

APPLICATION OF SPHAGNUM PEAT, CALCIUM CARBONATE, AND HYDRATED LIME FOR IMMOBILIZING RADIOACTIVE AND HAZARDOUS CONTAMINANTS IN THE SUBSURFACE

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ABSTRACT

Batch experiments, mineralogical studies, and geochemical modeling were conducted to evaluate the effectiveness of sphagnum peat, calcium carbonate, and hydrated lime in removing dissolved concentrations of As, Mo, NO₃, and U present in uranium-tailings pore water at Gunnison, Colorado. Amounts of As, Mo, and U removal by sphagnum peat, calcium carbonate, and hydrated lime at 5.0, 2.5, and 2.5 wt.%, respectively, were typically above 97%. Nitrate removal ranged between 55 and 80%. Significant contaminant removal was achieved by sphagnum peat alone at pH 3.18. Results from base potentiometric titrations and IR spectroscopy investigations suggest that U(VI) binds onto carboxylate and phenolate groups. Addition of 2.5 wt.% hydrated lime to the acidic tailings increased Mo concentrations by a factor of 2 under moderately alkaline conditions (pH 12). During neutralization of tailings-pore water, precipitation of ferric oxyhydroxides may provide additional removal of As, Mo, and U(VI) from solution through adsorption and coprecipitation processes. Sphagnum peat and other forms of solid organic matter effectively remove anthropogenic organic compounds from solution through hydrophobic sorption and partitioning processes.

INTRODUCTION

Impacts on groundwater quality from uranium-tailings leachate are extensive at Gunnison, Colorado (1). Proposed groundwater-restoration programs at Gunnison, Colorado would require a long-term effort using conventional pump and treat technologies. A geochemical approach to controlling contaminant migration associated with uranium tailings-leachate at this and other uranium tailings sites consists of using materials with high geochemical attenuation and neutralization capacities.

This investigation examined the effectiveness of sphagnum peat, calcium carbonate, and hydrated lime to immobilize As, Mo, NO₃, and U concentrated within uranium-tailings leachate at Gunnison, Colorado. Fixation of U onto peat and other forms of solid organic matter is well established (2-6). Solid organic matter is frequently observed within sandstone-type uranium deposits (7). Therefore, solid organic matter such as sphagnum peat may provide an excellent constituent of a geochemical barrier designed to remove redox sensitive elements and complexes from solution. Opitz et al. (8) conducted neutralization experiments on uranium tailings from Wyoming using calcium carbonate and hydrated lime, where contaminant concentrations decreased by 98%. The objective of this

investigation was to determine the combined effect of sphagnum peat, calcium carbonate, and hydrated lime on the solubilities and therefore, the mobilities of As, Mo, NO₃, and U.

SAMPLE CHARACTERIZATION AND EXPERIMENTS

Acid-leach tailings samples and pore-water samples were collected at the Gunnison Uranium Mill Tailings Remedial Action (UMTRA) site, Gunnison, Colorado from 1988 to 1989. The sphagnum peat samples were obtained from Los Alamos National Laboratory Peat Sample Library. Details of sample collection, preparation, and chemical analysis procedures for the sphagnum peat are provided by Raymond et al. (9). Peat is a precursor to coal and consists primarily of plant components and secondarily of mineral matter (9). Elemental composition of C, H, O, and N are 41.6, 6.8, 49.7, and 0.1 wt.%, respectively, for sphagnum peat used in the batch experiments. The wt.% distributions of ash and sulfur on dry-sphagnum peat (moisture free basis) samples are 1.82 and 0.05, respectively (9). The surface area of the sphagnum peat (1 mm particle diameter, minus No. 20 sieve) was found to be 25 m²/g, using the BET-N₂ method. The cation exchange capacity of sphag-

num peat ranges from 121 to 224 meq/100 g, with a mean value of 149 meq/100 g (10).

