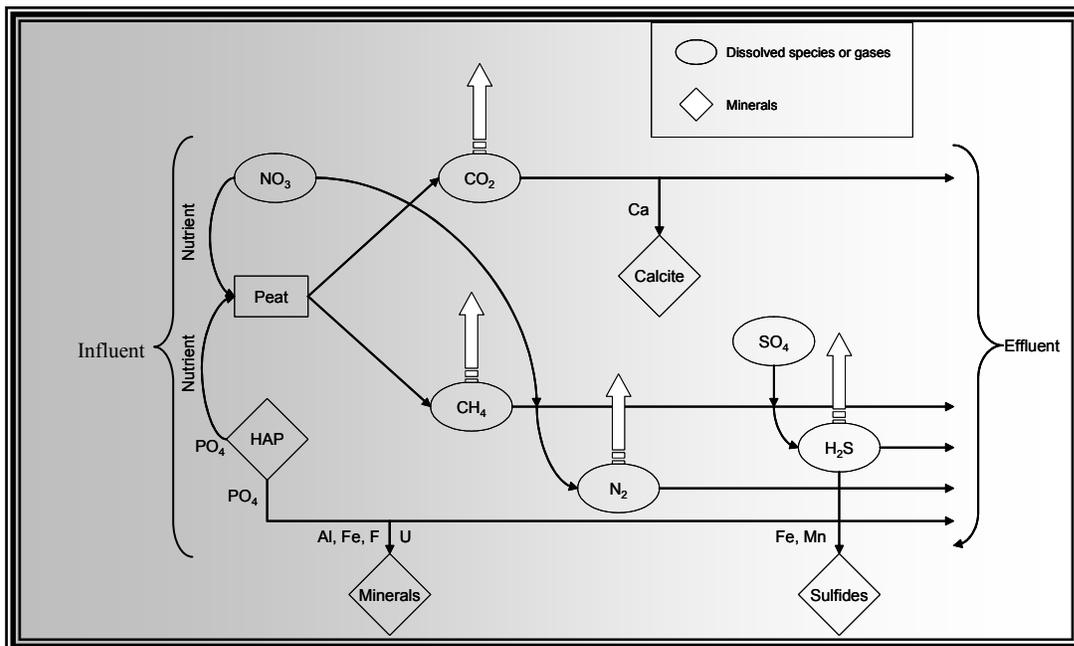


Recommended Amendment Mixture for *In Situ* Treatment of Waste Management Unit Groundwater, Ashtabula Closure Project



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January, 2004

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

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Executive Summary

This document provides recommendations for the composition of a mixture of peat, hydroxyapatite, and sand to treat dissolved TCE, uranium, and technetium-99 in groundwater at the Waste Management Unit (WMU) of the Ashtabula Closure Project. One option for treatment presented by the Department of Energy Office of Environmental Management sponsored technical assistance team was to remove the most contaminated soil and fill the engineered excavation with amendments for in situ clean up of the groundwater.

A mixture of peat and hydroxyapatite will produce conditions necessary for stabilization of uranium and technetium-99, as well as anaerobic degradation of TCE. There is an ample body of literature supporting the use of peat to maintain the methanogenic conditions required for reductive dechlorination of TCE. Likewise, peat has been used to remediate uranium in groundwater. Furthermore, reducing conditions that stabilize uranium will also stabilize technetium-99. Addition of hydroxyapatite, a natural phosphate mineral, will enhance stabilization of uranium by precipitation of low solubility phosphate phases. Hydroxyapatite will also provide phosphate, a critical nutrient, to promote microbial degradation of the peat required to maintain methanogenic conditions.

The recommended mixture per cubic meter is:

| Amendment | Mass (kg) per m ³ | Weight % |
|----------------|------------------------------|----------|
| Peat | 350 | 22 |
| Hydroxyapatite | 28 | 2 |
| Sand | 1200 | 76 |

This is based on the composition of WMU groundwater, the groundwater flow rate, and an assumed 30-year lifetime for the outermost meter of the treatment zone. The lifetime of the treatment system as a whole depends on the size of the treatment zone. It is recommended that laboratory treatability studies be conducted prior to any implementation of this system. The studies should focus on effectiveness and longevity. Two specific issues that may affect these are replacement of hydroxyapatite by fluorapatite and precipitation of calcite within the system.

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Introduction

A technical assistance team sponsored by the Department of Energy Office of Environmental Management (EM) was convened in June of 2003 to evaluate strategies for addressing contaminated groundwater at the Waste Management Unit (WMU) of the Ashtabula Closure Project (ACP). The recommendations of the team included the option of filling a trench or source material excavation with amendments to provide passive long-term treatment of the groundwater (WSRC-TR-2003-00340). In the optimal configuration, the excavated trench is hydraulically connected to the base of a nearby escarpment to maintain a lowered water table and induce the contaminant plume to flow back toward the amendments for treatment. The active amendment proposed was a mixture of solid phosphate (hydroxyapatite) and peat. A mixture of these, combined with sand for structural integrity, would fill the excavation and provide the geochemical conditions necessary for treatment of the contaminants. This document is a preliminary assessment of reasonable amendment proportions to provide a basis for laboratory treatability studies.

The contaminants of concern in the groundwater are primarily trichloroethylene (TCE) and uranium, but treatment of technetium-99 (^{99}Tc) would also be beneficial. Table 1 shows average concentrations of these in the WMU groundwater and regulatory limits for the groundwater and outfall.

Table 1: Average concentrations, groundwater cleanup limits and outfall limits for contaminants of interest at the WMU. (from Hughes, 2003)

| Contaminant | Average Concentration | Groundwater Cleanup Limit | Outfall Limit |
|------------------|-----------------------|---------------------------|---------------|
| TCE | 840 ug/L | 5 ug/L | 5 ug/L |
| Uranium | 666 ug/L | 30 ug/L | 430 ug/L |
| ^{99}Tc | 73 pCi/L | 900 pCi/L | 60,000 pCi/L |

The objectives for the amendment mixture are to provide conditions necessary for destruction of TCE, as well as stabilization of uranium and ^{99}Tc in low solubility phases. The optimal amendment mixture will achieve these conditions passively without violating any standards for pH, phosphate, or other constituent concentrations. No amendment mixture will perform indefinitely, but longevity should be a consideration in choosing amendment proportions. Likewise, structural stability may be important, though engineering controls can alleviate effects of subsidence. For this analysis, geochemical factors were given first priority, followed by longevity and structural integrity.

Target conditions for stabilization or destruction of each contaminant were identified by searching the literature and modeling uranium and technetium speciation. Interactions between peat and hydroxyapatite were then modeled to yield a mixture that best satisfies these target conditions. Summaries of contaminant geochemistry and the properties of peat and hydroxyapatite are, in part, from WSRC-TR-2003-00340.

Modeling of geochemical processes was done using PHREEQC, ver. 2.8 (Parkhurst and Appelo, 1999) and The Geochemist's Workbench®, ver. 4.0 (Bethke, 2002). When it was

appropriate to use specific chemistry of WMU groundwater, an analysis from January 2003 of groundwater from well 505B was used. This water had the highest TCE concentration (475 mg/L) for this sampling period and high nitrate concentration (2210 mg/L). The analysis is shown in Table 2.

