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Geochemical Processes Controlling Migration of Tank Wastes in Hanford's Vadose Zone

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Nuclear wastes from Hanford's processing for separation of plutonium are stored in massive, buried, single-shell tanks in 18 tank farms. These so-called tank wastes were initially thermally hot because of radioactive decay, and many exhibited extreme chemical character in terms of pH, salinity, and radionuclide concentration. At present, 67 of the 149 single shell tanks are suspected to have released over 1.9 million L of tank waste to the vadose zone, with most leak events occurring between 1950 and 1975. Boreholes have been placed through the largest vadose zone plumes to define the extent of contaminant migration and to develop conceptual models of processes governing the transformation, retardation, and overall transport of tank waste residuals. Laboratory studies with sediments so collected have shown that ion exchange, precipitation and dissolution, and surface complexation reactions have occurred between the tank wastes and subsurface sediments, moderating their chemical character and retarding the migration of select contaminants. Processes suspected to facilitate the far-field migration of immobile radionuclides including stable aqueous complex formation and mobile colloids were found to be potentially operative but unlikely to occur in the field, with the exception of cyanide-facilitated migration of ^{60}Co. Certain fission product oxyanions (Mo, Ru, Se, Tc) and nitrates are the most mobile of tank waste constituents because their adsorption is suppressed by large concentrations of waste anions, the vadose zone clay fraction is negative in surface charge, and, unlike Cr, their reduced forms are unstable in oxidizing environments. Reaction/process-based transport modeling is beginning to be used for predictions of future contaminant mobility and plume evolution.

Abbreviations: AmOx, ammonium oxalate; CEC, cation exchange capacity; DBP, dibutyl phosphate; DCB, dithionite-citrate-bicarbonate; DST, double-shell tank; EDTA, ethylenediamine tetraacetic acid; PUREX, plutonium and uranium recovery by extraction; SST, single-shell tank.

The Hanford Site in south-central Washington State produced plutonium for the USDOE weapons program from 1943 to 1989. Plutonium (Pu) production involved the fission of uranium fuels using nine nuclear reactors along the Columbia River, followed by the extraction and concentration of trace product Pu through chemically intensive processing regimes performed in the central portion of the site. Three primary processing schemes were used during the lifetime of Hanford (bismuth phosphate [1944–1956], redox [1952–1967], and plutonium and uranium recovery by extraction [PUREX; 1956–1972, 1983–1989]), as improvements were sought to reduce waste volumes, allow U separation for reuse, and enhance Pu recovery efficiency.

Large volumes of radioactive waste were generated by processing, and the waste chemistry and composition varied markedly between the three processing schemes. The most concentrated and radioactive of these wastes were sent to 177 underground waste storage tanks. The first of these were single-shell tanks. The 149 large, single-shell, steel/concrete underground storage tanks ranged in volume from 209,000 L (55,000 gal) to >3.8 million L (1.0 million gal) (See Fig. 1, the S-SX tank farm under construction) with a total storage volume of 357

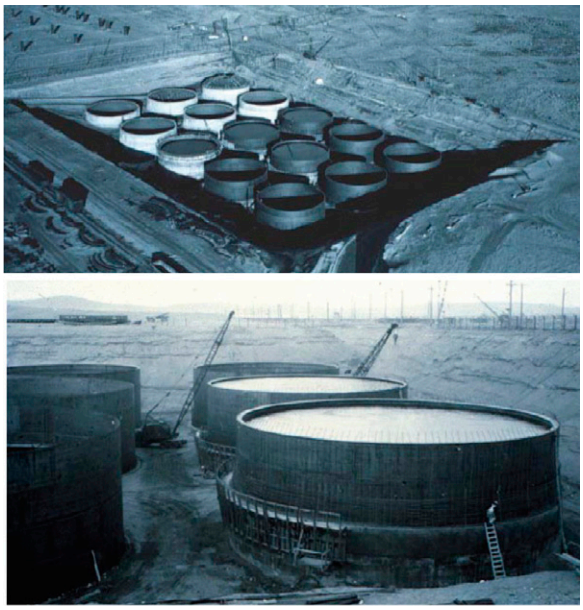

Fig. 1. The S-SX single-shell tank farm under construction in 1941. Note cranes for scales. The tank bottoms were 16.8 m below ground surface. (From Knepp, 2002a.)

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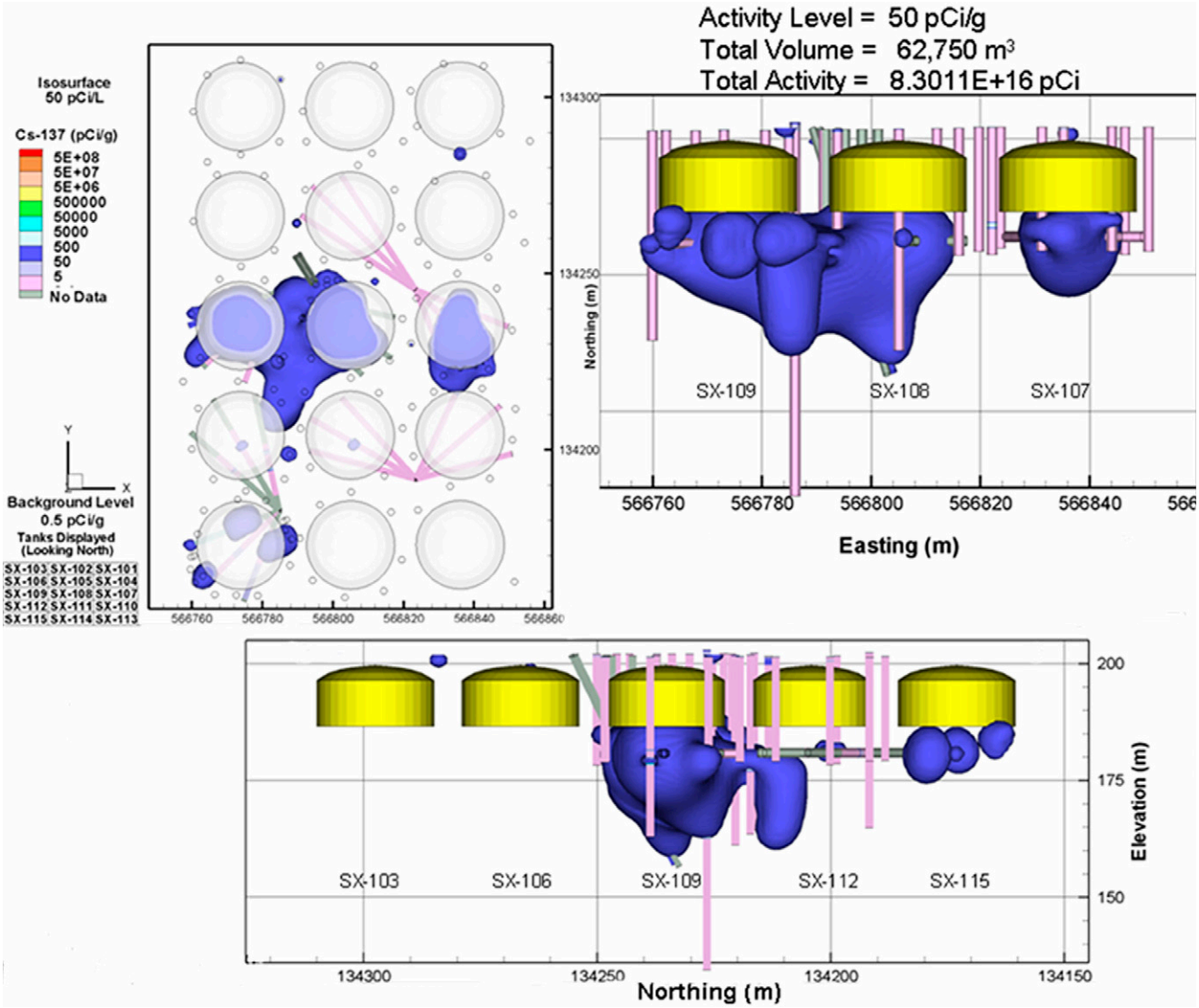

Fig. 2. Distribution of sorbed $^{137}Cs^{+}$ beneath leaked tanks SX-108, SX-109, and others in S-SX tank farm. Data collected by downhole spectral gamma monitoring through an extensive dry borehole array. Three-dimensional data obtained by kriging. (From Knepp, 2002a.)

million L (94 million gal). The larger tanks were massive: 13.7 m (45 ft) in depth and 22.9 m (75 ft) in diameter (Gephart and Lundgren, 1996). These were situated below ground and were covered with approximately 3 m of soil and gravel. The tanks are located within 18 different groupings, termed *tank farms*, in the central portion of the Hanford Site, some 11 to 16 km from the Columbia River. The wastes were stored to allow the decay of highly radioactive, short-lived isotopes and to allow the secondary extraction of U from bismuth phosphate wastes and other desired constituents. Tank storage was originally intended to be interim. It was the USDOE's intent to seek means for the permanent disposal of tank wastes within 20 yr of generation, but this has not been accomplished even to this day.

Leaks from single-shell tanks were first suspected in 1956 and confirmed in 1959. Monitoring systems were installed in the tank farms to ensure the integrity of the storage tanks and their entrained waste, including fluid depth monitors in the tanks and numerous cased, dry boreholes in the vadose zone to monitor soluble, gamma-emitting radionuclides such as short-lived, anionic ^{106}Ru, mobile ^{60}Co, and waste-dominant ^{137}Cs (Fig. 2). These monitoring systems have indicated the loss of tank waste from the single-shell tanks, or their respective ancillary piping, into the vadose zone, which extends 50 to 70 m below ground surface. The leakage resulted from tank failure, tank overfilling, and breaches in transfer lines that brought the waste to and from the tanks. The total volume of tank waste loss has been difficult to determine but ranges between 1.9 million L (500,000 gal) and 3.8 million L (1 million gal), containing about 1,000,000 curies of radioactivity. Some of the waste materials lost exhibited extreme chemistry and high heat. This leakage has been augmented with natural recharge of meteoric water in the tank farms enhanced by gravel covers (Khaleel et al., 2007) and artificial recharge resulting from water line leakage and other infrastructure sources. Leaked tank wastes have been in contact with surrounding vadose zone sediments for decades and have undergone significant geochemical and radiological transformations. Mobile, anionic tank waste contaminants [e.g., $^{99}Tc(VII)O_4^{-}$, $Cr(VI)O_4^{2-}$, NO_3^{-}] have been observed in groundwaters beneath some of the tank farms, leading to concern over the future mobility of the uncontained tank waste inventory in the vadose zone.