Minerals tentatively identified in the tailings samples by powder X-ray diffraction (XRD) analysis, using Cu-K α radiation with quartz as an internal standard, include ferrihydrite ($\text{Fe}_5\text{O}_7(\text{OH})\cdot 4\text{H}_2\text{O}$), ferrimolybdate ($\text{Fe}_2(\text{MoO}_4)_3\cdot 8\text{H}_2\text{O}$), rameauite ($\text{K}_2\text{CaU}_6\text{O}_{20}\cdot 9\text{H}_2\text{O}$), uranopilite ($(\text{UO}_2)_6(\text{SO}_4)(\text{OH})_{10}\cdot 12\text{H}_2\text{O}$), ilsemannite ($\text{Mo}_3\text{O}_8\cdot x\text{H}_2\text{O}$), gypsum ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$), scorodite ($\text{FeAsO}_4\cdot 2\text{H}_2\text{O}$), and goethite ($\alpha\text{-FeOOH}$). The mineralogical content of the sphagnum peat determined from XRD analysis included quartz (SiO_2), albite ($\text{NaAlSi}_3\text{O}_8$), corundum (Al_2O_3), muscovite ($\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$), and kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) (9).

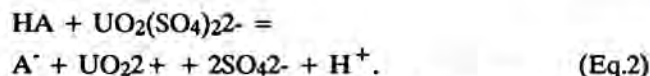
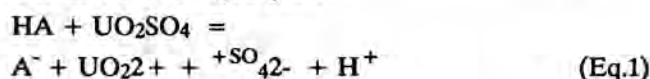
Tailings sand- and clay-sized material were collected and volumetrically mixed (75 % sand and 25 % clay) to obtain representative composite field samples for batch experiments. The batch experiments consisted of a mixture of 250 g of tailings material, 800 ml of deionized water, 12.50 g of sphagnum peat, 6.25 g of calcium carbonate, and 6.25 g of hydrated lime. Sphagnum peat was air dried for several hours prior to the batch experiments. Sphagnum peat by itself and with calcium carbonate and hydrated lime were added at 2.5 wt.% relative to the tailings samples. The experiments were conducted in 1 L glass erlenmeyer flasks. The flasks were tightly sealed and shaken for 72 hours at 25 C. All solutions were passed through a 0.45 micron filter prior to analysis.

Molybdenum, Fe, As, and major cations were analyzed by using Jarrell-Ash emission spectrometers with an inductively coupled plasma (ICP) source and graphite-furnace atomic absorption (GFAA) spectroscopy, respectively, at Barringer Laboratories, Denver, Colorado. Uranium solutions were analyzed by fluorometry. Sulfate and NO_3 concentrations and carbonate alkalinity were analyzed by ion chromatography and titration, respectively. Field and laboratory analyses included measurements of temperature, pH (Orion Ross), Eh (Orion 96-78 platinum electrode), alkalinity, and specific conductance.

Infrared spectra of sphagnum peat and its corresponding uranium adduct were recorded on a Bio-Rad FTS-40 spectrophotometer using the KBr-pellet technique. Potentiometric titrations, using an Orion 960 automatic titrator with 1-g sphagnum peat samples, were carried out under an argon gas atmosphere using degassed deionized water in order to eliminate any uranyl carbonate complexing. The accuracy of the measurement at 25 ± 0.1 °C at $u = 0.1\text{M}$ (Na_2SO_4) was ± 0.01 pH. The titrant consisted of 0.01M KOH and 0.05M U(VI), in the form of $\text{UO}_2\text{SO}_4\cdot 3\text{H}_2\text{O}$, was added to sphagnum peat prior to the titration experiments.

RESULTS

The infrared spectra of sphagnum peat and the corresponding uranium adduct within the range of 4000 to 500 cm^{-1} are shown in Figs. 1 and 2, respectively. The most dominant absorption maxima are also shown in these figures in which both spectra exhibit typical bands of terrestrial organic matter (11). The uranium-rich sample is characterized by 1) the presence of an absorption band at 890 cm^{-1} , which is attributed to the stretching band of the uranyl ion (12); 2) an increase of absorption of the 1710 cm^{-1} band, which only exhibits a slight shoulder; and 3) a slight widening of the 1400 cm^{-1} band. Features 2 and 3 indicate transformation of the carboxylic groups into carboxylate anions. The IR pattern similar to that in Fig. 2 have been observed in samples from uranium-rich bogs (4) and in laboratory experiments dealing with the fixation of uranyl ions by humic acids and brown coal (13). Shanbhag and Choppin (14) have used a solvent extraction technique to demonstrate the binding of uranyl with R-COO^- . Infrared spectroscopy suggests that uranyl undergoes complexing with carboxylate groups. The binding of uranyl ions onto sphagnum peat (denoted as HA) leads to the dissociation of UO_2SO_4 and $\text{UO}_2(\text{SO}_4)_2^{2-}$:



The presence of other functional groups such as phenolic hydroxyl groups, however, is not demonstrated by the IR data but may also participate in metal complexing (15).

