank is roughly the same as for the Hanford ground water, while the alkalinity of the leachates from the waste form 1 soil adsorption column continues to increase as more pore volumes of waste solution contact the soil. Figure 7.3 illustrates the total carbonate concentrations in solution as determined by the MINTEQ calculations. The carbonate concentration increases as the waste solution continues to contact the soil,

TABLE 7.1. Calculated Composition of Averaged Waste Solution

Constituent	Value
pH	9.46
Eh	287 mV
Alkalinity (as mg/L CO_3)	204.95 mg/L
Ca	20.15 mg/L
Mg	5.43 mg/L
K	25.68 mg/L
Na	197.00 mg/L
Ba	0.02 mg/L
Sr	0.20 mg/L
SO_4	164.32 mg/L
PO_4	5.76 mg/L
Si	12.73 mg/L
B	0.09 mg/L
Cl	23.53 mg/L

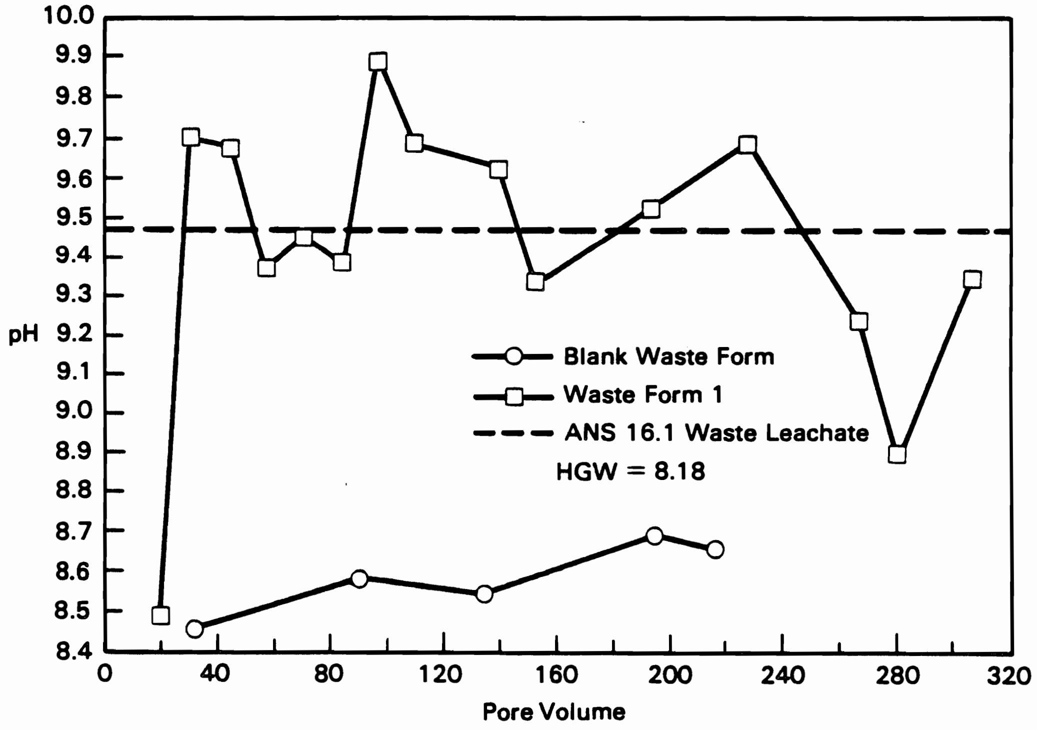


FIGURE 7.1. pH Values for the Soil Adsorption Column Leachates

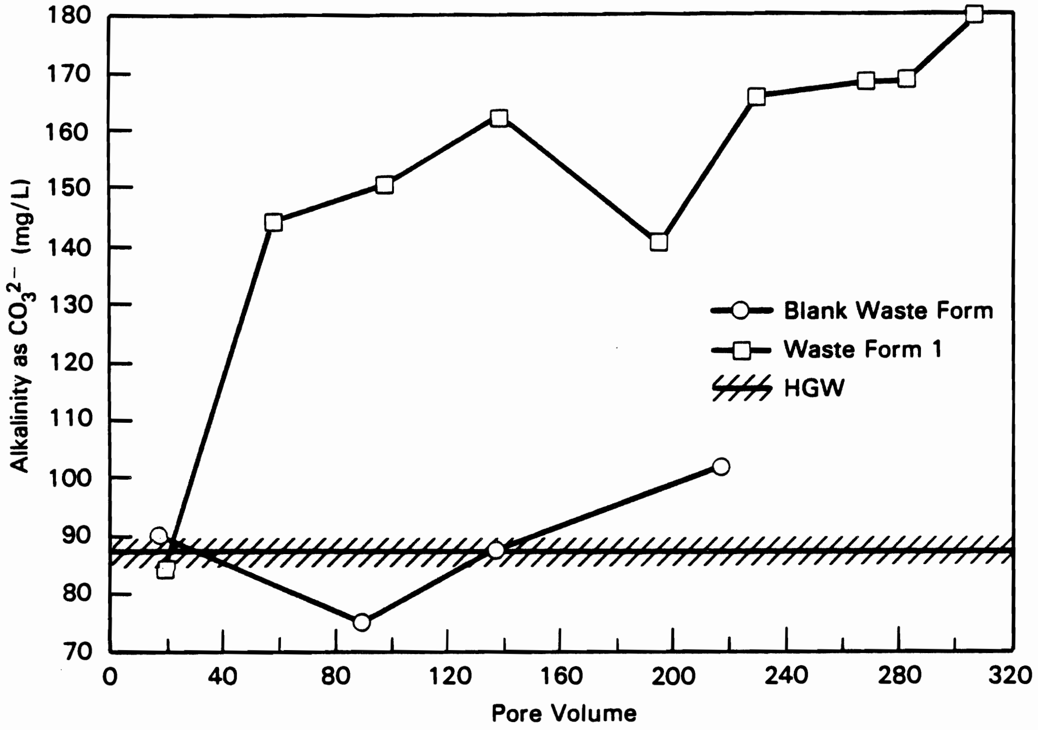


FIGURE 7.2. Alkalinity Values for the Soil Adsorption Column Leachates

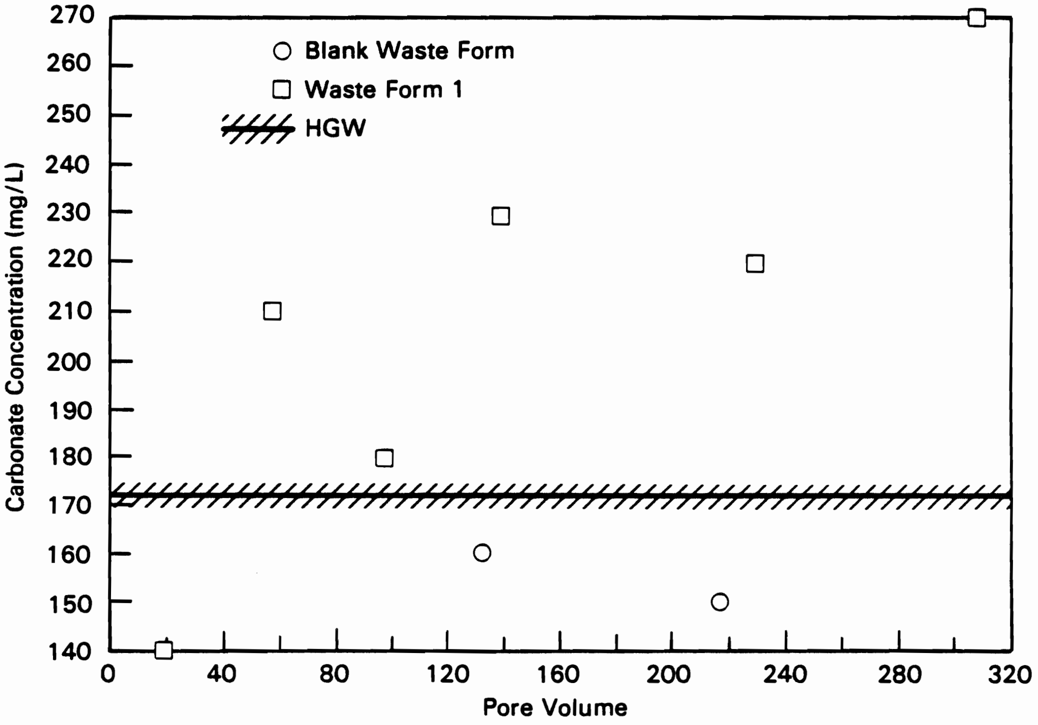


FIGURE 7.3. Carbonate Values Used in the MINTEQ Calculations for the Soil Adsorption Column Leachates

while the carbonate concentration appears to stay below that of the Hanford ground water in the leachates from the blank soil adsorption column.

Figures 7.4 and 7.5 illustrate the observed Ca and Mg concentrations in the leachates from these experiments. The Ca and Mg concentrations in the leachates from the blank soil adsorption experiment remain roughly the same as the concentrations in Hanford ground water, suggesting there is no reaction between the soil and the ground water. For the waste form 1 soil adsorption experiment, the Mg and Ca concentrations are initially high after 19 pore volumes of waste solution have passed through the soil column; the concentrations of Ca and Mg then decrease to less than the inferred Ca and Mg concentrations in the influent waste solution. These decreases in concentration, followed by continued low levels of Ca and Mg in solution, suggest that Ca- and Mg-bearing minerals precipitate as the waste solution reacts with the soil. Again, as in the ANS 16.1 batch leaching experiments, there is no correlation between the carbonate and Ca concentrations through time (compare Figures 7.3 and 7.4); for the waste form 1 soil adsorption column, carbonate concentrations increase while Ca concentrations remain between 2 and 10 mg/L.

Figures 7.6 and 7.7 show that, in the blank soil adsorption experiment, leachate concentrations of Na and SO_4^{2-} vary around the Hanford ground-water concentrations. Na concentrations in the leachates from the waste form 1 soil adsorption experiment increase from 110 to 210 mg/L in solution. SO_4^{2-} concentrations in the leachates from the waste form 1 soil adsorption experiment range from 170 to 200 mg/L. Increases and decreases in Na and SO_4^{2-} concentrations are parallel through time. However, Na concentrations only increase to the average Na concentration in the waste solution, while SO_4^{2-} concentrations are always higher than in the averaged waste solution. These observations suggest that Na is initially attenuated in the soil adsorption column, perhaps by ion exchange until all the available sites are filled; the Na^+ ions then travel freely through the soil. The high SO_4^{2-} concentrations suggest that the soil is contributing to the SO_4^{2-} content of the leachates, possibly by the dissolution of a sulfate-bearing mineral.

Except for an anomaly after 201 pore volumes of Hanford ground water have traveled through the soil adsorption column, PO_4^{3-} concentrations are at the

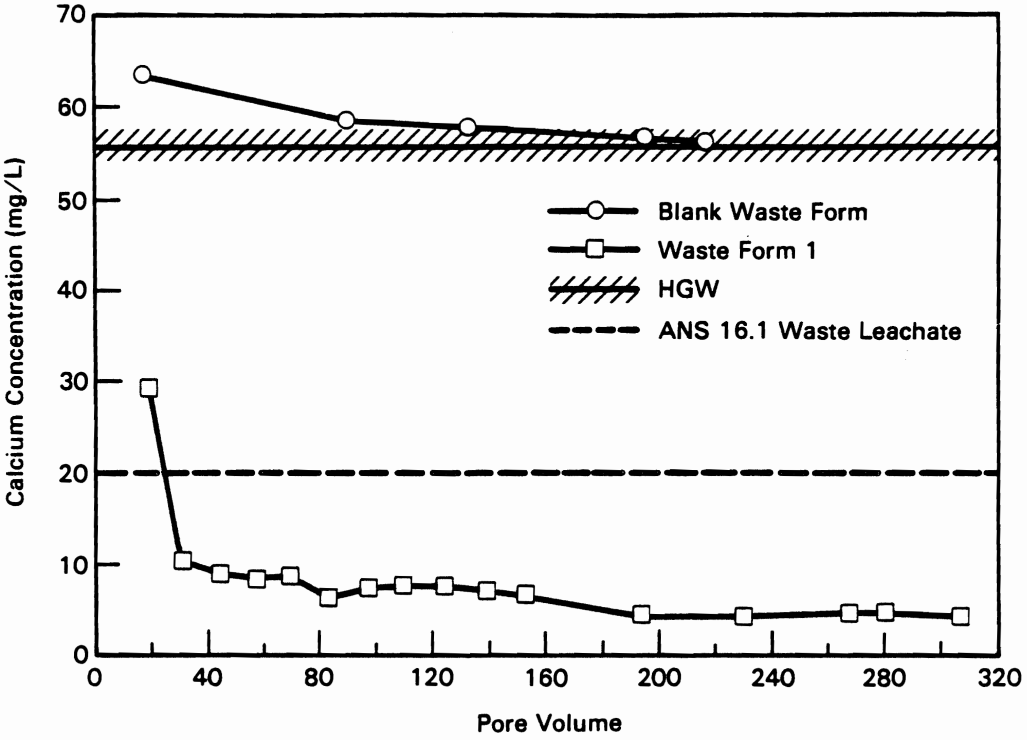


FIGURE 7.4. Calcium Concentrations in the Soil Adsorption Column Leachates

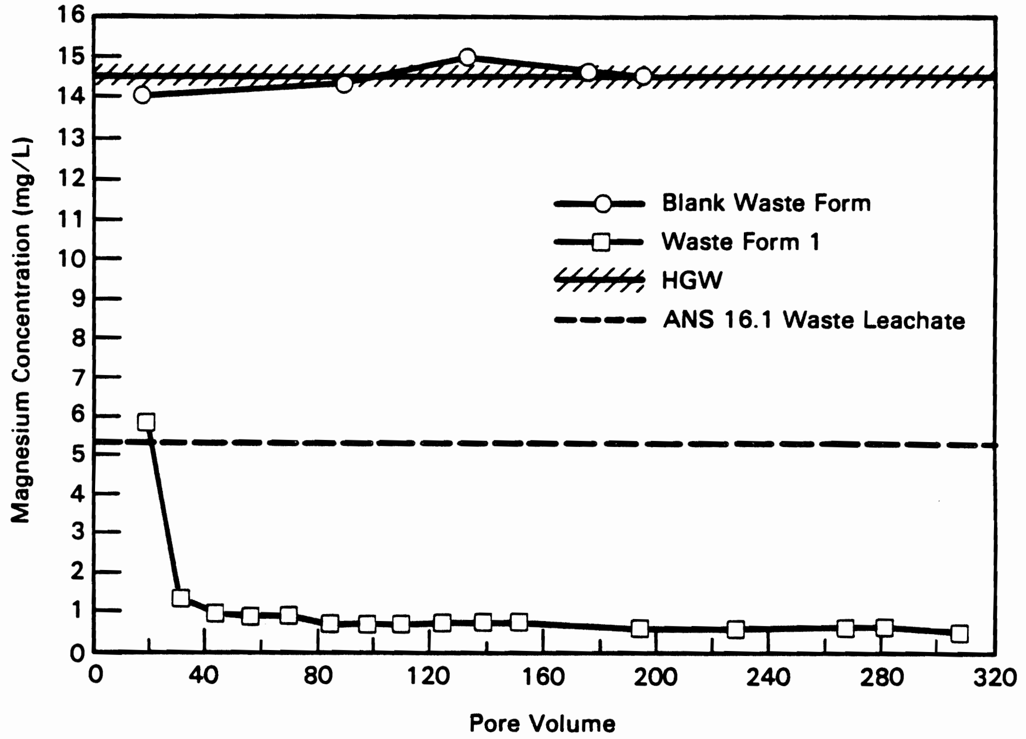


FIGURE 7.5. Magnesium Concentrations in the Soil Adsorption Column Leachates

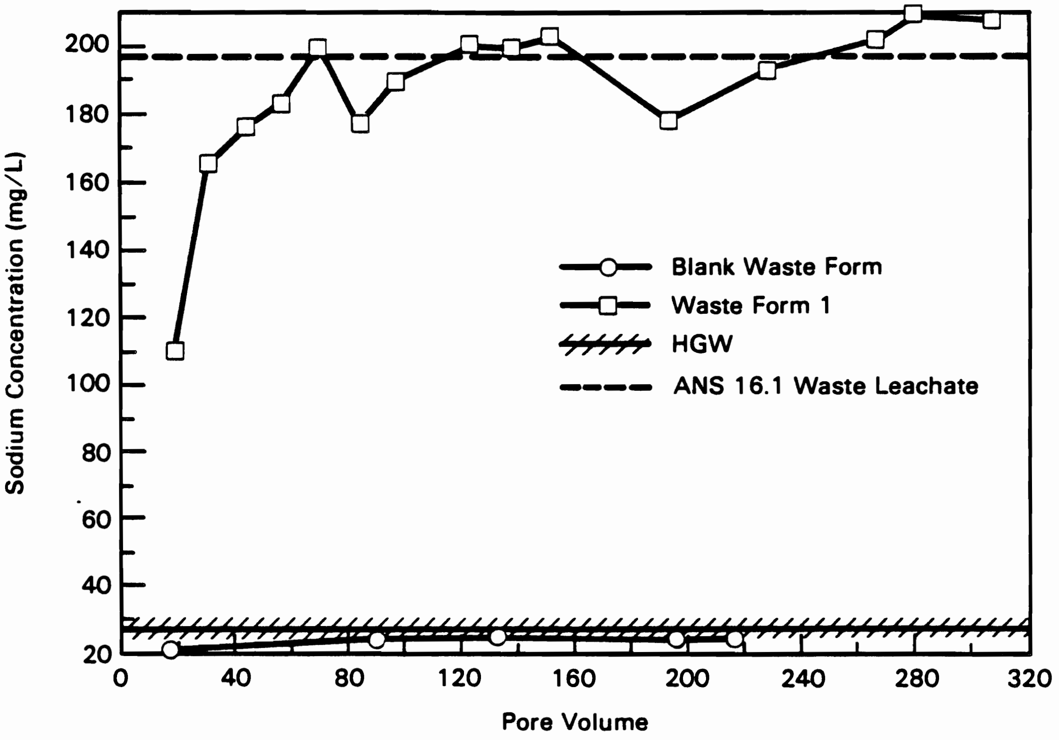


FIGURE 7.6. Sodium Concentrations in the Soil Adsorption Column Leachates

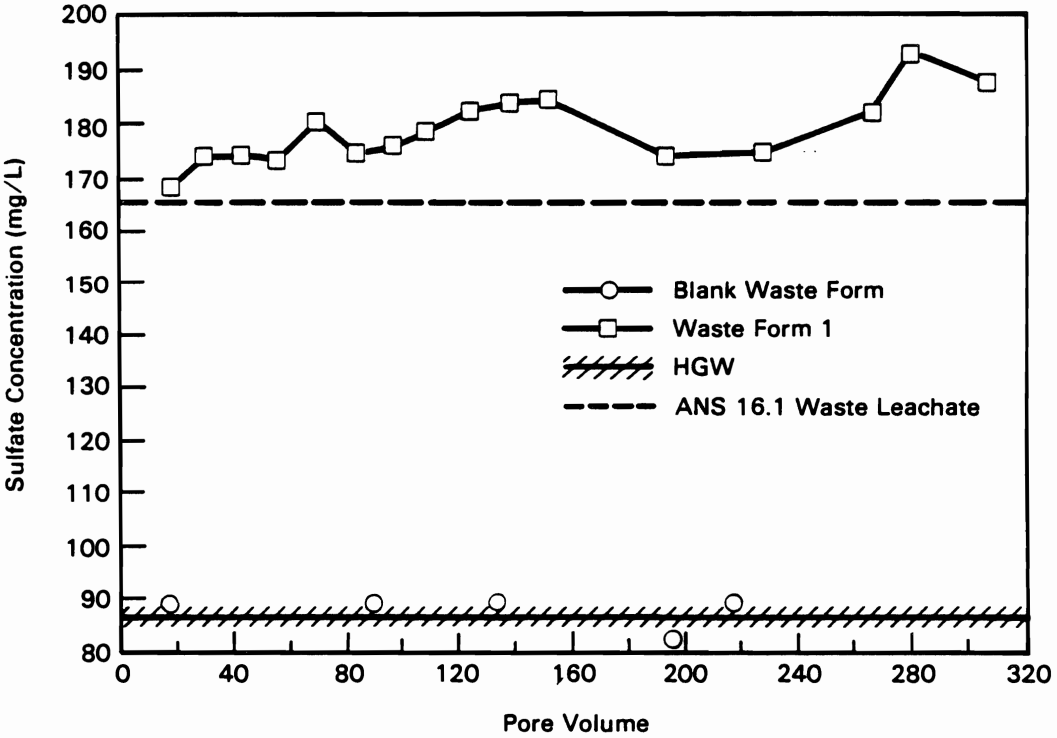


FIGURE 7.7. Sulfate Concentrations in the Soil Adsorption Column Leachates

detection limit for the blank soil adsorption leachates (Figure 7.8). For the waste form 1 soil adsorption leachates, PO_4^{3-} concentrations are always lower than in the averaged waste solution, suggesting that PO_4^{3-} is attenuated in the soil.

Silicon concentrations (Figure 7.9), are initially higher in the leachates from both experiments than in Hanford ground water. For the blank soil adsorption experiment, silicon concentrations in the leachates drop from 21 mg/L to 17 mg/L. These concentrations are all higher than that in the Hanford ground water; therefore, silicon must be dissolving from the soil. For the waste form 1 soil adsorption experiment, the silicon concentration is initially 28 mg/L and decreases to less than 10 mg/L, below the silicon concentration in both Hanford ground water and the averaged waste solution. Silicon apparently is dissolved from the soil as the first 100 pore volumes of waste solution travel through the column; a silicate mineral must then precipitate from solution during the remainder of the experiment, decreasing silicon concentration in the leachates.

Aluminum concentrations in the leachates from both the blank and waste form 1 soil adsorption experiments (Figure 7.10) rise above the detection limit. The Al concentration in both the Hanford ground water and the averaged waste solution is below the detection limit. All Al in the leachates must therefore come from the dissolution of an aluminum-bearing mineral in the soil.

