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OAK RIDGE Y-12 PLANT

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MODELING OF RADIONUCLIDE AND HEAVY METAL SORPTION AROUND LOW AND HIGH pH WASTE DISPOSAL SITES AT OAK RIDGE, TENNESSEE

(Classification Review Package)

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ABSTRACT

Modeling of mineral precipitation and metal sorption reactions using MINTEQA2 and the iron oxyhydroxide diffuse-layer model has provided insights into geochemical processes governing contaminant migration from low-level radioactive waste disposal sites at the U.S. Department of Energy's Oak Ridge National Laboratory and Y-12 Plant at Oak Ridge, Tennessee. Both acidic and basic nuclear-fuel reprocessing wastes, locally mixed with decontamination solvents, were disposed of in unlined trenches and lagoons. Model results show that as wastes move toward neutral pH due to reactions with surrounding soils and saprolite, mineral precipitation and sorption can limit the solubility of heavy metals and radionuclides. However, observed contaminant levels in monitoring wells indicate that at least locally, wastes are moving in faults and fractures and are not retarded by sorption reactions along such flow paths. Model results also support previous studies that have indicated organic complexing agents used in decontamination procedures can enhance radionuclide and heavy metal solubility when mixed with nuclear fuel reprocessing wastes. However, complex interactions between metal-organic complexes and mineral surfaces and natural organic matter, biodegradation, and fracture flow complicate the interpretation of contaminant mobility.

INTRODUCTION

From approximately 1950 to 1980 liquid low-level radioactive wastes of variable composition were disposed of in shallow trenches and lagoons on the U.S. Department of Energy's (DOE) Oak Ridge Reservation, Tennessee. Wastes came from nuclear fuel reprocessing and equipment decontamination, and consisted of fission products such as ^{137}Cs , ^{90}Sr , and ^{60}Co , transuranics, transition metals, and organic and inorganic solvents. Waste pre-treatment and disposal practices varied from facility to facility and over time. At the Oak Ridge National Laboratory (ORNL), sodium hydroxide and sodium carbonate were added to the wastes to raise pH to ~ 12 to induce precipitation of $\text{Ca}(\text{Sr})\text{CO}_3$ and the supernatant liquids were disposed of in buried trenches in weathered shale (Fig. 1) at the "Pits and Trenches area". At the Oak Ridge Y-12 Plant, acidic ($\text{pH} < 2$) wastes were locally discharged into shallow lagoons on weathered carbonate bedrock at the S-3 Ponds area. (Fig. 1).

Migration of contaminants out of the unlined trenches and lagoons has occurred over the years. For example, nitrate has been detected in monitoring wells at depths $> 300\text{m}$ around the S-3 ponds at Y-12 (Dreier et al., 1993; Shevenell et al., 1994) and radionuclide-bearing water seeps out of springs in low-lying areas near White Oak Creek at ORNL during wet seasons (e.g., Means et al., 1978a; Cerling and Spalding, 1982; Spalding, 1987). Extensive monitoring and remediation programs are ongoing at both sites. In addition, the waste disposal area at ORNL has been the site of numerous laboratory and field investigations of the chemical and physical processes that affect local contaminant migration. Because radionuclides at ORNL pose a persistent environmental risk to the biosphere, much

of the research to date has focused on the capacity of the natural soils to retard their movement.

At ORNL, the mobilities of the three principal radionuclides in the wastes vary greatly. ^{137}Cs is strongly adsorbed in interlayer sites in illite present in the weathered shale (Tamura and Jacobs, 1960; Jacobs, 1960; Spalding and Cerling, 1979). Consequently, it has migrated only a few cm into the soil along the sides and bottoms of the trenches and is generally not found in nearby monitoring wells (Lomenick et al., 1967). A large percentage of ^{90}Sr was initially removed from solution by caustic pretreatment of the wastes leading to deposition of $\text{Ca}(\text{Sr})\text{CO}_3$ as sludge at the bottom of the trenches. Approximately 90% of ^{90}Sr in sludge occurs in carbonate phases, with the remainder present in easily exchangeable sites on mineral surfaces (Lomenick et al., 1967; Olsen et al., 1986; Spalding, 1987). In the first few centimeters of soil surrounding the trenches, approximately half of the ^{90}Sr exists as carbonates and half in exchange sites (Lomenick, 1967; Jardine et al. 1993a). A minor amount is present in nearby groundwaters (typically <30 pCi/l; Olsen et al., 1986). ^{60}Co has reacted with the soils to some extent, but is locally present at relatively high concentrations in shallow groundwaters and seeps (~ 1000 - $25,000$ pCi/l) and has contaminated White Oak Creek (Spalding and Cerling, 1979; Cerling and Spalding, 1982; Olsen et al., 1986).