Results of base potentiometric titrations for blank- and uranium-loaded sphagnum peat samples are shown in Fig. 3.

The objective of these experiments is to determine the nature of U(VI) binding sites present on the sphagnum peat. Results of the potentiometric titration experiments for blank sphagnum peat indicate two regions where deprotonation reactions occur as a function of pH (Fig. 3). Deprotonation of the carboxylic acids result in a substantial buffering capacity of the sphagnum peat. Within the pH range between 4 and 8, sphagnum peat exhibited less buffering capacity, indicating that deprotonation reactions are not extensive. Above pH 8, sphagnum peat undergoes additional deprotonation reactions with phenolic functional groups. Deprotonation reactions produce negatively-charged surface sites on the sphagnum peat, which are potential binding sites for cations including the uranyl ion. Fixation of uranyl onto sphagnum peat occurs under acidic conditions, where the buffering capacity decreases (Fig. 3). Uranyl fixation is shown by the following reactions:

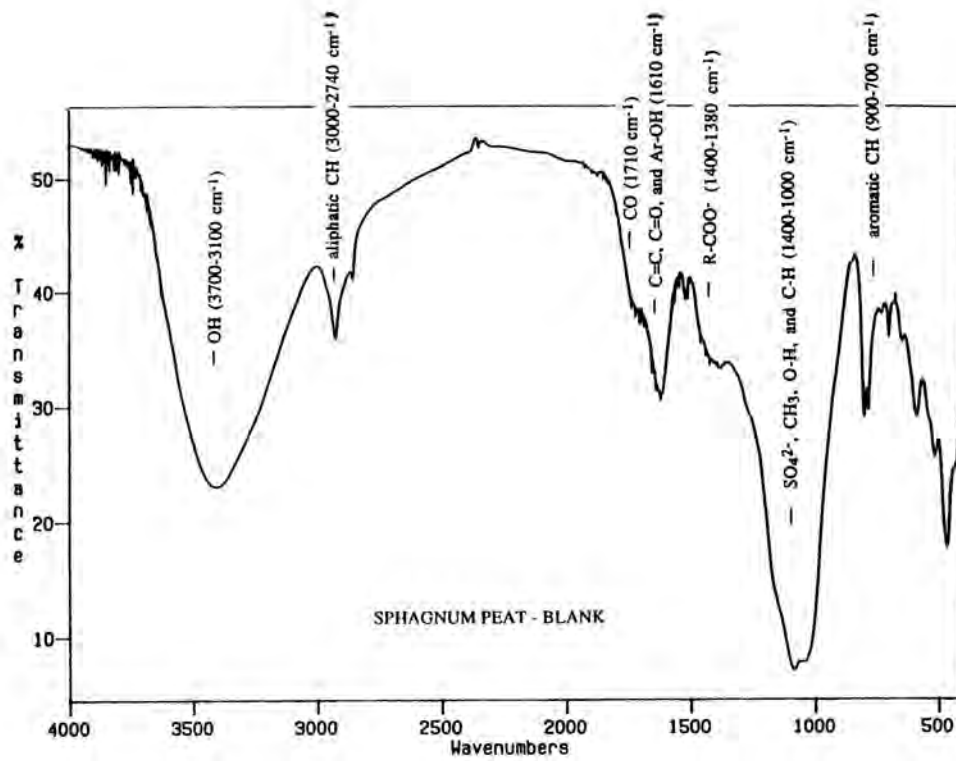


Fig. 1. Infrared spectrum of sphagnum peat.

