

RETARDATION OF URANIUM AND ASSOCIATED ELEMENTS BY CHEMICAL REDUCTION AND PRECIPITATION

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ABSTRACT

This paper details the results of a solution equilibria modeling study investigating the feasibility of constructing a geochemical barrier to attenuate dissolved selenium, vanadium, arsenic, molybdenum, and uranium in the interstitial water of the mill tailings at a Grand Junction, Colorado site which is part of the U. S. Department of Energy's Uranium Mill Tailings Remedial Action (UMTRA) program. Results indicate that the geochemical barrier concept is plausible, causing a significant decrease in the dissolved concentrations of these elements. The proposed geochemical barrier is an organic carbon bearing zone situated between the compacted clay base of the tailings pond and the tailings. Bacterial reduction of the tailings water sulfate within the barrier will engender a highly effective reducing environment that is rich in hydrogen sulfide/bisulfide. Thermodynamic modeling demonstrates that, within the barrier, equilibrium phases of the elements of concern are native selenium (Se), karelinite (V_2O_3), orpiment (As_2S_3), molybdenite (or jordisite) (MoS_2), and uraninite (UO_2). All are relatively insoluble, consequently their precipitation drastically lowers the dissolved equilibrium concentration of these elements. Specifically, dissolved selenium content would drop from 3 ppm to 0.006 ppm, dissolved vanadium from 11 ppm to 0.15 ppm, and the abundances of soluble molybdenum, arsenic, and uranium all drop to less than 0.005 ppm. The predicted removal of these elements under the conditions within the chemical barrier is substantiated by numerous natural analogs, for example, roll-type and tabular-type uranium ore deposits. Additionally at Weldon Spring, Missouri the removal of these elements appears to be occurring naturally from raffinate sludge seepage migrating into the underlying carbonaceous limestone.

It is estimated that approximately 10,000 dry tonnes of 70%-grade organic carbon will be necessary to form the barrier. This quantity comprises a ten-fold excess in organic carbon, ensuring sufficient bacterial carbon substrate to maintain the reducing environment for many thousands of years.

INTRODUCTION

As part of the U. S. Department of Energy's Uranium Mill Tailings Remedial Action (UMTRA) Project, the concept of incorporating a geochemical barrier to solution contaminant transport into a uranium mill tailings holding facility was proposed at a site near Grand Junction, Colorado. It was the relationship between precipitated uranium, selenium, molybdenum, vanadium, and arsenic and organic carbon in natural systems that inspired the concept of engineering an organic-rich blanket over the compacted clay base of the tailings cell to help attenuate these elements.

Dissolved heavy metals in uranium mill tailings pore water display either anionic or cationic behavior. Those behaving as cations (i.e., iron) are quickly and easily precipitated as hydroxo compounds in a neutral to alkaline environment. Uranium, selenium, molybdenum, vanadium, and arsenic, however, exist either as anionic complexes or oxyanions while in their oxidized valence states (1, 2, 3). Their solubility is less dependent on pH conditions, being more profoundly affected by the Eh (or redox potential) of the system. In low Eh solutions, these elements precipitate as relatively insoluble reduced phases.

The solubilization and transportation in oxidized valence states and subsequent precipitation in reducing envi-