Table 2: Analysis of groundwater from well 505B, January 2003.

| Constituent | |
|--------------------|------|
| pH | 6.66 |
| Alkalinity (mg/L) | 520 |
| ORP (mV) | 260 |
| Ca (mg/L) | 233 |
| Fe (mg/L) | 0.1 |
| Mg (mg/L) | 82 |
| K (mg/L) | 10 |
| Na (mg/L) | 3420 |
| Chloride(mg/L) | 132 |
| Nitrate (mg/L) | 2210 |
| Sulfate (mg/L) | 337 |
| Fluoride (mg/L) | 10 |

Peat

Peat can be generally defined as a partially fossilized plant matter that occurs in wetlands where there is a deficiency in oxygen and where the accumulation of plant matter is faster than its decomposition. Peat is a complex material consisting of plant fibers that contain cellulose and hemicellulose, humic and fulvic acids, waxes, resins, and other substances. As a result, peat contains polar functional groups such as alcohol, aldehydes, ketones, and ethers that can be involved in chemical bonding and ion exchange. The polar and ion exchange functionality of peat has been shown to support sequestration of metals such as uranium and polar molecules such as ammonia. Peat also has a high surface area and high organic carbon content, similar to activated carbon, resulting in sequestration of organic contaminants (see information from www.peatec.com).

In groundwater remediation systems peat can perform two functions. It acts as a sorbent for contaminants and promotes anaerobic/reducing conditions under which many contaminants are degraded or stabilized. Often, as with uranium (Nakashima et al., 1984), contaminants are initially sorbed to peat and subsequently reduced to more stable forms. The sorbent properties of peat for both organic and inorganic contaminants are well studied. Cohen et al. (1991) examined a variety of peats and found that all removed significant amounts of hydrocarbons from water. They concluded that organic sorption properties were best in peats with low fiber and high ash content. Metals sorb at the sites of carboxylic, phenolic, and hydroxylic functional groups (Gosset et al., 1986). Metal sorption is strongly dependent on pH (Gosset et al., 1986) because H^+ competes with metal cations for sorption sites. The optimum pH range for metal sorption seems to be

between 3.5 and 6.5 (Brown et al., 2000). At pH above 8.5 peat begins to degrade and metal sorption is decreased (Brown et al., 2000). The ability of peat to strongly sorb a wide variety of contaminants makes it a common component of many wastewater treatment systems (Couillard, 1994; Brown et al., 2000).

The chemical conditions generated by peat in a remediation system are critical to its success as a treatment medium. Most information on these conditions comes from studies of natural peat soils. Values of pH in natural peats range from 2.6 to 7.5 (Mitsch and Gosselink, 2000) depending on the nutrients available. In general, pH values increase as nutrient concentrations increase. Eutrophic (nutrient-rich) peats have pH values greater than 4.5. This is, in part, due to enhanced methane production in nutrient-rich peats that raises pH by consuming acid and reducing the partial pressure of CO₂.

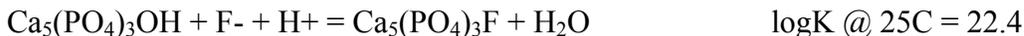
Redox conditions in peat are reducing and become more so the further removed the sample is from atmospheric oxygen. Within a meter from the surface most peat soils become anaerobic and can support sulfate reduction and methanogenesis (Bozkurt et al., 2001). The position of the water table is particularly important in establishing reducing conditions. Nedwell and Watson (1995) found that the water table was the boundary between oxic and anoxic conditions in a Scottish peat bog. Likewise, Rask et al. (2002) observed that methane flux in a peat was directly correlated with water level in a Canadian wetland. Nutrient influx, in particular nitrogen and phosphorus, into peat is also important to methane production (Amodor and Jones, 1995; Rask et al., 2002; Chapin et al., 2003).

Hydroxyapatite

Hydroxyapatite has proven effective for immobilization of several metals because of their formation of relatively insoluble phosphate phases (Gauglitz et al., 1992; Jeanjean et al., 1995; and numerous others). Three mechanisms of metal stabilization by hydroxyapatite are recognized. Hydroxyapatite may be dissolved and the solubilized phosphate may then force precipitation of the metal as a phosphate phase. Alternatively, the metal may be adsorbed to the hydroxyapatite and subsequent precipitation of metal phosphate may occur. The third mechanism is actual cation exchange of the metal for calcium in the apatite.

Hydroxyapatite also has an effect on water pH because of the hydrolysis of the phosphate ion. Figure 1 shows the calculated titration of two different waters by hydroxyapatite. In a sodium chloride solution with no alkalinity pH rises to an equilibrium value of 9.6. However, WMU groundwater has sufficient bicarbonate to buffer the pH at, or near, the initial value. Introduction of CO₂ into the water would also buffer the pH.

If there is significant fluoride in the groundwater it may substitute for hydroxyl ion and replace the hydroxyapatite with fluorapatite by the reaction:



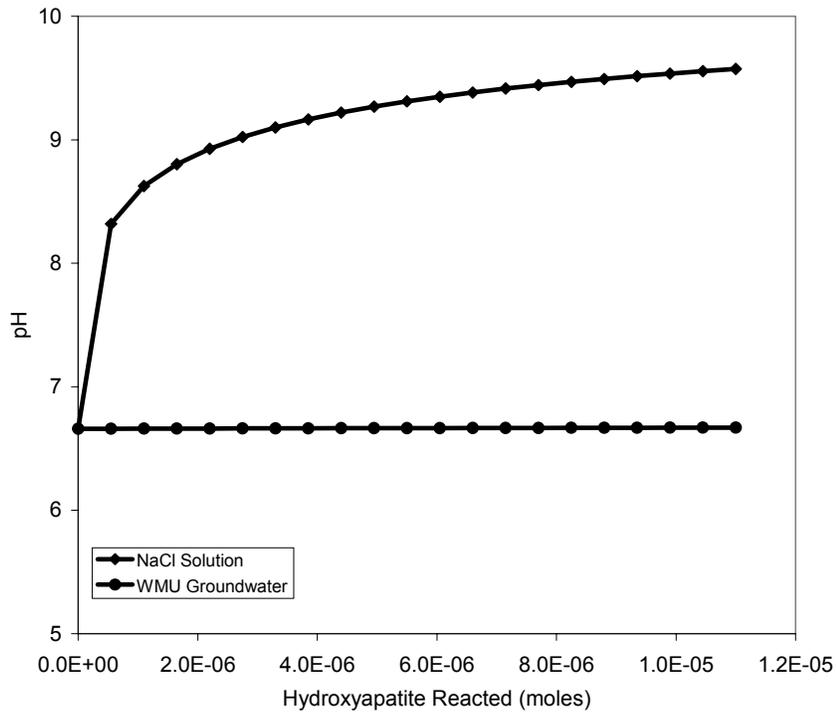


Figure 1: Titration of NaCl solution and WMU groundwater by hydroxyapatite.