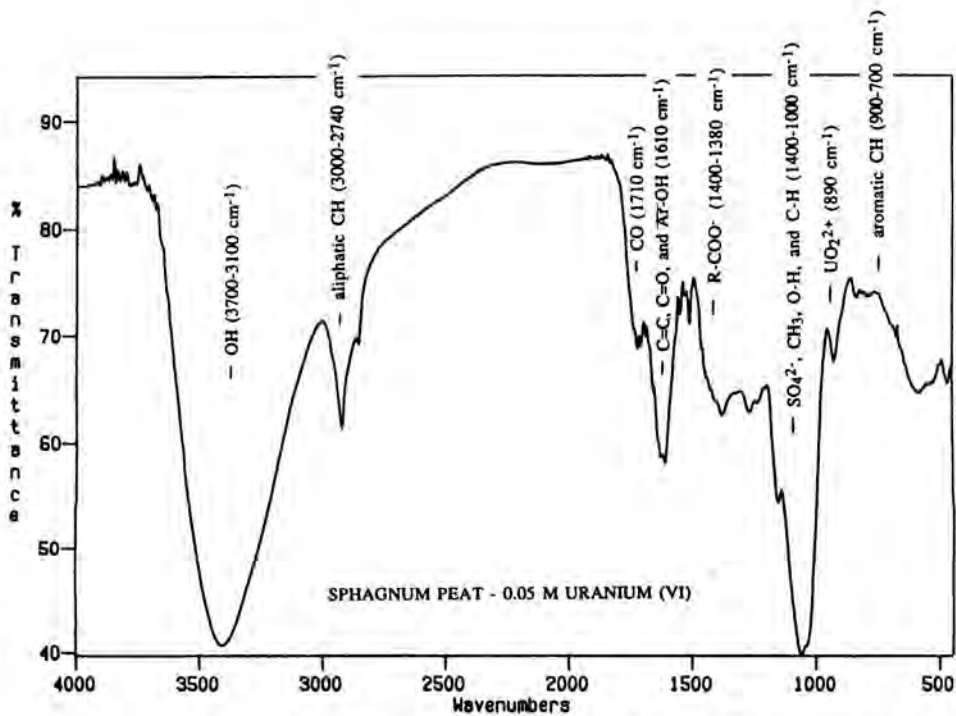


Fig. 2. Infrared spectrum of sphagnum peat and uranium adduct.

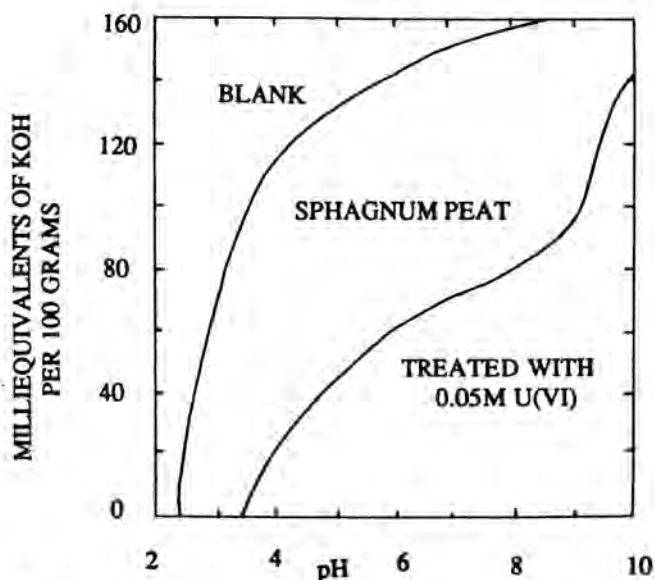


Fig. 3. pH titration of sphagnum peat and its uranium adduct.



Based on results of the titration experiments, uranyl ions displace protons associated with carboxylic acid and phenolic functional groups (Fig. 3). Fixation of uranyl ions onto sphagnum peat decreases the buffering capacity of the sphagnum peat. Results of the base-potentiometric titration experiments show that the sphagnum peat has a high capacity for removing uranyl complexes from aqueous solution under acidic to alkaline pH conditions.

Results of selected chemical analyses on tailings-pore water, obtained from suction lysimeters completed within the Gunnison tailings impoundment, are shown in Table I (16). The composition of the tailings-pore water is dependent on: (1) type of ore; (2) type of leach circuit; (3) by-product recovery; (4) initial quality of process water; and (5) surface evaporation. These factors account for the concentration distribution of species reported in Table I. Sulfuric acid and NaClO_3 were used during the ore-extraction process, which generated a SO_4 -rich tailings pore water (17).