Because of the abundance of iron oxyhydroxides in soils and saprolite on the Oak Ridge Reservation, this modeling study was undertaken in an attempt to evaluate their role in retarding the migration of some radionuclides and transition metals. Advances in the understanding of sorption phenomena by the development of surface complexation models (e.g., James and Healy, 1972; Davis and Leckie, 1978; Sposito, 1984; Farley et al., 1985; Westall, 1986; Davis and Hayes, 1986; Hayes and Leckie, 1987; Schindler and Stumm, 1987; and Dzombak and Morel, 1990) provide a framework to evaluate radionuclide and transition metal sorption at the Oak Ridge Reservation. Because of the abundance of ^{60}Co in the Oak Ridge waste streams, the potential for its sorption and precipitation will be evaluated in detail.

Cobalt Mobility in the Environment

Neither the mobility of ^{60}Co in groundwater nor the exact chemical processes involved with its retardation by natural soils are well understood. Previous studies at ORNL on the sorption of ^{60}Co by site soils (Means et al., 1976; Means et al., 1978a, 1978b) concluded that manganese oxyhydroxides were the principal sorbing phases for cobalt, even though iron oxyhydroxides were 3-30 times more abundant. A similar conclusion for Co sorption by stream sediments was reached by Cerling and Turner (1982) and Cerling and Spalding (1982). These studies have utilized the sequential dissolution procedure of Chao (1972) where a hydroxylamine hydrochloride extraction preferentially dissolves manganese phases including ^{60}Co nominally sorbed or coprecipitated by MnO_2 . Because the amount of ^{60}Co removed correlated well with the amount of Mn dissolved in the leachate, it was concluded that MnO_2 phases hosted sorbed cobalt. However, hydroxylamine hydrochloride

also dissolves a significant amount of amorphous iron oxyhydroxides (Chao and Theobald, 1976; Chao and Zhou, 1983), which also can sorb Co effectively (e.g., Kurbatov et al., 1951; Schenk et al., 1983). Furthermore, it also is possible that this procedure might liberate metals specifically adsorbed on iron oxyhydroxide phases without dissolving the parent material.

Laboratory studies and other evidence indicate that MnO_2 is probably a stronger adsorber of metals than other metal oxides, including iron oxides (e.g., Murray et al. 1968; Murray, 1975; Childs, 1975; Chao and Theobald, 1976; Catis and Langmuir, 1986). In addition, the probable higher adsorption capacity of MnO_2 over iron oxyhydroxides is even greater at low pH, because the point of zero charge of MnO_2 occurs at approximately pH=2.5, as opposed to near neutral pH for iron oxide phases (Means et al., 1978b; Drever, 1988). Because of the relatively low abundance of MnO_2 in site soils (typically <0.1wt.% MnO_2 , Arnseth and Turner, 1988) compared to iron phases, the present study was undertaken to evaluate the potential for iron phases to sorb metals in the study area. In particular, competition between surface complexation sites and both inorganic and organic ligands for metals present in waste are evaluated. Because the sorption capacity Mn -oxyhydroxides (or mixed Fe-Mn phases) would enhance the retardation of radionuclides and metals, results of this study should be considered a conservative approximation of the sorption capacity of metal oxyhydroxides in the study area soils.

The mixing of variable amounts of organic solvents such as ethylenediaminetetraacetic acid (EDTA), which was used in decontamination procedures, with fuel reprocessing wastes at ORNL led E.A. Bondietti (Auerbach et al., 1974) to propose that they could form stable aqueous complexes with ^{60}Co and lead to Co migration around disposal facilities at ORNL. This hypothesis was supported by investigations by Means et al. (1976, 1978c) who detected EDTA and high levels of ^{60}Co in a seep near a disposal trench at ORNL. In addition, Means et al. (1978c) used several different analytical procedures which indicated that the Co in the seep water occurred as low-molecular weight anionic organic complexes. However, subsequent laboratory experiments and field investigations have yielded conflicting results as to the mobility of Co-EDTA complexes in natural soils (e.g., Weiss and Columbo, 1980; Swanson, 1982 and 1983; Kirkham and Jones, 1982).

More recently, Jardine et al (1993b) showed that Co(II)-EDTA complexes can undergo redox reactions with natural ferro-manganese oxyhydroxides resulting in an extremely stable Co(III)-EDTA complex. However, Jardine et al. (1993b) also found that the Co(III)-EDTA complex itself was sorbed similar to inorganic Co^{2+} by undisturbed samples of ORNL soils, although sorption rate of the chelated complex was slower than that of Co^{2+} . Jardine et al. (1993b) attempted to reconcile conflicting observations on contaminant mobility in the presence of organic ligands. They emphasized the probable complex interplay between competitive sorption and co-sorption, aqueous and surface complexation, solid phase modification, and biological degradation.

