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Potential *In Situ* Remediation of ^{129}I and ^{99}Tc in Groundwater Associated with the F-Area Seepage Basins (U)

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Executive Summary

The purpose of this document is to provide the initial scientific basis for considering supplementary techniques for removing or stabilizing ^{129}I and ^{99}Tc in the subsurface. These methods must be deployable in conjunction with *in situ* pH adjustment or other *in situ* remediation of groundwater associated with the F-Area Seepage Basins. Other criteria for inclusion in this report are that the method satsifies generally accepted regulatory guidance, is relatively easy to apply, and is cost effective.

Iodine and technetium chemistries in groundwater are complicated by multiple possible oxidation states and the ability to form solid phases. At conditions common in groundwater, dissolved iodine can exist as I^-, I_2, or IO_3^-. Dissolved technetium generally occurs as TcO_4^- or hydrolyzed species of Tc(IV). Conditions in F-Area groundwater favor stability of I- whereas technetium may occur as TcO_4^- or a Tc(IV) species. Anionic species of iodine and technetium are mobile in groundwater and raising the pH of the groundwater may enhance their mobility. For this reason, techniques that are useful with *in situ* pH adjustment are sought to remove or stabilize these contaminants.

All of the methods discussed here involve emplacement of reagents in the aquifer. The purposes of the reagents are to alter the redox state of the contaminant or force precipitation of a solid phase that incorporates the contaminant. One reagent that may be particularly useful for remediation of ^{129}I is the non-radioactive natural isotope ^{127}I. Addition of ^{127}I stabilizes desirable forms of iodine making remediation of ^{129}I easier.

The following are summaries of ^{129}I and ^{99}Tc remediation methods discussed in this report.

Precipitation of ^{129}I

Injection of reagents into the aquifer can cause iodide salts to precipitate, removing ^{129}I from groundwater. Addition of univalent copper [Cu(I)] would be effective and the most likely reagent to be acceptable to regulators. This process can be enhanced by addition of non-radioactive ^{127}I to expand the stability field of copper iodide and force its precipitation. Uncertainties include kinetics of copper iodide precipitation, rate of ^{129}I release to groundwater as aquifer conditions change, and regulatory acceptance.

Redox Manipulation/Air Sparging of ^{129}I

If ^{129}I can be converted to diiodine (I_2), it can be purged from the groundwater by air sparging. This method would probably require addition of non-radioactive ^{127}I to expand the field in which diiodine is dominant and an oxidant to convert iodide to diiodine. This is the only method discussed that removes contaminant from the aquifer. Uncertainties include choice of oxidant, Henry's Law constant for diiodine, and the disposition of volatilized ^{129}I (collection, release to atmosphere, etc.).

Redox Manipulation/Precipitation for ^{99}Tc

If total ^{99}Tc concentrations are high enough, reduction of Tc(VII) to Tc(IV) will cause precipitation of a hydrated technetium oxide phase. At lower ^{99}Tc concentrations, reduction removes ^{99}Tc from groundwater by enhancing sorption onto soil. Reduction can be accomplished chemically by injection of reagents or biologically by injection of nutrients to stimulate microbial reduction. Uncertainties include the mechanism of ^{99}Tc stabilization, choice of reductant, and long-term stability.

Redox Manipulation/Co-precipitation of ^{99}Tc

Co-precipitation of ^{99}Tc after reduction from Tc(VII) to Tc(IV) may be a viable strategy for long-term stabilization. The method would require injection of one or two reagents to reduce technetium and force precipitation of the carrier phase. Stannous tin could both reduce technetium and cause co-precipitation in tin oxide. Uncertainties include the distribution coefficient of ^{99}Tc into the carrier phase, kinetics of carrier phase precipitation, long-term stability of the carrier phase, and regulatory issues regarding tin.

Solid Amendments for ^{129}I and ^{99}Tc

Solid reactants to stabilize ^{129}I or ^{99}Tc can be injected as slurries or emplaced in an aquifer as a permeable reactive barrier. The only effective solid amendments for ^{129}I are copper compounds or metallic copper. Amendments that reduce ^{99}Tc may be effective for this contaminant. These include zero-valent iron and metallic copper. Uncertainties include engineering of emplacement, interfering reactions, effect on nitrate (for reductants), and effects of amendment particle coating.

Evaluation of these methods should include consideration of regulatory issues, compatibility with in situ pH adjustment, and potential for collateral damage to the environment. The following table summarizes the potential remediation methods presented here with an assessment of each of these considerations. The numerical qualifiers indicate the relative concern associated with each of these methods for these issues. It must be emphasized that the numerical qualifiers indicate relative factors among the methods presented in this paper. For example, the 3 listed for the potential for reducing technologies to cause collateral damage means that these methods have the highest potential among the methods presented here. It does not mean that they will cause collateral damage. Likewise, for the copper technologies, the 3 listed for potential for regulatory issues does not mean these will be unacceptable to regulators. It means that regulators may require more bench-scale work for these methods than other methods to prove that copper will not exceed regulatory limits.