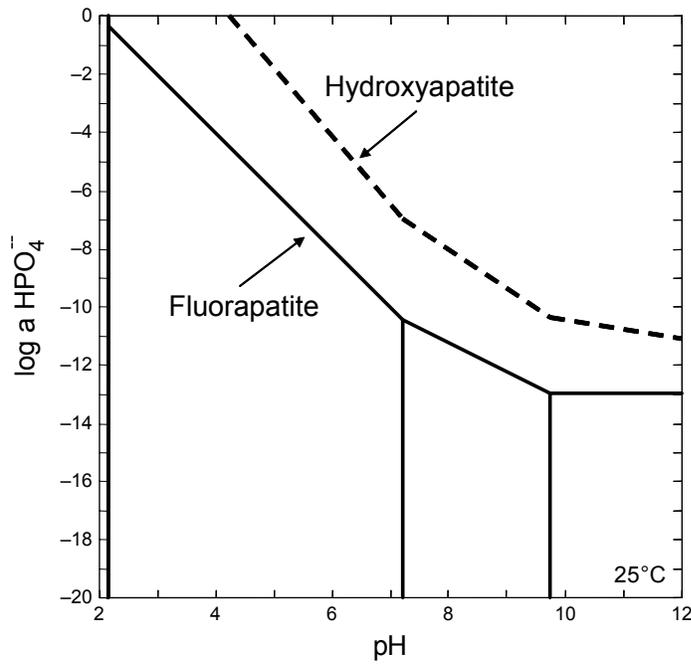


Figure 2: Solubility of hydroxyapatite [Ca₅(PO₄)₃OH] and fluorapatite [Ca₅(PO₄)₃F] versus pH. Vertical lines are boundaries between dissolved orthophosphate species.

The solubility of fluorapatite is several orders of magnitude lower than hydroxyapatite (Figure 2), and thus the availability of dissolved phosphate for reaction with metals would be diminished. However, the benefit of a coating of fluorapatite on hydroxyapatite grains would be lower phosphate concentrations at exposure points (e.g. outfalls) and increased longevity of the phosphate amendment. An additional benefit may be co-precipitation of uranium with fluorapatite. Figure 3 shows the relative stability fields of fluorapatite and hydroxyapatite as a function of fluoride concentration and pH. WMU groundwater contains sufficient total fluoride concentrations to suggest that fluorapatite would be the stable apatite phase. This is noted here as a reaction to be aware of in designing treatability studies using hydroxyapatite as a treatment amendment.

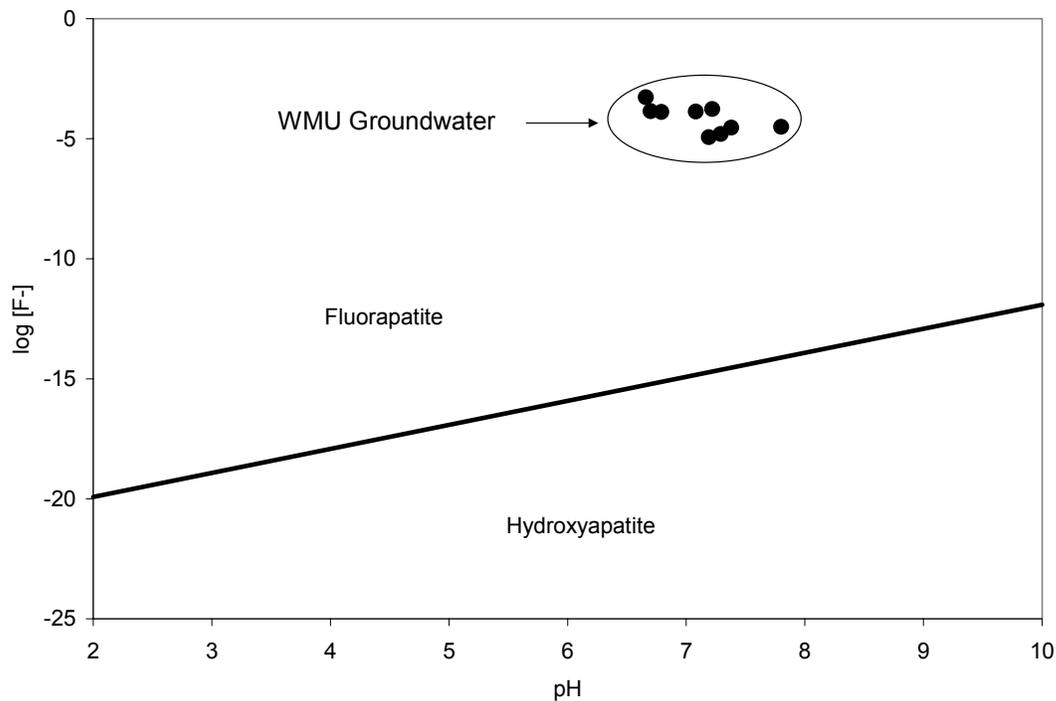


Figure 3: Stability of fluorapatite $[\text{Ca}_5(\text{PO}_4)_3\text{F}]$ and hydroxyapatite $[\text{Ca}_5(\text{PO}_4)_3\text{F}]$ with respect to fluoride concentration and pH. Analyses of WMU groundwater from January 2003.

Peat-hydroxyapatite Interactions

In the case of WMU groundwater, one purpose of blending hydroxyapatite with peat is to provide a critical nutrient for microbial degradation of the peat to CO₂ and CH₄. The goal is to drive the system to methanogenic conditions most conducive to stabilization or destruction of the contaminants. Natural peat readily achieves these conditions if isolated from oxygen influx (Nedwell and Watson, 1995; Amador and Jones, 1995; Bergman et al., 2000; Rask et al., 2002; Chapin et al., 2003; Blodau and Moore, 2003). The two most critical nutrients required to sustain these conditions in peat are nitrogen and phosphate (Amador and Jones, 1995; Rask et al., 2002; Chapin et al., 2003). WMU groundwater has relatively high nitrate concentrations and the hydroxyapatite would provide the necessary phosphate concentrations.

Figure 4 summarizes the reactions likely in the peat-hydroxyapatite system. Hydroxyapatite dissolves to produce orthophosphate which, combined with nitrate in the influent, provides nutrients for microbial degradation of the peat. The products of the degradation reaction are carbon dioxide and methane. Carbon dioxide can be removed from the water by degassing or precipitation of calcite. The remainder is dissolved in water and is released from the system in the effluent. The fate of the methane is more complicated. The net reactions are that some may degas, some may react with nitrate to produce nitrogen, and some may react with sulfate to produce hydrogen sulfide, but methanogenic conditions will not be reached until nitrate and sulfate are exhausted. The hydrogen sulfide will react with available iron and manganese to form sulfide phases, some will degas, and the rest will remain in the effluent. The dissolved orthophosphate from hydroxyapatite dissolution will react with metals, including uranium, to form precipitates and the rest will remain in the effluent. Hence, reactions in the amendment system are complex and depend on the influent composition and the configuration of the treatment zone (ability of gases to escape, length, etc.). Nevertheless, the major reactions that influence treatment performance can be modeled and these and others can be investigated in bench-scale tests.