HYDROGEOLOGIC SETTING

The two study areas are located in valley-forming units within the Valley and Ridge

province of east Tennessee. The S-3 Ponds waste area is located in the Nolichucky Shale, part of the Cambrian Conasauga Group, located in Bear Creek Valley. The pits and trenches waste area in Melton Valley is also underlain by the Conasauga Group because the major Copper Creek thrust fault caused a repetition of the Cambrian stratigraphy. The pits and trenches occur in the unit below the Nolichucky Shale, which is a slightly more carbonate-rich sequence called the Maryville Limestone.

Soils on the Oak Ridge Reservation derived from the weathering of Conasauga Group rocks contain quartz, illite, vermiculite, kaolinite, amorphous manganese oxyhydroxides and amorphous to partially crystalline iron oxyhydroxides (Tamura and Jacobs, 1960; Means et al., 1978a; Olsen et al., 1986; Arnseth and Turner, 1988). Unweathered Conasauga rocks contain the same clay minerals listed above along with chlorite, plagioclase, organic matter, calcite, dolomite, and ferroan dolomite (Haase, 1983; Lee et al., 1988; Foreman, 1991; Toran and Saunders, submitted). The weathering of ferroan dolomite and chlorite probably is the source of the ubiquitous iron oxyhydroxides, which give the soils and saprolite their distinctive red color.

The shallow groundwater adjacent to these waste areas is typically a Ca-HCO_3 or Mg-Ca-HCO_3 type due to dissolution of variable amounts of calcite and dolomite (e.g., Haase, 1991; Saunders and Toran, 1994). This zone is underlain by Na-HCO_3 -type water at depths ranging from 20 to 50 m (Solomon et al., 1992, Saunders and Toran, 1994; Toran and Saunders, submitted).

Groundwater generally flows from the ridges to the valleys in this setting, discharging to both valley-floor streams, and along strike to cross-cutting streams. The shallow soil zone where much of the waste is buried is intensely fractured (approximately 1 cm fracture spacing; Dreier et al., 1987). Fracture-controlled groundwater flow in bedrock occurs in three predominant fracture sets: along the bedding plane, perpendicular to the bedding plane, and vertical (Solomon et al., 1992). Fast flow along fractures has been documented in both the shallow and bedrock systems (Olsen et al., 1986; Jardine et al., 1990). In the S-3 Ponds area, density-driven flow is also a factor, due to the composition of wastes placed in the ponds (density=1.07; Shevenell et al., 1994). A plume of NO_3 has been detected up to 300 m deep in monitoring ports beneath the pond (Dreier et al., 1993). Since the ponds occurs in a regional discharge area, density-driven flow must be a factor in the depth of this contamination (Toran et al., 1993). The geochemical studies reported here are a first step to understanding the composition of this dense plume and the chemical interactions that could possibly enhance permeability and transport.

GEOCHEMICAL MODELING

Mineral precipitation and dissolution, and cationic sorption and desorption reactions were investigated in detail as a function of changing pH, which is likely the most important reaction-path variable as the high- and low-pH wastes react with the surrounding soils and saprolite. Modeling utilized the computer program MINTEQA2 (Allison et al., 1991), the

latest version of the MINTEQ family of programs (Felmy et al., 1984). A review of the literature and unpublished reports were used to reconstruct typical waste compositions used for modeling (Table 1). Because ^{90}Sr and ^{60}Co are principal contaminants of concern in the Oak Ridge wastes, their solubility and mobility are a principal focus of this study. Unfortunately, detailed records of all waste constituents were not kept. Therefore we have estimated the total amount of Co and Sr in the high-pH wastes from Trench 7 based on the reported activity of ^{60}Co and ^{90}Sr in the waste, and the measured amounts of Co and Sr in nearby monitoring wells (Olsen et al., 1986). EDTA content was estimated (1 mg/l) from measured concentrations in a seep discharging relatively concentrated waste along a fault zone (Means et al., 1978c), allowing for a dilution factor of ~ 3 . However, undocumented reports indicate that locally EDTA concentrations may have been as high as 10^{-3} M/l (276 mg/l) (Jardine et al., 1993b). In the S-3 ponds waste, total Co and Sr were measured directly (Table 1). EDTA would not be expected in the fuel reprocessing waste at the S-3 ponds area (as opposed to mixed decontamination and reprocessing wastes as in Trench 7).

Sorption reactions were modeled with the diffuse-layer surface complexation model of Dzombak (1986) and Dzombak and Morel (1990) in MINTEQA2. The existing sorption module in MINTEQA2 was modified to include surface complexation reactions for Sr, Co, and U from Dzombak and Morel (1990). Equilibrium constants for Co aqueous complexes and minerals were calculated from thermodynamic data in Naumov et al. (1974), Smith and Martell (1976) and Vaughan and Craig (1978). Equilibrium constants for Sr aqueous complexes and minerals were adjusted to reflect "best" values recommended by Nordstrom et al. (1990).