ronments is used to explain the localization of uranium, selenium, molybdenum, vanadium, and arsenic in both roll-type and tabular-type ore deposits (1, 4). The reduced facies of these, typically sandstone-hosted deposits, is usually characterized by relatively high amounts of organic carbon ($X\% - X\%$) and iron disulfides (pyrite and/or marcasite). Uranium mineralogy is typically dominated by reduced uranous compounds, such as uraninite or coffinite (UO_2 or $USiO_4$). Selenium may occur as native selenium, or ferroselite ($FeSe_2$), whereas molybdenite or jordisite (MoS_2), montrosite or karelinite (V_2O_3), and orpiment or realgar (As_2S_3 or AsS) comprise the remaining accessory minerals. The widely accepted genetic model for these deposits, in organic bearing systems, is that of oxidized uranium and the associated elements reduced through reaction with bacteriogenic hydrogen sulfide or bisulfide or with pyrite/marcasite of bacterial origin (2, 4, 6, 7, 8). Some of the deposits that supposedly formed as a consequence of biogenic sulfide production include: the Panna Maria uranium deposit of Texas (9, 10); the Shirley Basin uranium deposits of Wyoming (4); the Highland uranium deposit of Wyoming (11); most, or all, of the many uranium-vanadium deposits hosted within the Salt Wash member of the Morrison and the Shinarump strata of the central Colorado Plateau; the Rifle uranium-vanadium-lead-chromium deposit of Colorado; the Todilto uranium deposits of New Mexico (6); and

the Tony M uranium-vanadium deposit of Utah (5). Additionally, the copper deposits at White Pine, Michigan (12) and the Kupferschifer of Europe (13) are believed to contain a bacteriogenic sulfide component. Although this list is not comprehensive, it represents the remarkable ability of sulfate reducing bacteria to precipitate tremendous amounts of metal.

Bacterial reduction of sulfate to sulfide is documented as occurring in many anoxic, sulfate-bearing, organic-rich environments (14). This process is noted in a variety of solutions, for example in normal groundwater, seawater, sabhka brines, or gypsum-saturated alkaline lakes. Bacteria of the genus *Desulfovibrio* are usually attributed with the sulfide production. Because sulfate is kinetically inhibited from participating in redox reactions in low-temperature, inorganic systems, most if not virtually all sulfide in low-temperature, organic-bearing systems is probably of bacterial origin (14). (It is recognized that pyrite/marcasite in some south Texas and a few other low-temperature deposits is likely related to fault-leaked solutions containing nonbiogenic sulfide formed at depth. However, many nonfault related, organic-rich, uranium, copper, and silver low-temperature deposits definitely contain a biogenic sulfide component.)

The removal of uranium, molybdenum, vanadium, and arsenic from raffinate sludge seepage by geochemical reactions in a reducing environment is demonstrated by the low levels of these elements in the groundwater impacted by the Weldon Spring, Missouri raffinate water (15). Alkaline raffinate sludge from the processing of yellow cake for uranium metal have been stored in pits constructed in unconsolidated materials which overlay carbonaceous limestone bedrock since about 1958. Average concentrations in the raffinate solutions in the pits are as follows: uranium, 1.1 mg/l; molybdenum, 3.2 mg/l; vanadium, 1.1 mg/l; arsenic, 0.04 mg/l; and selenium, <0.01 mg/l. Groundwater monitoring wells located about 30 meters and 100 meters downgradient from the edge of the pit contain concentrations of elements, respectively, as follows: uranium, 0.02 mg/l and 0.005 mg/l; molybdenum, 0.1 mg/l and 0.04 mg/l; vanadium, <0.05 mg/l; arsenic, <0.01 mg/l; and selenium, <0.01 mg/l. The decrease in the concentrations of uranium, molybdenum, vanadium, and arsenic by several orders of magnitude within 30 to 100 meters from the raffinate pits suggests effective retardation processes in a naturally-occurring reducing environment. Consequently, increased effectiveness of retardation would likely result using an engineered barrier designed for the specific conditions of the tailings.

This study investigated the theoretical basis for and the feasibility and benefits of a chemical barrier designed for acidic uranium tailings. This investigation emphasized computerized solution equilibria modeling guided by postulated

behavior of natural systems. Through the use of equilibria modeling, it is possible to determine the activities and speciation of dissolved components and the degree of saturation of various solid phases for a solution. Equilibration of that solution with a given solid phase (or phases) allows the resulting impact on acidity, redox potential, activity of dissolved constituents, and relative saturation to other solid phases to be monitored. Given the solubilized or precipitated mass transfer quantities of the equilibrated phases, mass balance calculations for the overall system are possible.