Results of batch experiments using 5.0 wt.% sphagnum peat, 2.5 wt.% calcium carbonate, and 2.5 wt.% hydrated lime, relative to the mass of uranium tailings, are provided in Figs. 4 and 5. Sphagnum peat (with deionized water),

sphagnum peat-calcium carbonate, sphagnum peat-hydrated lime, and sphagnum peat-calcium carbonate-hydrated lime combined with tailings solids comprised the different batch systems investigated. Substantial concentration decreases of As, NO_3 , SO_4 , U, and total dissolved solids (TDS) in all batch systems are evident. Addition of sphagnum peat, without calcium carbonate and/or hydrated lime present, resulted in significant concentration decreases of Mo, NO_3 , and U. Maximum removal of As was achieved within the sphagnum peat-hydrated lime-tailings system. Concentrations of Mo increased by a factor of 1.8, however, within the sphagnum peat-hydrated lime-calcium carbonate tailings systems under alkaline pH conditions. Concentrations of Se were below analytical detection limit (0.005 mg/L) for all batch solutions analyzed by GFAA spectroscopy. Percentage removal of the different species is greater than 97%. Molybdenum concentrations, however, are an exception, where 60 to 250% of Mo was apparently released to solution for runs involving hydrated lime.

Relative effectiveness for contaminant removal by sphagnum peat, calcium carbonate, and hydrated lime is presented in Table II for As, Mo, NO_3 , and U. These affinities were determined from mass balance distributions of species associated with sphagnum peat, calcium carbonate, and hydrated lime. Sphagnum peat was present in all of the batch experiments conducted in this study. Solid organic matter, consisting of humic substances, is considered to be the dominant adsorbent for hydrophobic non-ionized organic compounds (18-20).

Calculated K_d values, at 5 wt.% sphagnum peat concentrations, for tributyl phosphate, benzene, carbon tetrachloride, trichloroethene, and tetrachloroethene are 300, 5, 14, 8, and 13 ml/g, respectively. These contaminants are frequently found at uranium and plutonium processing facilities. The K_d values were calculated from the relationship, $K_d = \text{KOC} \times (\text{wt.}\% \text{ solid organic matter}/100)$, where KOC is the soil organic matter-water partition coefficient (18). The KOC values for tributyl phosphate, benzene, carbon tetrachloride, trichloroethene, and tetrachloroethene are 6000, 102, 275, 166, and 257 ml/g, respectively. These calculations, along with other empirical data (20), suggest that sphagnum peat and other forms of solid organic matter are strong adsorbents for most hydrophobic organic compounds. Further experiments, however, are required to quantify the effectiveness of sphagnum peat to remove organic contaminants from solution.

GEOCHEMICAL MODELING

The geochemical code, PHREEQE (21) was used to compare theoretical to observed mineralogical assemblages to determine if precipitation reactions were thermodynamically possible within the batch experiments. Speciation calculations were also performed to assess importance of

TABLE I

Geometric Mean and Range of Selected Chemical Analyses of Suction Lysimeter Samples, Gunnison, Colorado (In mg/L, except as noted).

Parameter/Species	Value	Range	Number of Analyses
pH (SU)	3.73	1.43-4.17	10
Aluminum	309	15-653	11
Arsenic	1.19	0.04-17.05	11
Iron	575	0.31-6100	11
Molybdenum	0.32	0.03-12.50	11
Nitrate	5.80	10-190	7
Selenium	0.20	0.10-4.50	11
Sulfate	10,404	2400-23000	11
Uranium	4.72	0.02-50	11
Vanadium	0.51	0.10-13	11
Field Eh (mV)	+ 600	+ 550- + 650	10

humate complexing with U(VI). For meaningful model simulations, however, it is important that the thermochemical data base is accurate and internally consistent. The data base contained in PHREEQE has been reviewed critically by Noronha and Pearson (22). Equilibrium is assumed among aqueous species found in the different solutions; and species present in solution, but not included in the model, may cause misleading results. Dissolved concentrations presented in Figs. 4 and 5 were used as input for model simulations. The sphagnum peat-hydrated lime-tailings and sphagnum peat-hydrated lime-calcium carbonate-tailings

systems were not modeled with PHREEQE because of the extremely alkaline conditions.