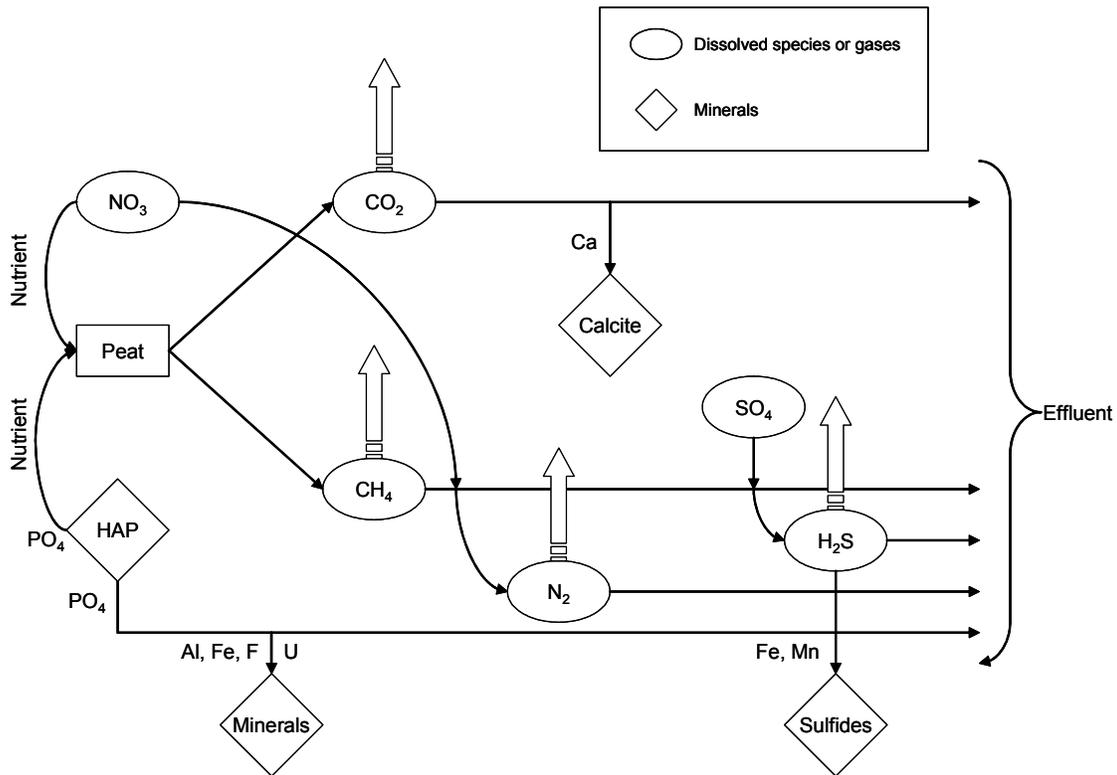


Figure 4: Diagram showing reactions expected in peat-hydroxyapatite system. Hydroxyapatite is denoted by HAP.

For example, the effect of peat degradation in the presence of hydroxyapatite on redox and pH conditions in WMU groundwater is modeled in Figure 5 by the reaction:



This does not account for kinetic effects of microbial mediated reactions, but does indicate the limits of conditions and the stoichiometry of the reactants. The three curves illustrate the effect of nitrate concentration on the reaction. Before conditions can become reducing enough to support methane accumulation, nitrate and sulfate must be reduced. Higher concentrations of these require higher amounts of carbon be reacted. At the WMU (for January 2003) the median nitrate concentration is 1280 mg/L compared to the maximum of 6700 mg/L. At the maximum nitrate concentration 0.6 moles of carbon must react to reach methanogenic conditions. This compares to 0.12 moles of carbon reacted for the median nitrate concentration. The sulfate concentrations are relatively constant and low compared to the nitrate concentrations. Figures 6 and 7 show the equilibrium conditions reached for the median nitrate concentration with respect to sulfur and carbon speciation. The boundaries on the diagrams represent equal activities of species, not

stability fields. At the conditions marked by the black circles, methane and hydrogen sulfide are produced.

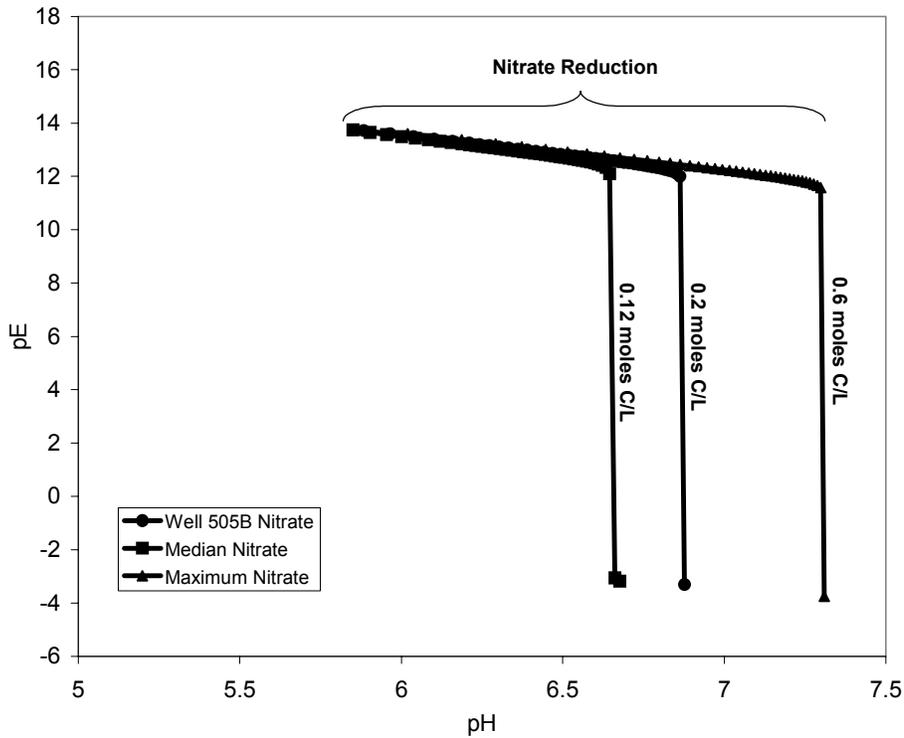


Figure 5: Evolution of pE and pH with degradation of carbon at different nitrate concentrations. Well 505B nitrate concentration is 2210 mg/L, median nitrate concentration is 1280, maximum nitrate concentration is 6700 mg/L.

The concentration of nitrate also affects the amount of hydroxyapatite dissolved, and thus the concentration of dissolved phosphate in the system. The calculations account for precipitation of calcite during carbon degradation. This is a likely reaction because the groundwater at the WMU is nearly saturated with calcite. As nitrate is reduced, pH increases and calcite precipitates. Removal of calcium from the system promotes additional hydroxyapatite dissolution. For example, at 6700 mg/L nitrate, the equilibrium phosphate concentration is over 10 times that for the median nitrate concentration of 1280 mg/L.