Potassium concentrations (Figure 7.11) in the blank soil adsorption leachates fluctuate around the Hanford ground-water concentration. The K concentrations in the waste form 1 soil adsorption leachates are initially less than the concentration in Hanford ground water. The K concentration then increases, surpassing the Hanford ground-water concentration (~7 mg/L) after 85 pore volumes of waste solution/soil contact, surpassing the concentration in the averaged waste solution (~25 mg/L) after 240 pore volumes of waste solution/soil contact, and reaching a maximum of 32 mg/L after 280 pore volumes of waste solution have traveled through the soil column. This trend in K concentration suggests that K is initially attenuated in the soil. Later, after 280 pore volumes of waste solution have traveled through the soil, K is released from

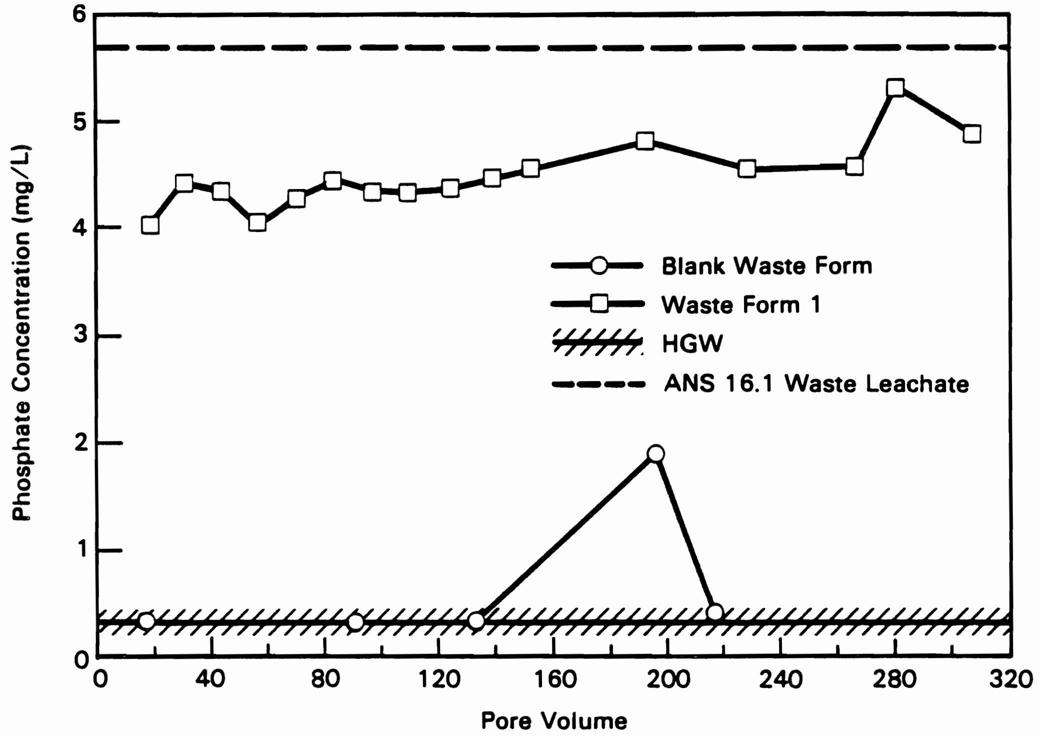


FIGURE 7.8. Phosphate Concentrations in the Soil Adsorption Column Leachates

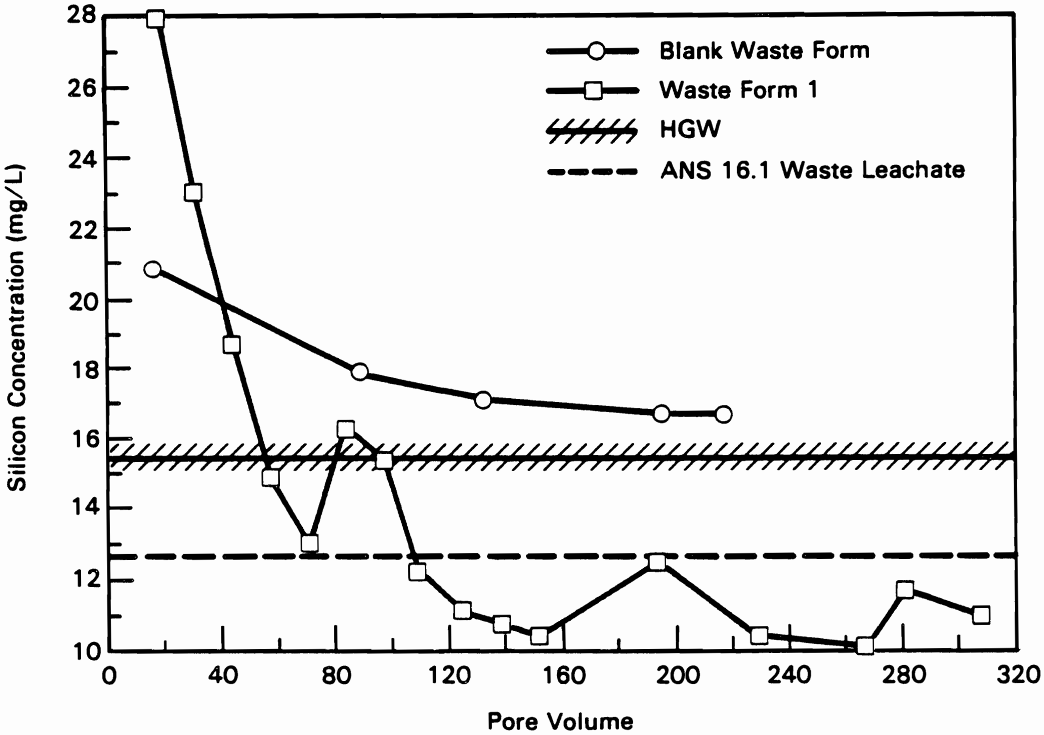


FIGURE 7.9. Silicon Concentrations in the Soil Adsorption Column Leachates

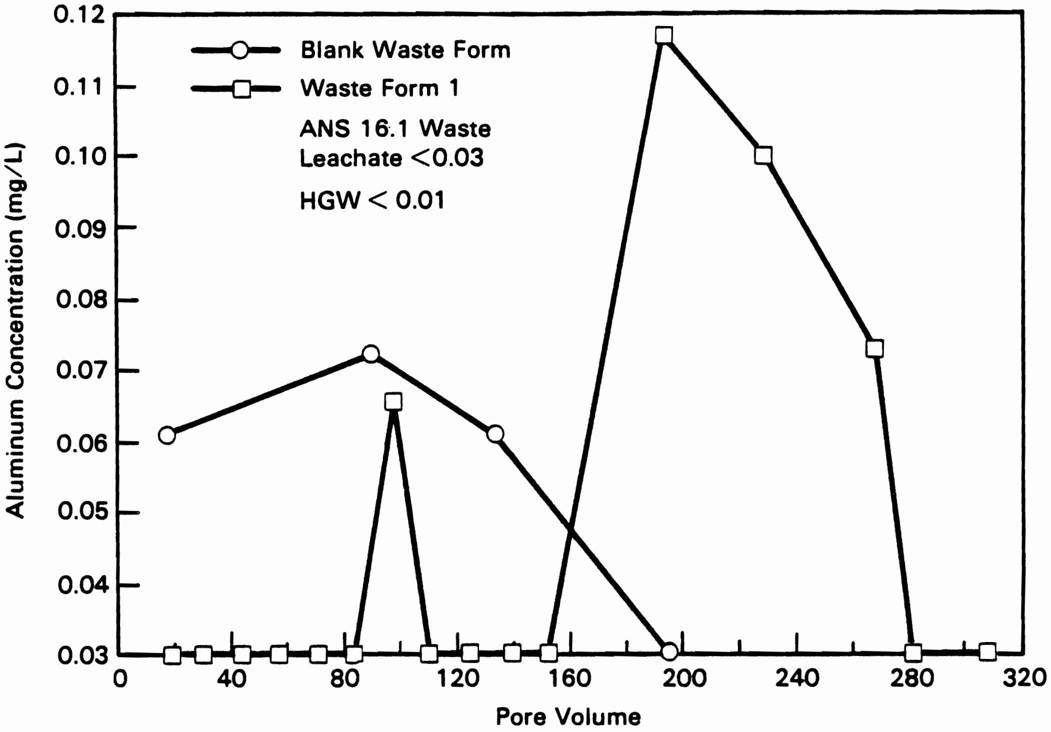


FIGURE 7.10. Aluminum Concentrations in the Soil Adsorption Column Leachates

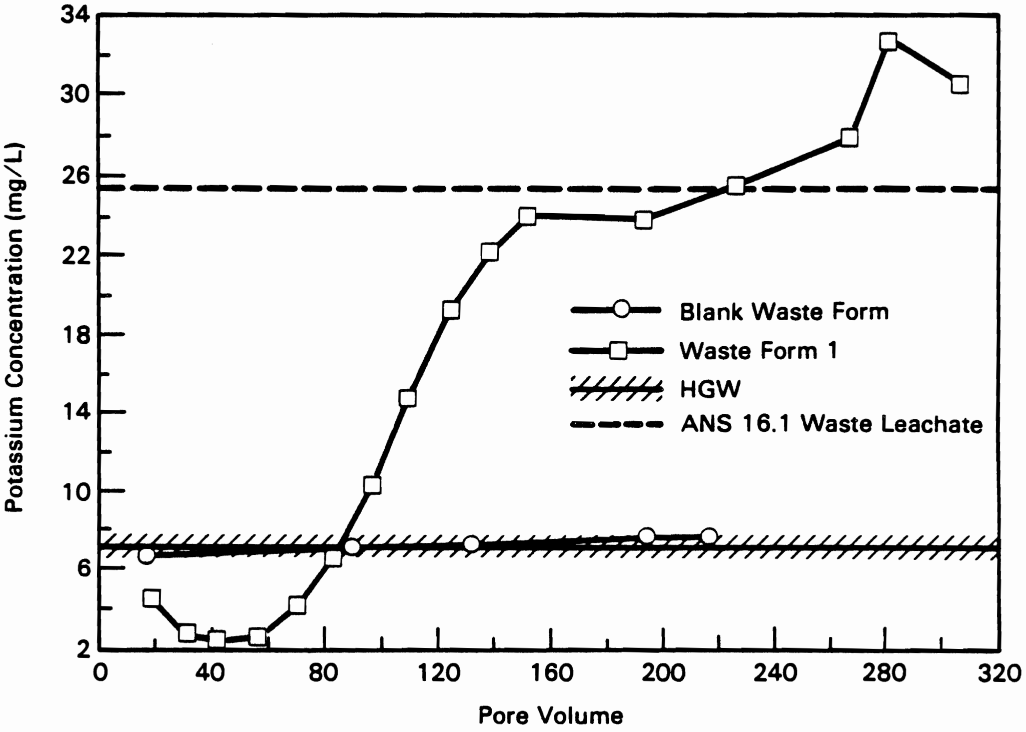


FIGURE 7.11. Potassium Concentrations in the Soil Adsorption Column Leachates

the soil. The behavior of K shows similarities to the behavior of Na. It is possible that both ions are competing for adsorption sites in the soil until these sites are completely filled.

Barium concentrations in the leachates are illustrated in Figure 7.12. The leachates from the blank soil adsorption experiment contain a little more barium (<0.01 mg/L) than the Hanford ground water. The average waste solution (>0.02 mg/L) contains less barium than the Hanford ground water (>0.05 mg/L). The Ba concentration in the waste form 1 soil adsorption leachates is initially higher than that in the waste solution, but after 20 pore volumes of waste solution/soil contact, Ba concentrations decrease to less than 0.01 mg/L. With continued contact between the waste solution and the soil, Ba concentration in the leachates increases slowly toward the Ba concentration in the averaged waste solution.

Boron concentrations (Figure 7.13) in the leachates from the blank soil adsorption experiment decrease slowly from 0.1065 mg/L to 0.0686 mg/L as Hanford ground water contacts the soil. Boron concentrations in the leachates from the waste form 1 soil adsorption experiment vacillate from 0.05 mg/L to 0.1 mg/L during the experiment. No trend in boron concentrations with increasing waste solution/soil contact time is apparent. Recall that the pH (Figure 7.1) also showed no apparent trend with time. However, although both the pH and boron concentration curves display erratic behavior with time, there does not appear to be any correspondence between these two properties.

Strontium concentrations (Figure 7.14) are maintained below the influent solution levels in both the blank and waste form 1 soil adsorption experiments. In particular, strontium concentrations in the leachates from the waste form 1 soil adsorption experiments are maintained at very low levels (~0.02 mg/L) after 30 pore volumes of waste solution/soil contact. These low strontium concentrations suggest that a strontium-bearing mineral is precipitating from solution. In addition, the variation in strontium concentration parallels the variations in Mg and Ca concentrations, suggesting that similar attenuation mechanisms are involved in controlling these concentrations in solution.

Chlorine concentrations in the leachates from both experiments are illustrated in Figure 7.15. In the leachates from the blank soil adsorption

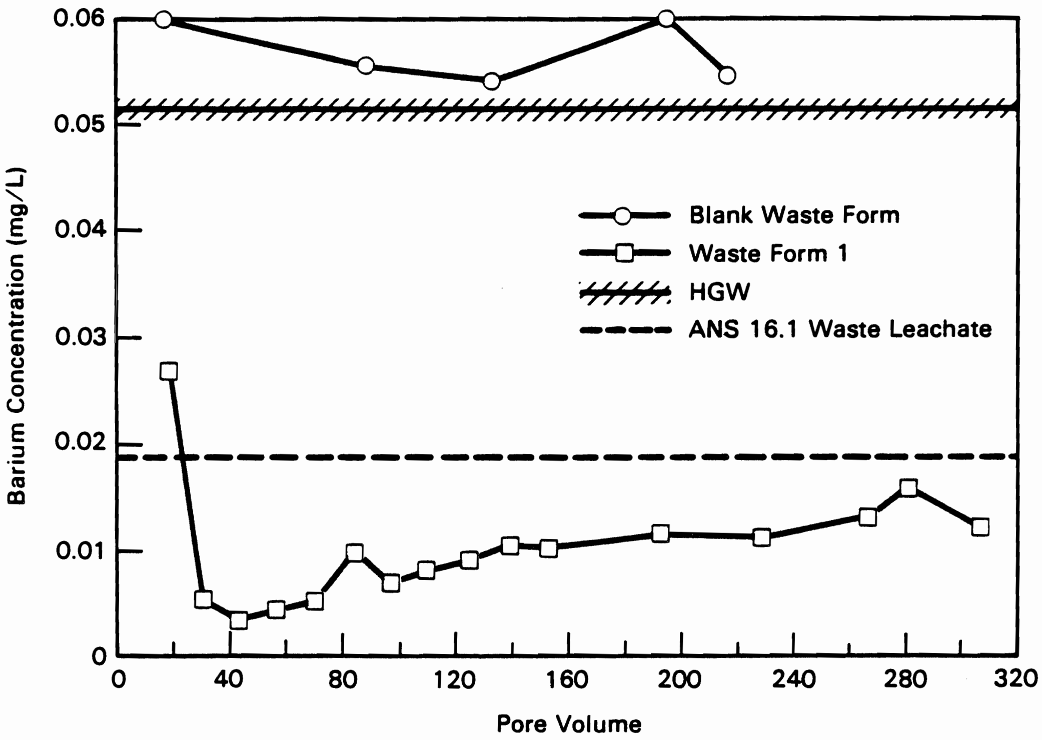


FIGURE 7.12. Barium Concentrations in the Soil Adsorption Column Leachates

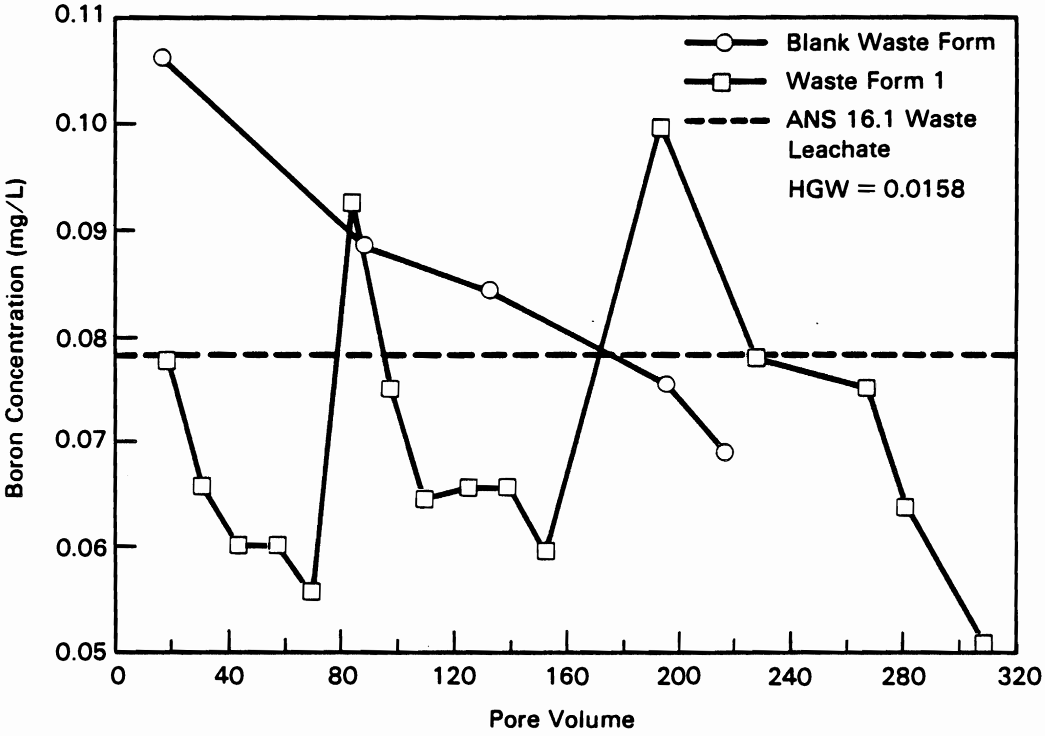
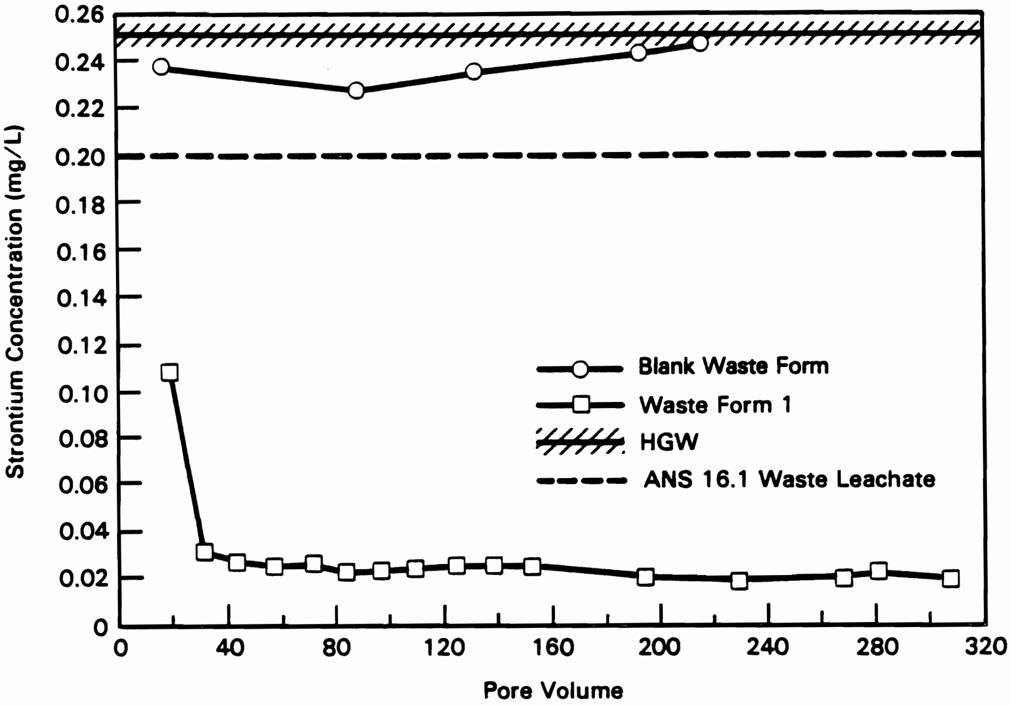
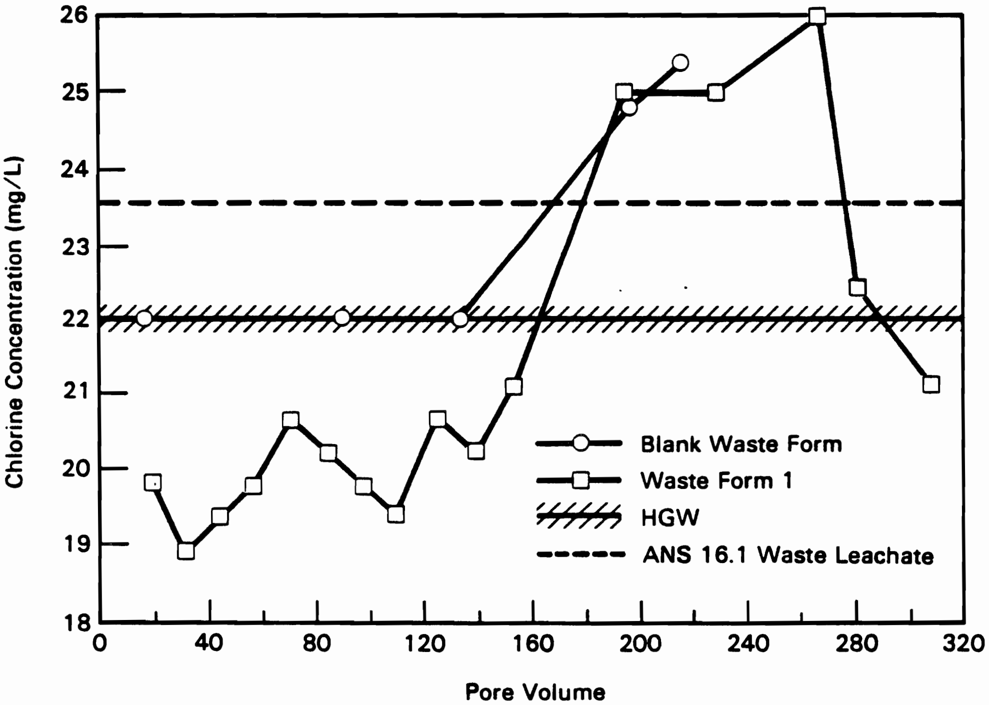


FIGURE 7.13. Boron Concentrations in the Soil Adsorption Column Leachates



<u>FIGURE 7.14</u>. Strontium Concentrations in the Soil Adsorption Column Leachates



<u>FIGURE 7.15</u>. Chlorine Concentrations in the Soil Adsorption Column Leachates

experiment, Cl concentrations are maintained at Hanford ground-water levels until more than 200 pore volumes of ground water have passed through the soil column. Then, the soil contributes some Cl to the leachate, increasing the Cl concentration to more than 25 mg/L. In the leachates from the waste form 1 soil adsorption experiment, Cl concentrations are maintained below the Cl concentration in the averaged waste solution, again until more than 200 pore volumes of waste solution have passed through the soil column. The Cl concentration then increases to more than the concentration in the waste solution.