CHARACTERIZATION OF MILL TAILINGS INTERSTITIAL SOLUTION

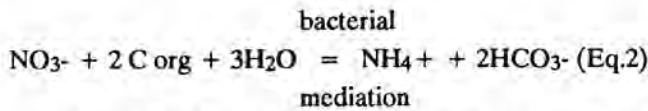
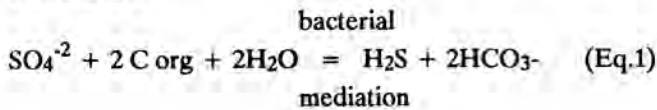
The chemistry of the mill tailings interstitial solution is important in determining the feasibility and characteristics of an organic-rich geochemical barrier. Modified analyses from lysimeter data of the Grand Junction tailings were used to characterize the tailings solution (Table I).

Computer modeling of this solution utilizing the PHREEQE solution equilibria computer program (21) defined the dominant aqueous species for each component. Note that sulfate and chloride complexes predominate for alkaline earth and transition metals, whereas oxy-anions prevail for selenium, molybdenum, vanadium, and arsenic. This tailings solution is not typical of a sulfuric acid leach system, deviating by exhibiting a higher pH, consequently less soluble iron and aluminum, and significantly more nitrate and ammonia. Saturation indices for solid and gaseous phases indicate that the solution is in approximate equilibrium with gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and chalcidony, slightly under saturated with SiO_2 gel and amorphous phases, and slightly over saturated with the molybdate minerals wulfenite (PbMoO_4), powellite (CaMoO_4), and SrMoO_4 . Extreme supersaturation of fluorite (CaF_2) and fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) exists, indicating slow kinetics to reach equilibrium. Importantly, all selenium, vanadium, arsenic, and uranium phases are substantially undersaturated in this solution. It is reasonable, therefore, to presume that dissolution of these elemental-bearing minerals is slow, ranging from a few years to a few tens of years. Thus, introduction of minor amounts of infiltrating groundwater should not solubilize significant new quantities of these elements over a similar period.

REACTION OF TAILINGS SOLUTION WITH THE GEOCHEMICAL BARRIER

Having defined the chemical parameters of the tailings solution, it is possible to computer model its reaction to an organic-rich geochemical barrier. Within the geochemical barrier, bacteriogenic reduction of dissolved sulfate will exert the dominant force on Eh. Biogenic nitrate reduction also should occur. [Simultaneous production of sulfide and ammonia is frequently observed in anoxic

near-shore marine sediments (14).] Specific reactions of concern are:



[Bacterial nitrate reduction is known to occur as a sequence of reduction reactions, with N₂ as an intermediate

product (14). The above reaction simply utilizes end-member components.]

Solution modeling, assuming the tailings water approximately equilibrates with an organic carbon mass, results in a pH increase to 6.6, and an Eh drop to -175 mV. Dissolved total sulfide becomes an important aqueous species, reaching a concentration of over 600 ppm. Under these conditions, numerous sulfide and reduced valence state phases are greatly supersaturated. Table II shows the degree of saturation of selected phases. The degree of oversaturation and the generally rapid kinetics associated with sulfide and reduced phase precipitation argue that removal of insoluble phases should occur, drastically lowering the concentrations of impacted dissolved components. Computer model-

TABLE I
Characterization of Initial Solution

pH = 5.5
Eh = 335 mV
Ionic Strength = 0.270
TDS (mg/kg) = 15,530
Temperature = 25°C