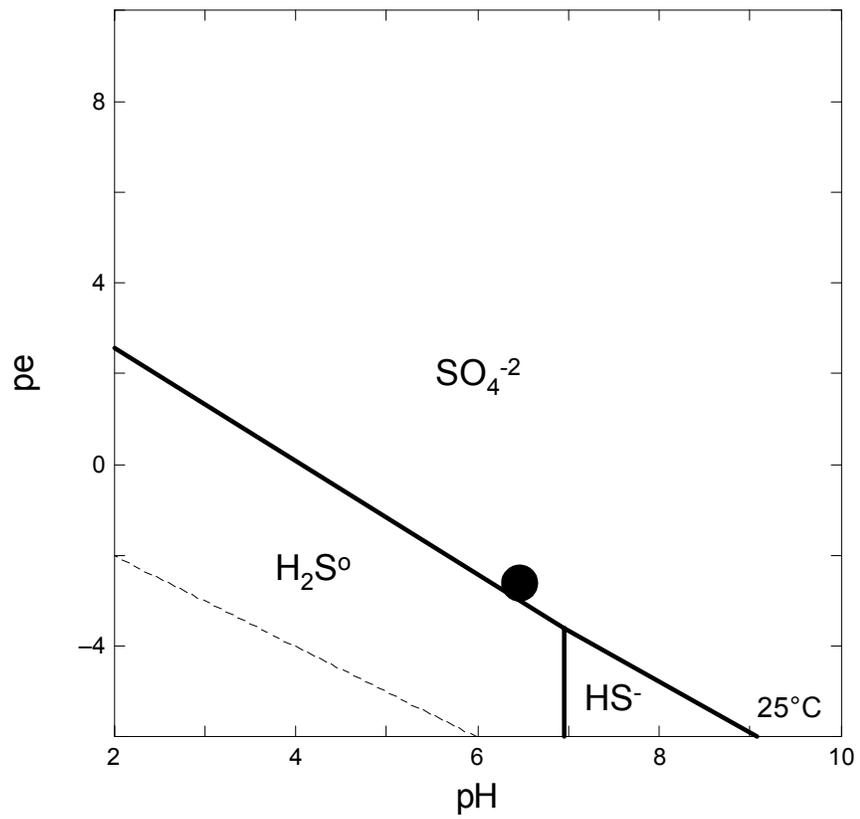


Figure 6: Equilibrium pE and pH (black circle) for degradation of carbon relative to sulfur speciation.

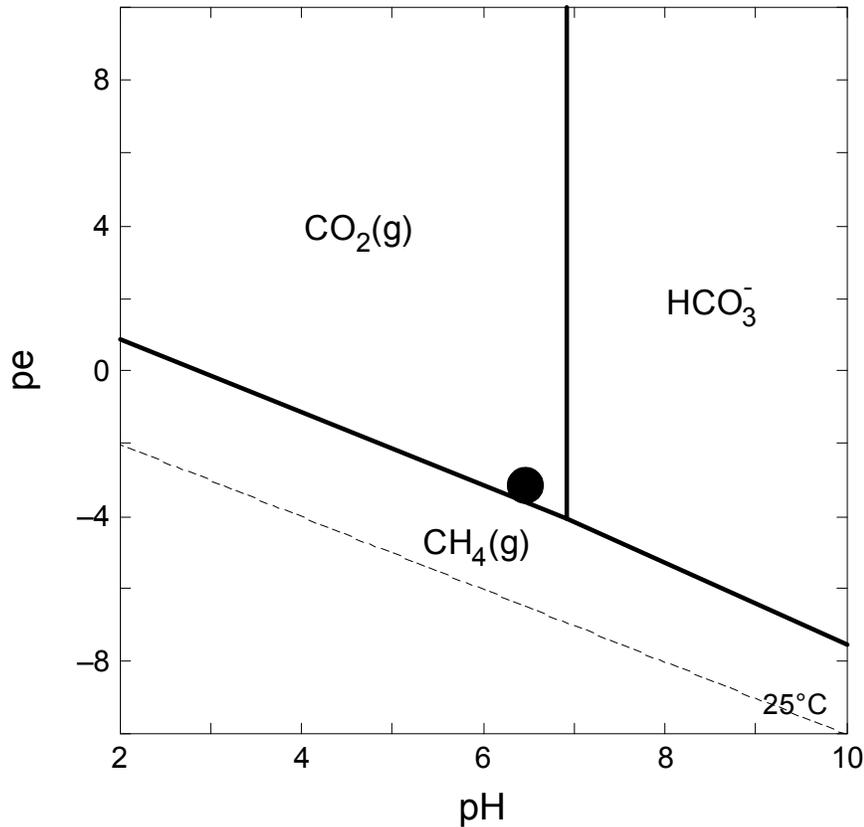


Figure 7: Equilibrium pE and pH (black circle) for degradation of carbon relative to carbon speciation.

Treatment of Trichloroethylene

Peat sorbs TCE (increasing its residence time in the system for reactions to occur) and acts as a source of carbon and other nutrients to promote TCE biodegradation. Kao and Lei (2000) studied the use of peat as a biobarrier to degrade TCE and PCE. In a biobarrier inoculated with sludge, degradation of both solvents was rapid. They documented that peat slowly released the nutrients necessary to stimulate growth of bacteria provided by the sludge. Sheremata et al. (2000) showed that TCE was degraded to cis-1,2,-DCE up to 8 times faster in the presence of composted peat than in control experiments. A novel system tested by Kao and Borden (1997) used nutrient briquets to provide nitrate and phosphate followed by a peat barrier to provide a substrate for denitrification. Significant BTEX removal by this system was observed. Kao and Borden (1997) concluded that peat alone would not be an efficient method of remediating BTEX, but with the nutrient briquets peat does provide substantial bioremediation. In laboratory microcosms of a peat and sand mixture, Rasmussen et al. (2002) observed substantial degradation of dissolved

organic compounds associated with creosote. Likewise, Khandelwal and Rabideau (2000) demonstrated that addition of natural humus enhanced sorption of TCE in a soil-bentonite barrier.

It is expected that degradation of TCE by reductive dechlorination will occur in a mixture of peat and hydroxyapatite. The influx of nitrate-rich groundwater and dissolved phosphate from hydroxyapatite will provide the nutrients necessary to drive the system to methanogenic conditions (Figure 5).

Treatment of Uranium

Three mechanisms of uranium stabilization may operate in a mixture of peat and hydroxyapatite. The uranium may be reduced from U(VI) to less soluble U(IV), it may be adsorbed onto the peat and the hydroxyapatite, or it may combine with orthophosphate from the hydroxyapatite to precipitate as an insoluble phosphate phase. A goal of the amendment mixture is to optimize stabilization by providing conditions that promote all of these mechanisms.

Reduction of uranium has been used successfully to stabilize uranium in the subsurface. In general, the solubility of U(IV) phases is lower than the solubility of U(VI) phases and U(IV) phases are stable over a wider range of pH. Figure 8 illustrates the latter for uranium oxide-hydroxide phases. Below a pE of 4 (an Eh of about 240 mV) reduced uranium phases are stable over a wide pH range. In contrast, at oxidizing conditions schoepite is only stable over a narrow pH range.