7.2 ION SPECIATION

The MINTEQ ion speciation/solubility calculations suggest that the speciation of the major components in the leachates from the blank soil adsorption experiment varies in only a minor way from the speciation in the Hanford ground water. On the other hand, the speciation of the major components in the leachates from the waste form 1 soil adsorption experiment reflects the speciation of the waste solution that contacts the soil.

For the leachates from the blank soil adsorption experiment, only minor variations in speciation are observed. No changes in Ca, Mg, SO_4, or PO_4 speciation in the leachates are observed. Minor changes in Si, B, and CO_3 speciation are observed; these changes bear a marked similarity to the changes observed in the leachates from the ANS 16.1 blank waste form experiment. A comparison of Figures 7.16, 7.17, and 7.18 with Figures 6.18, 6.19, and 6.20 points to these similarities. The silicon species $H_3SiO_4^-$ is more important (accounting for ~5% of the silicon present in solution) in both sets of leachates than in the Hanford ground water. The percentage of boron present in solution as $H_2BO_3^-$ increases from 10% in the ground water to 20% in the leachates. Minor amounts of CO_3^{2-} and $CaCO_3^0$ are present in the leachates, while a minor amount of $H_2CO_3^0$ is present in the ground water.

Because the composition of the mixed leachate from the ANS 16.1 batch leaching experiments has not been determined, it is difficult to evaluate how this waste solution had been affected by reaction with the soil. From Figures 7.19 through 7.26, which illustrate the aqueous speciation of the major components in solution, it appears that the waste solution is buffered by the

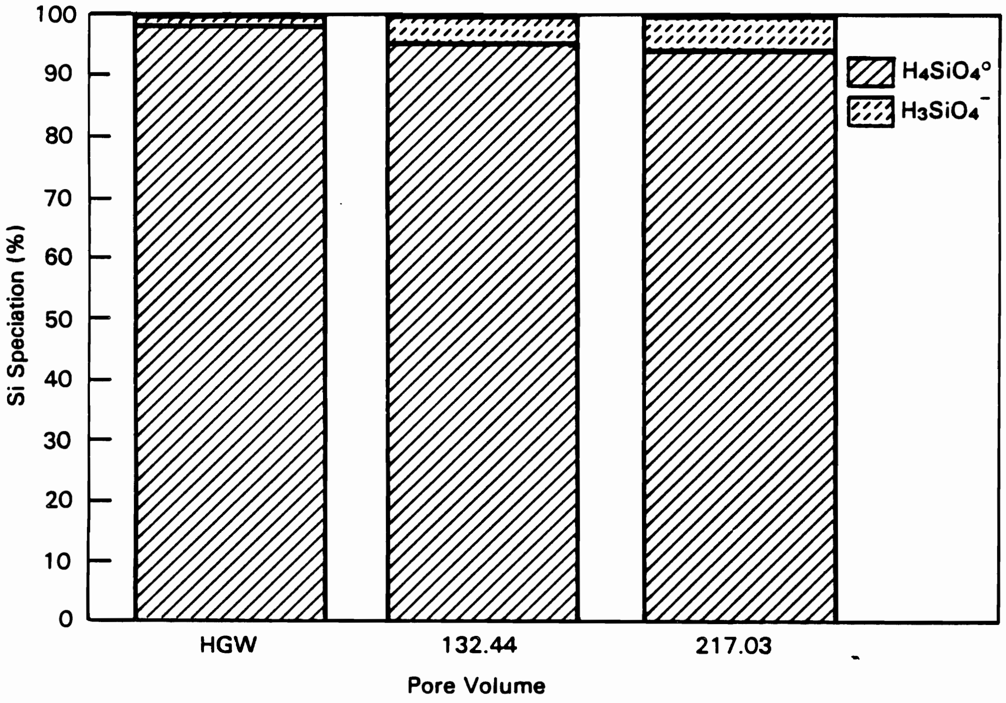


FIGURE 7.16. Silicon Species Present in the Blank Soil Adsorption Column Leachates

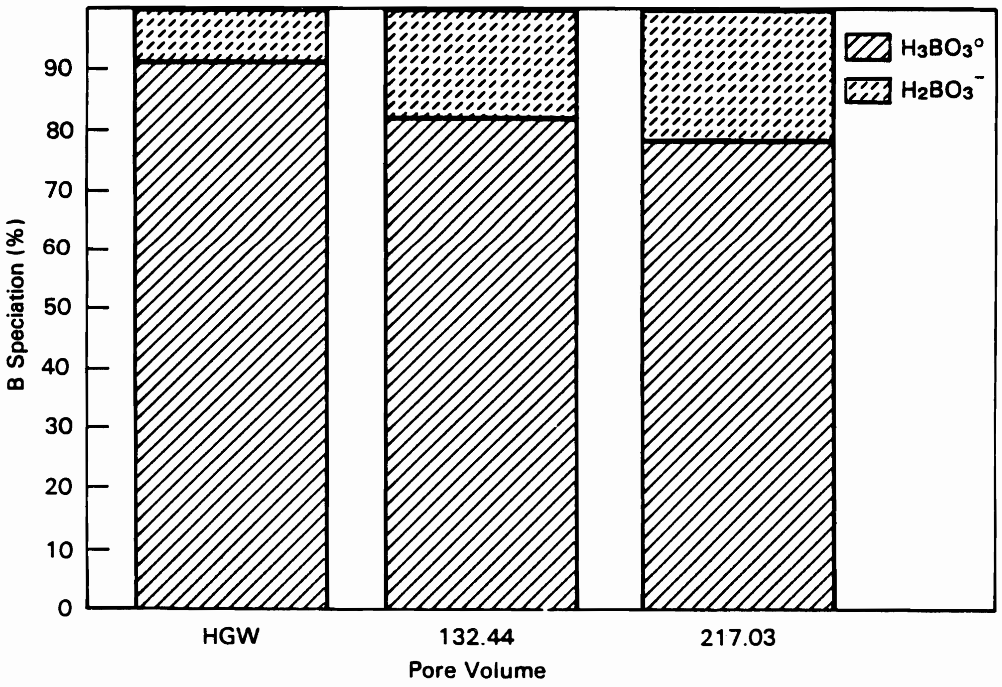


FIGURE 7.17. Boron Species Present in the Blank Soil Adsorption Column Leachates

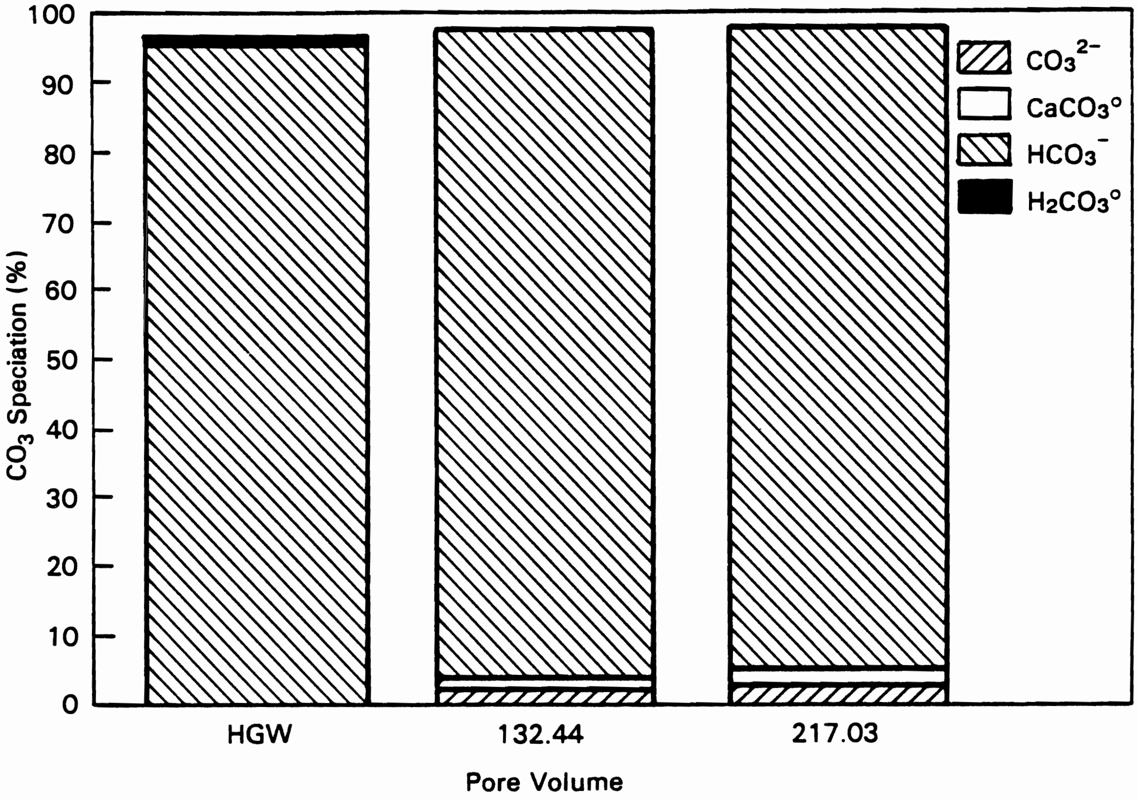


FIGURE 7.18. Carbonate Species Present in the Blank Soil Adsorption Column Leachates

soil for between the first 18 to 50 pore volumes of waste solution/soil contact. Table 7.2 lists the species distribution for the major components in the averaged waste solution. The following discussion of the species distribution for the major components in the soil adsorption waste form 1 leachates will compare these leachates to both the averaged waste solution and the sampled ANS 16.1 leachates.

Figure 7.19 illustrates that the calcium species $CaCO_3^{0}$ and $CaPO_4^{-}$ both play a role in calcium transport through the soil. Both these species were present in the ANS 16.1 waste leachates. Both species are not present in significant proportions in the leachates from the soil until after 18 pore volumes of waste solution have passed through the column. The soil must initially buffer the waste solution. $CaOH^{+}$ was present in minor amounts in some of the ANS 16.1 leachates; however, it is not present in the averaged waste solution.

TABLE 7.2. Species Distribution for the Averaged Waste Solution

Component	Percentage	Species
Ca	59.1	Ca^{2+}
	27.3	$CaCO_3^0$
	7.9	$CaSO_4^0$
	3.1	$CaPO_4^-$
	1.7	$CaHCO_3^+$
Mg	64.4	Mg^{2+}
	20.5	$MgCO_3^0$
	2.1	$MgHCO_3^+$
	7.5	$MgSO_4^0$
	4.6	$MgPO_4^-$
H_4SiO_4	72.2	$H_4SiO_4^0$
	27.6	$H_3SiO_4^-$
H_3BO_3	34.8	$H_3BO_3^0$
	65.2	$H_2BO_3^-$
CO_3	15.0	CO_3^{2-}
	2.6	$CaCO_3^0$
	1.5	$NaCO_3^-$
	79.4	HCO_3^-
SO_4	94.0	SO_4^{2-}
	2.3	$CaSO_4^0$
	2.5	$NaSO_4^-$
PO_4	50.4	HPO_4^{2-}
	17.1	$MgPO_4^-$
	2.3	$MgHPO_4^0$
	3.4	$CaHPO_4^0$
	25.9	$CaPO_4^-$

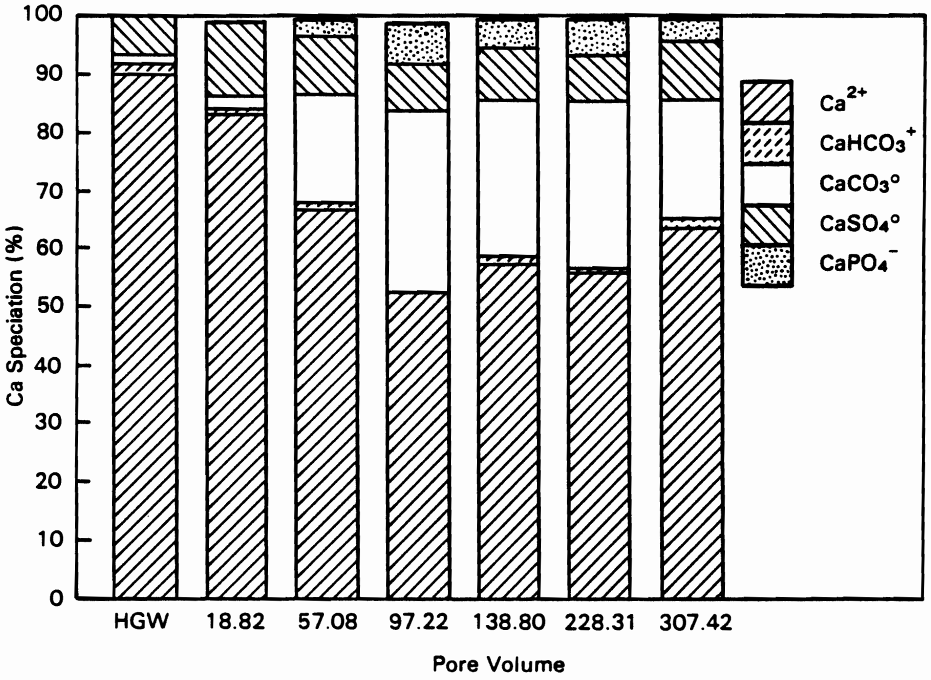


FIGURE 7.19. Calcium Species Present in the Waste Form 1 Soil Adsorption Column Leachates

Figure 7.20 illustrates the changes in magnesium speciation with increasing contact between the waste solution and the soil. The behavior of Mg and Ca show marked similarities. Again, no major changes in species distribution occurred during the first 18 pore volumes of waste solution/soil contact. The species $MgCO_3^0$ and $MgPO_4^-$ are significant magnesium complexes in solution after 57 pore volumes of waste solution have passed through the soil column. The species $MgOH^+$, which is present in the ANS 16.1 leachates, is not present in the averaged waste solution and is not a predominant species in the leachates from the soil adsorption column.

Figures 7.21 and 7.22 illustrate, respectively, the silicon and boron speciation in the leachates from the waste form 1 soil adsorption column experiments. Silicon species in solution include $H_4SiO_4^0$ and $H_3SiO_4^-$, with

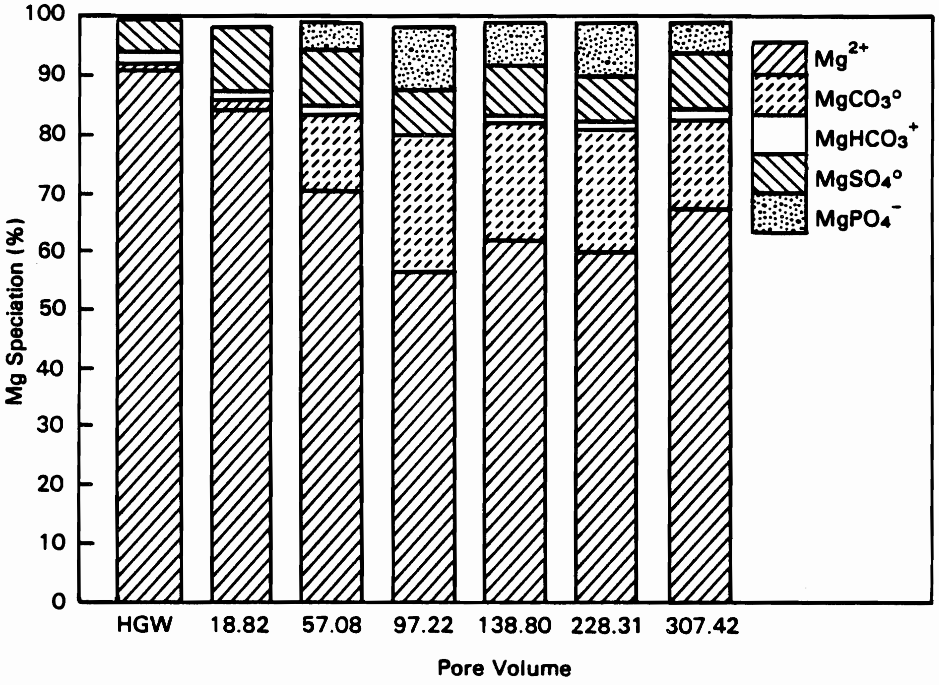


FIGURE 7.20. Magnesium Species Present in the Waste Form 1 Soil Adsorption Column Leachates

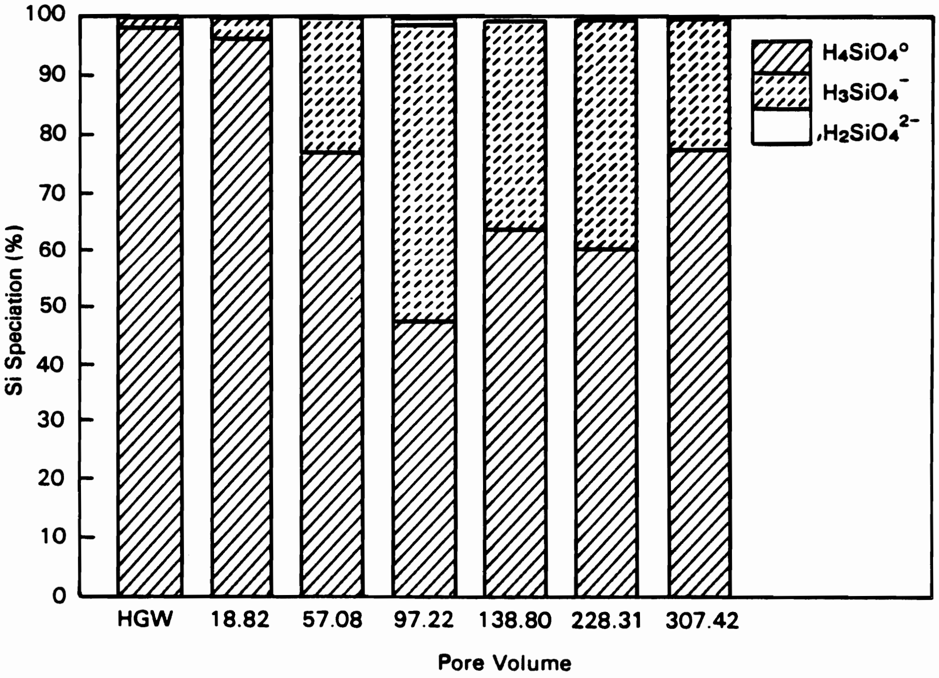


FIGURE 7.21. Silicon Species Present in the Waste Form 1 Soil Adsorption Column Leachates

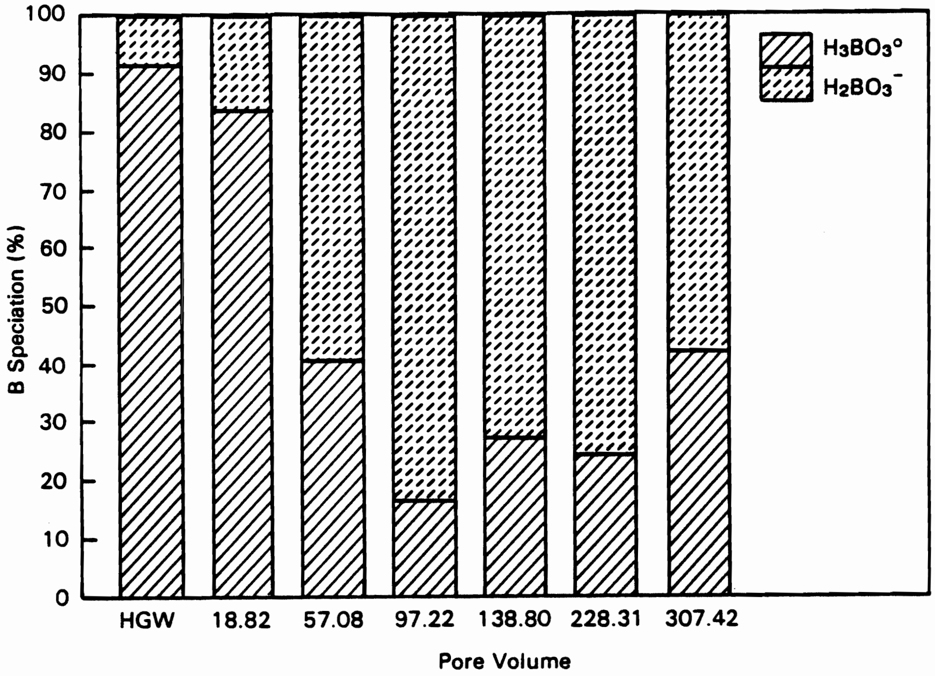


FIGURE 7.22. Boron Species Present in the Waste Form 1 Soil Adsorption Column Leachates

$H_3SiO_4^-$ accounting for between 20% and 50% of the silicon present. $H_2SiO_4^{2-}$, which is an important silicon species in the ANS 16.1 waste leachates (see Figure 6.25), is present only in negligible amounts in the soil adsorption column leachates. This difference in silicon speciation could be caused by reactions between the soil and waste solution or by the lower pH of the averaged waste solution. The predominant boron species in solution are $H_3BO_3^0$ and $H_2BO_3^-$; $H_3BO_3^0$ is the predominant boron species in Hanford ground water, and $H_2BO_3^-$ is the predominant boron species in ANS 16.1 waste leachates. Again, the difference in boron speciation probably results from the difference in pH between the ANS 16.1 waste leachates and the averaged waste solution.