The diffuse-layer surface complexation model of Dzombak and Morel (1990) is one of several surface complexation models currently used to model adsorption of ionic inorganic species on mineral or mineraloid surfaces. The model used here considers only adsorption on to amorphous oxyhydroxide and does not include surface precipitation at high sorbate concentrations, which is part of the complete model of Dzombak and Morel (1990). As incorporated into MINTEQA2, the diffuse-layer surface complexation model can evaluate the relative competition of surface adsorption sites and inorganic and organic ligands for cations, as well as potential solids that could precipitate. Although amorphous iron oxyhydroxides are not the only solids capable of affecting the solubility of aqueous species in the soils of the Oak Ridge Reservation, their abundance and relative reactivity justify evaluating their contribution as potential contaminant-retarding agents at the site.

The diffuse-layer model assumes that these pH-dependent ionization (surface acidity) reactions occur at the iron-oxide surface (Dzombak and Morel, 1990):

and for sorption of cations at the surface:

where M^{2+} represents a divalent cation, and $=FeOX$ represents a variably ionized iron-oxide surface site. Mass action expressions for surface complexation reactions are analogous to those for aqueous complex formation, but require an electrostatic term to account for the surface charge and potential. This term is essentially an activity coefficient for the long-range effects of charged surface groups (Dzombak and Morel, 1990). These terms are calculated by MINTEQA2 (Loux et al., 1989).

Dzombak and Morel (1990) reviewed the voluminous literature on laboratory experiments dealing with the adsorption of aqueous species on iron oxyhydroxides. For cations, they derived "intrinsic" equilibrium constants for two surface reactions that could be used to fit the carefully screened experimental data. For some elements such as uranium, Dzombak and Morel (1990) estimated the equilibrium constants for surface complexation reactions using linear free-energy relationships. These included a reaction between cations and a limited number of "high-energy" sites (strong complex) and a reaction between specific cations and more abundant "low-energy" sites (weaker complex). Furthermore, Dzombak and Morel (1990) specify in their model that: 1) the high-energy sites comprise $0.005 \text{ moles} \cdot \text{moles}^{-1}$ of Fe; 2) low-energy site density is $0.20 \text{ moles} \cdot \text{moles}^{-1}$; 3) specific surface area of the amorphous iron oxyhydroxide is $600 \text{ m}^2 \cdot \text{g}^{-1}$; and 4) the molecular weight of the iron phase is $89 \text{ g} \cdot \text{mole}^{-1}$. Although the intrinsic equilibrium constants are built into the diffuse-layer model in MINTEQA2, the concentration of iron surfaces must be input (Loux et al., 1989).

For the present study, the amount of amorphous Fe in the soils was averaged from 11 analyses (av. = 0.90 wt.% as amorphous $Fe(OH)_3$) from monitoring wells around the ORNL waste burial grounds (Means et al., 1978a). This value is significantly less than the range of total iron concentration (including crystalline goethite) reported in Oak Ridge Reservation soils (1.3-5.8 wt.% recalculated to $Fe(OH)_3$) reported by Arnseth and Turner (1988), and thus should be viewed as a conservative estimate of the amount of iron oxyhydroxide capable of competing for cations in groundwater. For the purpose of calculating the amount of iron that was in contact with groundwater, the soil porosity and dry density were assumed to be 40% and 2.5, respectively.

MINTEQA2 was used to model the effect that plausible mineral-waste reactions would have on the pH-dependent sorption of radionuclides and transition metals by iron oxyhydroxides in the site soils around the pits and trenches at ORNL and the S-3 ponds at Y-12. Predictions for the relative mobility of several species are then compared to their observed concentrations in nearby monitoring wells as a test of the utility of the model under real-world conditions.

RESULTS

Trench 7, ORNL

MINTEQA2 was used initially to calculate: 1) the distribution of aqueous species between uncomplexed ions and important ligands; and 2) the saturation index (log

[IAP/ K_{eq}]; where IAP = ion activity product) for minerals of geochemical interest as pH decreases from 12 (in the trenches) to 7, the approximate pH of shallow groundwaters around the trenches. Plausible minerals with positive saturation indices ($SI > 0$) were allowed to precipitate in subsequent model runs. In the case of the high-pH waste from Trench 7 at ORNL, the following minerals were allowed to precipitate in the model as they became saturated: calcite, strontianite ($SrCO_3$), and amorphous $Al(OH)_3$. It is likely that a mixed $Ca(Sr)CO_3$ as opposed to separate phases would have precipitated (e.g., Lomenick et al., 1967; Olsen et al., 1983, 1986) but the effect on strontium solubility would be similar for either phase. Model results show that approximately 90% of the Sr precipitates as strontianite at pH 12 (Fig. 2), but the amount drops sharply between pH 10 and 8, where strontianite redissolves. This process is accompanied by a changeover from $SrSO_4^0$ to Sr^{2+} as the principal strontium species in solution as well as an increase in the total dissolved Sr (Fig. 3). In contrast, because of aluminum hydroxide complexes, most Al is predicted to precipitate as amorphous aluminum hydroxide as the pH decreases (Fig. 2).