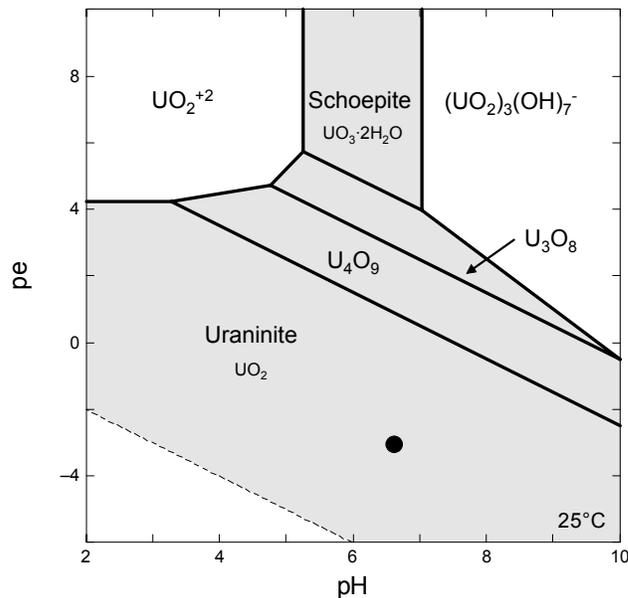


Figure 8: Equilibrium pE and pH (black circle) for degradation of carbon relative to uranium speciation. Gray areas are solid phases.

A variety of uranium reduction methods have been tested including application of zero-valent iron (Cantrell et al., 1995; Morrison et al., 2001; Morrison et al., 2002), application of mixed ferrous/ferric iron hydroxides (O'Loughlin et al., 2003), and bioreduction (Robinson et al., 1998; Istok et al., 2004). In addition, peat has been used as a reductant to remediate uranium in surface water (Looney et al., 1987; Veselic et al., 2002). Figure 8 shows that the conditions expected for degradation of peat are in the uraninite stability field.

Peat is also a potential adsorbent for uranium. In natural systems uranium is commonly associated with organic matter ranging from petroleum bitumen (Curiale et al., 1983) to lignite (Vassiliou, 1980; Ilger et al., 1987). Nakashima et al. (1984) found that the association of uranium to natural organic matter involved both adsorption and reduction. In their studies uranium was initially sequestered in lignite by formation of urano-organic compounds followed by reduction of U(VI) to less soluble U(IV). The association of uranium with organic matter has become the basis for using organic materials for removing dissolved uranium from water (Heitkamp and Wagener, 1982; Cullen and Siviour, 1982; Morrison and Spangler, 1992).

The presence of hydroxyapatite in a mixture with peat contributes to the stabilization of uranium in three ways. It provides phosphate, an important nutrient for the anaerobic degradation of peat. This promotes the reducing conditions that stabilize uranium. Uranium can also adsorb to the surface of hydroxyapatite (Fuller et al., 2002). Finally, uranium can react with orthophosphate released from the hydroxyapatite to form uranium phosphate phases (Gauglitz et al., 1992; Jeanjean et al., 1995; Arey et al., 1999; Fuller et al., 2002).

Figures 9 and 10 suggest that uranium precipitation as a phosphate phase under reducing conditions is more likely to achieve concentrations that meet regulatory limits than precipitation under oxidizing conditions. Experiments by RMIES using phosphate reagents did achieve uranium concentrations below the regulatory limit under oxidizing conditions, but the dissolved phosphate concentrations used were higher than expected from dissolution of hydroxyapatite. Figure 11 shows that the final dissolved phosphate concentrations for experiments that achieved the regulatory limit were significantly higher than those in experiments that failed to achieve the regulatory limit. All are higher than the phosphate concentration expected from dissolution of hydroxyapatite at pH 6. However, Jerden and Sinha (2003) and Jerden et al. (2003) report on a natural analogue in which uranium precipitation as a Ba meta-autunite limited uranium concentrations to below 30ug/L. Thus, it is uncertain, but feasible that precipitation of uranium phosphates under oxidizing conditions can achieve the regulatory limit for uranium concentration.

RMIES also conducted experiments using Hydrogen Release Compound (HRC[®]) and Metal Reducing Compound (MRC[™]), both products of Regeneration. Use of the HRC[®] never achieved the regulatory limit for uranium, but uranium concentrations did decrease with time. Thus, it is possible that duration of the experiments was not sufficient to allow the HRC[®] to reach its maximum effectiveness. The MRC[™] performed better and may be a useful amendment for uranium removal from groundwater. However, neither of these

amendments is sustainable for long periods of time without regular re-application. Nevertheless, they might be useful for accelerating the initial degradation of peat that would then drive reduction and precipitation of uranium.

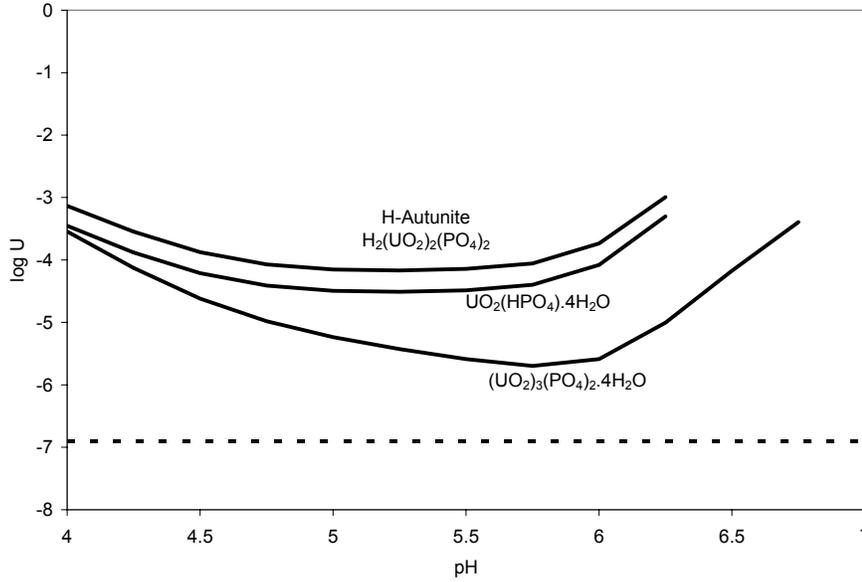


Figure 9: Solubility of U(VI) phases most likely to precipitate in equilibrium with hydroxyapatite. Dashed line is at clean-up criterion of 30 ug/L.

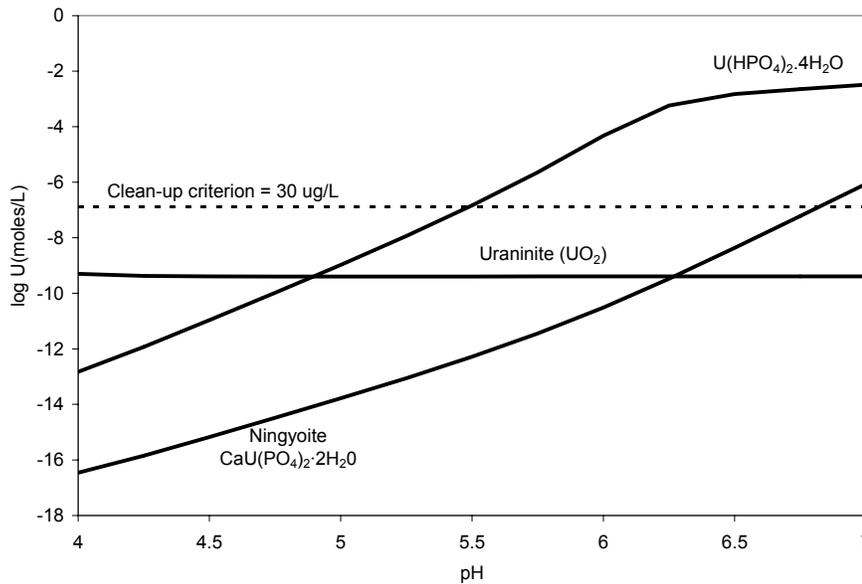


Figure 10: Solubility of U(IV) phases most likely to precipitate in equilibrium with hydroxyapatite.