The predominant carbonate species is HCO_3^- in both the Hanford ground water and the waste form 1 soil adsorption column leachates (see Figure 7.23). The marked change from predominantly HCO_3^- to predominantly CO_3^{2-} in the ANS 16.1 leachates is not reflected in the soil adsorption column leachates. CO_3^{2-} does, however, become an important species in these leachates, accounting for as much as 30% of the carbonate present in solution after 97 pore volumes have passed

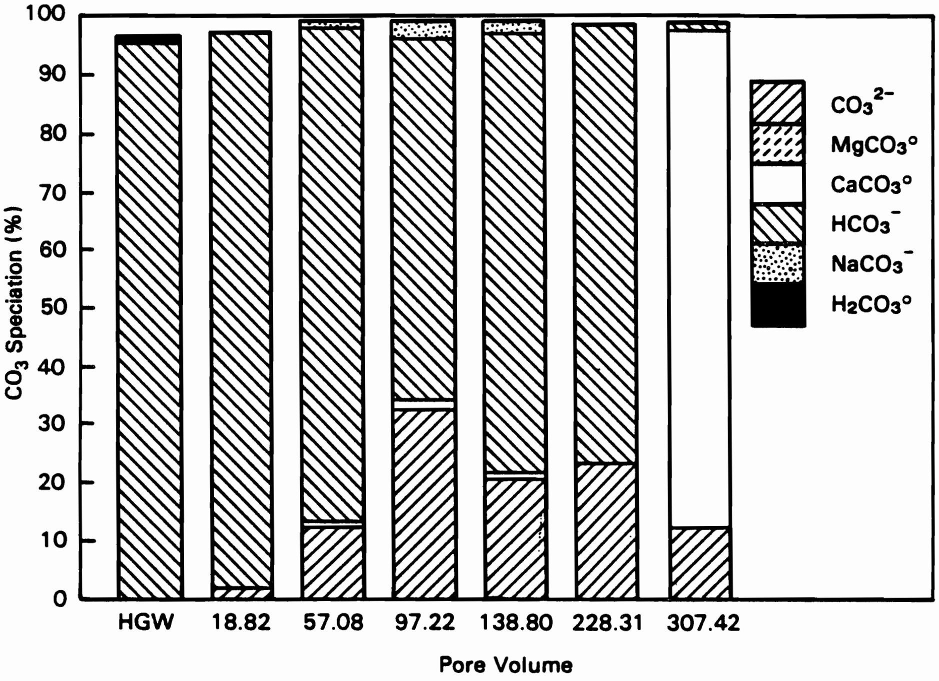


FIGURE 7.23. Carbonate Species Present in the Waste Form 1 Soil Adsorption Column Leachates

through the soil column. Note that CO_3^{2-} is a more important species in this leachate than in the averaged waste solution. $CaCO_3^0$ and $NaCO_3^-$ together represent less than 10% of the total amount of carbonate present in solution.

Figure 7.24 illustrates the sulfate speciation in the waste form 1 soil adsorption column leachates. The predominant sulfate species in solution is SO_4^{2-}; $NaSO_4^-$ is present in minor amounts (<5%). This sulfate species distribution is approximately the same as that found in the ANS 16.1 waste leachates.

Figure 7.25 illustrates the phosphate speciation in the waste form 1 soil adsorption column leachates. The predominant phosphate species is HPO_4^{2-}, followed by $CaPO_4^-$. This species distribution is significantly different from that of some of the ANS 16.1 leachates in which $MgPO_4^-$ or $CaPO_4^-$ is the major phosphate species. The predominant phosphate species in the averaged waste solution are HPO_4^{2-} and $CaPO_4^-$; however, the waste form 1 soil adsorption column leachates have more HPO_4^{2-} and less $CaPO_4^-$ than the averaged waste solution.

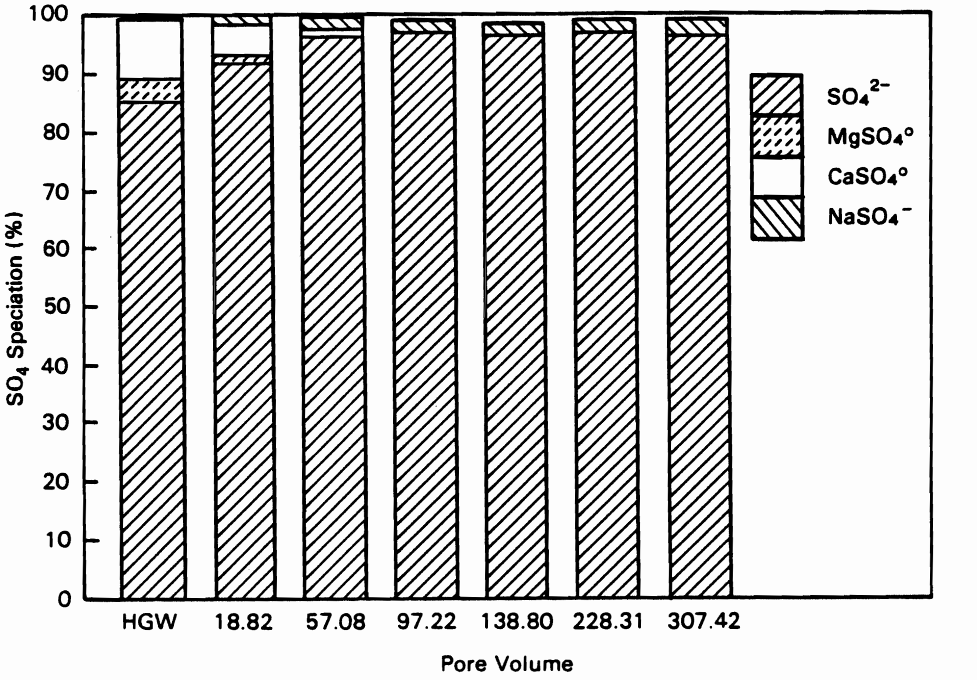


FIGURE 7.24. Sulfate Species Present in the Waste Form 1 Soil Adsorption Column Leachates

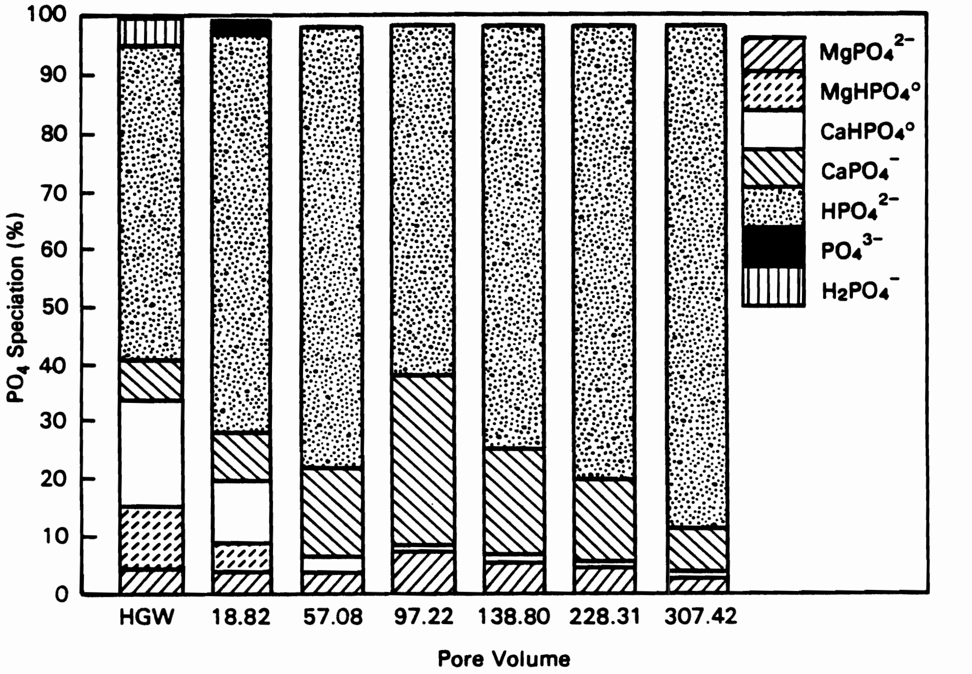


FIGURE 7.25. Phosphate Species Present in the Waste Form 1 Soil Adsorption Column Leachates

7.3 SATURATION INDICES FOR MINERALS

It is worth repeating that the nature of the soil adsorption column experiments is such that equilibrium between the influent solution and soil may never be achieved. The soil is continuously exposed to fresh influent that travels through the column. If the influent and the soil reacted completely to equilibrium, the soil would be altered to a solid assemblage in equilibrium with the influent solution. The leachates would therefore have the composition of the influent. Figures 7.1 through 7.15 illustrate that the Hanford ground water and Hanford sediment appear to be nearly in equilibrium with each other. If a steady-state condition was achieved, then the influent and the solid assemblage would always react in the same manner, resulting in identical leachates. The waste solution and sediment do not achieve a steady-state condition, although more than 300 pore volumes of waste solution pass through the soil. Several elements including Ca, Mg, Si, Ba, and Sr do, however, exhibit steady-state behavior.

Table 7.3 presents the saturation indices for some of the minerals that might participate in reactions between the influent solutions and the soil. The minerals considered here are the same as those considered for the ANS 16.1 batch leaching tests (see Table 6.2). The leachates from the blank soil adsorption column experiments and Hanford ground water are for the most part oversaturated and undersaturated with respect to the same minerals. The only discrepancies worth mentioning are the following: 1) the leachates from the blank soil adsorption column are more oversaturated with respect to calcite, dolomite, sepiolite, and hydroxyapatite than the Hanford ground water, and 2) the leachates from the blank soil adsorption column are more undersaturated than the Hanford ground water with respect to brucite and the cement minerals (lime, portlandite, ettringite, and monosulfate).

The leachates from the waste form 1 soil adsorption column are oversaturated with respect to both dolomite and calcite and slightly undersaturated with respect to magnesite. The saturation indices for these minerals are not very different from those determined for the leachates from the blank soil adsorption column. Barite is in equilibrium with the early waste form 1 soil adsorption column leachates and undersaturated in the later leachates. Gypsum

TABLE 7.3. Saturation Indices for Potential Solubility Controls in the Soil Adsorption Experiments

	HGW	Bln[a] 6	Bln 9	WF1[b] 1	WF1 4	WF1 7	WF1 10	WF1 13	WF1 16
Carbonates									
Calcite	0.663	0.999	1.063	0.567	0.905	1.082	1.002	0.817	0.670
Dolomite	1.017	1.689	1.817	0.708	1.122	1.468	1.324	1.024	0.695
Magnesite	-0.142	0.194	0.258	-0.376	-0.279	-0.110	-0.174	-0.289	-0.472
Otavite	0.828	0.906	0.919	0.879	0.975	0.981	0.981	0.981	0.978
Rhodochrosite	-1.282	-1.258	-1.179	-1.394	1.366	-0.126	-0.201	-0.171	-0.359
Strontianite	-1.205	-0.906	-0.805	-1.355	-1.017	-0.717	-0.771	-0.864	-1.064
Cerrusite	-0.860	-0.788	-0.798	-0.780	-1.054	-1.277			
Sulfates									
Barite	0.118	0.153	0.160	0.136	-0.666	-0.480	-0.266	-0.255	-0.203
Gypsum	-1.482	-1.463	-1.472	-1.493	-2.128	-2.294	-2.270	-2.503	-2.430
Celestite			-2.499	-2.574	-3.207	-3.251		-3.342	
Ettringite	-21.495	-18.362	-18.726	-20.274	-20.641	-18.761	-20.465	-20.520	-22.609
Monosulfate	-23.593	-20.498	-18.610	-22.349	-21.641	-19.234	-20.985	-20.574	-22.809
Phosphates									
$MnHPO_4$	0.200	-0.148	-0.078	1.080	2.883	0.971	1.076	1.119	
Strengite	-1.885	-2.761	-2.816	-1.355	-4.205		-4.994		
Hydroxyapatite	2.026	3.381	3.959	5.320	5.635	6.771	5.97	5.266	4.312
Hydroxides/Oxides									
Brucite	-0.446	-3.118	-2.911	-3.665	-2.838	-1.915	-2.449	-2.473	-3.161
Gibbsite	-0.254	-0.003	-0.422	-0.269	-1.131	-1.340	-1.403	-0.938	-1.114
Boehmite		0.189	-0.229	-0.076	-0.939	-1.147	-1.211	-0.746	-0.922
Diaspore		1.894	1.476	1.629	0.766	0.558	0.494	0.959	0.783
Portlandite	-9.372	-8.641	-8.435	-9.071	-7.983	-7.052	-7.601	-7.676	-8.348
Lime	-19.494	-18.763	-18.557	-19.193	-18.105	-17.174	-17.723	-17.818	-18.470
$Cr(OH)_3$ (A)[c]		0.173	-2.136						
γFeO_3	6.292	6.072	6.263						
Ferrihydrite	1.448	1.338	1.433	0.989	0.239	0.197	-0.025	0.624	0.460
Wulfenite		-0.598	-0.596	-0.475		-2.395	-2.404		-1.932
Silicates									
SiO_2 (A)	-0.561	-0.523	-0.539	-0.309	-0.680	-0.870		-0.936	-0.810
Chalcedony	0.252	0.290	0.274	0.504	0.133	-0.057	-0.089	-0.123	0.003
Cristobalite	0.316	0.354	0.338	0.568	0.197	0.007	-0.025	-0.059	0.067
Quartz	0.735	0.773	0.757	0.987	0.616	0.426	0.394	0.360	0.486
Sepiolite (C)[d]	0.163	1.737	2.101	1.285	1.823	3.099	1.936	1.786	0.790
Willemite	0.562	-1.157	-1.037	-0.966	-1.161	-0.634			-1.70

(a) Bln, blank waste form.
(b) WF1, waste form 1.
(c) A, amorphous.
(d) C, crystalline.

is more undersaturated in the waste form 1 soil adsorption column leachates than in the blank soil adsorption column leachates. Hydroxyapatite is more oversaturated in the waste form 1 soil adsorption column leachates than in the blank soil adsorption column leachates. The saturation indices for gypsum and hydroxyapatite reflect the properties of the waste solution. However, brucite is oversaturated in the leachates from the ANS 16.1 batch leaching experiments that make up the waste solution, and undersaturated in the leachates from the waste form 1 soil adsorption column experiment because of the drop in pH after contact with the soil. The waste form 1 soil adsorption column experiment leachates appear to be nearly in equilibrium with rhodochrosite, diaspore, ferrihydrite, and either chalcedony or cristobalite. The leachates from the ANS 16.1 batch leaching experiments were not in equilibrium with these minerals; reactions between the waste solution and soil must be responsible for these new mineral/solution equilibria.

Preliminary mass transfer calculations using MINTEQ suggest that calcite, quartz, and dolomite will precipitate from the waste solution as it passes through the soil column. This precipitation would explain the steady-state behavior of Ca, Mg, and Si in this experiment.

8.0 COMBINED SOIL/WASTE COLUMN EXPERIMENTS

This section discusses the results of the combined soil/waste form column experiments, the ion speciation of the leachates from these experiments, and potential solubility controls for these leachate compositions.

8.1 CHEMICAL ANALYSES

Three combined soil/waste form experiments were performed: one using Hanford sediment, ground water and a blank waste form, and two using Hanford sediment, ground water, and a real waste form. In this report, the combined soil/waste form column experiment using waste form 1 is compared to the combined soil/waste form column experiment using a blank waste form.

Figures 8.1 to 8.14 illustrate the changes in solution composition as a function of pore volumes of Hanford ground water that have traveled through the combined soil/waste form columns. Because the flow rate through the soil adsorption columns was much faster (15 pore volumes/day) than the flow rate through the combined soil/waste form columns (0.8 pore volumes/day), it may be inappropriate to compare the leachate compositions from these two types of experiments in detail. From a quick comparison of Figures 7.1 to 7.15 with Figures 8.1 to 8.14, it appears that the pH and the concentrations of the major components in solution vary more in the combined soil/waste form column leachates than in the soil adsorption column experiments. These differences in leachate compositions may result from the difference in the types of experiments or the fact that a longer reaction time is available in the combined soil/waste form column experiments than in the soil adsorption column experiments. The concentrations of the major components and the pH of the leachates from the combined soil/waste column experiments bear a greater similarity to the concentrations and pH observed in the leachates from the ANS 16.1 batch experiments (compare Figures 8.1 to 8.14 with Figures 6.1 to 6.15). The similarities and differences in these leachates are discussed in further detail.

Figure 8.1 illustrates the changes in pH with continued contact between the soil, waste forms, and Hanford ground water in the combined soil/waste form column experiments. The pH of the leachates from the blank soil/waste form

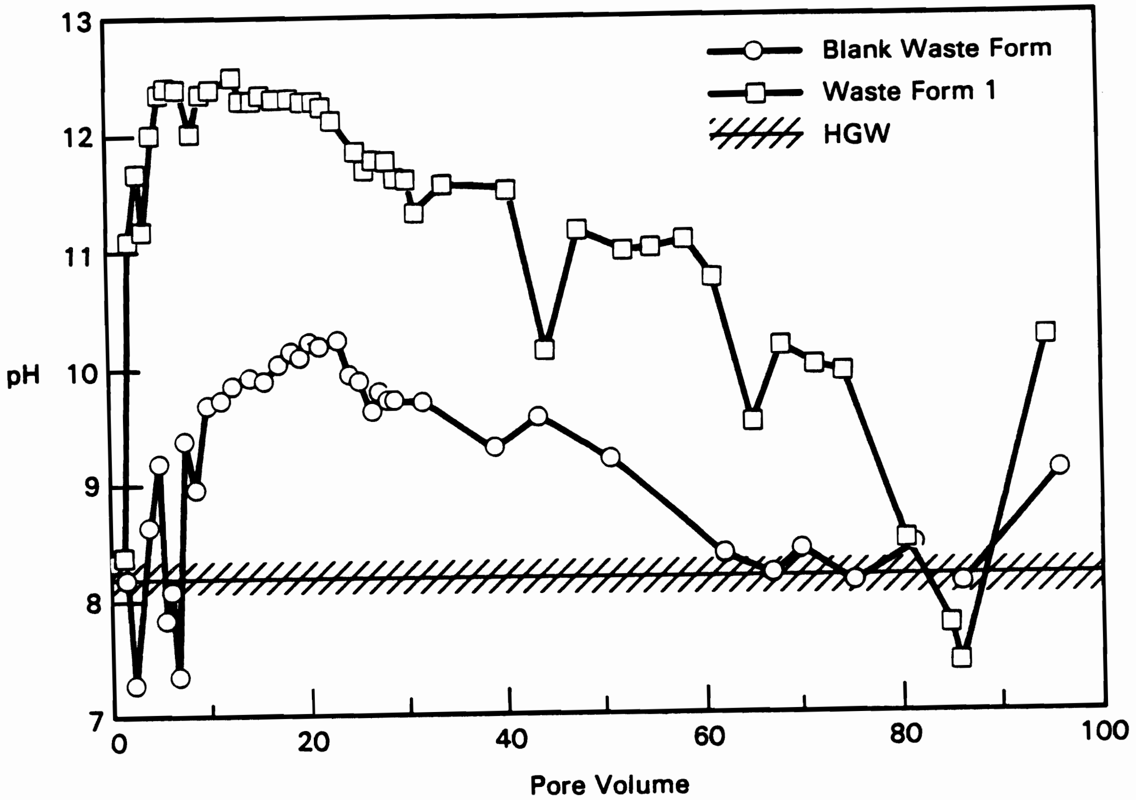


FIGURE 8.1. pH Values for the Combined Soil/Waste Form Column Leachates

column can be compared to the pH of the leachates from the blank ANS 16.1 batch experiments. In both types of experiments, the pH of the leachates rises to over 10, and then decreases back toward a pH of 8. No soil adsorption column experiment using the leachate from the blank ANS 16.1 batch experiment was performed. Therefore, the results from the blank combined soil/waste form column experiment cannot be directly compared to the results of an equivalent soil adsorption column experiment. The pH of the leachates from the waste form 1 soil/waste form column experiment can be compared to the pH of the leachates from both an equivalent ANS 16.1 batch leaching and an equivalent soil adsorption column experiment. The pH of the leachates from the waste form 1 soil/waste form column, like the pH of the leachates from the ANS 16.1 batch leaching experiment, increases to more than 12.0 pH units. Then the pH decreases to a more neutral pH with increased soil, waste form, and groundwater contact.

Figure 8.2 illustrates the change in alkalinity in the leachates from the combined soil/waste form column experiments. The alkalinity in the blank

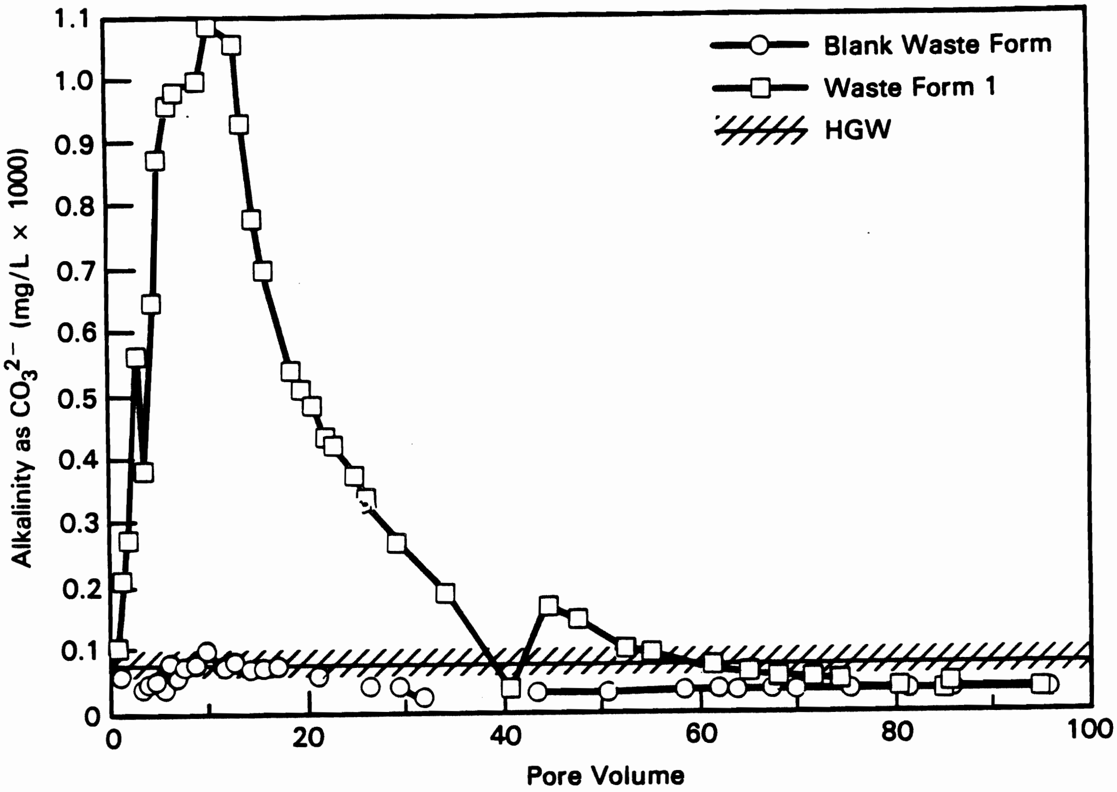


FIGURE 8.2. Alkalinity Values for the Combined Soil/Waste Form Column Leachates

soil/waste form column leachates remains near the alkalinity of the Hanford ground water, decreasing slightly with continued soil/waste form/ground-water contact. The alkalinity of the final leachates (30 to 35 mg/L CO_3^{2-}) is less than the alkalinity of the final leachates from the blank ANS 16.1 batch leaching experiments (70 to 75 mg/L CO_3^{2-}). The alkalinity of the waste form 1 soil/waste form column leachates rises to more than 1000 mg/L CO_3^{2-} during the first 15 pore volumes of soil/waste form/ground-water contact. These alkalinity values are much higher than the highest alkalinity values observed in the waste form 1 ANS 16.1 leachates (>400 mg/L CO_3^{2-}) and the highest alkalinity values observed in the waste form 1 soil adsorption column leachates (<200 mg/L CO_3^{2-}). Again, these results are difficult to compare to the results of the other two types of experiments because the fluids were replaced at different rates in each experiment. However, these results suggest that the reactions between the soil, waste forms, and Hanford ground water that occur in the combined soil/

waste form column experiments, but do not occur in either the ANS 16.1 batch leaching or the soil adsorption column experiments, play an important role in altering the fluid composition.