<u>Element</u>	<u>Total (mg/kg)</u>	<u>Dominant Species*</u>
As	1.68	HASO ₄ ⁻²
Ca	720	Ca ⁺² , CaSO ₄ ⁰
Cd	0.035	Cd ⁺² , CdCl ₂ ⁰ , Cd(SO ₄) ₂ ⁻²
Cl	2,990	Cl ⁻
Cu	0.256	Cu ⁺² , CuSO ₄
F	16	F ⁻
Fe	0.1	Fe ⁺² , FeSO ₄ ⁰
Hg	0.0003	HgCl ₃ ⁻ , HgCl ₂ ⁰
K	212	K ⁺
Mg	1,550	Mg ⁺² , MgSO ₄ ⁰
Mo	8.65	MoO ₄ ⁻²
Na	1,700	Na ⁺
NH ₄	467	NH ₃
NO ₃	1,110	NO ₃ ⁻
PO ₄	8.4	H ₂ PO ₄ ⁻
Pb	0.011	PbSO ₄ ⁰ , Pb ⁺² , PbCl ⁺
SO ₄	6,700	SO ₄ ⁻²
Se	1.69	HSeO ₃ ⁻
SiO ₂	16.6	Si(OH) ₄
Sr	4.09	Sr ⁺²
U	0.01	UO ₂ (HPO ₄) ₂ ⁻²
V	10.8	H ₂ VO ₄

*Calculated by PHREEQE

TDS = Total Dissolved Solids

pH in Standard Units

TABLE II
Degree of Supersaturation of Selected Phases for the Reduced Tailings Solution

Phase	Log Value* Degree of Saturation (Log IAP/KT)
Molybdenite (MoS ₂)	30.4
Orpiment (As ₂ S ₃)	25.3
Chalcocite (Cu ₂ S)	14.0
Fluorapatite (Ca ₅ (PO ₄) ₃ F)	12.4
Pyrite (FeS ₂)	9.4
Karelinite (V ₂ O ₃)	4.8
Native Selenium (Se)	2.7
Fluorite (CaF ₂)	1.5
Galena (PbS)	0.9
Calcite (CaCO ₃)	0.6
Uraninite (UO ₂)	0.5
Cinnabar (HgS)	0.4
Gypsum (CaSO ₄ *2H ₂ O)	-0.3

* A Log IAP/KT value of 1.0 indicates a ten-fold degree of supersaturation that phase. A value of 0.0 indicates equilibrium conditions. A value less than 0.0 indicates undersaturation.

IAP = Ion Activity Product

KT = Thermodynamic Equilibrium Product at Temperature "T"

ing allows one to determine the amount of precipitate formed and the equilibrium concentrations of dissolved constituents. Table III reports the final chemistry of the solution equilibrated with the geochemical barrier subsequent to mineral precipitation. Note the significant decrease in the dissolved concentrations of arsenic, copper, iron, mercury, molybdenum, selenium, and vanadium. Concentrations of these components all fall below the maximum concentration limits set by the EPA. Observe that several constituents are unaffected by the barrier. Specifically, chlorine, potassium, sodium, silica, and strontium remain at initial solution levels. Lead will be significantly affected although it is already relatively insoluble in the initial tailings solution. Cadmium probably will not be significantly depleted but will remain in approximate equilibrium with greenockite (CdS). Thermodynamic data indicate that the reduced tailings solution is greatly supersaturated with

fluorapatite, fluorite, and dolomite. Recall that the first two compounds also were supersaturated in the initial tailings solution, indicating that more than a few years' time interval is required to reach equilibrium. In natural systems, these phases usually form as a replacement of other calcium-bearing minerals, such as aragonite or calcite. Upon encountering calcite grains within the compacted clay base, some solid-state transformation may occur with alteration of the original calcite to fluorapatite, fluorite, or dolomite. This would not result in any decrease in permeability.