Saturation indices (SI) of several solid phases were calculated using analytical data for different solutions. These results are shown in Table III. Thermochemical data for uranyl-humate complexing were incorporated in the model simulations. Gypsum precipitation probably controls dissolved SO₄ concentrations within both the unamended tailings-pore water and sphagnum peat-calcium carbonate-tailings system. Sulfate fixation onto sphagnum peat may account for concentration decreases of this species when the solution is undersaturated with respect to gypsum. Pre-

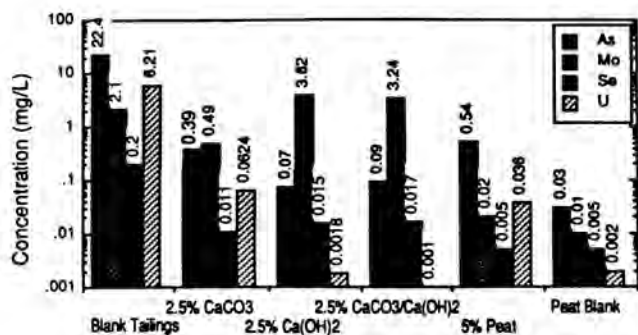


Fig. 4. Results of batch leach experiments (16).

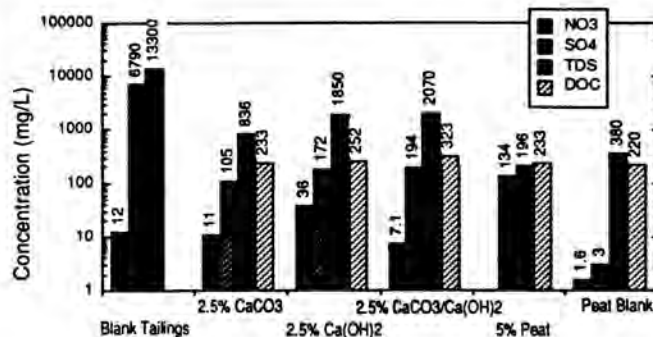


Fig. 5. Results of batch leach experiments (16).

TABLE II

Relative Effectiveness for Contaminant Removal

Species	Order
Arsenic	CaCO ₃ > Ca(OH) ₂ /CaCO ₃ >> Sphagnum Peat
Molybdenum	Sphagnum Peat CaCO ₃ >> Ca(OH) ₂
Nitrate	Sphagnum Peat > CaCO ₃ = Ca(OH) ₂
Uranium	Ca(OH) ₂ >> Sphagnum Peat > CaCO ₃

TABLE III

Saturation Index Values for Gunnison Batch Experiments

Solid Phase	Batch Tailings Solution	Lysimeter Tailings Solution	Blank Peat	Peat Plus Tailings	Peat Plus CaCO ₃
Gypsum	0.05	0.42	-4.10	-1.39	-0.96
Goethite	1.09	5.53	0.89	-0.44	3.98
B-UO ₂ (OH) ₂	-6.77	-4.68	-14.52	-15.25	-8.15
Uraninite	-13.76	-12.92	-20.42	-18.61	-9.98
Schoepite	-6.63	-4.50	-14.38	-14.76	-8.01
UO ₂ am	-19.40	-18.71	-26.06	-24.25	-15.62
Ilsemaninite	-0.01	-0.96	-9.15	-6.50	-22.91
pH	2.22	3.73	3.55	3.18	6.35
Eh (mV)	+650	+600	+540	+487	+254
S.I. = log ₁₀ $\frac{IAP}{Kf}$					

precipitation of metal sulfides is unlikely under the moderately oxidizing conditions that prevailed during the batch experiments. Ilsemaninite probably controls dissolved concentrations of Mo within tailings-pore water and batch-tailings solution, based on XRD analysis and SI calculations. Ilsemaninite is stable under oxidizing and acidic conditions (23), which prevailed in the tailings-pore water and blank-tailings solution. Dissolution of ilsemaninite occurs within sphagnum peat-tailings and sphagnum peat-calcium carbonate-tailings systems. Fixation of Mo onto sphagnum peat, however, results in a concentration decrease of this species (Fig. 3). All solutions are predicted to be undersaturated with respect to U(IV) and U(VI) minerals contained in the PHREEQE data base. Therefore, U concentrations are not controlled by precipitation reactions in the batch experiments, based on modeling results.