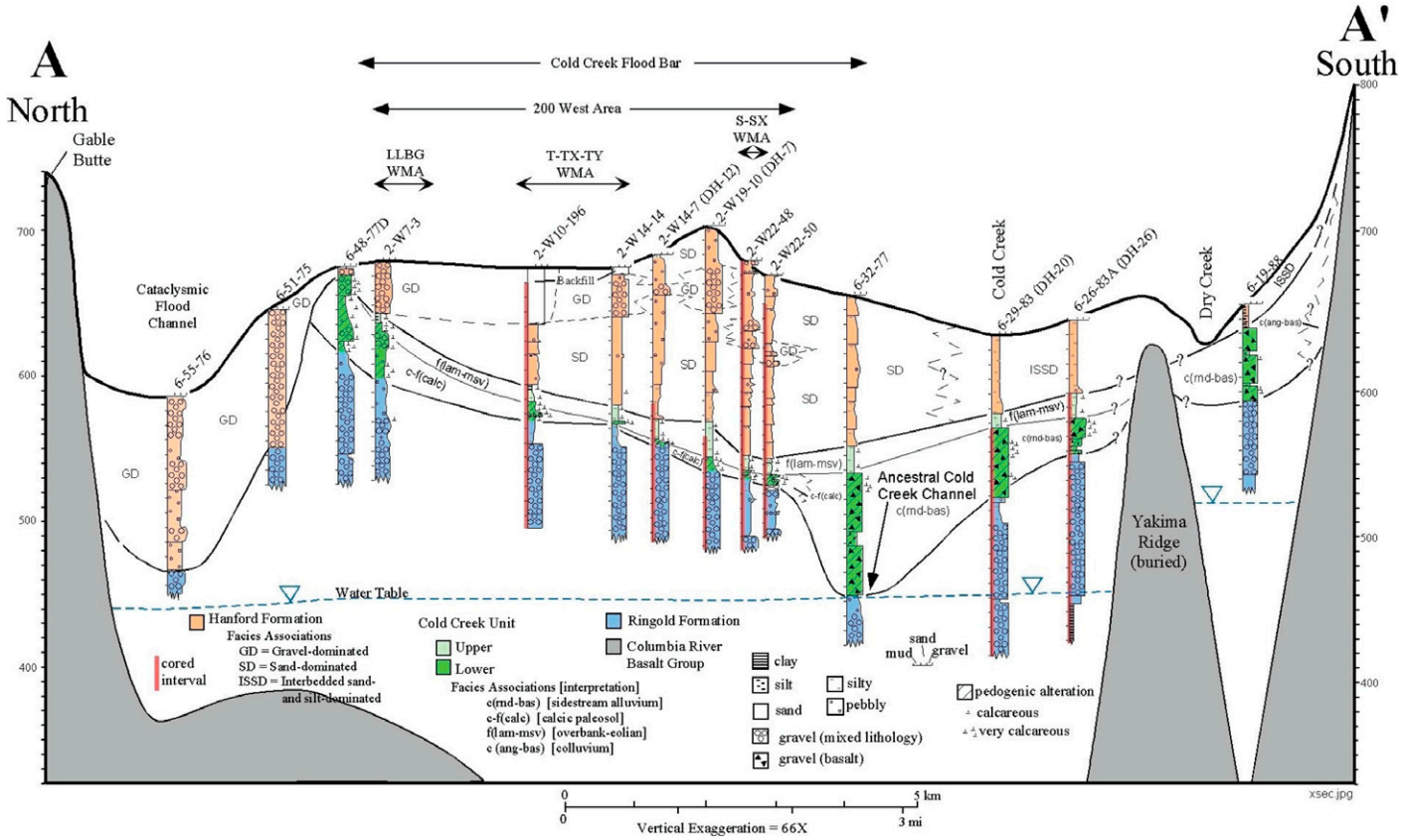

FIG. 3. North–south geological transect through Hanford's 200A plateau where waste processing facilities and tank farms exist. (From Serne et al., 2004a.)

Since 1998, the Hanford Site has been actively characterizing the in-ground distribution of contaminants within the largest tank waste releases and associated vadose zone contaminant plumes (e.g., SX-108; BX-102, T-106 [Knepp, 2002a,b; Myers, 2005]). The characterization objectives have been to assess the risk posed to groundwater of tank waste contaminants in the vadose zone and to develop improved conceptual models (e.g., Davis et al., 2004) of hydrologic and geochemical processes, and of geologic features controlling contaminant migration in the vadose zone. Additionally, recognizing the lack of scientific understanding of deep vadose zone processes, both the USDOE's Office of Environmental Management and Office of Science have supported significant applied and fundamental research on geochemical and hydrologic processes controlling the transport and fate of tank waste residuals in Hanford's vadose zone.

This paper integrates results from field characterization activities and from laboratory research to identify the primary vadose zone geochemical processes that have acted on leaked tank wastes to control their chemical evolution and the mobility of entrained contaminants in the vadose zone. The processes include ion exchange, dissolution–precipitation, abiotic redox transformations, colloid formation and migration, aqueous complexation, surface complexation, and microbiological transformations. Hydrologic processes are integral to contaminant transport and in situ reaction kinetics; they are addressed by Khaleel et al. (2007) and Ward and Zhang (2007) in this issue. First, we provide background information on geochemical reactants in this complex system, including the mineralogy of Hanford's vadose zone sediments, and tank waste chemical composition and thermal characteristics. Then, we illustrate the effects of the above features on waste neutralization, transformation, contaminant retardation, sequestration, and migration, using case studies from field and laboratory campaigns performed to understand the subsurface behavior of different tank waste types and specific contaminants. We conclude by discussing (i) the integration of these processes into reactive transport models and (ii) the remaining critical gaps in scientific understanding of processes and other issues controlling the subsurface fate and transport of tank wastes.

Background

Subsurface Geology and Mineralogy

Approximately 30.5 to 122 m of unconsolidated sediments of Pleistocene and Pliocene age overlie Miocene age tholeiitic basalt flows (Columbia River Basalt Group) at the Hanford Site. The Pleistocene-age Hanford formation (catastrophic flood deposits from glacial Lake Missoula) and Pliocene-age Ringold Formation (overbank deposits from the ancestral Columbia River) are the primary geologic units in the unconsolidated sediments (Fig. 3). The Hanford formation contacts the Ringold Formation at an erosional discontinuity, and occasionally, the intervening Pliocene-age Cold Creek unit consisting of calcified paleosols is found between the two units. Hanford's unconsolidated sediments reach their greatest depths in the central or 200 Area plateau, where the processing facilities and tank farms are located. At these locations the vadose zone is approximately 61 to 85.4 m in thickness, and the unsaturated sediments override

Hanford's unconfined aquifer in suprabasalt sediments. The generalized stratigraphy of the Hanford site is shown in Fig. 3 (USDOE, 1988, 2002; Lindsey, 1995, 1996). Considerable variability in the thicknesses and properties of the three primary vadose zone geologic units exist across Hanford's central plateau in both east–west and north–south directions. The general character of these three units is described in Table 1.

The sand and gravel mineralogy of the Hanford and Ringold formations is similar because of common geologic provenance. Gravel-sized clasts generally consist of >50% subangular to subrounded basalt rock fragments (USDOE, 2002). Sand facies generally contain 50% basaltic lithic fragments and 50% granitic fragments, whereas silt is typically dominated by quartz, various feldspars, and micas (biotite and muscovite) (Ginder-Vogel et al., 2005; Tallman et al., 1979; Zachara et al., 2002). The clay fraction is remarkably consistent between different vadose zone samples (Knepp, 2002a; Myers, 2005; Zachara et al., 2002) and is dominated by expansible phyllosilicates (smectite), ferroan chlorite (chlinochlore), and mica (both biotite and muscovite) (Fig. 4), with serpentine-group minerals (antigorite and lizardite) also being reported (Ginder-Vogel et al., 2005).

The sediments invariably contain a magnetic, Fe-rich mineral fraction (at $\leq$2 mass %) that contains magnetite, ilmenite, Fe(II)/Fe(III) phyllosilicates, and Fe(III) oxides (ferrihydrite; goethite) (according to X-ray diffraction and transmission Mössbauer spectroscopy). This potentially reactive fraction has not been well studied and is expected to show considerable variation between the Hanford and Ringold formations and specific vadose zone samples from within them. In a study of four <2.0-mm size isolates of U(VI)-contaminated, Hanford formation vadose zone sediments from the 300 Area U plume near the Columbia River, extractable crystalline Fe(III) oxides (dithionite-citrate-bicarbonate [DCB]) varied from 29 to 67 μmol g^{-1} while poorly crystalline Fe(III) oxide (ammonium oxalate [AmOx]) displayed a range of 48 to 91 μmol g^{-1} (Bond et al., 2007). A deeper vadose zone sediment from the Hanford plateau displayed extractable Fe(III) concentrations of 37.7 μmol g^{-1} (DCB) and 9.85 μmol g^{-1} (AMOX) (Um et al., 2007). Additional measurements of this type in deeper vadose zone sediments from Hanford's 200 Area plateau are needed as the above data is insufficient to define a representative range of extractable Fe(III) concentrations.

Table 1. Geologic character of the Hanford, Cold Creek, and Ringold formations at the Hanford Site.†

Name	Age	Character
Hanford formation	Pleistocene	Catastrophic, flood deposits ranging from boulder-size gravel to sand, silty sand, and silt. Sorting increases with decreasing texture. Common cm-scale layers.
Cold Creek formation	Pliocene	Pedogenically altered fluvial, eolian, and/or colluvial deposits. Occasional pedogenic calcretes.
Ringold Formation	Pliocene	Fluvial-lacustrine deposits including semi-indurated clay, silt, fine- to coarse-grained sand, and variably cemented granule to cobble gravel.

† From Serne et al. (2004a).

The total manganese concentration of Hanford sediments is relatively high because of copious mafic/basaltic lithic fragments. However, the Mn(III/IV) contents of Hanford sediments that derive from the weathering of the primary mineral pool of Mn are highly variable (see Zachara et al., 1995, for several examples) and not well characterized. Manganese(III/IV) oxides are strong sorbents and oxidants (Eary and Rai, 1987; Zachara et al., 1995) that may influence the solid–liquid distribution and valence speciation of polyvalent metals and radionuclides in Hanford sediments (e.g., Cr, Co, Tc). Hanford formation sediments are, in general, only modestly weathered because of youthful age, and significant concentrations of Mn(III/IV) oxides are not expected except under isolated and specific conditions. Consequently, ranges expected for extractable Mn(III/IV) in the Hanford vadose zone cannot be defensibly stated at present.

Detrital and pedogenic calcite are consistently observed throughout the vadose

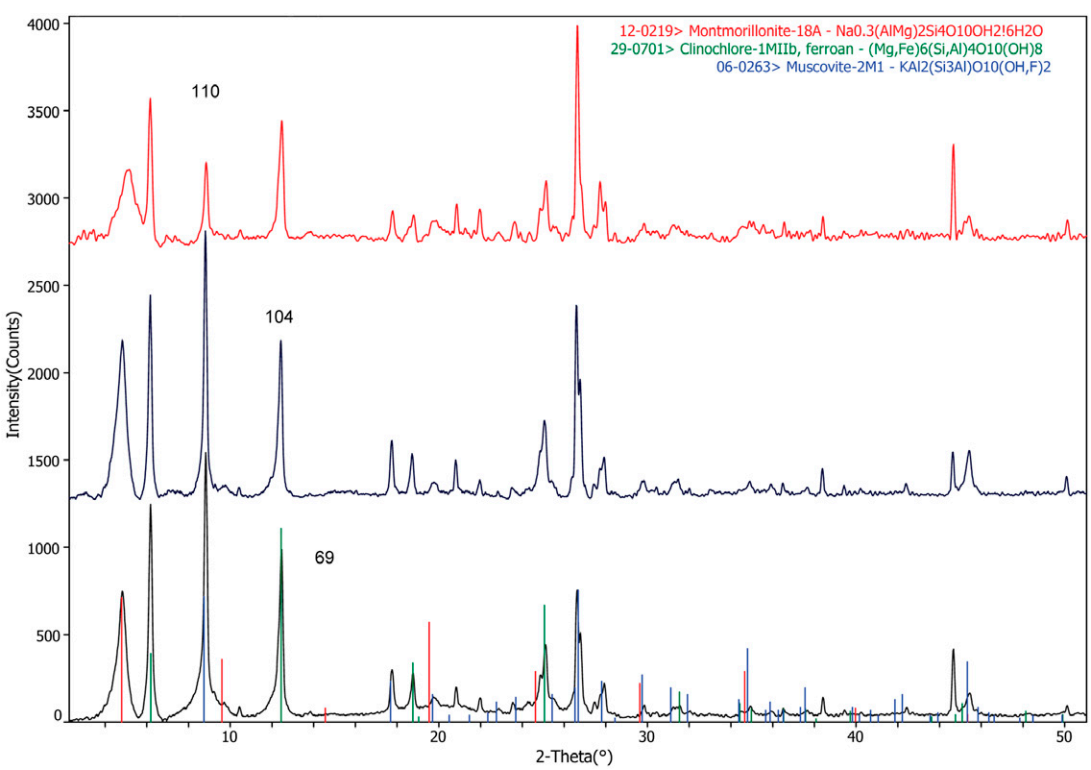

Fig. 4. X-ray diffractograms of the clay-sized fraction (<2.0 μm) isolated from deep vadose zone sediments collected beneath the TX tank farm (borehole C3832). Samples 69 and 104 are from the Hanford formation; sample 110 is from the Cold Creek formation.

zone ranging in concentrations from 1 to 5% and averaging 1.79 mass % (Serne et al., 2004a). Pedogenic calcite exists in the form of discrete, but infrequent caliche layers (~25 cm in thickness) that formed beneath surfaces that were exposed for extended interflood periods during the Pleistocene. These past pedogenic land surfaces are relatively infrequent. A calcite-indurated paleosol (calcrete; 35–45% calcite) frequently occurs in the Upper Cold Creek unit immediately below the contact with the Hanford formation (Fig. 3; Serne et al., 2004a). All Hanford sediments not impacted by Hanford wastes exhibit a soil water pH near neutrality because of high dissolved bicarbonate in pore water and the frequent presence of calcite.