Figures 8.3 and 8.4, which illustrate the concentrations of Ca and Mg in the leachates from the combined soil/waste form column experiments, show that for the waste form 1 leachates both Ca and Mg are initially leached from the soil and/or waste form; the concentrations of both elements then decrease to levels below those found in Hanford ground water. Similar behavior is observed for these elements in the waste form 1 leachates from both the soil adsorption and ANS 16.1 batch leaching experiments, although the initial rise to more than 240 mg/L Ca and to 40 mg/L Mg is unique to the waste form 1 combined soil/waste form experiment. In addition, both Ca and Mg concentrations drop to lower concentrations (<2 mg/L and <0.1 mg/L, respectively) in the combined soil/waste form 1 column leachates than in either the waste form 1 ANS 16.1 batch experiment or the soil adsorption column experiment. Calcium concentrations in solution begin to rise again after 60 pore volumes of soil/waste form/groundwater contact. The Ca and Mg concentrations in the leachates from the blank combined soil/waste form experiment bear some similarities to those in the blank ANS 16.1 batch leaching experiment. Calcium concentrations decrease to less than 10 mg/L and then increase toward the Hanford ground-water concentration of 55.4 mg/L. On the other hand, Mg concentrations in the leachates from the blank combined soil/waste experiment remain below 5 mg/L throughout the experiment, but increase up to Hanford ground-water concentrations after 5 days of contact in the ANS 16.1 batch leaching experiments.

Figures 8.5 and 8.6 show that both Na and SO_4 concentrations in the blank soil/waste form column leachates fluctuate around the Hanford ground-water concentrations, while they soar to more than 1100 mg/L and 2400 mg/L, respectively, in the combined soil/waste form 1 column leachates. These concentrations are much higher than those observed in either the ANS 16.1 batch leaching experiments (compare Figures 8.5 and 8.6 to Figures 6.6 and 6.7, respectively) or in the soil adsorption column experiments (compare Figures 8.5 and 8.6 to Figures 7.6 and 7.7, respectively). In addition, both Na and SO_4 concentrations in the leachates from the soil/waste form 1 column experiments drop to

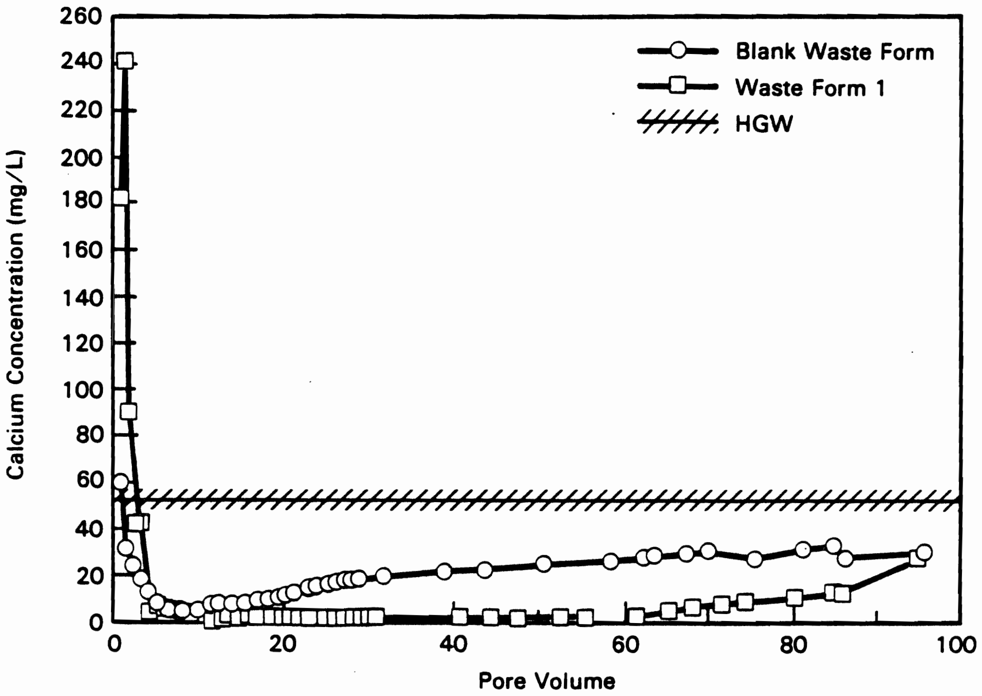


FIGURE 8.3. Calcium Concentrations in the Combined Soil/Waste Form Column Leachates

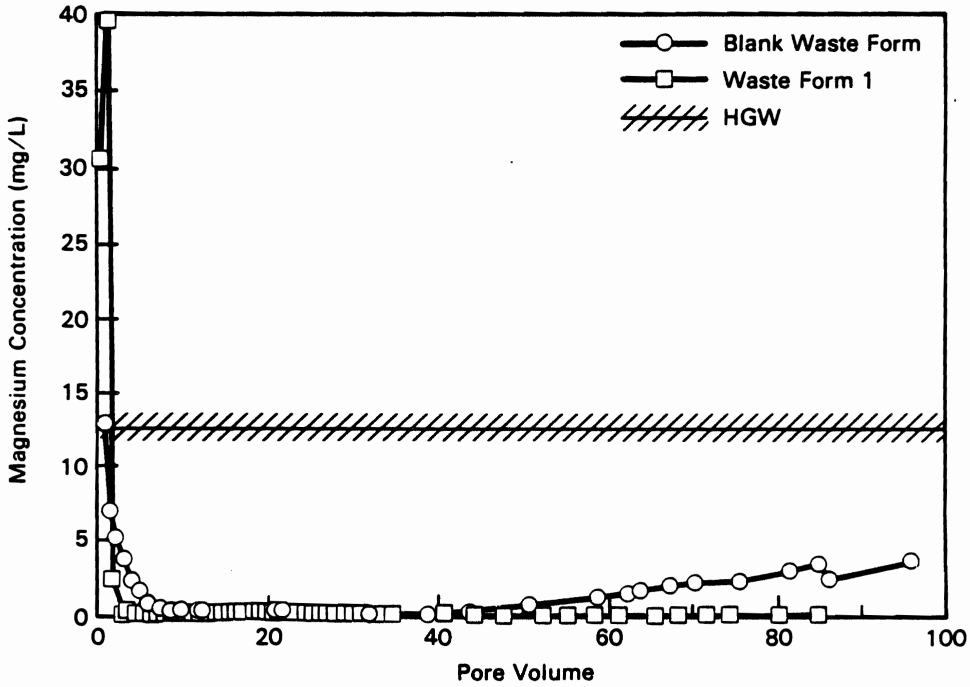


FIGURE 8.4. Magnesium Concentrations in the Combined Soil/Waste Form Column Leachates

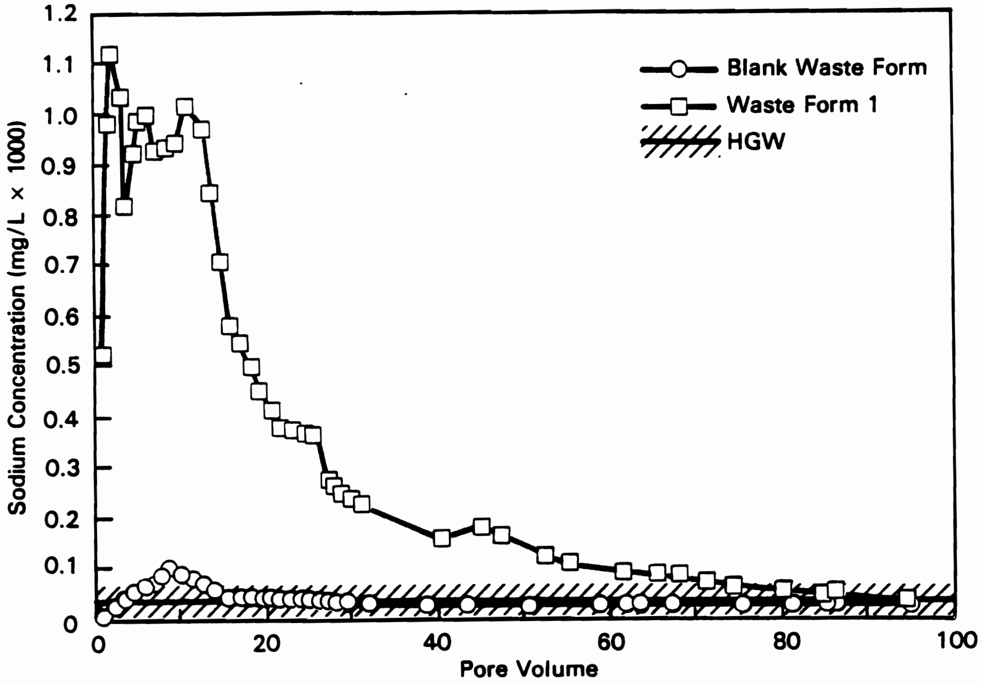


FIGURE 8.5. Sodium Concentrations in the Combined Soil/Waste Form Column Leachates

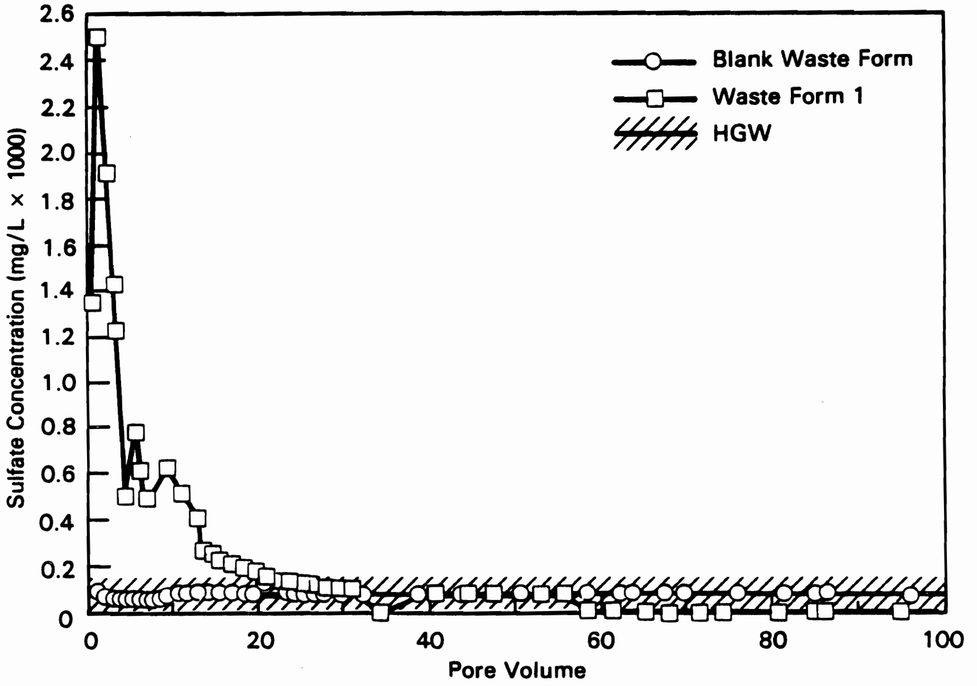


FIGURE 8.6. Sulfate Concentrations in the Combined Soil/Waste Form Column Leachates

below the minimum concentrations observed in the other two types of experiments; Na concentrations decrease to the Hanford ground-water concentration of 26.13 mg/L and SO_4 concentrations decrease to below the Hanford ground-water concentration. Decreases in Na and SO_4 concentrations are observed in the waste form 1 ANS 16.1 batch leaching experiments but not in the soil adsorption column experiments. Again the results from the ANS 16.1 batch leaching experiments are more similar to the combined soil/waste form column experimental results than the results from the soil adsorption column experiments. The combined soil/waste form column experiments continued for a longer period of time than the ANS 16.1 batch leaching experiments, allowing for the continued decrease in Na and SO_4 leaching from the waste form.

Phosphate concentrations (Figure 8.7) remain fairly constant in the leachates from the blank combined soil/waste form column experiment. The phosphate concentrations in the leachates from the waste form 1 combined soil/waste form column experiment mimic those of Ca, Mg, and SO_4, reaching a maximum after 1.5 pore volumes (~2 days) of soil, waste form, and ground-water contact. Phosphate concentrations then decrease to less than 10 mg/L.

Silicon concentrations (Figure 8.8) are initially high in both the leachates from the blank and waste form 1 combined soil/waste form column experiments. Silicon concentrations initially increase in the leachates from both experiments; the silicon concentrations in the leachates from the blank experiment reach a maximum of 80 mg/L and the silicon concentrations in the leachates from the waste form 1 experiment reach a maximum of 233 mg/L. The observation that the silicon concentrations in the blank experiment leachates are higher than the Hanford ground-water concentrations suggests that reactions among soil, blank waste form, and ground water are affecting leachate compositions. The silicon concentrations for the leachates from the ANS 16.1 blank experiment were always less than those found in Hanford ground water. While silicon concentrations must be controlled by the precipitation of a silicon-bearing mineral in the ANS 16.1 batch leaching experiments, silicon must be leaching from the soil in the combined soil/waste form experiment. Again, a comparison with the soil adsorption column experiments cannot be made. Silicon concentrations in the leachates from the waste form 1 combined soil/waste form experiment

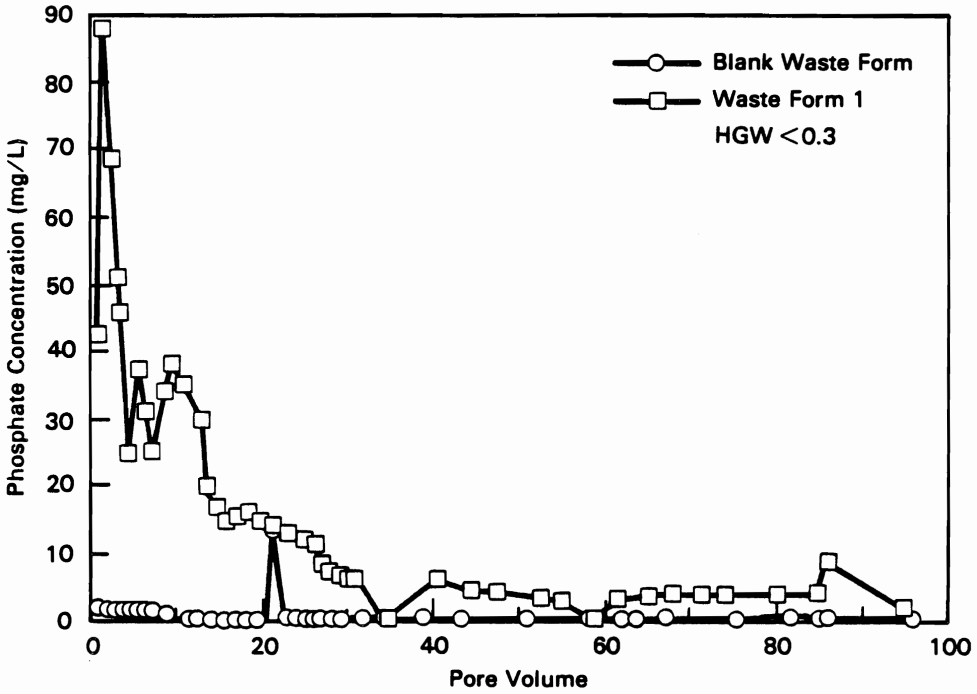


FIGURE 8.7. Phosphate Concentrations in the Combined Soil/Waste Form Column Leachates

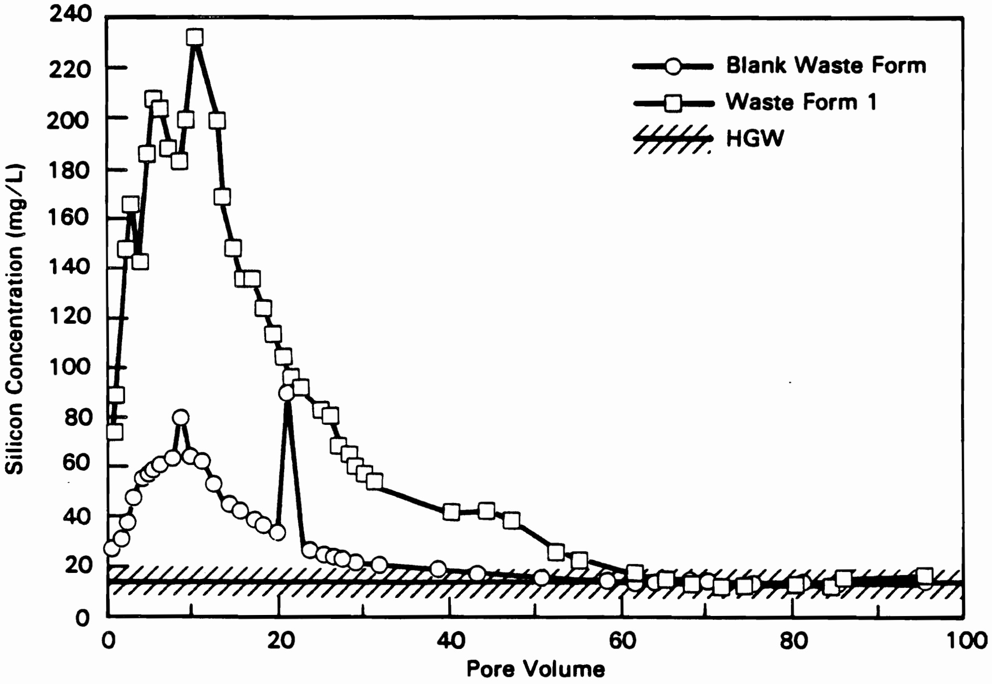


FIGURE 8.8. Silicon Concentrations in the Combined Soil/Waste Form Column Leachates

reach higher levels than in either the ANS 16.1 or soil adsorption column experiments. Then they decrease to the Hanford ground-water concentration, which differs from the soil adsorption column leachates in which the silicon concentration decreases to less than the Hanford ground-water concentration, suggesting the precipitation of a silicon-bearing mineral.

Figure 8.9 illustrates that Al concentrations remain below detection level for the blank combined soil/waste form column leachates, and increase to greater than 7 mg/L in the waste form 1 leachates. These concentrations are much higher than those observed in the soil adsorption column leachates, in which the highest concentration observed is less than 0.12 mg/L. Again, this difference in maximum Al concentration could result either from the difference in reaction time allowed in the soil adsorption and combined soil/waste form experiments, or from additional reactions among soil, waste form, and ground water that are eliminated from the experimental design of the ANS 16.1 batch leaching and soil adsorption column experiments.

As in the ANS 16.1 batch leaching experiments, the K concentrations in the leachates from the combined soil/waste form column experiments (Figure 8.10) are higher in the leachates from the blank experiment than in the leachates from the waste form 1 experiment (compare Figure 6.11 with Figure 8.10).

Figures 8.11 through 8.14 illustrate the concentrations of barium, boron, strontium and chlorine, respectively, in the leachates from the combined soil/waste form column experiments. Figure 8.11 shows that with the exception of an initial increase in the waste form 1 leachates, barium concentrations are maintained below that of the Hanford ground water in both experiments. The barium concentrations are lower in the waste form 1 leachates than in the blank leachates. Figure 8.12 illustrates that boron concentrations vacillate through time for both the blank and waste form 1 combined soil/waste form column leachates. This behavior is not unlike that seen in the waste form 1 soil adsorption column leachates. Strontium concentrations (Figure 8.13) are maintained below the Hanford ground-water concentration in the waste form 1 combined soil/waste form column leachates, suggesting the precipitation of a strontium-bearing mineral; at the same time, strontium concentrations rise to about 1.2 mg/L in the blank combined soil/waste form column leachates. Finally,

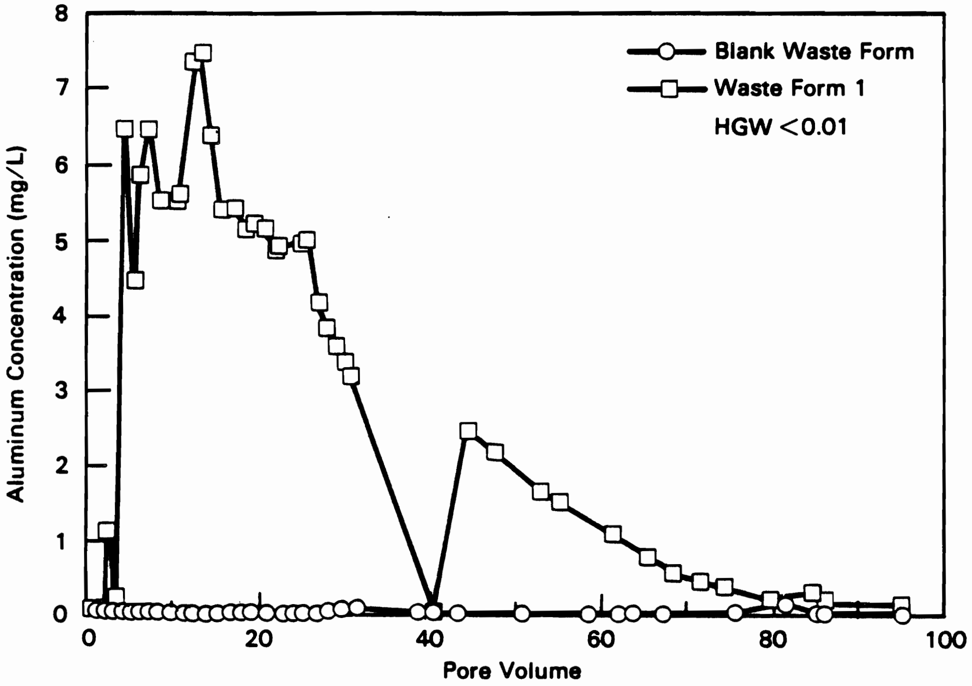


FIGURE 8.9. Aluminum Concentrations in the Combined Soil/Waste Form Column Leachates