Surface complexes between Sr and iron oxyhydroxide are relatively weak, which is reflected in the general low amount of Sr sorption, except for a spike at pH=8 (Fig. 2). Likewise Co^{2+} is not readily sorbed at high pH (Fig. 2). Only at the lower end of the pH range does Co begin to sorb appreciably (Fig. 2), due to the decreased stability of the Co(II)-EDTA complex (and the increased stability of Co^{2+}) at lower pH (Fig. 4). When the model is rerun without any EDTA, Co behaves quite differently. Almost all of the Co is sorbed between pH 11 and 7, with the relative amount of adsorption decreasing with decreasing pH. This is the typical "adsorption edge" response of uncomplexed cations. In contrast, at pH 12, the amount of Co sorbed drops rapidly to ~35% due to the increasing stability of the $Co(OH)_3^-$ species (Fig. 5 and 6). If the model is rerun assuming the dissolved EDTA content is $10^{-3}M$ (the upper end of the reported EDTA content of the ORNL wastes), the model shows that all Co remains in solution as Co(II)-EDTA complexes. However, laboratory experiments by Jardine et al. (1993) showed that Mn-oxyhydroxides in Oak Ridge have the capacity to oxidize Co^{2+} to Co^{3+} , and that a Co(III)-EDTA complex forms that is much more stable than Co(II)-EDTA ($\log K_{stab.}$ 41 vs. 17.4 for Co(II)-EDTA). Furthermore, they found that once the Co(III) complex forms, it is sorbed by the natural soils to the same extent as uncomplexed Co^{2+} . More recently, Szecsody et al. (1994) found that solutions containing Co(II)-EDTA have "anion-like" sorption behavior (increased sorption as pH decreases). In addition, the Co(II)-EDTA apparently causes the dissolution of iron oxides and the formation of an aqueous Fe(II)-EDTA complex and Co^{2+} , the latter of which can then be sorbed by remaining iron oxides. Thus, it is clear that the system Co-EDTA-natural solids is very complex, and that more research is required to substantiate previous conclusions about EDTA greatly enhancing Co mobility (e.g., Means et al. 1976, 1978c).

Due to the weakness of the Sr-EDTA complex, modeling shows that increasing the EDTA content does little to change the precipitation or sorption of Sr. Transition metals Pb (Figs. 2,5) and Zn (not plotted) are almost totally adsorbed by iron oxyhydroxide in the pH range modeled at low EDTA concentration (0 and 1 mg/l), but at $10^{-3}M$ EDTA, they are not sorbed by the model iron oxyhydroxide and are present in solution as EDTA complexes.

S-3 Ponds, Y-12

Data from monitoring wells indicate that wastes from the S-3 ponds have migrated at least 800 m down dip (e.g., Dreier et al., 1993). MINTEQA2 was used to model the interaction of the waste with the partially weathered Nolichucky Shale. The most important geochemical process was judged to be the neutralization of the waste by calcite dissolution. Progressive dissolution of calcite leads to calcite saturation at 0.07 m/l added and a pH of approximately 5.5 (Fig. 7). The pH of contaminated groundwater in the deep monitoring wells is typically >7 , indicating significant far-field mixing and dilution with ambient Ca-Mg- HCO_3 and Na- HCO_3 groundwaters. Thus model results presented are more representative of possible processes in the vicinity of the S-3 ponds prior to significant dilution. Modeling shows that raising the pH and dissolved carbonate content as a result of calcite dissolution leads to the supersaturation of siderite (FeCO_3) and otavite (CdCO_3) (Fig. 8) and causes other carbonate phases such as rhodochrosite (becomes supersaturated at $\text{pH}=7$), strontianite, spherocobaltite (CoCO_3), and cerrusite (PbCO_3 , not plotted in Fig. 8) to move toward saturation. This process (dissolution of calcite by Fe- and Mn-rich groundwater) is similar to the one proposed by Saunders and Swann (1992) to explain the origin of authigenic calcite in an aquifer in Mississippi. In addition, Loux et al. (1989) conducted laboratory experiments with natural aquifer materials and solutions spiked with Cd and other trace metals as a partial validation test of the diffuse-layer module in MINTEQA2. They concluded that otavite might be an important phase controlling Cd solubility (in addition to sorption) in their experiments. As in the case of the ORNL wastes, neutralizing waste pH also leads supersaturation of amorphous aluminum hydroxide and several iron oxide and hydroxide phases (e.g. ferrihydrite, $\text{Fe}(\text{OH})_3$, a kinetically favored, fast-forming phase; Stollenwerk, 1994).