Hanford vadose zone sediments exhibit a cation exchange capacity (CEC) that varies strongly with sediment texture and that increases with decreasing particle size (Ward et al., 2006a). The CEC is primarily contributed by fine-grained phyllosilicates (e.g., Fig. 4), including smectite, vermiculite, and mica, that contain fixed charge from isomorphic substitution (Zachara et al., 2002). The weathering of basaltic glass in lithic fragment interiors may also produce smectite-like secondary phases with significant CEC (McKinley et al., 2007). An average CEC value for medium <2.0-mm Hanford sand with 9.3% silt and clay content is 40 μeq g^{-1} (Zachara et al., 2004, 2002). Ward et al. (2006a) reported a range of 20 to 240 μeq g^{-1} for a variety of <2.0-mm Hanford sediments. Many Hanford sediments contain a sizable mass fraction that is >2.0-mm in size, and CEC values for whole sediment are often calculated (rightly or wrongly) by assuming that the >2.0-mm fraction has no exchange sites (Serne et al., 2002c; Ward et al., 2006a). Cation exchange capacity values show positive linear correlation with silt and clay content and negative correlation with sand (Ward et al., 2006a). Under natural conditions, the exchanger phase is saturated with a mixture of Ca^{2+}, Mg^{2+}, Sr^{2+}, and Na^{+}, with Ca^{2+} in predominance. The exchanger phase composition is closely linked with the presence of calcite through solubility reaction (McKinley et al., 2007).

Tank Waste Composition

Each Pu processing scheme (bismuth phosphate, redox, and PUREX) and the uranium recovery process generated a series of three or more waste streams that differed in composition. These, in turn, differed between processing schemes (Anderson, 1990; Gephart and Lundgren, 1996). Waste streams included cladding dissolution wastes, the primary stream with maximum fission products, and start-up and rinse cycle wastes of different sorts. At least 50 different radioactive waste streams are recognized, which have been categorized into 23 or more distinct waste types (Remund et al., 1995). All Hanford tank wastes were initially acidic (HNO_3) but were overneutralized with NaOH to high pH to minimize tank corrosion. Waste compositions changed significantly after initial routing to the tank farms (i) as the waste solutions boiled and self-concentrated, (ii) as wastes were mixed and intentionally condensed through evaporation to maximize storage space that became limited with time, (iii) as atmospheric CO_2 was absorbed by high pH supernate, (iv) as bismuth phosphate ($BiPO_4$) wastes were subjected to uranium recovery in the U Plant, and (v) as redox and PUREX wastes were reprocessed in the B Plant to remove heat-generating isotopes ^{137}Cs and ^{90}Sr. Because of these operational and chemical complexities, it is difficult to estimate average compositions for different waste types that were lost to the vadose zone.

For all but three of the older, single-shell tanks (SSTs), free liquid tank wastes have now been pumped into newer, double-shell tanks (DSTs) for storage until final vitrification. Wastes remaining in many of the SSTs contain some interstitial liquids. Wastes from different sources have been mixed in the DSTs and eight general waste types are recognized (Gephart and Lundgren, 1996; Table 2).

To appreciate the chemical complexity and extreme character of these materials, it is helpful to survey the estimated compositions of waste materials released in specific high-volume tank leaks (e.g., Table 3). These three examples span the range in chemical character of Hanford tank wastes. The redox waste leaked from tank SX-108 in 1971 was a caustic Na-NO_3/NO_2-OH-$Al(OH)_4$ brine that self-concentrated through boiling caused by radioactive decay. The waste had high ionic strength (I = 18), high solution density (2.09 g cm^{-3}), and temperature greater than 100°C. It was discharged into a vadose zone that was also elevated in temperature because of heat transfer from multiple boiling waste tanks in the 241-SX tank farm (Pruess et

Table 2. Waste inventory totals for double-shell tanks.†

Waste	Waste inventory total
	L
Dilute noncomplexed waste	19,394,000
Double-shell slurry and double-shell slurry feed	20,829,000
Concentrated complexant	15,117,000
Neutralized current acid waste	7,086,000
Concentrated phosphate	4,160,000
Dilute complexed waste	3,528,000
Neutralized cladding removal waste	2,979,000
Plutonium finishing plant sludge and other solids	2,266,000
Total	75,759,000

† Hanlon (1995).

Table 3. Tank waste compositions for three of the Hanford Site's largest tank leaks.

Tank waste type	SX-108† redox waste	BX-102‡ neutralized $BiPO_4$ metal waste	T-106§ B-Plant isotope recovery waste
Leak volume (L):	57,539	347,000	75,700
Temperature (C°):	100(+)	80	NR
$Al(OH)_4^-$ (mol L^{-1})	3.36	5.9 x 10^{-4}	0.47
K^+ (mol L^{-1})	0.074	2.7 x 10^{-3}	0.02
Na^+ (mol L^{-1})	19.6	2.92	4.34
OH^- (mol L^{-1})	5.25	0.1	0.8
NO_3^- (mol L^{-1})	5.46	0.53	1.25
NO_2^- (mol L^{-1})	4.42	0.046	0.84
$CO_{3\,(TOT)}^-$ (mol L^{-1})	0.032	0.643	0.18
HPO_4^{2-} (mol L^{-1})	0.00	0.36	0.011
SO_4^{2-} (mol L^{-1})	0.028	0.23	0.089
CrO_4^{2-} (mol L^{-1})	0.41	0.0016	0.043
UO_2^{2+} (mol L^{-1})	8.79 x 10^{-3}	0.114	0.003
Dibutyl phosphate (mol L^{-1})	NE¶	NE	4.84 × 10^{-2}
$^{137}Cs^+$ (Ci L^{-1})	7.71 x 10^{-1}	1.02 x 10^{-2}	4.97 × 10^{-2}
$^{90}Sr^{2+}$ (Ci L^{-1})	1.22 x 10^{-1}	NR	1.34 × 10^{-4}
^{99}Tc (Ci L^{-1})	2.27 x 10^{-4}	9.42 x 10^{-6}	2.8 × 10^{-5}
Pu (Ci L^{-1})	5.33 x 10^{-4}	8.68 x 10^{-6}	2.5 × 10^{-5}
Am (Ci L^{-1})	8.52 x 10^{-5}	NR#	1.37 × 10^{-2} (note other isotopes especially $Eu^{154/155}$ & Se^{79})

† Jones et al. (2000b).
‡ Jones et al. (2001).
§ Jones et al. (2000a).
¶ NE, not expected.
# NR, not reported.

al., 2002). Contaminants in especially high concentration were CrO_4^{2-}, $^{137}Cs^+$, and ^{99}Tc. The neutralized $BiPO_4$ metal waste released at BX-102 by tank overfilling in 1951 was a concentrated, 80°C, alkaline solution of U(VI) dissolved in Na-HCO_3 with PO_4 and SO_4, and a wide array of fission products. This was an early Hanford waste that had not been subject to uranium recovery. Fluids leaked from tank T-106 were a later Hanford waste (PUREX) that had been subject to isotope recovery in B plant. It contained high levels of Na-NO_3/NO_2-OH, ^{137}Cs, ^{90}Sr, and ^{99}Tc, and dibutyl phosphate (DBP), an organic complexant. In addition to the constituents in Table 3, B- and T-plant waste contained elevated concentrations of a number of more exotic fission products including ^{79}Se, ^{125}Sb, ^{151}Sm, $^{154/155}Eu$, and multiple isotopes of Pu and Am (Jones et al., 2000a).

Geochemical Processes Influencing Tank Waste Migration in the Vadose Zone

Approximately 67 single-shell tanks have leaked tank waste into the vadose zone in the 200 Area plateau (Gephart and Lundgren, 1996). Generally, the leak volumes have been small relative to the waste tank volumes. Three of the largest known leaks are reported in Table 3; these range from 57,540 to 347,000 L. Despite these relatively small waste fluid volumes, great concern exists because of the high contaminant concentrations present in the wastes and their extreme chemical and thermal character. The SX-108 spill, for example, released a total of 44,363 Ci of ^{137}Cs and 13.1 Ci of ^{99}Tc (Knepp, 2002a), while the BX-102 overfill event contained an estimated 9430 kg of U (Knepp, 2002b). T-106 released more than 21,000 Ci of ^{137}Cs, 21,600 Ci of ^{90}Sr, 32.5 Ci of Pu, and 60 Ci of ^{99}Tc (Myers, 2005). These radioactive and chemical contaminants were released in point source fashion, and groundwater monitoring data indicate that the most mobile of tank waste constituents from these leaks [NO_3^-, $^{99}TcO_4^-$, CrO_4^{2-}, U(VI)] have migrated to groundwater in places (Knepp, 2002a,b; Myers, 2005). However, it is still not certain that the source of all these mobile contaminants in groundwater was tank farm waste because, in many instances, the tank farms are surrounded by cribs, trenches, and pipelines that were used to purposefully dispose of similar contaminant-bearing liquids in much larger volumes (>10^6 L).

A number of drilling and sampling campaigns have placed boreholes directly through the centers of mass of tank waste plumes in the vadose zone (Freeman-Pollard et al., 1994; Knepp, 2002a,b; Myers, 2005; Serne et al., 2002a,b,c,d,e, 2004a,b). These have been challenging sampling campaigns because of limited access; constrained quarters; environmental, health, and safety issues; and the extremely high radioactivity of many samples (e.g., $\sim 10^8$ pCi g^{-1} ^{137}Cs). One of these campaigns (Knepp, 2002a; Serne et al., 2002d) used an angled drilling method to access highly radioactive sediment directly beneath leaked tank SX-108. The study of sediments from these boreholes as well as (i) laboratory interaction experiments with tank waste simulants in contact with specimen or synthetic mineral material or pristine sediments and (ii) reactive transport modeling to describe current subsurface contamination profiles or monitoring data from past leak events have provided important insights on the dominant geochemical processes controlling contaminant migration in the Hanford vadose zone. An extensive data and information base has resulted from these and other related Hanford studies that this paper attempts to summarize, integrate, and evaluate with regard to future science needs.

Ion Exchange

High sodium waste fluids such as those shown in Table 3 are in gross disequilibrium with the sediment exchanger phase that is predominantly saturated with Ca^{2+} and Mg^{2+} with minor Na^+ and Sr^{2+}. Indigenous exchangeable ions are displaced from the exchanger phase into pore water by mass action at the leading edge of the migrating waste plume (Fig. 5), leading to a distinct ion exchange front of Ca^{2+}, Mg^{2+}, and Sr^{2+} that is nearly coincident with unretarded, anionic NO_3^-. The migration of Na^+ is correspondingly attenuated by its adsorption to the sediment exchanger phase. The high concentrations of Na in tank wastes relative to native pore water cations leads to almost complete saturation of the exchanger phase by waste Na^+. The displacement of ion exchangeable Ca^{2+} can lead to calcite supersaturation and precipitation at the ion exchange front (Wan et al., 2004a,b,c), with an associated decrease in pH within this zone: $Ca^{2+} + HCO_3^- = CaCO_3(s) + H^+$. Magnesium-containing phases may also supersaturate in this region (Zhang et al., 2005). The field ion exchange profile beneath SX-115 in Fig. 5 was well described with a reactive transport simulator (FLOTRAN; Lichtner et al., 2004) containing multicomponent ion exchange described by the Gaines–Thomas convention (Sposito, 1981). The timing, volume, and contaminant concentrations of the tank leak were major uncertainties in the modeling.