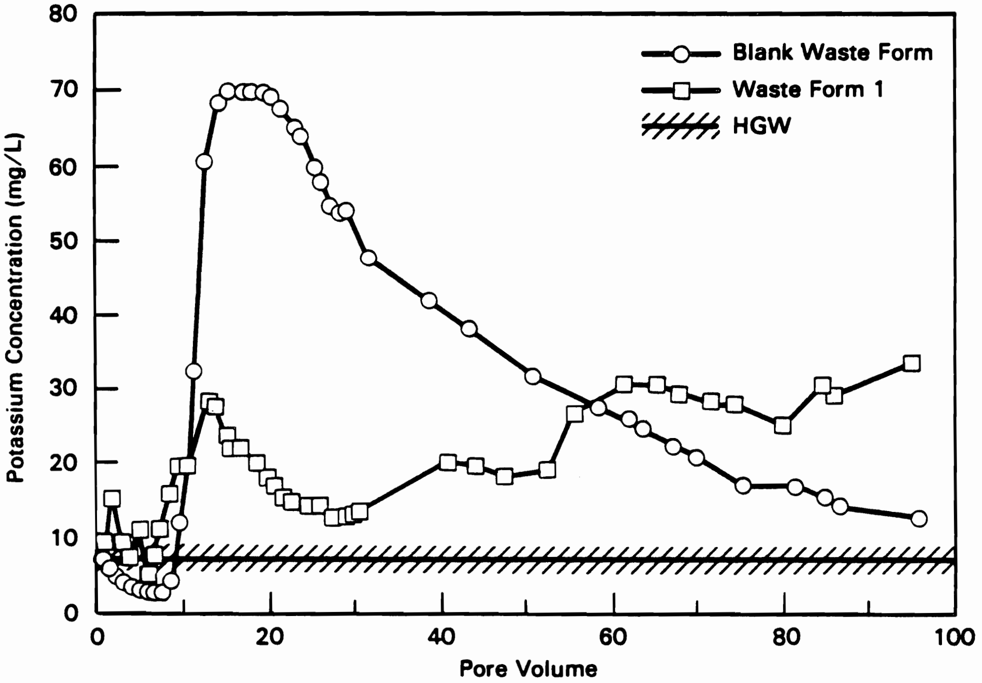


FIGURE 8.10. Potassium Concentrations in the Combined Soil/Waste Form Column Leachates

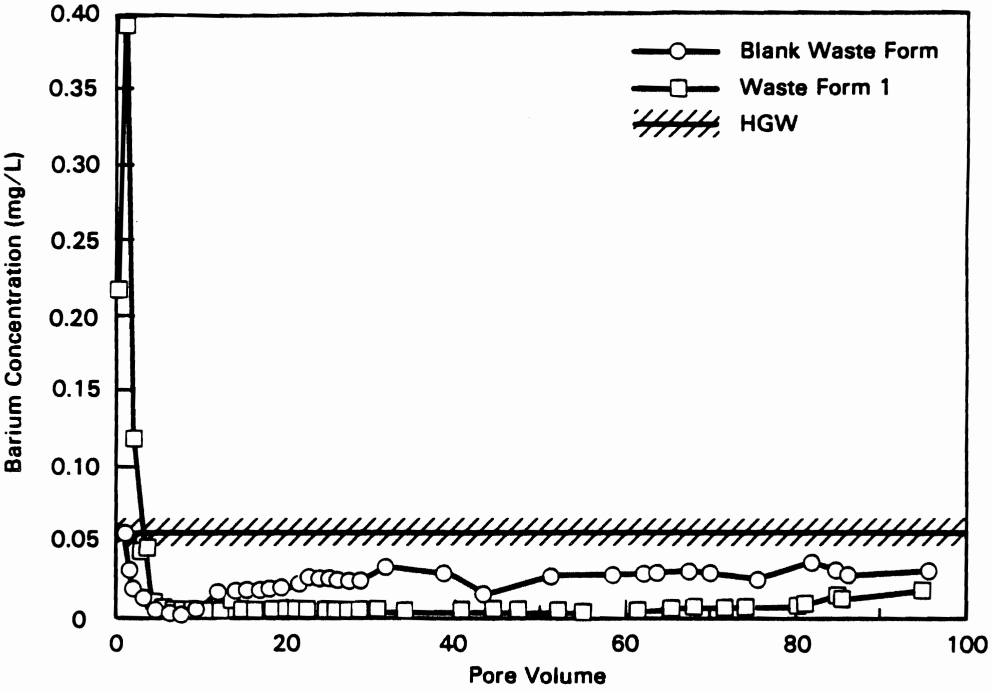


FIGURE 8.11. Barium Concentrations in the Combined Soil/Waste Form Column Leachates

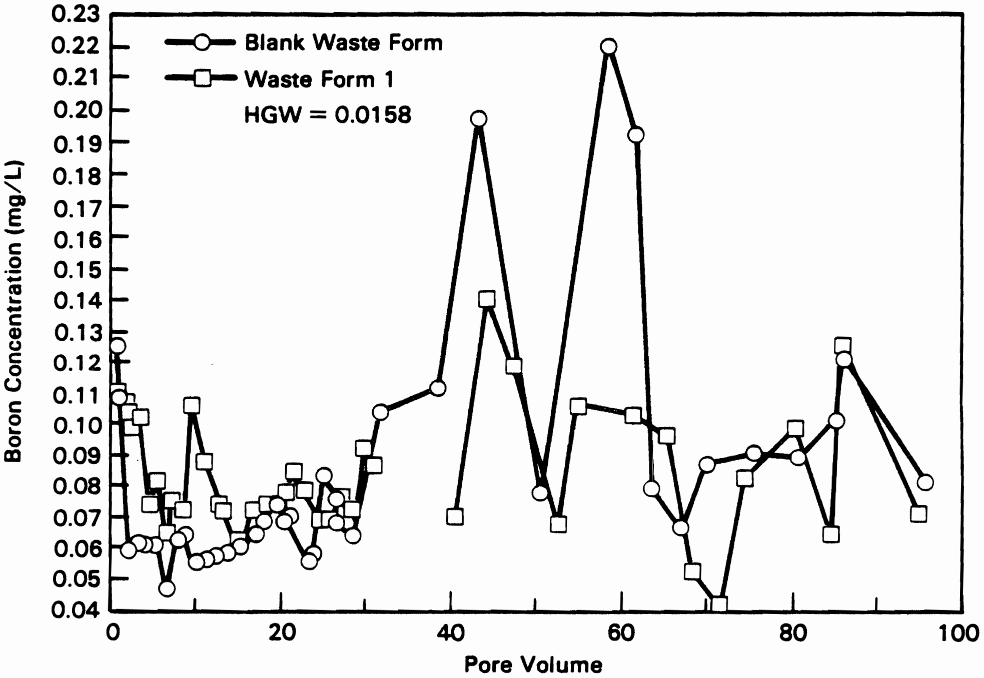


FIGURE 8.12. Boron Concentrations in the Combined Soil/Waste Form Column Leachates

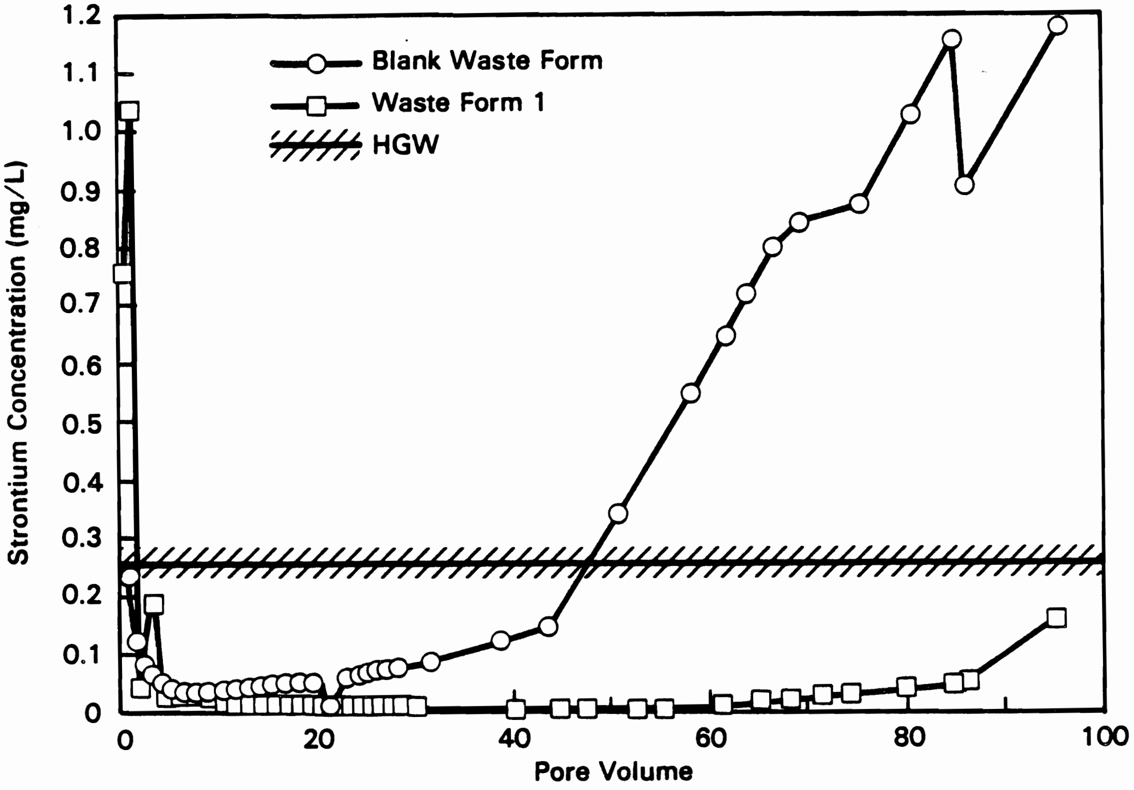


FIGURE 8.13. Strontium Concentrations in the Combined Soil/Waste Form Column Leachates

chlorine concentrations (Figure 8.14), after an initial rise to more than 55 mg/L in the waste form 1 leachates, vary between 15 and 25 mg/L for both the blank and waste form 1 experiments.

8.2 ION SPECIATION

Figures 8.15 through 8.21 illustrate the species distribution for the major components in the leachates from the blank combined soil/waste form experiment. These figures show that changes in major component speciation occurred as the Hanford ground water and soil reacted with the blank cement waste form. These changes are greater than the changes in speciation that occurred in the blank ANS 16.1 batch experiment leachates. (Compare Figures 8.15 through 8.21 with Figures 6.16 through 6.22.)

For example, Figures 8.15 and 8.16 illustrate that $CaPO_4^-$, $MgPO_4^-$, and $MgOH^+$ are important in the transport of calcium and magnesium in the leachates from

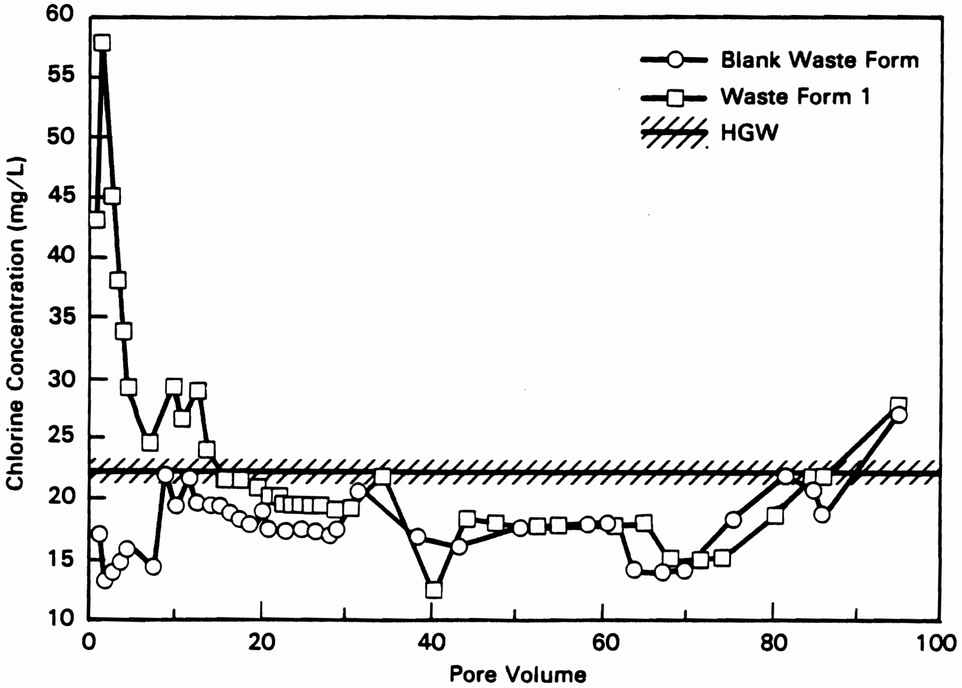


FIGURE 8.14. Chlorine Concentrations in the Combined Soil/Waste Form Column Leachates

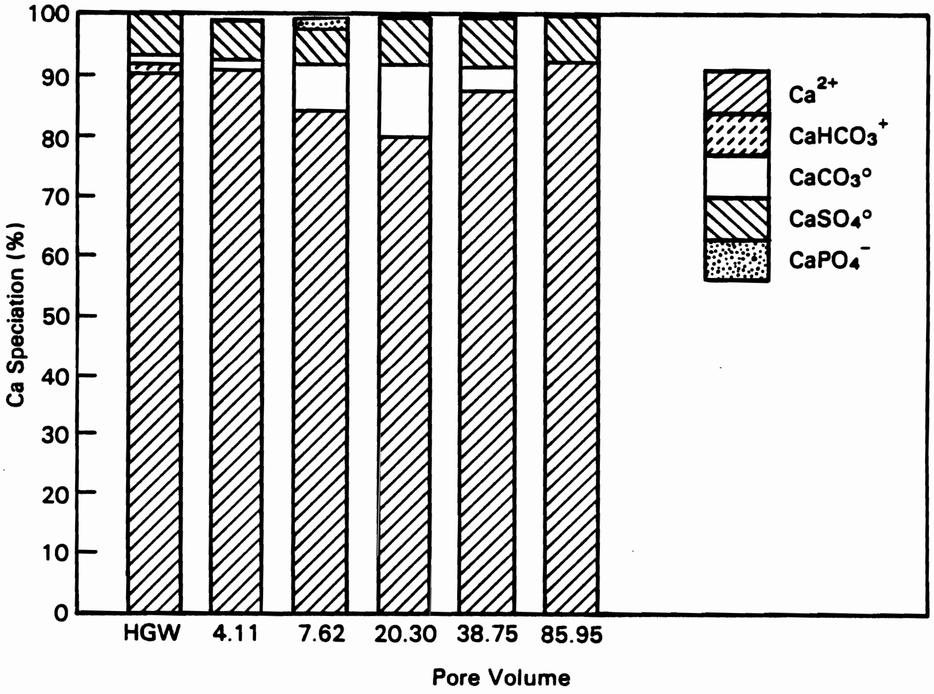


FIGURE 8.15. Calcium Species Present in the Blank Combined Soil/ Waste Form Column Leachates

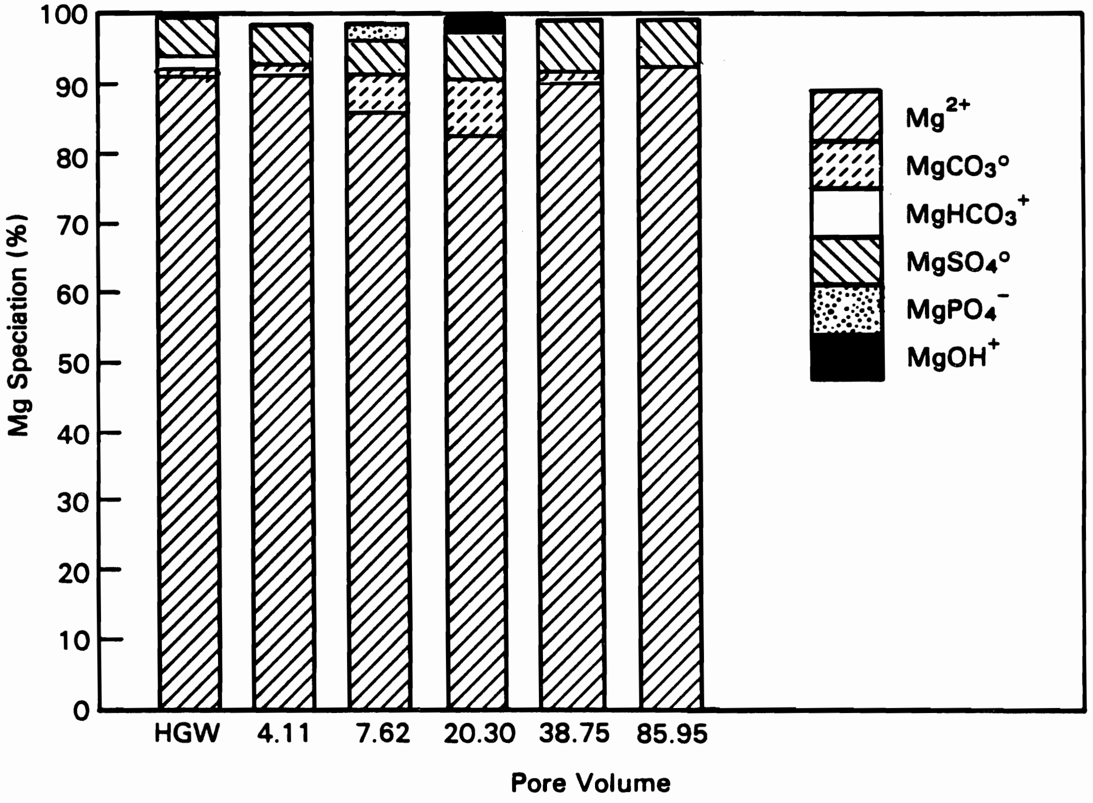


FIGURE 8.16. Magnesium Species Present in the Blank Combined Soil/Waste Form Column Leachates

the blank soil/waste form column experiment. These species were also found in significant proportions in the leachates from the waste form 1 ANS 16.1 batch experiments. Figures 8.17 and 8.18 illustrate that the predominant silicon and boron species are $H_4SiO_4^0$, $H_3SiO_4^-$, $H_3BO_3^0$, and $H_2BO_3^-$, and that these species are present in proportions similar to those found in the waste form 1 soil adsorption column leachates (see Figures 7.21 and 7.22). After 20 pore volumes of contact between the soil, ground water, and blank waste form, CO_3^{2-} and $CaCO_3^0$ are important carbonate species (Figure 8.19). In the same leachate, $CaPO_4^-$ rather that PO_4^{3-} is the predominant phosphate species (Figure 8.20). Figure 8.21 illustrates that $MgSO_4^0$ is not an important sulfate species in the blank soil/waste form column leachates, although it is an important species in the Hanford ground water. This figure also shows that $NaSO_4^-$ is an important species after 7 pore volumes of soil/ground-water/waste form contact. $NaSO_4^-$ was not an important species in the blank ANS 16.1 leachates. These observations suggest that the interaction among the soil and the leachates from the

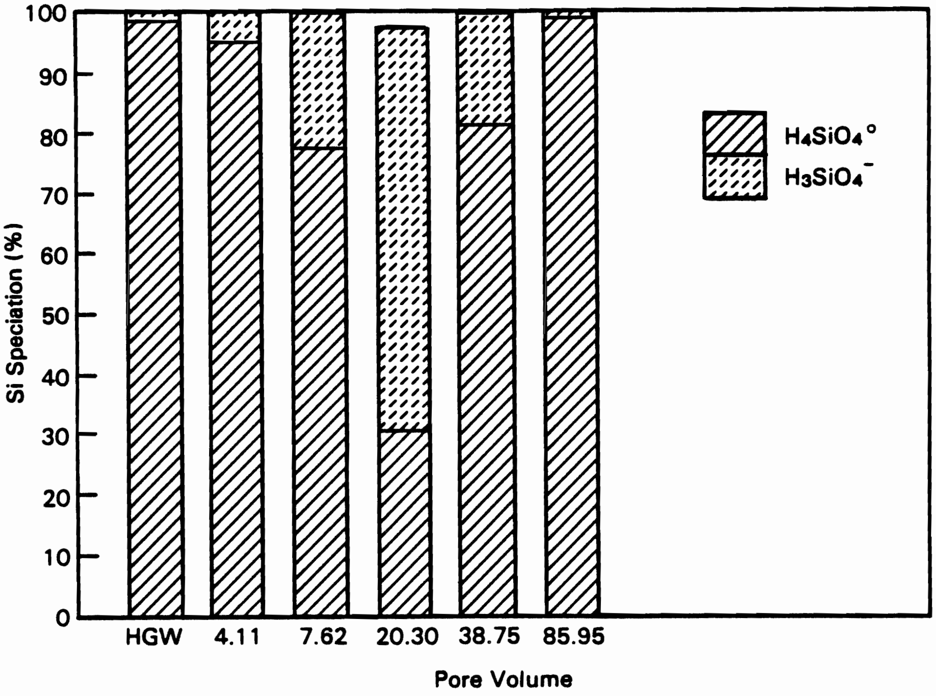


FIGURE 8.17. Silicon Species Present in the Blank Combined Soil/Waste Form Column Leachates

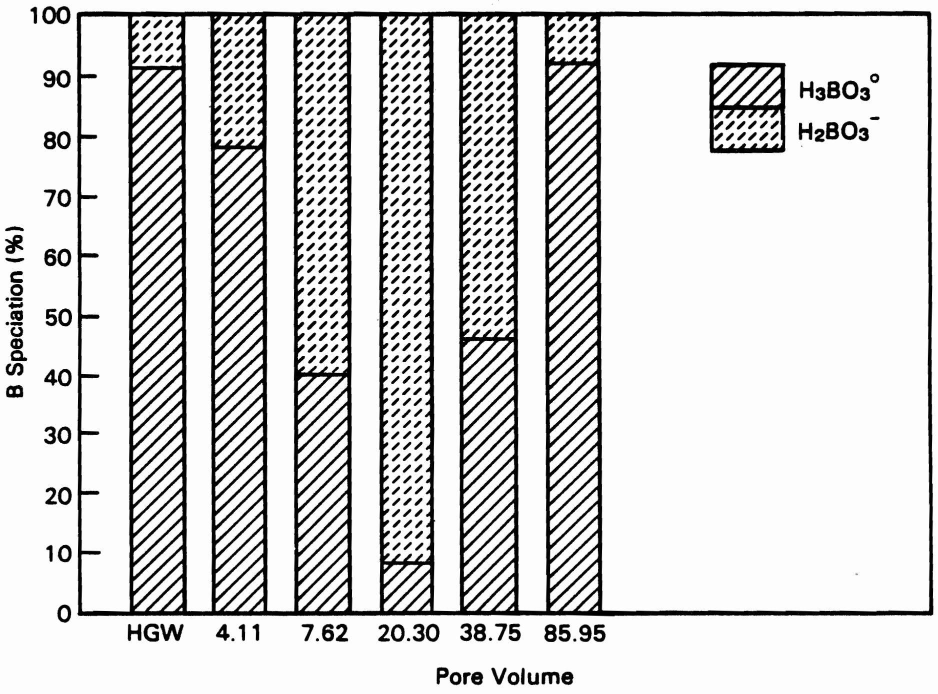


FIGURE 8.18. Boron Species Present in the Blank Combined Soil/Waste Form Column Leachates