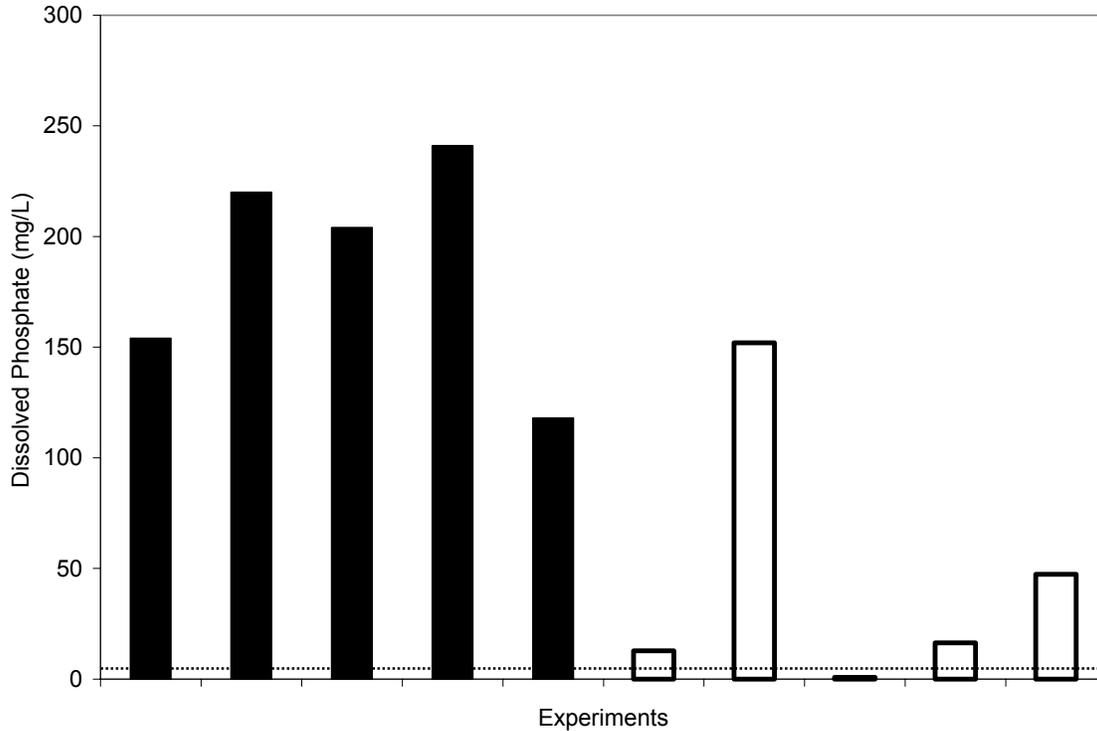


Figure 11: Uranium-phosphate stabilization experiments done by RMIES using dissolved orthophosphate. Black bars are experiments that achieved the regulatory limit for uranium; white bars are experiments that did not achieve the regulatory limit for uranium. Dotted line shows phosphate concentration in equilibrium with hydroxyapatite.

Treatment of Technetium

Technetium can exist in multiple oxidation states that range from -1 to $+7$. The most prevalent forms in groundwater are Tc(IV) and Tc(VII). The Tc(VII) form is generally soluble and dominated by the species TcO_4^- throughout the pH range of 2 to 10. Tc(IV) is much less soluble and tends to form the oxide TcO_2 or a hydrated phase $\text{TcO}_2 \cdot n\text{H}_2\text{O}$. Figure 12 shows the speciation of technetium as a pE versus pH diagram. At mildly reducing conditions, TcO_4^- is reduced to Tc(IV) that hydrolyzes to form $\text{TcO}(\text{OH})^+$ and $\text{TcO}(\text{OH})_2^0$. At low pH technetium speciation is dominated by TcO_4^- , whereas $\text{TcO}(\text{OH})_2^0$ dominates at high pH.

One approach to remediation of ^{99}Tc is to reduce it to the Tc(IV) state to precipitate the relatively insoluble oxides. The reduction can be done chemically or by stimulating microbes that reduce technetium. Chemical reduction by aqueous solutions of sodium dithionite has been studied extensively at the Hanford site (e.g. Amonette et al., 1994; Williams et al., 2000). Other aqueous solutions such as those containing Fe(II), Cu(I), or Sn(II) may also reduce technetium, though Cui and Eriksen (1996) found that reduction by Fe(II) was quite slow.

Any decrease in ^{99}Tc concentrations caused by reduction of Tc(VII) to Tc(IV) is likely to be due to enhanced sorption rather than precipitation of a stable phase. In Figure 13 the solubilities of TcO_2 and $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}$ are shown versus pH. Though the solubility of TcO_2 is much lower than the solubility of $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}$, TcO_2 does not precipitate readily at low temperatures. For example, Meyer and Arnold (1991) found that $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}$ was the stable stoichiometry of the solid phase precipitated by electrodeposition. This is consistent with other studies. Nevertheless, ^{99}Tc concentrations may decrease upon reduction to Tc(IV) because of enhanced sorption of the aqueous species $\text{TcO}(\text{OH})^+$ and $\text{TcO}(\text{OH})_2^0$ (Walton et al., 1986; Lieser and Bauscher, 1987; Liang et al., 1996). Another reduction option is to reduce Tc(VII) to sparingly soluble Tc metal.

In addition to establishing a reducing environment, peat will adsorb ^{99}Tc . Adsorption may be an effective process for the removal of ^{99}Tc from groundwater even under oxidizing conditions. Gu et al. (1996) found that activated carbon strongly adsorbed TcO_4^- over a wide range of pH, with K_d values that exceeded 10^4 ml/g in some cases.