Ion exchange also serves as the dominant attenuation mechanism for ^{90}Sr, a high-yield fission product present in some tank wastes (Table 3). However, the process is actually one of isotopic exchange between contaminant $^{90}Sr^{2+}$ and the native, concentration excess, stable Sr isotope pool ($^{86}Sr^{2+}$, $^{87}Sr^{2+}$) that exists as a minor component of the exchanger phase (McKinley et al., 2007). Tracing the mineralogic locations of $^{90}Sr^{2+}$ adsorption in coarse-textured sediment beneath leaked waste tank B-110 (Knepp, 2002b; Serne et al., 2002a) by digital autoradiography (Zeissler et al., 2001) (Fig. 6) has identified the presence of unique phyllosilicate (saponite) ion exchange domains in the intersticies of basaltic lithic fragments (Fig. 7) that apparently result from the weathering of glass (McKinley et al., 2007). Ion exchange within these lithic fragment interiors strongly limits desorption and further plume migration in otherwise extremely coarse-textured Hanford sediment.

Cesium-137 is a high-energy, gamma-emitting radionuclide ($t^{1/2}$ = 30 y) that is in high concentration in tank waste supernatant (Table 3). A highly selective ion exchange process occurs for $^{137}Cs^+$ on frayed edges and interlamellae of micaceous mineral phases (Fig. 8)—including biotite, muscovite, and vermiculite—that are ubiquitous in Hanford sediment (McKinley et al., 2001; Zachara et al., 2002). Most of the ^{137}Cs that currently exists in subsurface sediments beneath leaked single-shell tanks is sorbed and is immobilized by strong ion exchange to and diffusion within these micaceous sorbents (Liu et al., 2003). High electrolyte concentrations (e.g., >10^{-1} mol L^{-1}) of strongly sorbing monovalent ions (K^+, Rb^+, or NH_4^+) are required to remobilize sorbed $^{137}Cs^+$ (Liu et al., 2003). A significant research campaign was undertaken to understand why the migration of large amounts of $^{137}Cs^+$ was expedited beneath leaked waste tank

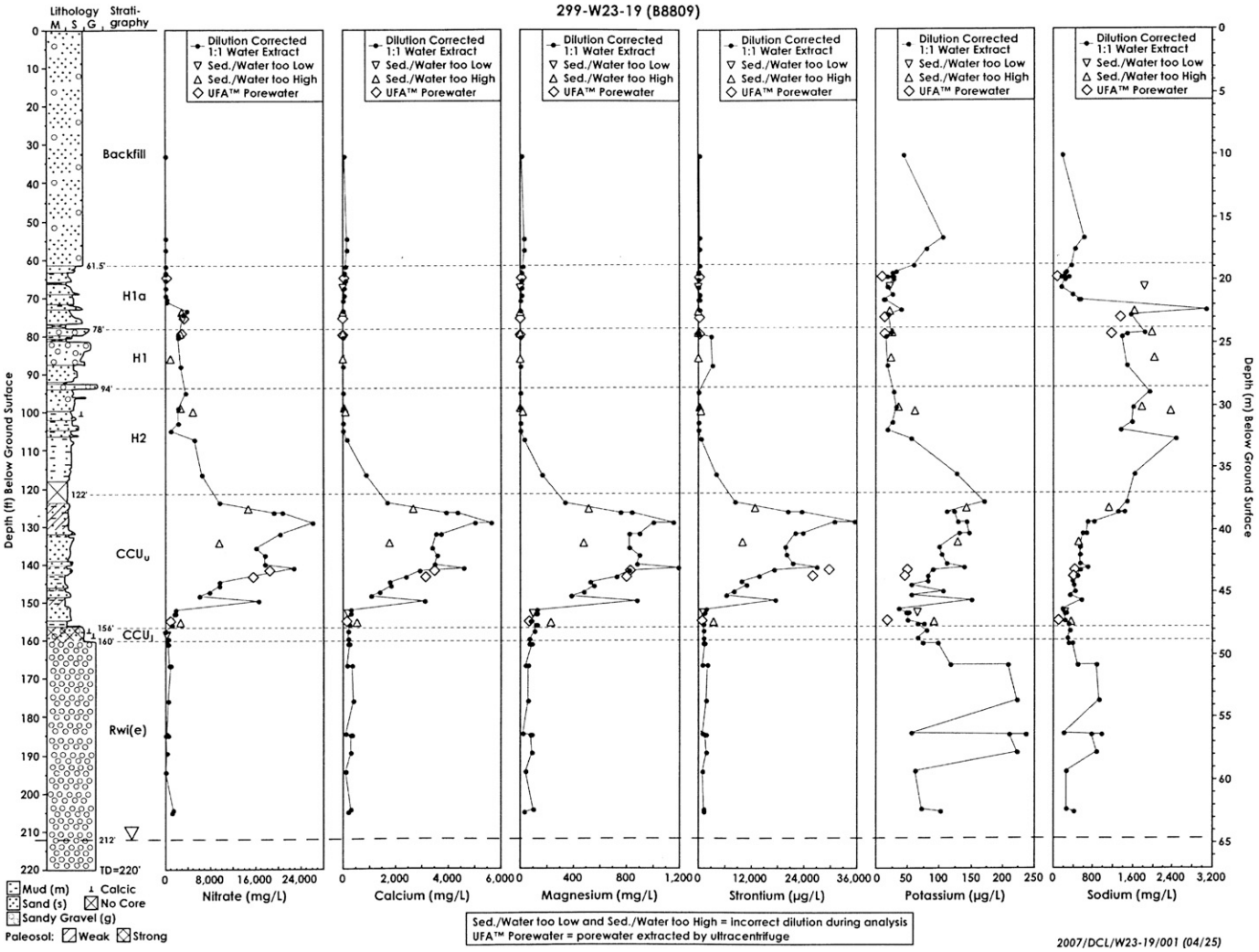

Fig. 5. Depth distribution of water-extractable ions in sediments beneath leaked single-shell tank SX-115. Note the tank waste front at 45.8 m (150 ft) below ground surface. SX-115 released tank waste of intermediate composition. (From Serne et al., 2002e.)

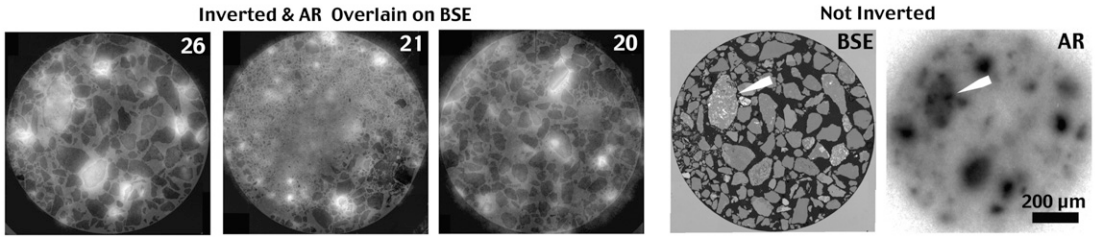

Fig. 6. Digital autoradiography of ^{90}Sr contaminated sediments from borehole 299-E33-46 (Serne et al., 2002a) near tank B-110; ^{90}Sr-containing lithic fragments are white (inverted) or black (not inverted). The backscattered electron (BSE) image shows millimeter-sized lithic fragments (from McKinley et al., 2007).

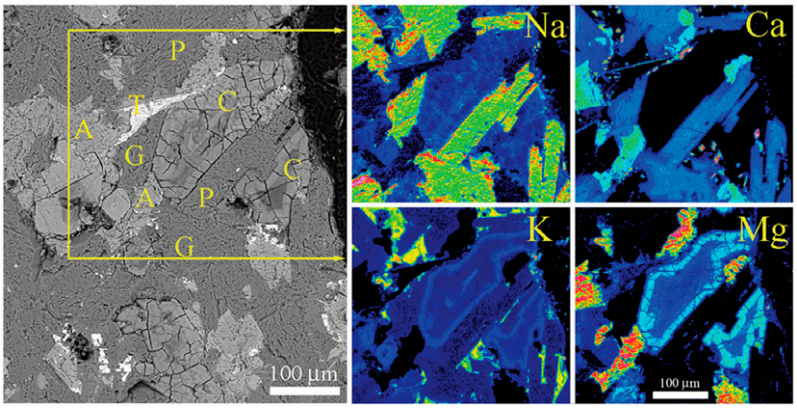

Fig. 7. Chemical composition of ^{90}Sr-containing domains from Fig. 6. All are secondary phyllosilicate domains (saponites-C) with characteristic Mg-zonation. (From McKinley et al., 2007.) P, plagioclase; A, augite, G, glass, C, cmectite; T, titanomagnetite.

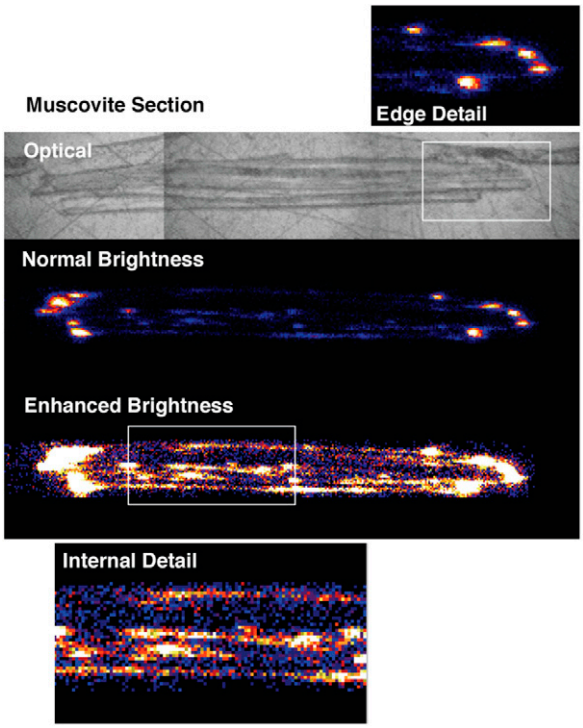

FIG. 8. Distribution of Cs^+ within muscovite collected from Hanford's S-SX tank farm as measured by synchrotron X-ray fluorescence. Cesium is strongly localized at selected regions on the crystallite edge. (From Liu et al., 2003.)

SX-108 in the S-SX tank farm. It was found that mass action and water activity effects from extremely high Na^+ concentrations in the self-boiling waste (~19 mol L^{-1}) (Liu et al., 2004; Zachara et al., 2002) and enthalpy effects from high subsurface temperature (>70°C; Liu et al., 2003) were mainly responsible for the anomalous ^{137}Cs behavior. The current subsurface distribution of ^{137}Cs can be well accounted for when these combined effects are considered (Liu et al., 2004).

Dissolution–Precipitation

Most Hanford tank wastes were intentionally overneutralized to alkaline pH (Table 3). Some of the waste solutions, such as redox, became concentrated through extended boiling periods driven by radioactive decay of short-lived radioisotopes to yield $NaNO_3$ brines with high OH^- (e.g., 5 mol L^{-1}, Table 3). Radiolysis in the alkaline waste solutions may have influenced the speciation of polyvalent metals and radionuclides (e.g., ^{99}Tc) in tank waste with high organic content (Lukens et al., 2001, 2002). These high pH, caustic solutions were extremely reactive when discharged to native, circumneutral Hanford sediments composed of aluminosilicate minerals. In certain cases, tank wastes with residual heat (e.g., >50°C) from processing operations or radioactive decay leaked into the vadose with ambient temperature, while in other cases, tank wastes were discharged to the vadose zone that had itself been heated by extended waste tank boiling (Liu et al., 2003; Pruess et al., 2002). Elevated temperature accelerates the rate of base-induced (OH^-) hydrolysis of aluminosilicates and certain precipitation reactions. Moreover, the aqueous phase that results from waste-sediment reaction at elevated temperature may become highly supersaturated with various mineral phases as temperatures decrease with transport distance from the waste source.