Modeling results suggest that low-solubility carbonate phases might limit the solubility of other metals in the S-3 ponds waste but not considered in this study (e.g., transuranics). However, due to the relative competition of sorption sites for cations, such predictions are not always straightforward. The increase in pH attending calcite dissolution also raises the sorption efficiency of Fe-oxyhydroxides for trace metals (Fig. 9), which would tend to remove cations from solution and thus potentially lowering the ion activity product controlling the solubility of the carbonate phase. For example, increasing the model pH to 7.5 leads to supersaturation of rhodochrosite, dolomite, and magnesite (MgCO_3). However, otavite, which was supersaturated at $\text{pH} < \sim 5.5$ (Fig. 8), becomes undersaturated at $\text{pH} > \sim 7$ due to increased sorption of Cd^{2+} at higher pH by Fe-oxyhydroxides (e.g., Fig. 9). Similarly, smithsonite (ZnCO_3) and NiCO_3 never reach saturation in the model due to increased sorption of Zn^{2+} and Ni^{2+} at higher pH. Added to these competing effects are the complexities of increasing the dissolved carbonate but diluting the waste due to progressive mixing with groundwater away from the disposal site.

With increasing pH, Co^{2+} and Cd^{2+} are increasingly sorbed onto iron oxyhydroxides (Fig. 9), and by pH of 7, approximately 99% of each is sorbed in the absence of EDTA. Uncomplexed Co^{2+} is the most important Co specie in the neutral pH range. In contrast to the transition metals, Sr is not appreciably adsorbed in the model until pH 7, where the

amount increases significantly (18% at pH=7, 59% at pH 8). Uncomplexed Sr^{2+} and SrHCO_3^+ are the principal Sr species at this pH, as was the case for the Trench 7 model (Fig. 3). Large concentrations of uranium are present in the S-3 ponds waste (Table 1), and the model indicates that approximately 96% is sorbed by pH 4, increasing to ~99% at pH 7. Uranium remaining in solution is present predominantly as $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$.

DISCUSSION

The S-3 ponds area was one of the major sites of contaminant release at the Y-12 plant (Shevenell et al., 1994) and the pits and trenches area at ORNL "...poses perhaps the largest risk for future environmental contamination for ORNL" (Spalding, 1987). Thus a better understanding of the geochemical processes controlling the migration of radionuclides and other contaminants is a prerequisite to monitoring and assessing risk at the sites.

In the present study, geochemical modeling indicates that mineral precipitation and sorption reactions are the principal mechanisms that have the potential for retarding the migration of radionuclides and heavy metals at the two sites. In particular, this study demonstrates the importance of Fe oxyhydroxides in adsorbing ^{60}Co and transition metals.

Model Predictions

At the ORNL pits and trenches area, modeling indicates that most Sr is stabilized as a Sr or Ca-Sr carbonate at high pH but is not adsorbed appreciably by iron oxides. Infiltration of slightly acidic groundwater could lead to dissolution of strontianite or $\text{Ca}(\text{Sr})\text{CO}_3$ over time, leading to a slow release of ^{90}Sr , as suggested by Lomenick et al. (1967), Spalding (1981; 1987) and Olsen et al. (1986). Most transition metals (including Co) should be stabilized at the pits and trenches area due to high pH's and sorption on iron oxyhydroxides unless high levels of EDTA are present.

Modeling of plausible reactions at the S-3 ponds site at Y-12 indicates that some heavy metals could be stabilized as carbonates (Fe, Cd) at the S-3 ponds, others should be sorbed appreciably by iron oxyhydroxides over a wide pH range (Pb, and to a lesser extent Zn), while others are not sorbed appreciably until pH >7 (Ni, Co, Cd). Thus the model predicts significant mobility of Co, Ni, Cd, and possibly Zn, but not lead. Sr should not be appreciably adsorbed by iron oxyhydroxides but apparently does exchange for Ca and Mg on clays in the site soils and stream sediments (Lomenick et al., 1967, Cerling and Spalding, 1982; Olsen et al. 1983; and Jardine et al., 1993a). However, a study of the mobility of Sr in a sandy aquifer has shown that Sr will not undergo exchange reactions with clays if the concentration of $\text{Ca}+\text{Mg} \gg \text{Sr}$ in groundwater (King and Killey, 1990). Even though uranium is adsorbed to a large extent in the model, several mg/l are still possible in groundwater due to the high levels of uranium in the waste.

Modeling indicates that the solubility of important mineral species and sorption

reactions capable of retarding contaminants at the Oak Ridge Reservation are highly pH dependent. Thus the degree of neutralization of highly acidic or basic wastes relative to the order of encounter of solid phases (carbonates, clays, Fe oxyhydroxide) in site soils and saprolite is important in controlling the relative mobility of most species considered in this study.

Monitoring Well Data

Because the present study only considers waste-solid phase reactions, modeling results are most appropriate for approximating observed groundwater abundances of trace metals in close proximity to the waste disposal sites. With increasing distance outward, dilution and other subsurface geochemical and hydrologic processes would play a greater role in controlling groundwater chemistry.