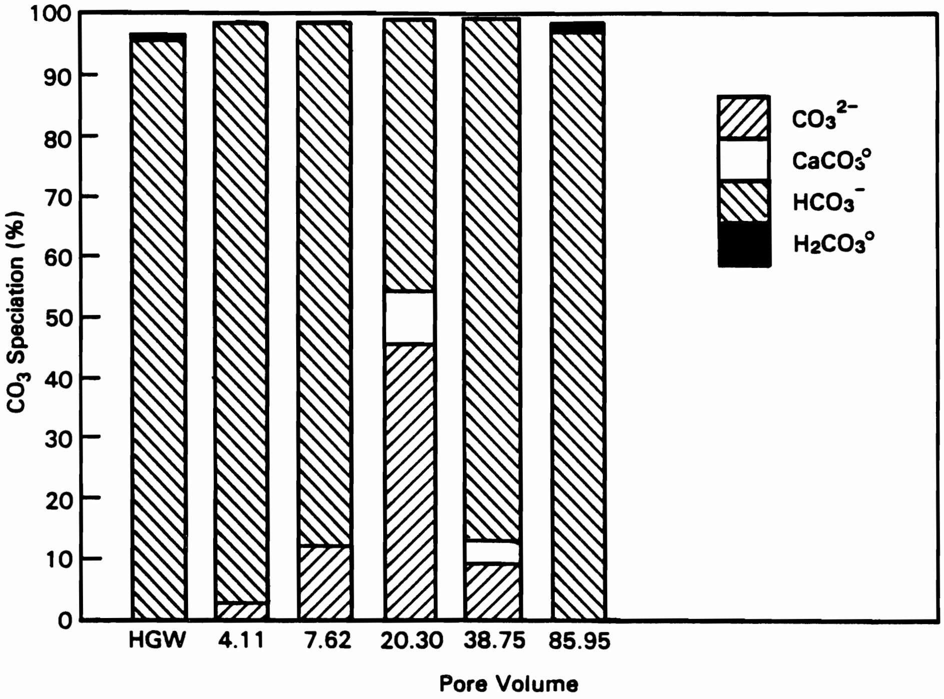


FIGURE 8.19. Carbonate Species Present in the Blank Combined Soil/Waste Form Column Leachates

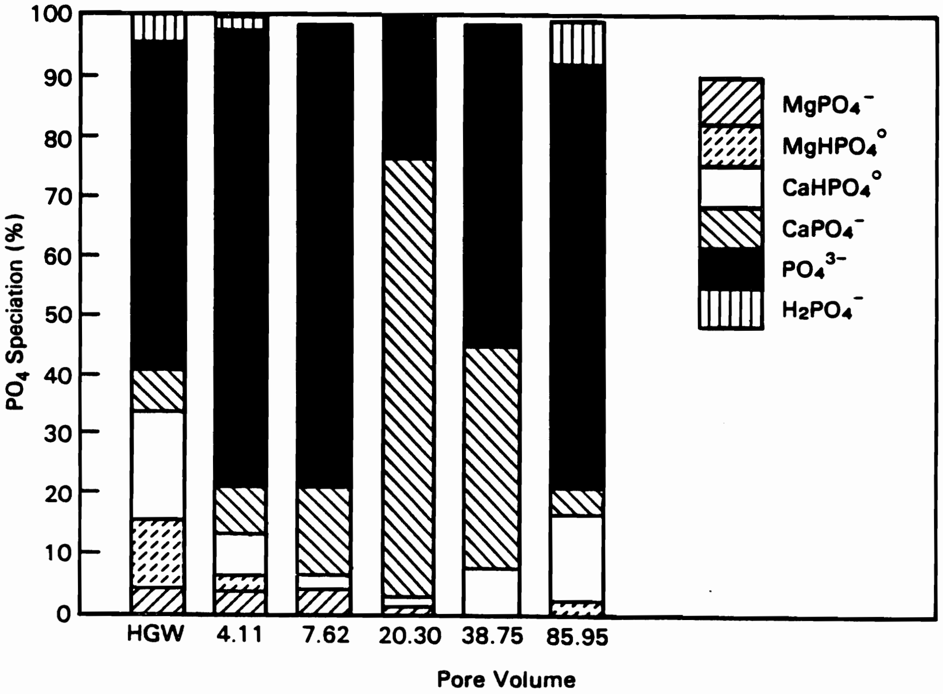


FIGURE 8.20. Phosphate Species Present in the Blank Combined Soil/Waste Form Column Leachates

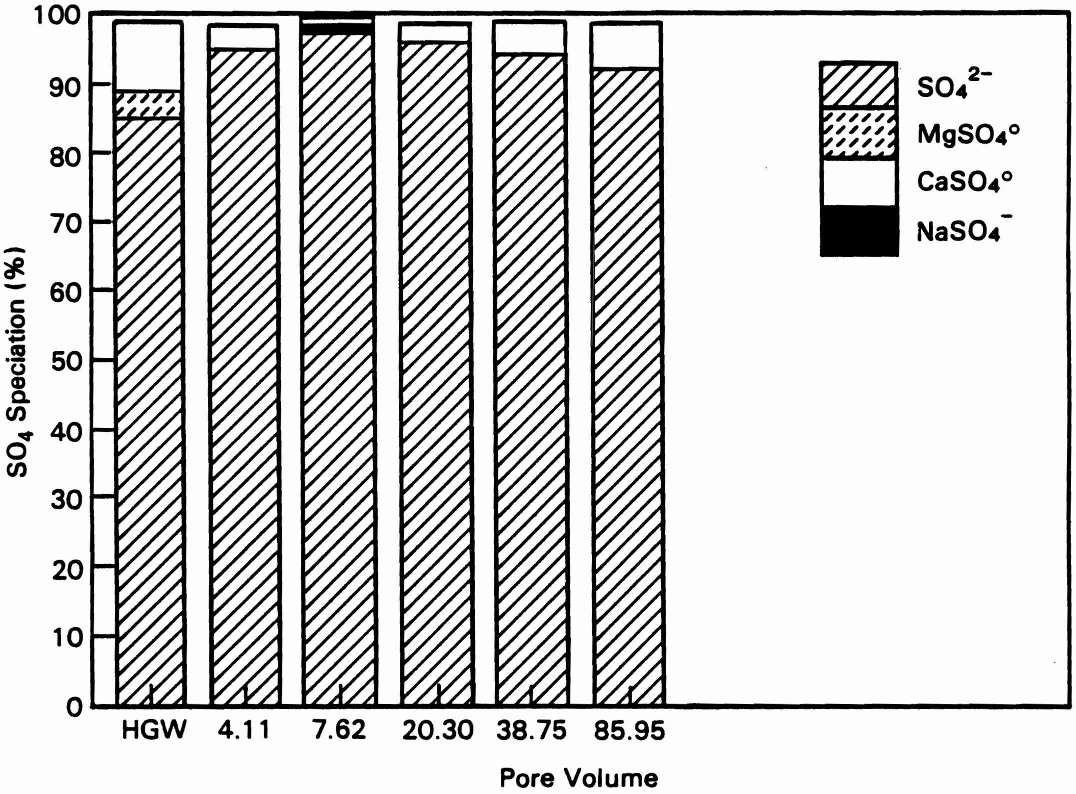


FIGURE 8.21. Sulfate Species Present in the Blank Combined Soil/Waste Form Column Leachates

blank waste form, and/or the interaction between the three components (cement, soil, and ground water) in the blank combined soil/waste form experiments, play a significant role in determining the leachate compositions.

Before continuing with a discussion of the species distributions calculated for the waste form 1 combined soil/waste form column experiments, a discussion of the MINTEQ calculations is required. The reader should recall that the MINTEQ calculations on each solution composition are iterative, changing the CO_3 concentration until the solution is charge balanced. Many of the leachate compositions for the waste form 1 combined soil/waste form column experiments could not be charge balanced in this manner. The MINTEQ calculations showed that even by excluding carbonate as a component in solution altogether, many of the leachates contained too many anions. These leachates were calculated to be between 15 and 30% out of charge balance.

Several explanations for this problem are possible. First, these solutions are distinct when compared to the leachates from the ANS 16.1 batch and the soil adsorption column experiments. They have some of the highest pHs (many over 11.5) measured in any solution analyzed. In addition, many of these solutions were analyzed to have high phosphorous concentrations (>10 mg/L). Both of these analytical measurements may be in doubt: pH measurements in highly alkaline, sodium-rich solutions are difficult to make, and the high phosphorous contents reported are not confirmed by the phosphate measurements. As an experiment, phosphate was removed as a component from the MINTEQ input decks; however, the leachate compositions were still calculated to be out of charge balance with too many anions. These leachates are also characterized by very high alkalinity and much higher concentrations of organic carbon than the other leachates analyzed. It is possible that organic compounds are responsible for a major percentage of the cations present in these solutions. It is also possible that an important cation in these solutions has not been measured (i.e., NH_4^+).

In addition to analytical uncertainties that might generate a cation/anion imbalance, uncertainties in the MINTEQ thermodynamic data base can also become significant when considering solutions with pHs of 10 to 12. For example, the equilibrium constants for the reactions

$$H_4SiO_4^0 \rightleftarrows H^+ + H_3SiO_4^- \qquad (1)$$

and

$$H_3SiO_4^- \rightleftarrows H^+ + H_2SiO_4^{2-} \qquad (2)$$

are not very well known. The value for the logorithm of the equilibrium constant for reaction (1) ranges from -9.77 (Volosov et al. 1972) to -9.93 (Helgeson 1969), and the value for the logarithm of the equilibrium constant for reaction (2) ranges from -11.70 (Ryzhenko 1967) to -13.17 (Volosov et al. 1972). Calculations using these different equilibrium constants generate different ratios of $H_3SiO_4^-$ to $H_2SiO_4^{2-}$ at high pHs. Varying the proportions of $H_3SiO_4^-$ to $H_2SiO_4^{2-}$ changes the anion/cation balance. As an experiment, several MINTEQ calculations were done in which silicon was not allowed to speciate (all silicon present was retained in the component H_4SiO_4). It was concluded that the leachates were still out of charge balance with too many anions. In summary, it appears that one or more major cations are not being considered in the MINTEQ calculations.

The observations that some of the leachates could not be charge balanced, and that a major cation might be missing from the compositional data used, suggest that carbonate is not the only unknown entity in these solutions. As a result, there is some doubt as to whether the leachates that could be charge balanced by changing the carbonate concentration are in fact being evaluated correctly. Bearing this in mind, Figures 8.22 through 8.28 illustrate the species distributions calculated for the major components in solutions that have been successfully charge balanced. Figures 8.22 through 8.25, which illustrate the speciation of calcium, magnesium, silicon, and boron, respectively, tend to suggest that the leachate compositions go through a major change until they almost completely reflect the composition of the waste stream after four pore volumes of contact; they then change back toward the speciation seen in the Hanford ground water.

For example, after 4 pore volumes of soil/waste form/ground-water contact, calcium is present almost entirely as $CaPO_4^-$ (Figure 8.22), and magnesium is present almost entirely as $MgPO_4^-$ (Figure 8.23). After 70 pore volumes of soil/waste form/ground-water contact, calcium and magnesium are present predominantly as Ca^{2+} and Mg^{2+}. Silicon and boron show similar behavior patterns: After 4 pore volumes of soil/waste form/water contact, all boron present is tied up in the species $H_2BO_3^-$ (Figure 8.24), and about 80% of the silicon in solution is present as $H_2SiO_4^{2-}$ (Figure 8.25).

Figures 8.26 through 8.28 illustrate the speciation of carbonate, sulfate, and phosphate, respectively. Figure 8.26 shows that the species $NaCO_3^-$ is a more important carbonate species in the leachates from the waste form 1 soil/waste form column experiment than in the waste form 1 ANS 16.1 batch leachates and that this species becomes increasingly important through time. Figure 8.27 illustrates that sulfate is present primarily as SO_4^{2-} throughout the experiment. This is consistent with the observations from both the ANS 16.1 batch

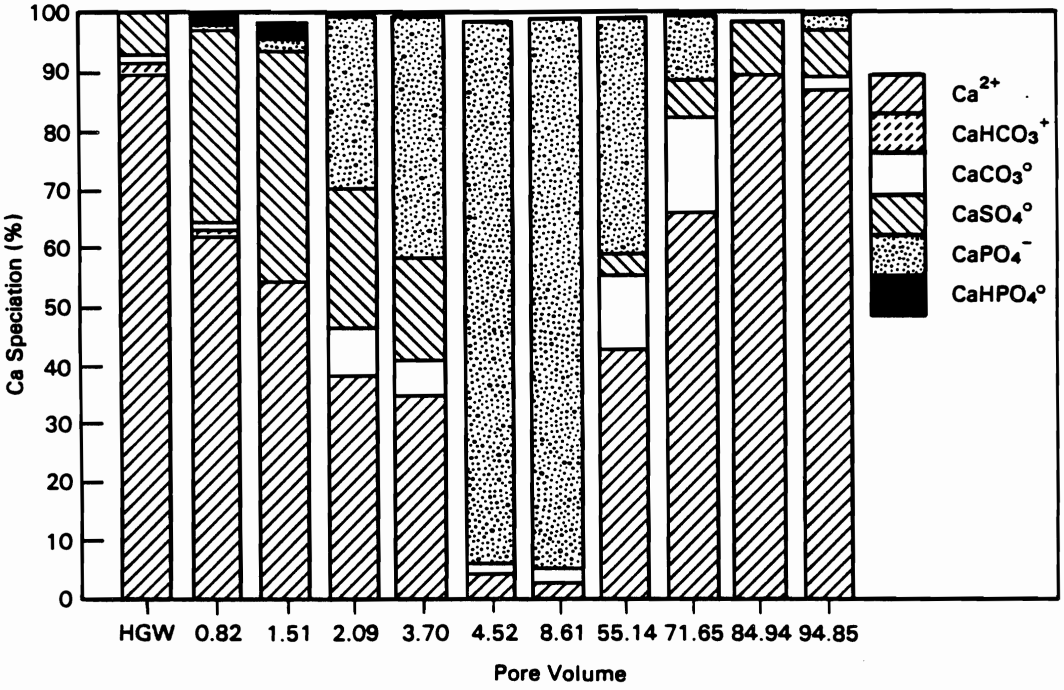


FIGURE 8.22. Calcium Species Present in the Waste Form 1 Combined Soil/Waste Form Column Leachates

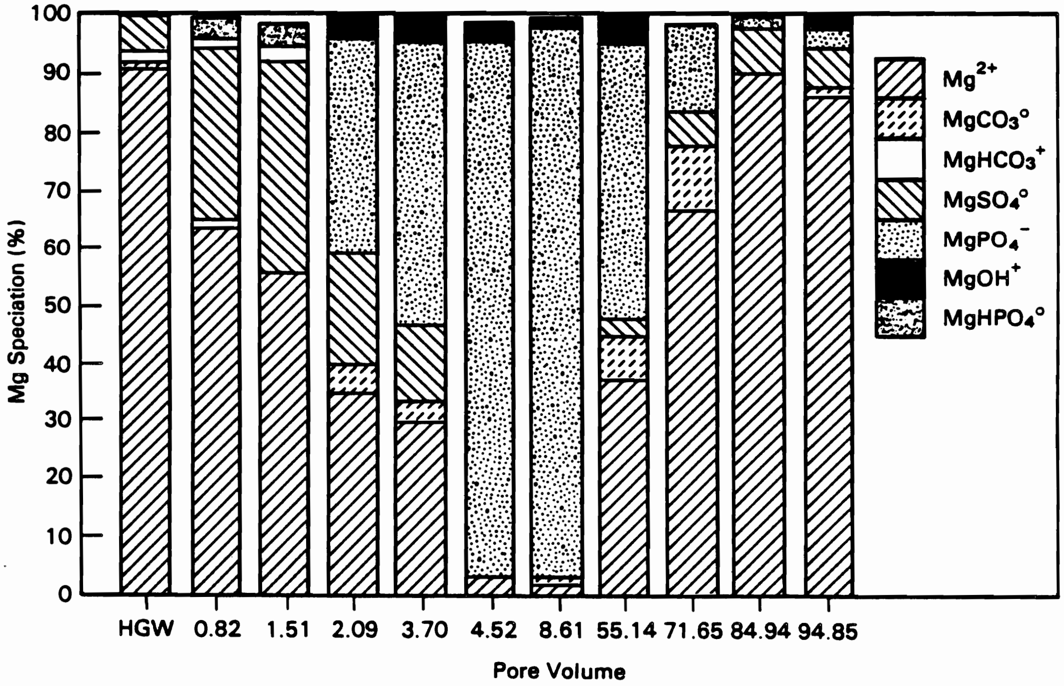


FIGURE 8.23. Magnesium Species Present in the Waste Form 1 Combined Soil/Waste Form Column Leachates

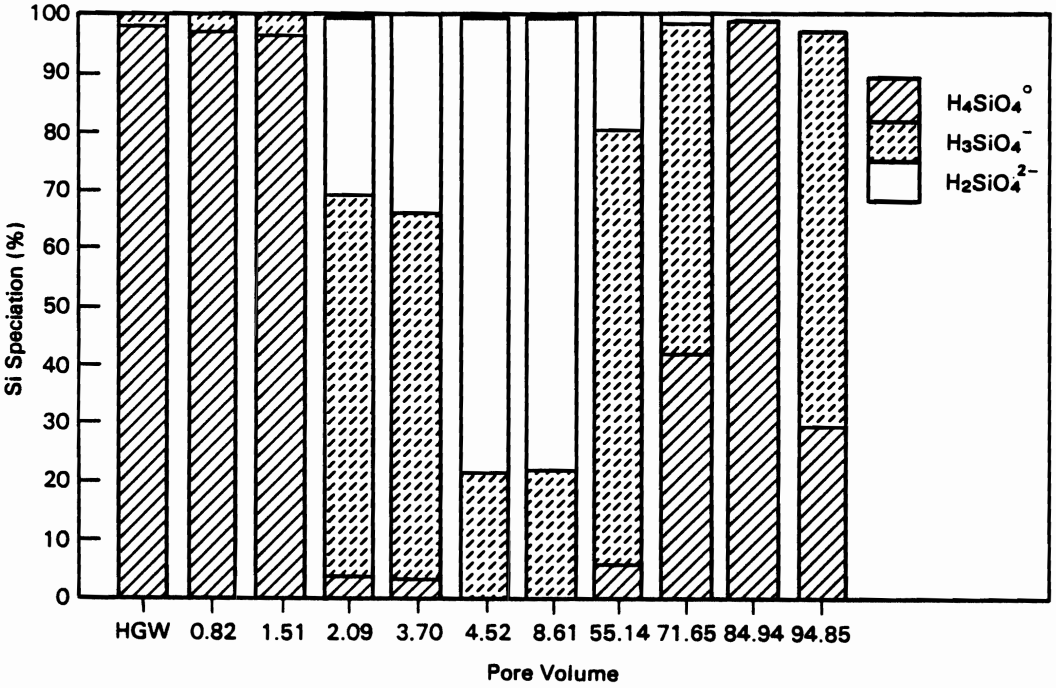


FIGURE 8.24. Silicon Species Present in the Waste Form 1 Combined Soil/Waste Form Column Leachates

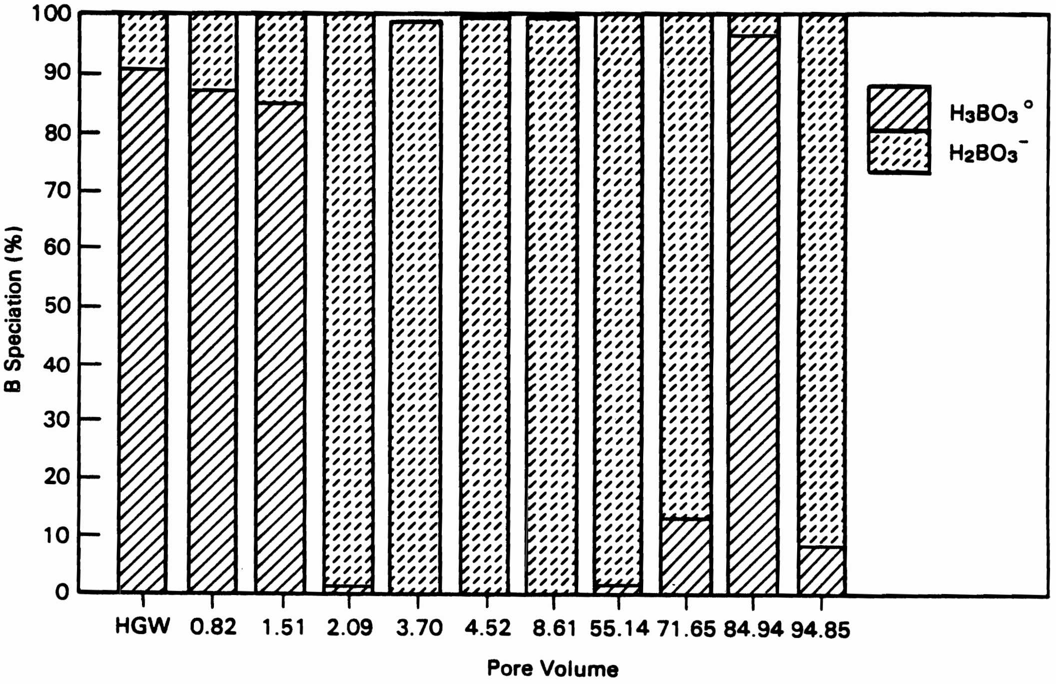


FIGURE 8.25. Boron Species Present in the Waste Form 1 Combined Soil/Waste Form Column Leachates