Laboratory studies to simulate the reaction process of highly alkaline tank waste (e.g., upper range with pH >14) with Hanford sediment have identified two primary reaction zones (Qafoku et al., 2004; Wan et al., 2004a,b) that progress hydrologically downgradient from the source of release. The zone nearest the source is dominated by silicate (e.g., quartz) and fine-grained aluminosilcate dissolution reactions that moderate pH (from pH 14 to pH 11–12) by hydroxide consumption. Important micaceous sorbents including biotite may also dissolve in this zone (He et al., 2005; Samson et al., 2005). Hydroxide alkalinity is transformed to silica and aluminate alkalinity (Marshal et al., 2004). Below this zone, whose depth is controlled by the volume of tank waste release, exists a pH neutralization zone (pH 6.5–10), where protons are released for additional base neutralization by the secondary precipitation of complex suites of zeolitic phases including cancrinite; feldspathoids including sodalite, ettringite, gibbsite; and other unnamed aluminosilicates (Ainsworth et al., 2005; Bickmore et al., 2001; Chorover et al., 2003; Deng et al., 2006; Qafoku et al., 2004; Um et al., 2005; Wan et al., 2004a.b; see Fig. 9). Hydroxide concentration and anion identity/concentration are critical variables determining secondary mineral precipitate morphology and identity. The precipitates exist as both grain coatings (Ainsworth et al., 2005; Bickmore et al., 2001; Qafoku et al., 2004) and suspended colloids in the aqueous phase exhibiting negative surface charge (Marshal et al., 2004). The importance of nitrate is worth noting because in high concentrations, it accelerates the formation of nitrate-bearing aluminosilicate (zeolitic) precipitates in laboratory simulation of weathering fronts (Wan et al., 2004b; Zhang et al., 2005).

Many have speculated that these secondary precipitates may influence tank waste contaminant migration by internal seques-

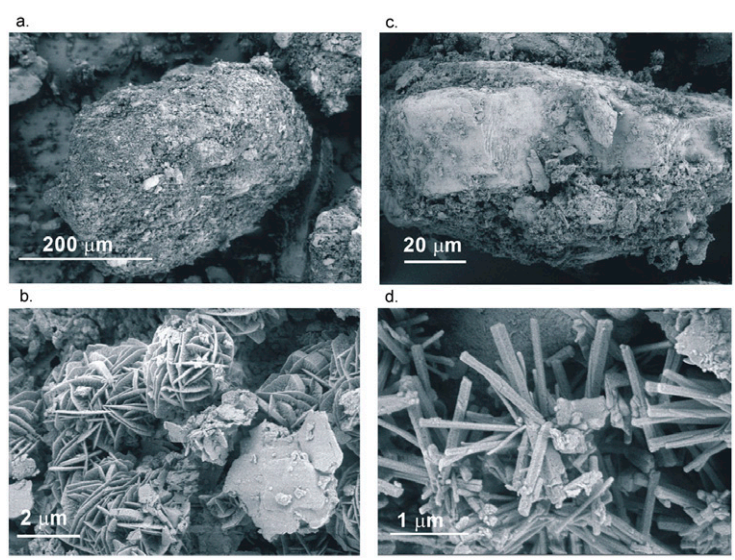

FIG. 9. Secondary feldspathic precipitates resulting from the reaction of $Na^+/NO_3^-/OH^-$ tank waste simulant with Hanford sediment. The dissolution of primary aluminosilicates and reprecipitation of various secondary phases neutralizes the high pH of tank waste. (From Qafoku et al., 2003.) Reproduced with permission from *Environ. Sci. Technol.* 2003. 37:3640–3646. Copyright 2003 American Chemical Society.

tration or surface adsorption. However, these issues have only been partially explored in the laboratory, with variable effects noted in mineral (Catalano et al., 2005; Choi et al., 2005a,b; Chorover et al., 2003; Mon et al., 2005) and sediment systems (Ainsworth et al., 2005; Marshal et al., 2004). Zhuang et al. (2003) observed that $^{137}Cs^{+}$ adsorbed to feldspathic colloids resulting from waste-sediment reaction, but sorption strength was below that of the native micaceous fraction. Ainsworth et al. (2005) observed only minor effects of high-base weathering on $^{137}Cs^{+}$ adsorption by Hanford sediment. Enhanced sorption of Sr^{2+}, apparently driven by coprecipitation processes, has been observed in suspensions of phyllosilicates contacted with alkaline tank waste simulants (Choi et al., 2005a,b).

Mineralogic studies have been performed on field samples collected from boreholes beneath waste tanks that leaked highly alkaline wastes (Knepp, 2002a; Zachara et al., 2004). While these sediments show distinct evidence for alteration in the near-source region (Zachara et al., 2004), they have not shown the high degree of mineral transformation or the distinct morphologies of secondary zeolite and feldspathoid mineral precipitates that have been observed in the laboratory (e.g., Deng et al., 2006). Because of constraints of sampling very near to the tanks themselves, the closest that field samples have been obtained successfully is 1.5 m from the sides or bottom, and most field samples have been collected no closer than 3 m from the tanks. In fact, the mineral and crystalline nature of these phases has been very difficult to assess in the field samples because of high associated radioactivity. The differences may result from the use of higher OH^{-} to sediment ratios in the laboratory than actually occurred in the field, or alternatively, that initial zeolites and feldspathoids have transformed to different, more stable phases with environmental exposure. Careful attention needs to be paid to select realistic reactant:sediment ratios when attempting to simulate field-scale waste-sediment interactions in the laboratory. Alternatively, perhaps the zone of intense base-sediment reaction occurs in a volume of sediment no larger than 3 m distance from the leak events.

Redox Processes

In its natural state, the Hanford vadose zone contains low volumetric moisture content (<10%) because of the semiarid climate. The water unsaturated pore space is generally fully oxygenated because of slow rates of microbial respiration. Most polyvalent contaminants with intermediate redox potentials (e.g., Tc and Cr) released to the Hanford vadose zone in near-neutral or poorly buffered wastewaters, in consequence, remain in the fully oxidized state because the surfaces of potential mineral reductants (e.g., illmenite and magnetite) are passivated by reaction with oxygen or by physical coating with secondary mineral phases such as calcite or Fe(III) oxides (Ginder-Vogel et al., 2005).

One important consequence of the dissolution–precipitation reactions that are promoted by alkaline tank wastes as described above is the release of redox reactive, structural Fe(II) that is present in primary mineral phases such as biotite and chlorite (Ginder-Vogel et al., 2005; He et al., 2005; Qafoku et al., 2003; Zachara et al., 2004). Ferrous iron so released may adsorb to mineral surfaces, precipitate as $Fe(OH)_2(s)$ or other Fe(II) phases, or migrate with the pore fluid. The ferrous iron can react with (i) dissolved oxygen, lowering Eh, and (ii) oxidized, polyvalent tank waste contaminants such as CrO_4^{2-}, causing changes to lower, less-soluble valence states. In laboratory studies, alkaline tank waste simulants dissolved Fe(II) from biotite and Hanford sediments that reduced soluble, weakly adsorbed CrO_4^{2-} to insoluble Cr(III) (Ginder-Vogel et al., 2005; He et al., 2005; Qafoku et al., 2003). Chromate reduction increased with base concentration and ionic strength and was hypothesized in both cases to involve a homogeneous reduction pathway. Field samples from beneath leaked waste tank SX-108 showed an anomalous retardation profile for Cr, which was shown through X-ray absorption near edge structure (XANES) analysis to result from the base-induced reductive immobilization of a portion of the waste Cr as Cr(III) (75–31%) (Zachara et al., 2004; Fig. 10). The extent of reduction decreased with increasing distance from the source as hydroxide was neutralized through mineral reaction. The resulting Cr(III) remains immobilized in the vadose because of its slow reoxidation rate by molecular oxygen (Zachara et al., 2004) and an apparent lack of sediment-associated Mn(III/IV) oxides that could function as heterogeneous oxidants (as noted by Eary and Rai, 1987).

Evans et al. (2007) analyzed trace fission oxyanions, including Mo, V, and Se, in water and acid extracts of a tank waste plume; out of this broader oxyanion analyte suite, only Mo showed evidence for reductive attenuation. Differences in oxyanion behavior result from their variable thermodynamic properties, kinetic pathways of reaction with $Fe(II)_{aq}$ and sorbed Fe(II), and the susceptibility and rate of oxidation of the reduced valence states. Similar laboratory experiments to those of Qafoku et al. (2003) have been performed with the oxyanion $^{99}Tc(VII)O_4^{-}$ (Hess, personal communication, 2007), a major risk-driving contaminant at Hanford. Technetium-99 exhibits some similarities in

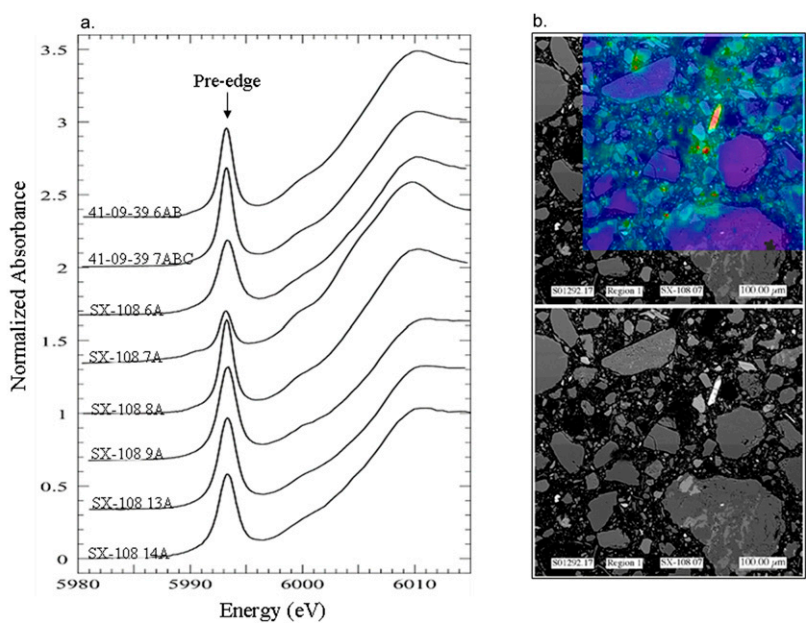

Fig. 10. (a) X-ray absorption near edge structure (XANES) spectra of Cr-contaminated sediment from SX-108 borehole C3082 where the height of the pre-edge feature is proportional to the Cr(VI) content. (From Zachara et al., 2004.) (b) Synchrotron X-ray fluorescence map of SX-108 sediment 7A, overlain on a backscattered electron micrograph. Cr concentration increases from green to red.

redox thermodynamics, reaction mechanisms with Fe(II), and solubility of oxidized and reduced states to CrO_4^- (Zachara et al., 2007). It, too, is reduced by Fe(II) liberated by base-induced mineral dissolution, yielding an insoluble Tc(IV) precipitate. This reduced form, however, apparently reoxidizes rapidly when oxidizing conditions return. Thus, the reductive immobilization process noted for Cr in association with alkaline tank waste is probably only important for those oxyanions whose reduced species reoxidize slowly.

Colloid Formation and Migration

The attachment (by adsorption to or precipitation on) of strongly sorbing radionuclides to colloidal-sized materials (1 nm to 1 μm) that are transported by mobile pore fluids is potentially an important transport mechanism (Honeyman, 1999; Kersting et al., 1999; McCarthy and Zachara, 1989; Sen and Khilar, 2006) that needs to be considered for certain contaminants at the Hanford Site. Susceptible contaminants include those of very low solubility (e.g., Am, Pu, Th) or those that strongly adsorb to mineral phases of clay-size (e.g., <2.0 μm) and below (e.g., $^{137}Cs^+$). Mobile colloids are generated when subsurface water systems experience chemical perturbations that cause relatively rapid, in situ precipitation events or ionic strength induced particle disaggregation (McCarthy and Zachara, 1989; Roy and Dzombak, 1997). These conditions have occurred at Hanford as caustic, saline tank wastes have been neutralized by dissolution–precipitation reactions with surface sediments, and as low ionic strength recharge waters resulting from meteoric water infiltration and infrastructure water losses have migrated behind relatively small volumetric releases of tank wastes causing salinity fronts. Critical questions for the Hanford Site are whether mobile colloid-contaminant associations form and whether such associations are stable against dissociation and filtration during transport through the highly structured vadose zone that is generally, but not always, low in moisture content. Indeed, the importance of colloid-facilitated transport is under debate in the field of environmental science since few studies have clearly shown its importance in the field (Honeyman, 1999).