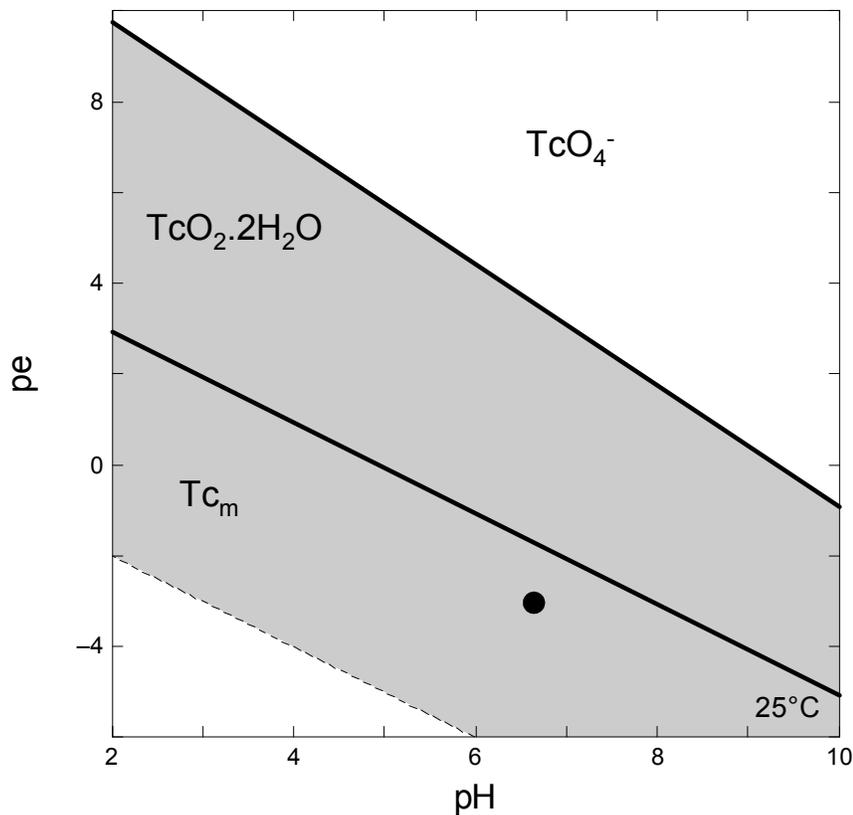


Figure 12: Stability of reduced technetium phases (gray areas). Black circle shows conditions expected for degradation of carbon in peat.

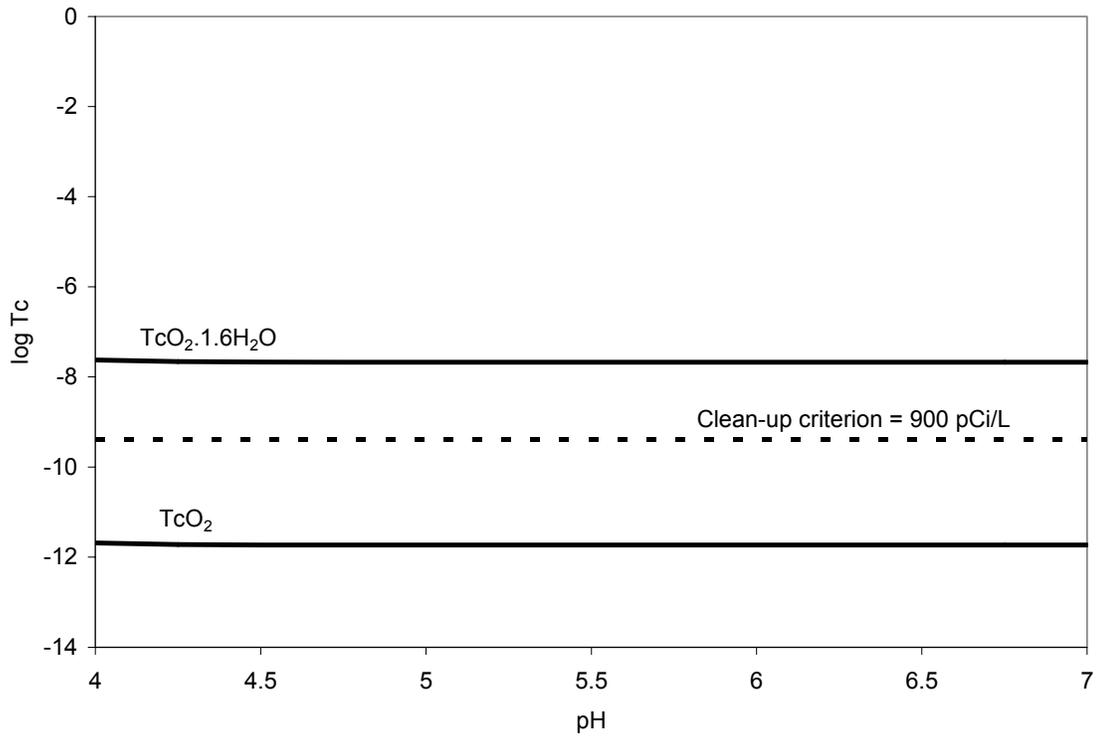


Figure 13: Solubility of Tc(IV) phases.

Amendment Design

The recommended amendment mixture is based on the stoichiometry of the carbon degradation reaction, the groundwater flow rate, and an assumed life span of 30 years for the first meter of amendment. The estimated total life span would be greater and depend on geometry and geochemical issues (to be assessed in treatability experiments). The stoichiometry used was for the median nitrate concentration of 1280 mg/L. The flow rate was based on calculations in WSRC-TR-2003-00340 (Appendix D). These calculations were made for the outermost meter of the hypothetical treatment zone – a cylinder with a 15 m radius and 8 m depth. The total flow rate into this cylinder was divided by the surface area of the cylinder to yield a flow of $1.6 \times 10^{-7} \text{ m}^3/\text{sec}/\text{m}^2$. The amendment mixture calculations were done for a block of 1 m^3 of soil with a porosity of 0.3. The result is that 17 pore volumes flow through the 1 m^3 block each year. Thus the mass of amendments must be sufficient to last through 510 pore volumes to sustain a 30 year life span. Table 3 shows the recommended mixture of amendments for a 1 m^3 block representing the outermost meter of amendment in the trench.

Table 3: Recommended amendment mixture for 30 year life span and a nitrate concentration of 1280 mg/L.

| Amendment | Mass (kg) per m^3 | Weight % |
|----------------|----------------------------|----------|
| Peat | 350 | 22 |
| Hydroxyapatite | 28 | 2 |
| Sand | 1200 | 76 |

Precipitation of calcite may eventually reduce the effectiveness of the amendments and the permeability of the system. The amount of calcite precipitation can be predicted, but the affect on performance can not without laboratory treatability experiments. In terms of the model described earlier, consider the reaction:



Thus, nitrate concentration can be a primary determinant of the amount of calcite precipitation. For every mole of nitrate reduced 1.25 moles of calcite may be precipitated. When nitrate is completely consumed and methanogenic conditions prevail, calcite precipitation will decrease or cease altogether. Hence, it is expected that a zone of calcite precipitation will begin at the upgradient end of the amendment trench and will advance as treatment capacity is diminished by coatings of calcite on amendment surfaces. However, decreasing treatment capacity is less of a concern than decreasing permeability at the upgradient end of the treatment zone. The amendment trench will be wide enough to provide sufficient long-term treatment of the contaminants, but if permeability decreases to values less than the aquifer, groundwater may not enter the trench. Based on the carbon degradation model, a nitrate concentration of 1280 mg/L, other concentrations from Table 2, and flow into a 1 m^3 volume, 128 cm^3 of calcite can potentially precipitate per year. The actual volume of treatment medium over which this precipitates depends on the rate of nitrate reduction. This can only be estimated by laboratory or field experiments.

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