Fixation of U(VI) onto sphagnum peat has been shown to be attributed to ligand exchange and sorption processes with carboxylic and possibly phenolic functional groups

(2-6). We have used published dissociation and conditional stability constants for humic acid and uranyl humate complexing to simulate surface reactions occurring on sphagnum peat. Dissociation constants of humic acid (pK₁ = 4.10±0.06, H₂L; pK₂ = 10.97±0.09, HL⁻ at u = 0.1) reported by Kribek and Podlaha (24) have been added to the PHREEQE thermochemical data base to assess the importance of uranyl-humate complexing within the sphagnum peat-tailings and sphagnum peat-calcium carbonate-tailings systems. H₂L represents part of a micelle containing two protonized functional groups, which may include carboxylic and phenolic binding sites. Dissolved organic carbon (DOC) concentrations provided in Fig. 5 were used as input for humic acid concentrations for the PHREEQE code. A number-average molecular wt. of 2000 for dissolved humic acid (19,25) was selected for model calculations. Conditional stability constants (log B₁ = 5.11±0.02, UO₂(HA)⁺ and log B₂ = 8.94±0.03, UO₂(HA)₂ at pH = 4.04, u = 0.1) were taken from values given by Shanbhag

TABLE IV

Dominant Aqueous Species for Different Batch Solutions

Species (log m)	Blank Tailings Solution	Peat-Tailings Solution	CaCO ₃ -Peat-Tailings Solution
U	UO ₂ SO ₄ (-4.98)	UO ₂ (HA) ₂ (-6.82)	UO ₂ (HA) ₂ (-6.58)
As	H ₂ AsO ₄ ⁻ (-3.76)	H ₂ AsO ₄ ⁻ (-5.19)	H ₂ AsO ₄ ⁻ (-6.23)
Mo	MoO ₄ ⁺ (-4.65)	MoO ₄ ²⁻ (-6.73)	MoO ₄ ²⁻ (-6.46)

and Choppin (14) for uranyl-humate complexing. Humic acid is denoted as HA. Results of the simulations indicate that the complex, UO₂(HA)₂ dominates (100 %) in both of the sphagnum peat-tailings and sphagnum peat-calcium carbonate-tailings systems. The dominant aqueous species in the different batch experiments are tabulated in Table IV. The batch solutions are undersaturated with respect to U(VI) minerals due to acidic conditions and uranyl-humate complexing.

DISCUSSION AND CONCLUSIONS

The successful decrease in contaminant concentrations of As, Mo, NO₃⁻, and U(VI) has been demonstrated from batch experiments as a function of pH. Active surfaces present on sphagnum peat evidently cause enhanced fixation of U(VI) under the acidic pH conditions during the batch experiments. The uranyl ion is a hard acid that has a strong preference for carboxylate groups (14). Infrared studies conducted by Koglin et al. (13) on uranyl-humate complexing also have strong interactions with the carboxylate sites.

Adsorption of As, Mo, and U onto ferric oxyhydroxides may also account for contaminant removal. These findings are consistent with those of Opitz et al. (8), in which neutralization, using calcium carbonate and hydrated lime, enhanced precipitation of amphoteric solid phases including ferric oxyhydroxides. Buffering of pH is an important waste-processing step for removing contaminants from solution. Iron concentration within the sphagnum peat is 3.4 wt.% (9), which may be due to the presence of ferric oxyhydroxide since pyrite was not observed during XRD analyses. Adsorption of oxyanions of As and Mo occurs onto ferric oxyhydroxides below the pH_{zpc} ranging between 6 and 7 (26). However, desorption of Mo from hydrous oxides, in addition to dissolution of ilsemannite, may have taken place under alkaline pH conditions in the presence of hydrated

lime. This phenomenon has been observed by Hingston et al. (27). These results suggest that a careful balance of neutralizing material is necessary to achieve optimum removal of Mo.

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