Flury, Harsh, and colleagues have comprehensively evaluated questions of colloid migration for contaminant $^{137}Cs^+$ at the Hanford Site (Chen and Flury, 2005; Chen et al., 2005; Cherrey et al., 2003; Czigany et al., 2005; Flury et al., 2002; Marshal et al., 2004; Zhuang et al., 2003, 2004). The results of these publications are summarized briefly here. The authors found that native colloids are mobilized by salinity fronts from sand-textured Hanford sediments and that feldspathic colloids are formed by alkaline waste-sediment reaction with a maximum observed concentration of 900 mg L^{-1}. Both of these colloid types behave similarly and exhibit net negative charge, form stable colloid suspensions in simulated Hanford pore water for extended time periods, and are readily transported through disturbed, water-saturated Hanford sediment that has been repacked in laboratory columns. Colloid retention increases, and colloid transport decreases, with decreasing water content as a result of colloid retention in water films of variable thickness. Both native and tank waste–induced feldspathic colloids (neo-formed phases) sorb $^{137}Cs^+$ and can induce a small amount of colloid-facilitated migration in repacked laboratory columns under water-saturated conditions. However, colloid-associated $^{137}Cs^+$ was stripped from this mobile fraction by downgradient stationary sorbents that were present in the sediment in far greater site concentration than present in the fluid phase. The coprecipitation of $^{137}Cs^+$ within neo-formed phases may lower its exchangeability and increase its colloidal-facilitated mobility over the case referred to here, where $^{137}Cs^+$ was adsorbed onto preformed colloids before introduction to the column system.

Strong adsorption of $^{137}Cs^+$ by immobile colloids and clay- and silt-sized phyllosilicates, along with the dramatic decrease in colloid transport that parallels water desaturation, leads to the general conclusion that colloid-facilitated migration of $^{137}Cs^+$ is unlikely to be important unless water contents and flow rates are locally and temporally increased by snowmelt or episodic artificial recharge (Czigany et al., 2005). Moreover, in situ colloid migration at Hanford may be markedly less than in laboratory repacked columns because of particle filtration by ubiquitous, structured, fine-textured layers as colloids move downward (Blume et al., 2002; Cherrey et al., 2003). Indeed, modeling simulations of Cs^+ migration in the S-SX tank farm based solely on chromatographic separation through multicomponent ion exchange to the immobile micaceous fraction of vadose zone sediment showed close agreement to field profiles (Lichtner et al., 2004). Along these same lines, Dai et al. (2005) found no defensible evidence for colloid-enhanced migration of Pu downgradient of source terms associated with spent nuclear fuel in Hanford's 100K basins.

Laboratory studies show that colloid formation can be significant at tank waste plume fronts as high waste Na^+ displaces Ca^{2+}, Mg^{2+}, and Sr^{2+} from the exchanger phase and induces the supersaturation of calcite and other phases (Wan et al., 2004a,c). Calcite precipitation is enhanced with wastes of elevated temperature (a typical occurrence) because of the retrograde solubility of calcite. The colloid load so produced accumulates in the aqueous phase and significantly exceeds the concentrations produced by salinity gradients (Flury et al., 2002; Wan et al., 2004c). The precipitation reactions neutralize and lower pH at the plume front allowing the supersaturation and precipitation of other phases including uranyl solids (J. Wan, personal communication, 2007), that may also migrate for unknown distances as colloidal material.

Aqueous Complexation

Synthetic chelating agents including EDTA (ethylenediamine tetraacetic acid), NTA (nitrilotriacetic acid), gluconate, citrate, TBP and DBP (tributyl and dibutyl phosphate), and a variety of others were used for the complexation of target cationic metals during separation processes for Pu, for the selective removal of radionuclides from waste streams, and for decontamination activities. These compounds and their residues ended up in tank wastes and were subject to complex aging and radiolysis reactions during tank waste storage (Toste, 1991; Toste and Lechner-Fish, 1993; Toste et al., 1994). The characterization of these residual organic compounds is extremely difficult because of high radioactivity, but the organic speciation of select tank waste samples has been performed (Campbell et al., 1996, 1998), showing the presence of EDTA, oxalate, glycolate, formate, acetate, and radiolysis products.

The significance of these compounds (primarily EDTA) is that they may form stable anionic aqueous complexes with normally insoluble cationic radionuclides (e.g., Co, Pu, and

Am) enhancing their subsurface migration if discharged to the vadose zone. For example, EDTA has mobilized radionuclides to groundwater at shallow waste disposal sites (Balk and Lee, 1994; Means and Alexander, 1981; Means et al., 1978; Olsen et al., 1986). It greatly enhances the solubility of Pu(IV) at circumneutral pH (Rai et al., 2001), the primary valence state of contaminant Pu in Hanford sediments. The complexants are slowly degraded by subsurface microorganisms and may therefore persist in ground for extended periods (Bolton and Girvin, 1996; Bolton et al., 1996, 2000; Liu et al., 2001; VanBriesen et al., 2000). Co(II)EDTA^{2-} exhibits complex behavior in circumneutral Hanford vadose zone sediments (Zachara et al., 1995). If small amounts of Mn oxides are present, the complex is oxidized to the highly stable, kinetically inert, and freely mobile Co(III)EDTA^{-} complex that is not adsorbed by Hanford sediment. If Mn oxides are not present, the Co(II)EDTA^{2-} complex slowly degrades through a ligand-induced dissolution reaction with Hanford sediment to yield immobile, sorbed Co^{2+} and mobile Al(III)- and Fe(III)EDTA^{-} complexes.

Despite the above reports, there is no definitive field evidence that organic complexants have facilitated the migration of tank waste contaminants through the vadose zone at Hanford. Moreover, there are no confirmed reports of the loss of high complexant waste to the Hanford vadose zone. Immobile $^{239/240}$Pu(IV) showed anomalously deep migration at T-106 (Freeman-Pollard et al., 1994), and immobile ^{155}Eu(III) demonstrated a significant migration distance in core C4104 from the T tank farm (Serne et al., 2004b). Both of these observations have led to speculation of chelator-facilitated migration. Organic analyses of extracted pore waters from the proximity of T-106 (Serne et al., 2004b), however, detected no chelators or elevated dissolved organic carbon. It is possible that the complexant concentrations were below detection or that they degraded over the 30-plus years of in-ground contact. Nonetheless, there is no analytical documentation of chelators associated with mobile radionuclides in field samples to substantiate the hypothesis of organic complexant–facilitated migration at the Hanford Site.

The most dramatic evidence for the far-field migration of a metal ion complex occurs with ^{60}Co ($t^{1/2}$ = 5 yr). As a bare divalent cation, $^{60}Co^{2+}$ is adsorbed strongly (e.g., log distribution coefficient [K_d] [mL g^{-1}] > 10^3) by Hanford sediment (Zachara et al., 1995) and is effectively immobile. ^{60}Co, however, exhibited unretarded migration through the vadose zone beneath the BY cribs soon after the disposal of liquid process effluents from U Plant containing ferrocyanide wastes in 1954–1955 (Hartman, 2000; Thornton and Lindberg, 2002). Elevated concentrations of ^{60}Co with coassociated cyanide (CN^{-}), the presumed complexant, have existed in groundwaters downgradient and surrounding the BY cribs from the year of disposal to the present day (Hartman et al., 2005). Low molar concentrations of the mobile complex (e.g., <10^{-10} mol L^{-1}) have, however, prevented identification of its identity (structure, stoichiometry, and coordination number) and valence [e.g., Co(II) or Co(III)]. By analogy to the ferrocyanide complex [Fe(III)CN_6^{3-}] used for $^{137}Cs^{+}$ complexation, the ^{60}Co complex may be hexacyanocobaltate [Co(III) CN_6^{3-}]. Cobalt-60 also shows high mobility (e.g., K_d [mL g^{-1}] $\leq$ 1), albeit low concentration, in tank waste leaks (e.g., borehole C3831 near TX-107; Serne et al., 2004a), but it is unclear whether its migration is cyanide facilitated.

Surface Complexation and Uranium Migration

Surface complexation is an adsorption process by which dissolved solutes form complexes with reactive functional groups on mineral surfaces (Davis and Kent, 1990; Stumm, 1992). The surface functional groups are typically hydroxylated metal ion centers on the surfaces of Fe, Si, Al, and Mn oxides, and on the truncated edges of phyllosilicates. Surface complexation may also occur on the surfaces of carbonate minerals, including calcite and phosphates (Cowan et al., 1990; Savenko, 2001; Wu et al., 1991; Zachara et al., 1991). Because it is an adsorption process, surface complexation leads to a reduction in the mobility of solutes that might otherwise be mobile. Surface complexation has been widely studied in the literature, and several surface complexation models exist that compute adsorption and attendant surface speciation (Sposito, 1984). As a general rule, the adsorption of metal cations (e.g., Co^{2+}) is low at lower pH ($\sim$4) and increases with increasing pH, whereas the adsorption of metal anions (e.g., CrO_4^{2-}) is low at high pH ($\sim$9) and increases with decreasing pH. These behaviors result from ionization reactions of the surface functional groups that lead to surface charge development. Outer- (intervening water between the sorbate and absorbent surface) and inner- (no intervening water) sphere surface complexes are identified, with the latter being more strongly bound. The importance of surface complexation for a given sorbate is controlled by (i) the magnitude of its equilibrium constant with surface functional groups, (ii) the total concentration of surface sites present in the sediment, (iii) pore water pH, and (iv) the concentrations of like ions that may compete for surface sites. These, in turn, are dependent on the mineralogy of the sediment, its surface-charging properties, its surface area, and the tank waste composition.

The hexavalent uranyl cation [U(VI)O_2^{2+}] is an important contaminant of Hanford's vadose zone, originating in bismuth phosphate metal waste (Table 3) and numerous other sources (Simpson et al., 2006). The subsurface migration of U(VI) is slowed in certain cases by surface complexation adsorption reactions (Curtis et al., 2006; Gabriel et al., 1998; Kohler et al., 1996). [Note McKinley et al., 2007, on U(VI) precipitation process in the Hanford vadose zone.] Preliminary studies have investigated U(VI) surface complexation reactions in Hanford vadose zone sediments (Barnett et al., 2002; Bond et al., 2007; Um et al., 2007). Experimental difficulties have been encountered because of the coarse-textured, unweathered character of the sediments and the presence of minor calcite. Neither the surface speciation of adsorbed U(VI), the predominant U(VI) sorbents, or plausible surface reaction networks have been definitively identified. Hence, a generalized surface complexation model does not exist for Hanford sediments that is comparable, for example, to that reported for the Naturita uranium mill-tailings site in Colorado (Davis et al., 2004).

The surface complexation of UO_2^{2+} in suspensions of minerals common to the Hanford vadose zone and open to atmospheric CO_2 (e.g., ferrihydrite and smectite; Pabalan and Turner, 1997; Pabalan et al., 1998; Prikryl et al., 2001; Waite et al., 1994) shows behavior that is comparable to that observed with U(VI) adsorption to Hanford vadose zone sediment (Barnett et al., 2002; Dong et al., 2005; Um et al., 2007). By analogy, it is assumed that the same reaction types that occur on these model mineral phases occur in Hanford sediment. With a fixed concen-

tration of U(VI) and sorbent, the amount of U(VI) adsorption increases with increasing pH at low pH (3.5–4.0), and decreases above pH 7 (Fig. 11). Surface complexation modeling suggests that the increase in adsorption results from strong surface binding of UO_2^{2+} and UO_2OH^+, with weaker surface binding of $UO_2(CO_3)_2^{2-}$ and other carbonate complexes as pH increases (Pabalan and Turner, 1997; Waite et al., 1994). The decrease in adsorption above pH 7 results from a change in the predominant U species to higher charged anionic [$UO_2(CO_3)_3^{4-}$] and poorly sorbing neutral ones [$Ca_2UO_2(CO_3)_3$; Fig. 12; Dong et al., 2005; Fox et al., 2006], and surface ionization that yields increasing negative surface charge with increasing pH (Waite et al., 1994; Wazne et al., 2003). Surface complexation modeling has been performed on Hanford sediment based on the assumption that poorly crystalline Fe(III) oxide is the sorbent (Barnett et al., 2002). Although this approximation may eventually prove correct, it has not been documented directly.