The solution equilibria modeling results also indicate that approximate equilibrium is maintained with gypsum during sulfate and nitrate reduction. It is therefore pre-

TABLE III
Change In Chemistry of Tailings Solution Upon Reaction With
Geochemical Barrier and Precipitation of Reduced Phases

Element	Elemental Compound	Reported As	Tailings Solution	Reduced Tailings Solution Before Precipitation	Precipitated Phase (w/S.I.)*	Reduced Tailings Solution After Precipitation	Proposed EPA MCL (for reported comp.)
Arsenic	AsO ₄ ⁻	ppm	3.1	3.1	Orpiment (1.0)	0	0.093
Calcium	Ca ⁺²	ppm	720	720	Fluorapatite (1.0) Fluorite/Dolomite (1.0)	236	
Cadmium	Cd ⁺²	ppm	0.035	0.035	--	0.035	0.01
Chlorine	Cl ⁻	ppm	2990	2990	--	2990	
Copper	Cu ⁺²	ppm	0.256	0.256	Chalcocite (1.0)	0	
Fluorine	F ⁻	ppm	16	16	Fluorapatite (1.014)		Fluorite (1.0)
Iron	Fe ⁺²	ppm	0.1	0.1	Pyrite (1.0)	4x10 ⁻¹⁰	
Bicarbonate	HCO ₃ ⁻	ppm	0	4532	Dolomite (1.0)	309	
Mercury	Hg ⁺²	ppm	0.0003	0.0003	Cinnabar (0.0)	0.0001	0.01
Potassium	K ⁺	ppm	212	212	--	212	
Magnesium	Mg ⁺²	ppm	1550	1550	Dolomite (1.0)	1260	
Molybdenum	MoO ₄ ⁻²	ppm	14.4	14.4	Molybdenite (1.0)	0	0.167
Sodium	Na ⁺	ppm	1700	1700	--	1700	
Ammonium	NH ₄ ⁺	ppm	467	786	--	786	
Nitrate	NO ₃ ⁻	ppm	1100	0	--	0	44
Phosphorus	PO ₄ ⁻³	ppm	8.4	8.4	Fluorapatite (1.0)	0.007	
Lead	Pb ⁺²	ppm	0.011	0.011	Galena	7x10 ⁻⁹	0.05
Hydrogen Sulfide	H ₂ S	ppm	0	677	--	677	
Sulfate	SO ₄ ⁻²	ppm	6700	2562	--	2562	
Selenium	SeO ₄ ⁻²	ppm	3.1	3.1	Native Selenium (0.0)	0.006	0.018
Silica	Si(OH) ₄	ppm	26.6	26.6	--	26.6	
Strontium	Sr	ppm	4.09	4.09	--	4.09	
Uranium	U ⁺⁴	ppm	0.01	0.01	Uraninite (0.0)	0.004	
Vanadium	V ⁺³	ppm	10.8	10.8	Karelinite (1.0)	0.143	
	pH	std.units	5.5	6.6	--	6.6	
	Eh	mV	335	-175	--	-175	

Note: Values less than 10⁻¹² reported as zero

* Recognizing that full equilibrium may not immediately be achieved, several phases have an S.I. value conservatively set at 1.0 (10X supersaturation).
S.I. = Saturation Index = Log IAP/KT

dicted that major precipitation of gypsum will not occur, thereby not causing impermeability problems.

KINETIC CONSIDERATIONS

Although this discussion has primarily emphasized thermodynamic equilibria, we must also consider the time element of these proposed reactions. Fundamental to the geochemical barrier concept is the metabolization of organic carbon by sulfate-reducing bacteria with the concomitant production of hydrogen sulfide. This process is aided by the degree and amount of non-refractory organic carbon available (14). For example, relatively refractory carbon sources, such as subbituminous or bituminous coals, provide an inadequate substrate for bacterial sulfate reduction. Using labile carbon sources such as peat or plant and animal debris, onset of anoxia and sulfide production is very swift. In natural systems, sulfate reduction can begin within a few days or months after development of a water-saturated organic-rich milieu. This is demonstrated by numerous studies of near-shore marine sediments and coastal and freshwater swamps. Consequently, reducing conditions should develop quickly in the engineered geochemical barrier. The ten-fold excess in consumable carbon should help ensure rapid sulfide production upon initial contact with the tailings pore fluid.