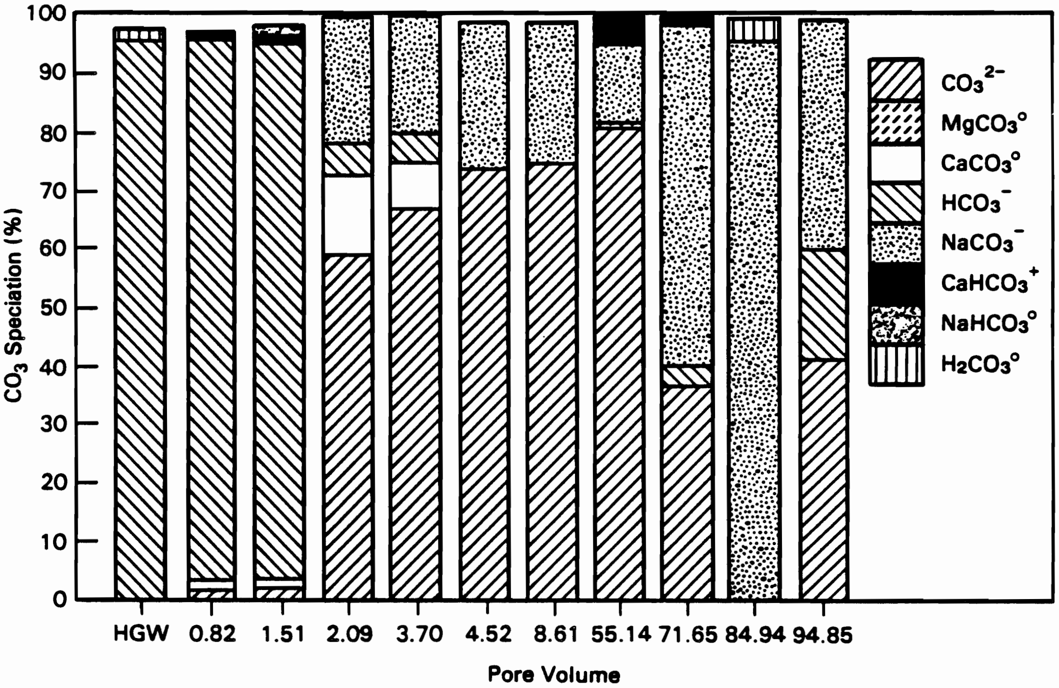


FIGURE 8.26. Carbonate Species Present in the Waste Form 1 Combined Soil/Waste Form Column Leachates

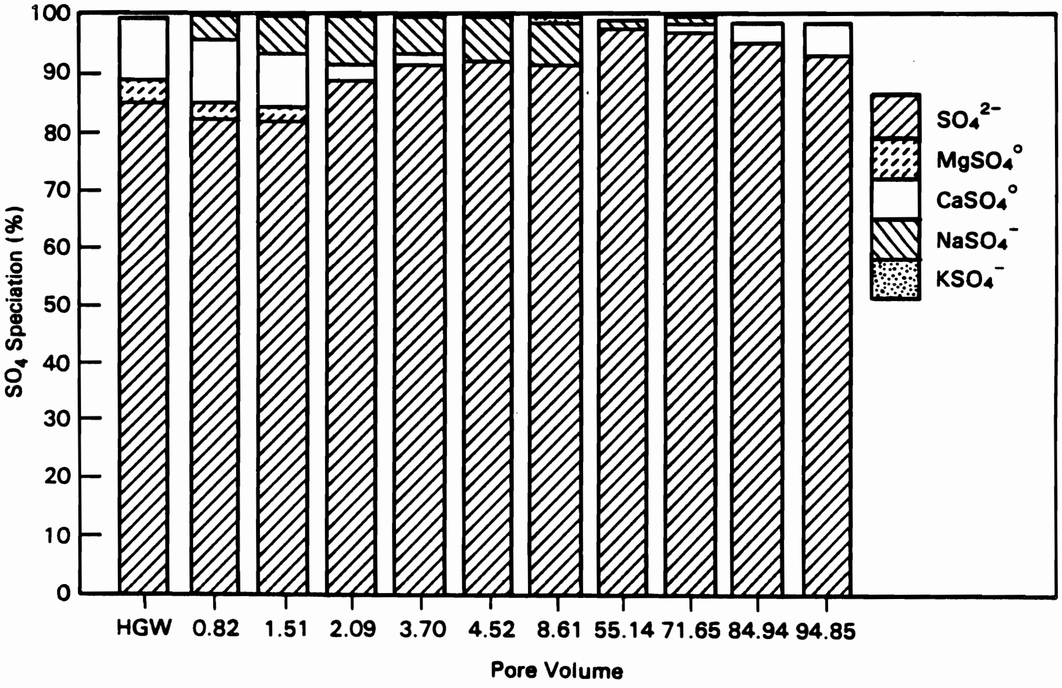


FIGURE 8.27. Sulfate Species Present in the Waste Form 1 Combined Soil/Waste Form Column Leachates

leaching and soil adsorption column experiments. Figure 8.28 illustrates that many phosphate species are present in solution. The predominant phosphate species are HPO_4^{2-}, PO_4^{3-}, and $CaPO_4^-$.

8.3 SATURATION INDICES FOR MINERALS

Table 8.1 lists the saturation indices for possible solubility controls in the combined soil/waste form column experiments. These experiments are similar in nature to the soil adsorption column experiments in that a steady state between the leachate, soil, and waste form could potentially be achieved. Figures 8.3 through 8.9 indicate that a steady state has almost been achieved by the end of the experiment.

From Table 8.1, it can be observed that the leachates from the blank soil/waste form column experiment are nearly in equilibrium with calcite and

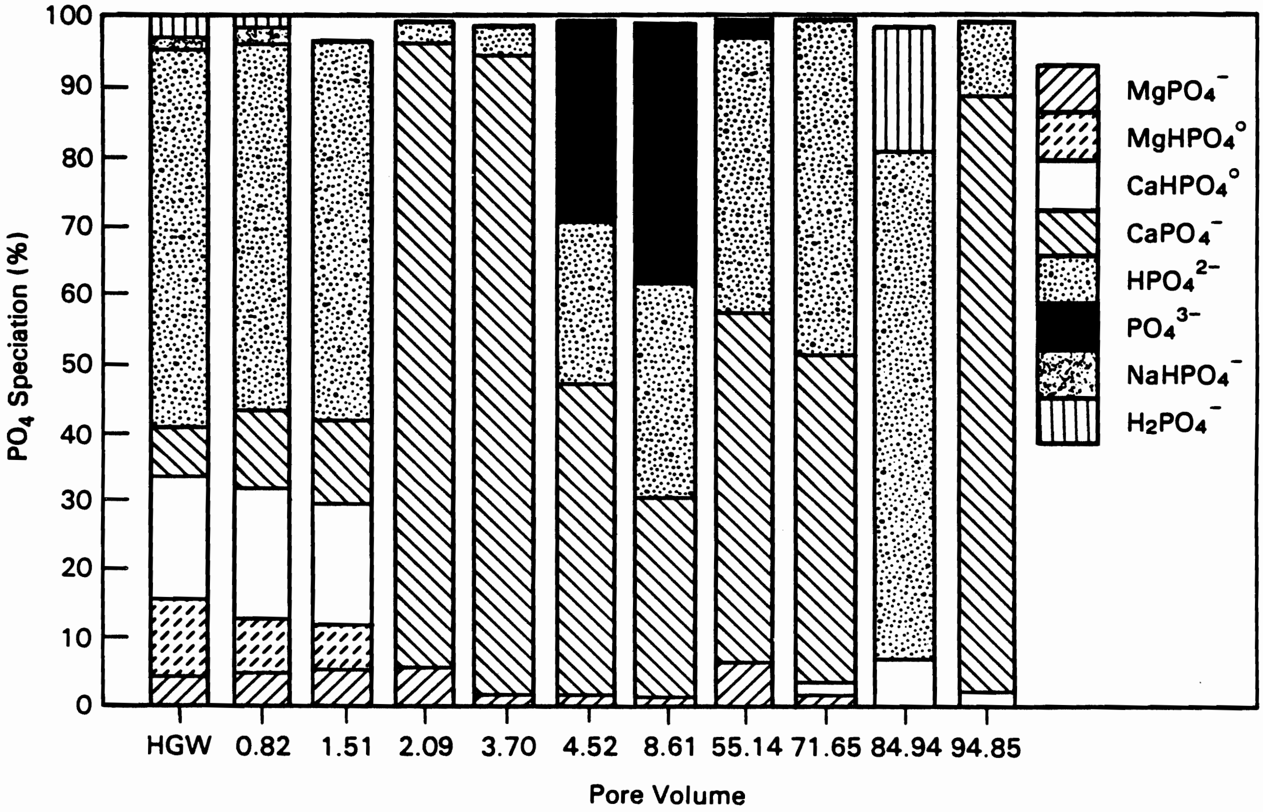


FIGURE 8.28. Phosphate Species Present in the Waste Form 1 Combined Soil/Waste Form Column Leachates

TABLE 8.1. Saturation Indices for Potential Solubility Controls in the Combined Soil/Waste Form Column Experiments

Sample	HGW	BL[a] 5	BL 10	BL 20	BL 30	BL 41	WF1[b] 1	WF1 2	WF1 3	WF1 5	WF1 6	WF1 10	WF1 35	WF1 40	WF1 43	WF1 45
Carbonates																
Calcite	0.663	0.149	0.267	0.868	0.693	0.288	1.096	1.061	1.588	1.156	-0.351	-0.245	0.039	0.782	-0.835	0.523
Dolomite	1.017	-0.157	-0.114	-0.054	-0.485	-1.371	1.706	1.628	1.852	0.421	-2.274	-2.000	-0.936	-0.026	-3.249	-1.115
Magnesite	-0.142	-0.802	-0.877	-1.419	-1.675	-1.578	0.114	0.072	-0.232	-1.2341	-2.419	-2.252	-1.471	-1.303	-2.909	-2.134
Otavite	0.828	0.875	0.953	0.934	0.927	0.549	0.791	0.719	0.679	0.525	-0.614	-0.180	0.734	0.965	0.310	-1.510
Rhodochrosite	-1.282	-1.441	-0.880	-0.358	-1.134	-2.218	-1.643	-1.794	-0.977	-1.101	-1.625	-1.191	-0.811	-0.525	-2.444	-1.212
Cerrusite	-0.860	-0.771	-0.885	--	-0.821	-0.765	-0.796	-0.798	-1.608	--	-5.544	-5.056	--	--	--	--
Strontianite	-1.205	-0.808	-1.697	-0.972	-1.065	-1.291	-0.668	-0.642	-0.933	-0.360	-0.944	-0.830	-1.679	-1.046	-0.553	-1.677
Sulfates																
Barite	0.118	-0.668	-0.990	-0.221	-0.059	-0.109	1.577	1.959	1.379	0.897	-0.321	-0.585	-1.210	-0.707	-0.315	-0.302
Gypsum	-1.482	-2.168	-2.632	-2.133	-1.824	-1.731	-0.283	-0.076	-0.721	-1.179	-3.429	-3.652	-3.244	-2.384	-2.029	-1.744
Celestite		-2.283	-3.754	-3.132	-2.740	-1.891	-1.204	-0.935	-2.399	-1.853	-3.178	-3.395	-4.120	-3.349	-8.118	-2.638
Ettringite	-21.495	-22.498	-22.336	-16.108	-18.333	-22.349	-15.881	-15.049	-6.718	-7.957	-13.995	-15.786	-16.576	-16.474	-23.741	-12.423
Monosulfate	-23.593	-23.222	-22.134	-16.813	-19.747	-23.949	-20.372	-19.949	-10.328	-10.654	-12.194	-13.537	-15.150	-16.767	-24.743	-13.996
Phosphates																
$MnHPO_4$	0.200	0.595	0.756	0.598	-0.044	0.095	1.590	1.750	0.078	0.137	-0.297	0.006	0.344	0.131	1.256	-0.099
Strengite	-1.885	-2.737	-4.130	-8.404	-5.046	-1.887	0.652	-0.423	-9.816	-10.00	-11.139	-11.076	-8.981	-6.354	0.853	-8.031
Hydroxyapatite	2.026	2.810	3.964	5.791	4.511	0.876	--	--	--	--	--	--	6.782	7.723	1.18	9.108
Hydroxides/Oxides																
Brucite	--	-3.664	-2.857	-1.909	-3.626	-4.729	-3.559	-3.452	0.599	-0.112	0.037	-0.243	-0.749	-2.419	-6.620	-1.845
Gibbsite	-0.446	-0.412	-1.136	-1.861	-1.027	0.096	-0.132	-0.196	-2.384	-2.104	-1.493	-1.542	-1.048	-0.645	1.509	-1.299
Boehmite	-0.254	-0.220	-0.943	-1.669	-0.835	0.288	0.060	-0.004	-2.192	-1.911	-1.301	-1.350	-0.856	-0.453	1.701	-1.107
Diaspore	--	1.485	0.762	0.036	0.870	1.993	1.765	1.701	-0.487	-0.206	0.404	0.355	0.849	1.252	3.406	0.598
Portlandite	-9.372	-9.042	-9.042	-5.951	-7.588	-9.768	-8.906	-8.791	-3.910	-4.053	-4.224	-4.565	-5.568	-6.663	-10.875	-5.516
Lime	-19.494	-19.164	-18.164	-16.073	-17.710	-19.89	-19.028	-18.913	-14.032	-14.175	-14.346	-14.686	-15.690	-16.785	-20.997	-15.638
$Cr(OH)_3(A)$[c]	--	0.551	-2.661	-7.123	-4.815	0.884	2.664	2.380	-10.186	-10.755	-13.679	-12.961	-9.775	-6.644	1.634	-8.507
γFeO_3	6.292	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Ferrihydrite	1.448	0.885	0.773	-0.613	0.432	1.169	2.267	1.030	-1.519	-1.599	-1.491	-1.764	-0.893	-0.485	1.962	-0.632
Wulfenite	--	-0.482	-0.915	-1.638	1.593	0.534	0.412	0.262	-1.730	-3.071	-6.337	-6.343	-3.247	-1.565	0.689	-1.401
Silicates																
$SiO_2(a)$	-0.561	-0.026	-0.049	-0.763	-0.570	-0.615	0.123	0.207	-1.009	-1.118	-2.324	-2.292	-1.611	-1.034	-0.662	-1.064
Chalcedony	0.252	0.787	0.764	0.050	0.243	0.198	0.936	1.020	-0.196	-0.305	-1.511	-1.479	-0.798	-0.221	0.151	-0.251
Cristobalite	0.316	0.851	0.828	0.114	0.307	0.262	1.000	1.084	-0.132	-0.241	-1.447	-1.415	-0.734	-0.157	0.215	-0.187
Quartz	0.735	1.270	1.247	0.533	0.726	0.681	1.419	1.503	0.287	0.178	-1.028	-0.996	-0.315	0.262	0.634	0.232
Sepiolite(C)[d]	0.163	2.135	3.68	3.436	0.579	-1.764	2.792	3.259	7.712	5.961	2.644	2.180	3.208	1.600	-5.685	2.659
Willemite	0.562	0.462	1.002	2.803	0.553	-0.925	3.152	3.374	4.272	1.162	-0.951	-0.779	-0.350	0.276	-2.029	0.403

(a) BL, blank waste form.
(b) WF1, waste form 1.
(c) A, amorphous.
(d) C, crystalline.

dolomite, undersaturated with respect to magnesite, strontianite, and cerrusite, and oversaturated with respect to otavite. The sulfates considered, barite, gypsum, ettringite, and monosulfate, are all undersaturated in these solutions. The leachates are undersaturated with respect to all of the hydroxides and oxides considered, with the two exceptions of diaspore and ferrihydrite. The silicates considered are all oversaturated in the leachates with the exception of amorphous silica, which is undersaturated.

The mineral saturation indices for the leachates from the waste form 1 soil/waste form column experiment vary more than the mineral saturation indices for the ANS 16.1 batch leachates or the soil adsorption column leachates. From the successful MINTEQ calculations, it appears that calcite and dolomite are initially oversaturated in solution, and become undersaturated with continued soil/waste form/ground-water contact. Magnesite is initially in equilibrium with the leachates and then becomes undersaturated with respect to these solutions. These minerals may precipitate near the waste form, altering the solution such that it is undersaturated with respect to the carbonate minerals by the time it leaves the column. Some of the leachate compositions are oversaturated and others are undersaturated with respect to otavite, with no apparent trend with increasing soil/waste form/ground-water contact. Strontianite and cerrusite are undersaturated with respect to the waste form 1 soil/waste form column leachates.

The sulfate minerals barite and gypsum are nearly in equilibrium with the early waste form 1 soil/waste form column leachates, and are undersaturated with respect to the later leachates. Ettringite and monosulfate are undersaturated throughout.

The phosphate minerals vacillate between over- and undersaturation with respect to the waste form 1 soil/waste form column leachates. $MnHPO_4$ is still nearly in equilibrium with these solutions. Strengite is usually very undersaturated ($SI = -10.0$), but in the first sample and the forty-third sample taken from this experiment, strengite is oversaturated ($0 < SI < 1$). Hydroxyapatite is again oversaturated in all of the leachates.

Most of the hydroxides also vacillate between over- and undersaturation with respect to the waste form 1 soil/waste form column leachates. The only interesting observation to be made is that the fifth, sixth, and tenth samples taken during the experiment, after 3.7, 4.5, and 8.6 pore volumes of fluid, respectively, have passed through the column, are nearly in equilibrium with brucite. The silicates also vacillate between over- and undersaturation with respect to the waste form 1 soil/waste form column leachates.

9.0 CONCLUSIONS

In conclusion, the laboratory experiments involving both a blank cement form and a waste form provide much information on cement/waste form/soil/ground-water interactions. The experiments performed by Walter et al. (1986) were designed to separate the outcome of reactions involving the following: cement and ground water; a cement waste form and ground water; leachates and soil; and a cement waste form, soil, and ground water.

The batch leaching experiments suggest that the blank cement form reequilibrates with the ground water more quickly than the waste form. The Portland III cement reacts with the ground water on initial contact, precipitating Ca- and Mg-bearing minerals, probably dolomite and calcite. With further cement/ground-water contact, Ca and Mg concentrations in the leachates increase through time toward the Hanford ground-water concentrations. In the waste form leachates, both Ca and Mg concentrations are low throughout the experiment, suggesting that Ca- and Mg-bearing minerals, possibly calcite, dolomite, and/or sepiolite, continue to precipitate, removing these elements from solution.

Aluminum and silicon are major components in the Portland III cement, but neither element appears to leach from the cement or waste forms. The preliminary mass transfer calculations, however, suggest that silicon concentrations in solution may be controlled by quartz precipitation in the cement/ground-water experiment and by sepiolite precipitation in the waste form/ground-water ANS 16.1 batch leaching experiment.

In the waste form ANS 16.1 batch leaching experiment, more than 2 moles of Na enter the ground water for each mole of SO_4^{2-}. This suggests that one or more sulfate-bearing minerals are removing sulfate from solution. The higher sulfate concentrations that are present may promote the formation of monosulfate or ettringite within the cement block, causing the cement to hydrate more quickly. The saturation indices for the cement minerals support this possibility: The leachates from the waste form ANS 16.1 batch leaching experiment are closer to equilibrium with portlandite, ettringite, and monosulfate than the leachates from the blank ANS 16.1 batch leaching experiment.

No major differences in the species distributions for Ca, Mg, Si, B, CO_3, SO_4, and PO_4 in the Hanford ground water and in the leachates that contacted the blank cement form are evident. Major changes in the species distribution for the same components do occur during the waste form batch leaching experiment. For example, $CaPO_4^-$ and $MgPO_4^-$ become the predominant calcium and magnesium species in solution after 11 days of waste form/solution contact. These changes, and the others discussed previously, reflect the influence of the waste stream.

The ANS 16.1 experiment is one in which equilibrium may never be achieved. From the concentration and speciation data for the waste form 1 leachates, it can readily be observed that the waste form has not come to equilibrium with the Hanford ground water; reactions are still occurring. The leachates from the blank cement form experiment are very similar in composition to the Hanford ground water. It is unclear whether the blank waste form is in equilibrium with the ground water.

The soil adsorption column experiments in which the Hanford ground water percolated through Hanford soil suggest that no further reactions occur; that is, the ground water and soil are in equilibrium. The species distribution for the major components in the leachates from the mixed ANS 16.1 leachate/soil experiments reflect the speciation of the waste form leachate. The pH of the waste form leachate appears to be buffered by the soil for the first 18 pore volumes of contact. Potassium and sodium are initially attenuated, probably by adsorption onto clay minerals in the soil. With continued waste form leachate/soil contact, these elements break through in larger concentrations.

The nature of the soil adsorption column experiments is also such that equilibrium between the influent solution and soil may never be achieved. If the soil-column leachate compositions are all identical but differ from that of the influent solution, a steady-state condition may be achieved. Although not all the components exhibit steady-state behavior after 300 pore volumes of waste solution/soil contact, Ca, Mg, Si, Ba, and Sr do so. Preliminary mass transfer calculations suggest that calcite, dolomite, and quartz will precipitate from solution, controlling the concentrations of Ca, Mg, and Si. The leachates from the waste solution/soil adsorption experiments are nearly in equilibrium with rhodochrosite, ferrihydrite, diaspore, and cristobalite. These potential equilibria were not found in the leachates from the ANS 16.1 batch leaching experiments; they are clearly the result of waste solution/soil interactions.

Because the flow rates in the soil adsorption column and the combined soil/waste form column experiments differ, and because the solution/waste form ratio differs between these experiments and the ANS 16.1 batch leaching experiments, it is difficult to compare directly the results of these experiments. In general, the pH and the concentrations of most of the major constituents increase to higher values in the leachates from the combined soil/waste form 1 column experiments than in the leachates from the other two types of experiments. This suggests that reactions involving the soil, waste form, and ground water play an important role in altering the fluid composition.

The MINTEQ calculations indicate that most of the leachate compositions measured for the combined soil/waste form 1 column experiments are out of charge balance, with too many anions present. It appears that a major cation, possibly an organic cation, that has not been measured analytically is important in these solutions. The MINTEQ speciation calculations from those leachates with a reasonable charge balance suggest that the leachate compositions go through a major change until they almost completely reflect the composition of the waste stream after four pore volumes of contact, then change back toward the speciation seen in the Hanford ground water.

Calcite and dolomite are oversaturated in the early leachates and undersaturated in the later ones. It is possible that these minerals precipitate on or near the waste form (where the chemical environment may differ from that of the sampled leachate), resulting in leachates out the bottom of the column that are undersaturated with these minerals.

In summary, the variations through time in the composition and the pH of the leachates from the combined soil/waste form column experiments are similar to those in the ANS 16.1 batch leachates. Because more water contacted the waste form at any given time in the ANS 16.1 batch leaching experiments, the component concentrations in the ANS 16.1 leachates are generally lower than in the combined soil/waste form column leachates.

The trends observed in the ANS 16.1 batch leaching and combined soil/waste form column experiments were not observed in the soil adsorption column experiments, possibly because the ANS 16.1 leachates were mixed together before being added to the soil.

The flow rate is slowest in the combined soil/waste form column experiments; hence more time for reaction between the waste form, soil, and ground water is available. As is typical of many diffusion-controlled leaching studies, the waste form initially has a major influence on the leachate compositions. This influence dissipates with continued waste form/soil/ground-water contact. The major changes in component speciation that result from the waste stream are an increase in phosphate- and sodium-bearing species. In all three types of experiments, the precipitation of calcite, dolomite, sepiolite, and/or quartz probably plays a role in controlling the solution concentrations of calcium, magnesium, and silicon.

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