The real difficulty in quantifying the surface complexation processes for U(VI) in Hanford vadose zone sediments results from the natural pH range of the sediments and the presence of relatively small concentrations of sorbents that are known to strongly adsorb U(VI). The natural pH of Hanford vadose zone sediments ranges from approximately 7 to 8.5. The presence of alkaline tank waste solutions in contaminated regions extends this pH range to higher values (e.g., pH $\approx$ 10) even after waste neutralization occurs through aluminosilicate hydrolysis. This pH range overlaps the region where U(VI) surface complexation to mineral surfaces decreases dramatically (Fig. 11 and 12) from changes in aqueous speciation (e.g., carbonate complexation) and surface charge. Consequently, U(VI) adsorption in Hanford sediment is a sensitive consequence of pH, carbonate concentration, and texture that controls surface area and total site concentration (see, e.g., Um et al., 2007). Measurements of U(VI) adsorption to different Hanford sediments vary widely because of differences in these properties. The interplay of these important variables has not been unraveled sufficiently to allow formulation of a workable, generalized surface complexation model that applies to the numerous sediment facies types that exist throughout the Hanford vadose zone, although efforts are currently underway to do so and preliminary results are promising (Um et al., 2007). Moreover, Pleistocene-age Hanford vadose zone sediments (e.g., Hanford formation) are relatively unweathered due to semiarid conditions, and the concentrations of ferrihydrite (e.g., Fig. 11), the strongest and most important sorbent in soils and weathered sediments, are small (e.g., typically <25 μmol g^{-1}) and difficult to quantify by extraction (e.g., ammonium oxalate or hydroxylamine hydrochloride) without significant ambiguity.

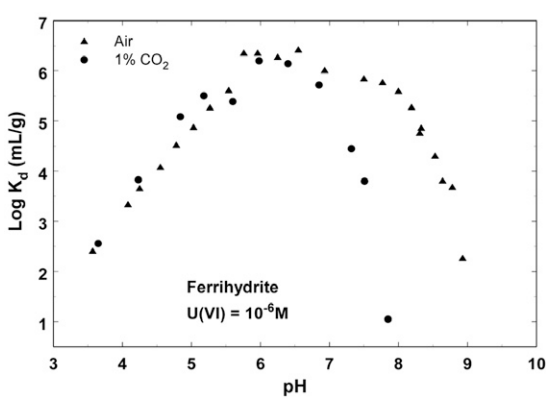

Fig. 11. Adsorption measured by distribution coefficient (K_d) of 1 μmol L^{-1} U(VI) on 1 mmol L^{-1} of ferrihydrite, one of the most important subsurface sorbents of uranium. (From Davis et al., 2004.)

The ubiquitous presence of calcite in small concentration further complicates our understanding of the surface complexation of U(VI). Calcite can adsorb the uranyl ion to its surface (Elzinga et al., 2004; Savenko, 2001) and incorporate it within its structure (Kelly et al., 2003; Wang et al., 2005). However, at low concentration (e.g., <10%) calcite appears to form particle coatings that block higher affinity adsorption sites on oxides and phyllosilicates, and release Ca^{2+} through solubility reaction that forms the poorly sorbing $Ca_2UO_2(CO_3)_3^0$ aqueous complex (Dong et al., 2005; Fox et al., 2006). Both of these effects appear to decrease the intrinsic sorptivity of Hanford sediment for U(VI). In contrast, preliminary observations of contaminant U(VI) behavior in high calcite (e.g., >35%), paleosol sediments from the Cold Creek unit beneath leaked tank TX-104, indicate that calcite at high concentration may strongly adsorb and immobilize soluble U(VI) in tank waste (Myers, 2005). Ongoing research seeks to resolve the role of calcite as a sorbent when present in Hanford sediment at high concentration.

Oxyanion Migration

Oxyanions are important components of tank waste resulting from fission (e.g., $^{98,100}MoO_4^{2-}$, $^{79}SeO_4^{2-}$, $^{101,102,104}RuO_4^{-}$, $^{99}TcO_4^{-}$) and/or processing (CrO_4^{2-}).

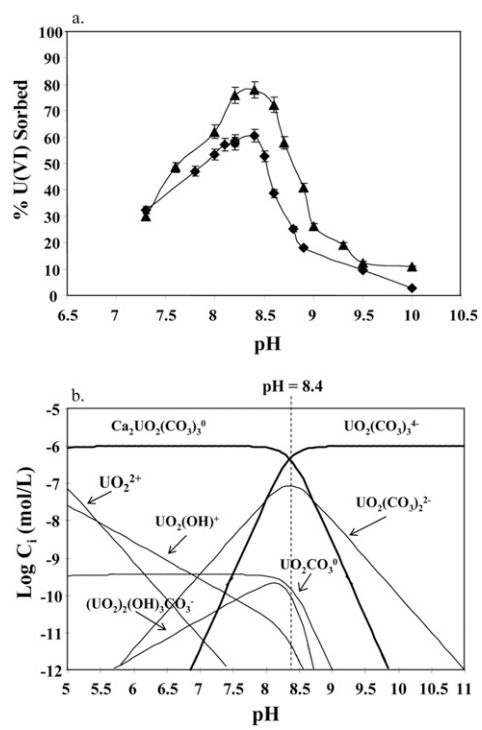

Fig. 12. (a) Adsorption of μmol L^{-1} U(VI) on a calcite-containing, deep vadose zone sediment (100 g L^{-1}) from Hanford's 200A plateau (S-SX tank farm) ♦ = untreated sediment; ▲ = sediment with calcite removed. (b) Computed aqueous speciation of U(VI) in calcite-saturated 0.05 mol L^{-1} $NaNO_3$. (From Dong et al., 2005.) Reproduced with permission from *Environ. Sci. Technol.* 2005. 39:7949–7955. Copyright 2005 American Chemical Society.

Surface complexation can retard the migration of metallic oxyanions through formation of both inner- and outersphere complexes on Fe(III) and Al(III) oxides that carry net positive charge at circumneutral pH (Davis and Leckie, 1980; Goldberg et al., 1996, 2002; Hayes et al., 1988; Zachara et al., 1989; Zachara et al., 1987). This process, however, appears to be suppressed when tank wastes contact Hanford vadose zone sediment. It is typically observed that in the absence of reduction, the monovalent oxyanions $^{101,102,104}Ru$ and ^{99}Tc are found at the leading edge of tank waste plumes along with NO_3^-, with CrO_4^{2-} and $^{98,100}Mo$ following close behind (Fig. 13; Evans et al., 2007; Serne et al., 2004b). Technetium-99 [as pertechnetate, $Tc(VII)O_4^-$] shows virtually no retardation under fully oxidizing conditions (Kaplan and Serne, 1998; Myers, 2005; Um and Serne, 2005). Consequently, ^{99}Tc and more recently, $^{101,102,104}Ru$ (Brown et al., 2006) have been used to trace tank waste migration through the vadose zone, and serve as indicators of tank waste contamination in groundwater (Dresel et al., 2002). Technetium-99 is important because it is a significant contributor to overall risk at the Hanford Site (USDOE, 2006). The extreme mobility of all of these anions in tank waste results from low concentrations of anion-adsorbing Fe(III) oxides in the Hanford vadose zone (the primary potential adsorbent), generally high pH that encourages negative charge development on amphoteric surfaces, and high concentrations of competing major anions including NO_3^- and CO_3^{2-} (of waste origin), and $H_3SiO_4^-$ (from basic mineral

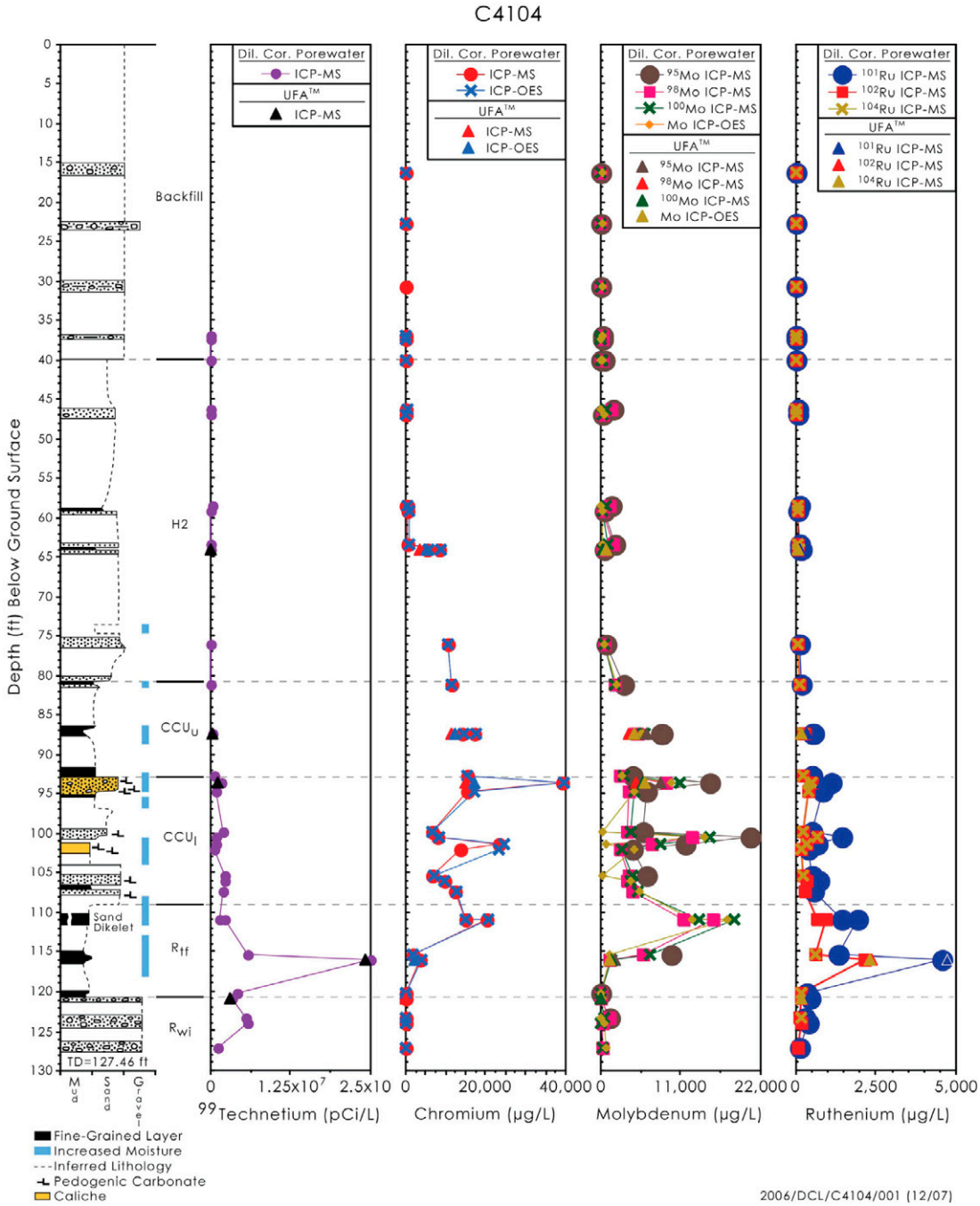

Fig. 13. Derived (Dil. Cor.) and actual (UFA) pore water composition of mobile metals in borehole C4104 collected near T-106. The leading edge of the tank waste plume is defined by ^{99}Tc. (From Serne et al., 2004b.)

hydrolysis) that compete for and saturate available surface sites (Hayes et al., 1988; Zachara et al., 1987).

Microbiological Processes

Microorganisms may be significant to the long-term fate of tank wastes in the vadose zone because they can mediate a variety of biogeochemical reactions that may influence vadose zone pore water composition and the chemical form, valence, and solid–liquid distribution of tank waste contaminants (Fredrickson and Onstott, 2001). For example, subsurface bacteria can transform mobile $^{99}Tc(VII)O_4^-$, $U(VI)O_2^{2+}$, and $Cr(VI)O_4^{2-}$ into immobile, reduced precipitates and denitrify NO_3/NO_2 into gaseous, volatile nitrogen forms. Microorganisms populate Hanford's vadose zone (Brockman et al., 1992; Fredrickson et al., 1993; Kieft et al., 1993), with activities and numbers controlled by water content and the concentration of organic matter that is generally sparse. The biogeochemical function and contribution of Hanford's vadose zone microorganisms, however, remains uncharacterized. The activities of subsurface microorganisms are believed to be quite low under ambient conditions and very much limited by low moisture content and nutrient fluxes.