Precipitation reaction kinetics for most of the elements of concern (V, Mo, As, U) are known only generally. Research has shown, however, that selenium, in the selenite (SeO_3^{2-}) form, is quickly and easily precipitated in a reducing environment (3). Distribution of elements in natural systems precipitated under low Eh conditions provide some measure of their reaction kinetics. Analysis of geochemical data collected in roll-type uranium deposits demonstrates that elemental content of uranium, selenium, vanadium, arsenic, and molybdenum decreases to background levels within a few to tens of meters from the oxidation-reduction boundary (4). Data from the Shirley Basin deposit of Wyoming in Table IV document the lateral distance of anomalous elemental content beyond the redox interface.

Assuming a flowrate of 3 meters per year within the Shirley Basin mineralized sediments, only 1 to 30 years are calculated before equilibrium is established with the initially oxidized solution and the reduced sediment. Note that selenium quickly reaches equilibrium as predicted.

At the Weldon Spring site in Missouri, a decrease of several orders of magnitude is observed in concentrations of uranium, molybdenum, vanadium, and arsenic between the raffinate water and the groundwater about 30 meters from the edge of the raffinate pits. This decrease in concentrations at Weldon Spring has occurred during the past 30 years.

Berner (14) and Kaplan (16) have estimated the rate of sulfate reduction in near-shore marine sediments between

TABLE IV

Elemental Data From Shirley Basin Wyoming Uranium Deposit

Element	Meters Beyond Redox Boundary for Return to Background Level	Time in Reducing Environment to Precipitate (Yrs.)
Se	3	1
U	13	4
As	13	4
V	16	5
Mo	90	30

1.8 and 6×10^{-14} moles $\text{H}_2\text{S}/\text{cm}^3/\text{sec}$. Using the more conservative rate, one computes the yearly sulfide production within the geochemical barrier equaling 16,080 moles H_2S .

The annual quantity of H_2S needed to equilibrate with all reactive constituents equals 4177 moles.

Interestingly, U, V, Mo, Se, and As are also attenuated by adsorption onto organic compounds. In fact, this sorption stage may be a precursor to reduction (2, 17). Adsorption may account for lower concentrations measured in groundwater at Weldon Spring than is predicted by precipitation reactions calculated by PHREEQE. Adsorption by peat will provide a two-fold benefit: first, to help attenuate dissolved concentrations; and secondly, to slow the rate of passage of adsorbed elements through the geochemical barrier. (Note that this does not suggest any impediments to solution flow.) Adsorption kinetics tend to be quite fast. For example, Szalay (17) exposed porous nylon bags of peat to natural waters for a week and noted a several thousand-fold enrichment in uranium. Bloomfield and Kelso (18) observed adsorption of U, V, and Mo on anaerobically rotted plant debris over a three-week period. Anaerobiosis may be important for adsorption of molybdenum in that Kabeck and Runnels (19) did not find molybdenum concentrated within oxygenated, organic-rich, stream sediments. However, Tompson, et al. (20) observed significant depletion of U and Se, among others, during a 72-hour reaction of tailings solution and peat.

Adsorption will help provide the residence time necessary for reduction and precipitation of slow-reacting species such as molybdenum. Adsorption alone, however, will not achieve the very low dissolved concentration levels provided by reduction or sulfidization.

SUMMARY AND CONCLUSIONS

Solution equilibria modeling studies validate the concept of an organic-rich zone attenuating dissolved selenium, molybdenum, vanadium, arsenic, and uranium. Incorporating 10,000 tonnes of organic carbon within a tailings cell

should engender precipitation of reduced phases of those elements, lowering their dissolved equilibrium concentrations below the proposed EPA maximum concentration limits. The computer modeling results are confirmed by many natural analogs. Reaction kinetics suggest that both sulfide production and reduction of the elements of concern should begin relatively soon.

The proposed geochemical barrier should maintain strongly reducing conditions for many thousands of years.

Whereas the geochemical barrier idea appears applicable to this site, there is nothing to indicate that it is also not applicable to other sulfuric acid leach locations, although the required quantity of organic carbon is site specific.

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