At ORNL, numerous monitoring wells are located ~ 10-50m from the buried pits and trenches. The present-day groundwater pH in these wells ranges from ~ 6.5-8 (Olsen et al., 1983), which is a range typical of the Oak Ridge Reservation as a whole (Haase, 1991). The pits and trenches still contain extensive amounts of a solid material ($\text{Ca}(\text{Sr})\text{CO}_3$) stabilized by the addition of caustic soda and sodium hydroxide to the waste (and locally to the soil) at the time of waste disposal. Monitoring wells around Trench 7 contained relatively high levels of ^{60}Co (~ 5-90 pCi/l) in 1983, but only minor amounts of ^{90}Sr (~ .01-2.5 Ci/l; Olsen et al., 1983). A down-gradient monitoring well only 10m from Trench 7 contained 0.4-0.5 mg/l of both Pb and Zn, and <0.013 mg/l Co. Due to the relatively short half life of ^{60}Co (5.25 years), even a high level of radioactivity does not require much dissolved Co. For example 10^5 pCi/l ^{60}Co is equivalent to only 0.1 $\mu\text{g/l}$ dissolved Co.

Monitoring wells ~ 50-150m from the S-3 ponds contain up to 53 mg/l U, 9 mg/l Zn, 8 mg/l Cd, 2.3 mg/l Co; 42 mg/l Ni; and 21 mg/l Sr, but only up to 0.15 mg/l Pb (Shevenell et al., 1994, and unpublished data). In addition, up to 375 pCi/l ^{90}Sr have been detected in shallow monitoring wells close to the S-3 ponds, and 60-80 pCi/l ^{90}Sr have been detected in relatively deep intervals in multiport monitoring well GW-134 (Fig. 3). Most heavy metals are below detection limits in the deep monitoring wells (Dreier et al., 1993). The concentration of most metals in the monitoring wells is pH dependent, where metal abundance typically drops with increasing pH (Figs. 10, 11). This is consistent with the increased amount of sorption and mineral precipitation at higher pH, and perhaps due to dilution effects along the edges of the contaminant plume. Observed lead concentrations (Fig. 10) show little if any correlation with pH, which is consistent with the high degree of lead sorption at low pH in the MINTEQA2 model (Fig. 9). Model-predicted concentrations of Cd and Zn are shown in Figures 10 and 11 (respectively). The degree to which the model results compare to the observed metal concentrations can only be viewed as a semi-quantitative test of the model, because the contaminant plume contains at least some input from the other 3 disposal ponds at the S-3 site and possibly other point sources of contamination (e.g., Geraghty & Miller, 1989).

Additional Complexities

Several factors not considered in this study are probably important also in controlling contaminant mobility in the study area. These include: 1) presence of additional solid species capable of sorbing cations; 2) kinetics of mineral precipitation and dissolution; 3) effects of fracture flow of groundwater and contaminants in saprolite and partially weathered bedrock; and 4) dilution by groundwater. In addition to the possibility of added cation sorption by clays and MnO_2 discussed above, model-predicted authigenic aluminum and iron oxide phases may add to cation sorption capacity of the soils over time. Stollenwerk (1994) demonstrated and modeled the contribution of authigenic $\text{Fe}(\text{OH})_3$ (ferrihydrite) in a study of the neutralization of iron-rich acid-mine discharges by aquifer minerals. Clearly, the rate at which cations and solid surfaces approach local equilibrium, and rates of calcite dissolution and authigenic phase precipitation, are important in a more extensive treatment of contaminant behavior.

Recent studies on the Oak Ridge Reservation (Olsen et al., 1986; Solomon et al., 1992, Moore and Toran, 1992; Shevenell et al., 1994) have shown that contaminants and groundwater preferentially move in fractures and faults in saprolite and bedrock. If pH neutralization, precipitation of authigenic phases, and sorption reactions have not reached their approximate local equilibrium values prior to reaching the fractured saprolite, then contaminants may be more mobile than modeling predicts. For example, contaminants are exposed to much lower effective surface areas in fractures, and solids capable of sorbing cations may reach local equilibrium, and have little capacity for sorbing additional cations moving through the fracture.

Olsen et al. (1986) documented contaminant migration along faults and other geologic structures at ORNL. Means et al (1978c) suggested the possibility that if Co-EDTA complexes were not causing Co mobility at the ORNL pits and trenches area, then fracture flow of contaminants should be considered. Because ^{60}Co in the absence of EDTA should be effectively sorbed by iron oxyhydroxides as this study suggests, and Co-EDTA complexes also are adsorbed (Jardine et al., 1993b), then the observed mobility of ^{60}Co at ORNL is likely a function of fracture flow. Future modeling using coupled geochemistry and transport models (e.g., Yeh and Tripathi, 1991) is planned to calculate how pH changes with distance from the source and to evaluate the effects of dilution or plume mixing on pH and sorption.