Microorganisms colonize, inhabit, and even flourish in some of the earth's most inhospitable environments (Konhauser, 2007). With this in mind, the microbiological characteristics of one of Hanford's most extreme environments, sediments beneath leaked waste tank SX-108 (C3082), were investigated (Fredrickson et al., 2004). This borehole penetrated a tank waste plume in the vadose zone that received caustic, saline, and highly radioactive redox waste (Table 3). Residual heat in the core of the plume was high when the borehole was drilled in 2001 (~70°C at 19.8 m below ground surface). This same region experienced temperatures in excess of 100°C with steam recirculation at the time of waste spillage in 1962 because of boiling redox waste throughout the tank farm (Pruess et al., 2002). The discharged waste contained large amounts of short-lived radioisotopes (e.g., ^{106}Ru, ^{144}Ce, ^{147}Pm, and others; Jones et al., 2000b) in addition to ^{137}Cs that presented a significant dose to subsurface organisms.

Despite the incredibly harsh thermal, chemical, and radiologic regime beneath tank SX-108, low concentrations ($\leq 10^5$ bacteria per gram of sediment) of viable microorganisms were recovered from 9 of 16 core samples studied (Table 4). These numbers may underestimate the microorganism population because of the limitations of cultivation-based methods (Amann et al., 1995). No correlation between moisture content or sediment radiation level (^{137}Cs) was observed (Table 4). Organisms were cultured from waste-impacted sediment that appeared "bone-dry" (e.g., sediments 4 and 10). The cultures obtained (Table 5) were dominated by common dry-soil dwelling, Gram-positive microorganisms, most closely related to *Arthrobacter* species that are known to be good survivors of stressful environments. Two isolates from a high radiation sample containing >20 μCi g^{-1} of ^{137}Cs were closely related to radiation tolerant *Deinococcus radiodurans* (Fig. 14) and were able to survive high doses of applied radiation (20 kGy). Activity measurements on the sediments indicated that the cells were mostly inactive or dormant under the current conditions of low moisture and high salinity. This community could increase in size and activity significantly, with unknown implications to contaminant solubility, if the moisture content were to increase through recharge.

Table 4. Culturable bacteria observed in tank SX-108 sediments.

Sample ID	Depth	^{137}Cs	Water content	Number of bacteria
	m (ft)	pCi g^{-1}	%	log $gram^{-1}$
1	16.61 (54.48)	3.06E+06	4.3	4
3	20.50 (67.27)	1.95E+07	2.8	bd†
4	21.80 (71.51)	1.38E+06	2.8	3.7
5	23.08 (75.73)	6.52E+06	4.7	bd
6	24.37 (79.94)	5.31E+07	3.7	bd
7	25.64 (84.13)	2.14E+07	6.2	3.2
8	26.92 (88.32)	5.55E+05	6	bd
9	28.19 (92.48)	1.71E+02	2.4	2.6
10	29.46 (96.64)	4.51E+02	1.9	2.1
11	30.80 (101.04)	9.12E+02	3.2	bd
12	31.98 (104.92)	3.37E+02	21.4	2.7
13	34.48 (113.14)	5.21E+02	7.6	bd
14	36.97 (121.3)	8.37E+02	12	bd
15	39.45 (129.44)	5.92E+02	17.4	2.1
16	41.92 (137.54)	9.79E+01	7.5	3.3
17	43.89 (143.99)	1.75E+02	19.7	>4.3

† bd, below detection.

Reactive Transport Modeling

Geochemical and biogeochemical processes of the types described above can be simulated within multicomponent, reaction-based reactive transport models (Steefel et al., 2005) that synthesize mineralogic, water chemical, hydrologic, geologic, and if necessary, biologic and biogeochemical details of the subsurface system. The resulting models can be used to match historic or current subsurface contamination distribution profiles or to predict future contaminant migration and plume evolution. Different processes are integrated through their influence on a common set of chemical components that are described using a series of mass action relationships termed a *reaction network*. This way to describe the chemical or biochemical contribution to the retardation factor (Freeze and Cherry, 1979) as a function of system chemical or biologic components is in contrast with the "constant-K_d" approach that has been the mainstay of performance assessment modeling for regulatory compliance (Bethke and Brady, 2000; Steefel et al., 2005).

The reaction-based approach has extensive conceptual model and parameter requirements (Davis et al., 2004) that can be time consuming or just plain difficult to determine, but an appropriately parameterized reaction network can accurately describe complex systems with chemical and biogeochemical change, gradients, multiple processes, and kinetic phenomena. Such an approach can reduce modeling uncertainty because

Table 5. Phylogeny of selected tank SX-108 cultures.

Isolate ID	Phylogeny	GenBank accession number
1b-1	*Arthrobacter globiformus*	M23411
1c-1	*Arthrobacter oxydans*	AJ243423
4a-4	*Rhodococcus corynebacteroides*	X80615
4b-2	*Staphylococcus warneri*	AJ223451
4b-3	*Nocardioides plantarum*	Z78211
7b-1	*Deinococcus radiodurans*	Y11332
9c-3	*Blastobacter* sp. Str. BF10	AJ223453
10c-2	*Sphingomonas* sp. Str. Koll-1	AJ224938
12a-1	*Pseudomonas* sp. Str. BRW3	AF025351
12b-1	*Pseudomonas* sp. Str. BRW3	AF025351
15a-1	*Terrabacter tumescens*	X83812
17a-1	*Arthrobacter aurescens*	X83405
17a-2	*Arthrobacter oxydans*	AJ243423
17a-3	*Pseudomonas* sp. Str. BRW3	AF025351
17b-1	*Arthrobacter pascens*	X80740

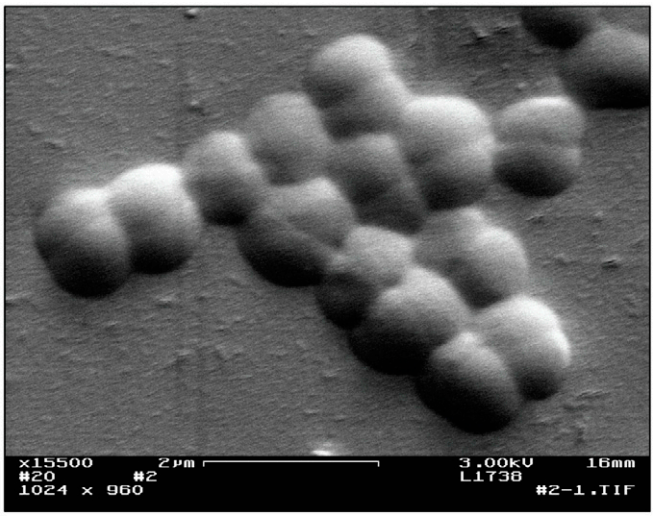

FIG. 14. Scanning electron micrograph of radiation-resistant bacteria *Deinoccus radiodurans* isolated from sediments collected from beneath leaked single-shell tank SX-108.

spatial and temporal variations in system chemical, mineralogic, surface chemical, and microbiologic properties and processes can be explicitly taken into account. The approach does require that reaction networks be well defined through experimentation and that the subsurface domain to be modeled is adequately characterized in terms of process-controlling properties. Valuable Hanford examples of this approach include the modeling of $^{137}Cs^{+}$ migration (Lichtner et al., 2004; Steefel et al., 2003; Zachara et al., 2002) and tank waste neutralization (Wan et al., 2004a; Wan et al., 2004b; Wan et al., 2004c; Zhang et al., 2005). The "constant-K_d" approach is more simple to parameterize unless a response surface is developed, but it can be inconsistent with the geochemical nature of the retardation process and with laboratory and field behavior/observations through its assumption of linear distribution (Liu et al., 2004; Yeh and Tripathi, 1989; Zhu, 2003).

Debate exists in the literature over which of the two modeling approaches (reaction-based or constant-K_d) are the most practical to forecast contaminant migration and future behavior (Bethke and Brady, 2000; Brady and Bethke, 2000; Steefel et al., 2005; Zhu, 2003). This same debate occurs at Hanford regarding the modeling of tank waste residuals in the vadose zone. However, the K_d approach is completely inappropriate for the early stages of tank waste-sediment interaction, where kinetically controlled dissolution–precipitation reactions occur in response to a gross state of disequilibrium between mineral solids and waste fluids, or where solubility reactions control desorption under variably saturated conditions (Liu et al., 2004). However, K_d is a useful concept that can be integrated into nonequilibrium, reactive transport calculations for meaningful field application (Qafoku et al., 2005).

Additional Needs and Opportunities

The research summarized here demonstrates that considerable knowledge regarding the geochemical behavior of Hanford tank waste in the vadose zone has been gained over the last 10 yr through field characterization, laboratory studies with tank-waste contaminated sediments and model mineral–tank waste systems, and reactive transport modeling. It has been observed that most tank wastes released to the vadose zone have reacted with subsurface sediments to reach "steady-state"–like conditions governed by long-term processes because of the length of time that they have been in ground. Many contaminants in tank waste have been strongly retarded by adsorption and precipitation reactions (Cs, Pu, Am, Eu), while others have remained mobile (Mo, Ru, Se, Tc). Still others show variable, waste-specific behavior (Sr, Cr, and U) that is closely tied to evolving pore water chemistry and, for Cr, temporal redox conditions. The temperature of in-ground tank waste has moderated by heat exchange with the mineral fraction, and high basicity has been neutralized through mineral hydrolysis and secondary mineral precipitation. Rapid initial kinetic reactions have approached completion, while slower ones have continued in response to water drainage, chemical gradients between particle interiors and exteriors, and mineral transformations of metastable phases.

One of many important future science challenges for Hanford's tank farms is to accurately project the future migration potential of tank waste residuals in the deep vadose zone and the risks posed by mobile contaminants to groundwater. Such projections provide the basis for remedial action decisions and for the development and testing of appropriate remediation strategies. The following fundamental geochemical science needs for the Hanford vadose zone are deemed critical to that end.

- Microscopic chemical speciation, mineral residence, and spatial location of reactive, semimobile contaminants (e.g., U and Cr) in deep vadose zone plumes originating from different tank waste types.
- New understanding of the adsorption process of U(VI) to deep vadose zone sediments of variable texture and calcite content over the pH range of 7 to 10, and better-linked aqueous-surface speciation models and associated parameters for reactive transport calculations.
- Effects of low and variable water saturation on contaminant desorption (or dissolution) and adsorption rates of weakly [e.g., $^{99}Tc(VII)O_4^-$] and more strongly (but variably) sorbing [U(VI)] contaminants for sediment textures ranging from gravel to silt.
- Characterizing long-term contaminant sequestration (including the nature of products formed and their kinetic reversibility) resulting from slow subsurface processes, including microbiologic activity, microscopic transport and intragrain reaction, and mineralogic transformation reactions of metastable phases (aluminosilicates and feldspathoids).
- Reactions controlling pore water composition in different lithologic units and facies types at different water contents and times, and strategies to simulate and predict the composition.
- Mass transfer processes controlling apparent reaction rates, contaminant distributions, and advective transport at different scales ranging from macroscopic to mesoscopic, causal factors, and modeling strategies.

While this paper has emphasized geochemical processes that control the migration of tank wastes in Hanford's vadose zone, water migration is the essential transport vector that controls the migration pathway and the nature and properties of the sediments to which the waste fluids are brought in contact with for geochemical reaction. As for geochemical reaction, the understanding of unsaturated water migration combined with

geochemical reaction through Hanford's geologically complex vadose zone has dramatically improved over the last 10 yr (Ward et al., 2006a,b)], along with recognition of the important role of thin, fine-grained sediment layers in inducing horizontal anisotropy and lateral water flow (Pace et al., 2004; Ward et al., 2006a,b). Improved hydrologic models have resulted (Raats et al., 2004; Zhang et al., 2003) that when coupled with geochemical models for the processes described herein and as may be evaluated in future research, hold great promise for more accurate and realistic predictions of the future migration of tank waste residuals in Hanford's vadose zone.

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