CONCLUSIONS

Due to their relative abundance, iron oxyhydroxides are apparently important adsorbers of transition metals (including inorganic ^{60}Co species) in soils and saprolite on the Oak Ridge Reservation. The relative abundance of iron oxide phases at these sites and a reevaluation of previous studies that proposed that manganese oxyhydroxides were more important metal sorbers illustrates their potential importance. Thus, metal sorption was

modeled using the diffuse-layer surface complexation module of MINTEQA2 in this study, and it was assumed that amorphous iron oxyhydroxide is the principal sorbing agent at the site.

Modeling indicates that amorphous iron oxyhydroxides are capable of sorbing heavy metals over a wide pH range. In particular, they are capable of sorbing inorganic ^{60}Co species. However, iron oxyhydroxide does not appear to limit the mobility of ^{90}Sr appreciably. Modeling with MINTEQA2 also suggests that precipitation of authigenic solid phases also may limit the solubility of Sr, Al, Fe, and possibly some other metal phases. Modeling of the effects of variable amounts of the organic solvent EDTA on metal mobility in the high-pH wastes indicates that: 1) Co will not be adsorbed even at low concentrations of EDTA (1mg/l); 2) at higher EDTA concentrations, other transition elements (Cd, Zn, Pb, Ni) are also more soluble; and 3) EDTA does little to affect the mobility of Sr due to the low stability of the Sr-EDTA complex. In summary, predictions about pH-dependent mineral precipitation and metal sorption reactions from the modeling generally match field observations for the acidic wastes disposed at the S-3 Ponds area and the high-pH wastes at ORNL. Thus, the present study demonstrates the utility of the iron-oxyhydroxide diffuse-layer surface complexation model to assess metal sorption at sites where amorphous iron phases are abundant.

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FIGURE CAPTIONS

Figure 1. Map showing location of the S-3 ponds area at the Y-12 facility and the Pits and Trenches area at ORNL.

Figure 2. Plot of MINTEQA2 model results showing relative amounts of contaminants adsorbed or precipitated as a function of pH at Trench 7, 1mg/l EDTA.

Figure 3. Plot of aqueous strontium speciation as a function of pH for Trench 7 area, 1mg/l EDTA.

Figure 4. Plot of aqueous cobalt speciation as a function of pH at Trench 7, 1mg/l EDTA.

Figure 5. Plot showing relative amounts of contaminants sorbed or precipitated at Trench 7, no EDTA considered in modeling.

Figure 6. Plot of aqueous cobalt speciation as a function of pH for Trench 7, no EDTA.

Figure 7. MINTEQA2 model results showing the effect of calcite dissolution on pH by acidic S-3 ponds waste.

Figure 8. Model results showing change in the Saturation Indices of carbonate phases as a result of the progressive dissolution of calcite. Note: CdCO_3 is otavite and CoCO_3 is spherocobaltite.

Figure 9. Model results showing relative amounts of metal sorption as a function of amount of calcite dissolved by S-3 ponds waste.

Figure 10. Plot of Cd (+), Pb (x), Co (o), and Ni (solid triangles) concentration as a function of pH in monitoring wells near the S-3 ponds (based on unpublished data). Also shown is the model-predicted concentration of Cd from MINTEQA2.

Figure 11. Plot of U (boxes), Zn (solid dots), and Al (solid triangles) concentration as a function of pH in monitoring wells close to the S-3 ponds. Also shown is the model-predicted concentration of Zn from MINTEQA2.

TABLE 1
COMPOSITION OF WASTES USED IN MODELING

(in mg/l except pH)

	Trench 7, ORNL ¹	S-3 Pond (Southwest), Y-12 ²
NO ₃ ⁻	4760	20,460
OH ⁻	360	-
CO ₃ ²⁻	2600	-
SO ₄ ²⁻	1280	-
PO ₄ ³⁻	150	-
Cl ⁻	104	789
Na ⁺	4350	1262
K ⁺	45	109
Ca ²⁺	12	250
Mg ²⁺	<10	199
Al ³⁺	165	1370
Fe	<0.5	347
Cu	<3	10.5
Pb	0.5	27
Zn	0.5	4.0
Cd	-	2.0
Co	0.1	0.5
Sr	0.5	1.2
U	-	111
EDTA	1.0	-
pH	12	1.2

- =not reported or not detected

¹ Data from Means et al. (1978a) except for: 1) Cl, reported in Means et al. (1976); 2) Pb and Zn, estimated from concentrations found in nearby monitoring wells, reported in Olsen et al. (1983); 3) Sr and Co based on activity of ⁹⁰Sr and ⁶⁰Co in the waste and Sr and Co concentrations in nearby monitoring wells, data from Olsen et al. (1983; 1986).

² Data from Jeter and Napier (1986)

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

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