	Method	**Technical Uncertainties**	**Potential for Regulatory Issues**	**Potential for Collateral Damage**	**Compatibility with Base Injection**
^{129}I	Precipitation of CuI	• Kinetics of CuI precipitation • Future ^{129}I release	3 – Cu in aquifer	2 – Cu in surface water	1
	Redox Manipulation/ Air Sparging	• Best oxidant • Henry's Law constant for diiodine	1 – Disposition of purged ^{129}I	1	2
	Solid Cu Amendments	• Engineering of Emplacement • Effect of Coatings	3 – Cu in aquifer	2 – Cu in surface water	3
^{99}Tc	Reduction/ Precipitation or Enhanced Sorption	• Mechanism of Tc stabilization • Best reductant • Long-term stability	1	3 – reducing conditions in surface water	1
	Reduction/ Co-precipitation	• Distribution coefficient for Tc • Kinetics of carrier phase precipitation • Long-term stability of carrier phase	2 – Sn in aquifer	3 – reducing conditions in surface water	1
	Solid Amendments	• Engineering of emplacement • Effect of coatings • Effect on nitrate	2 – fewer issues with Fe than Cu	2 – Reducing conditions in surface water (worse for Fe than Cu)	3

1 – least potential for regulatory issues and collateral damage; most compatible with base injection

2 – intermediate potential for regulatory issues; intermediate potential for collateral damage; requires some additional infrastructure

3 – most potential for regulatory issues; most potential for collateral damage; least compatible with base injection

Introduction

The Environmental Restoration Department of the Savannah River Site is currently evaluating *in situ* pH neutralization by addition of base solutions to groundwater associated with the F-Area Seepage Basins. This groundwater is acidic and contains elevated concentrations of metals and radionuclides. A main objective of base injection is to raise the pH of the aquifer to a point where natural aluminum and uranium are no longer leached from subsurface sediments in substantial quantities. A potential added benefit is enhanced adsorption of cationic contaminants such as ^{90}Sr. However, some of the contaminants of concern, in particular ^{129}I and ^{99}Tc, are present in groundwater as anions. Raising pH alone will provide no remediation benefit for these contaminants and may enhance their mobility. The purpose of this document is to provide the initial scientific basis for considering supplementary techniques for removal or stabilization of ^{129}I and ^{99}Tc in the subsurface.

The only method currently in widespread use for removing ^{129}I and ^{99}Tc from groundwater is ion exchange. This is normally used in pump-and-treat systems such as those in operation at the F- and H-Area Seepage Basins. Proposals to place ion exchange resins in engineered recirculation systems in the subsurface have been made (Brown, 1997). However, resins used in such systems must be highly selective for the target ions and will require frequent maintenance. Likewise, most ion exchange resins are organic and are subject to degradation and biofouling by microbial activity. Thus, they are not ideal media for *in situ* remediation.

Many of the ideas presented here are untested because of the lack of focus on *in situ* remediation of ^{129}I and ^{99}Tc. Others, such as redox manipulation for ^{99}Tc, are currently under study by several research groups. For inclusion in this paper the methods of ^{129}I and ^{99}Tc remediation must meet certain criteria. They must satisfy generally recognized regulatory acceptance criteria. Proposed methods must be suitable for use in conjunction with base injection. Technologies that counter the effect of base injection or are only useful in highly acidic water were not considered. Cost was also important. There are many examples of reagents that might be useful, but are too expensive. Finally, the methods considered must be relatively easy to apply, preferably using the same infrastructure required for base injection.

Chemistry of F-Area Groundwater

Groundwater associated with the F-Area Seepage Basins has been affected by disposal of predominantly acidic solutions contaminated with a variety of metals and radionuclides. The groundwater typically has high concentrations of sodium and nitrate from process solutions and elevated concentrations of aluminum and silica from dissolution of native minerals. Table 1 lists analyses of groundwater from well FSB-95DR from the 1st quarter of 1997. The well is a water table well located just downgradient from Basin 3. This composition was used for many of the geochemical calculations presented here.

Table 1: Composition of groundwater from well FSB-95DR (1Q97).

Constituent	**Concentration**
pH	3.2
Aluminum (mg/L)	27.8
Calcium (mg/L)	1.2
Magnesium (mg/L)_	4.6
Sodium (mg/L)	155.0
Silica (mg/L)	112.0
Chloride (mg/L)	1.3
Sulfate (mg/L)	13.8
Nitrate-nitrite as nitrogen (mg/L)	145.0

The most important parameters for remediation of ^{99}Tc and ^{129}I are pH and oxidation-reduction (redox) potential. Measurement of pH is routinely done when sampling monitoring wells at the SRS, but measurements of redox potential are not. The few redox potential measurements that are made must be interpreted cautiously because it is often unclear which redox couples most influence the measurement.

Nevertheless, an understanding of redox conditions in an aquifer is important to remediation of redox sensitive constituents.

One method of estimating redox conditions is to use the ferric-ferrous iron couple. Electrons tend to transfer easily from Fe(II) to Fe(III) and there is abundant solid phase iron in the aquifer. If this iron is present as hematite, its dissolution in the pH range of 3.5 to 7.3 is described by the reaction:

$Fe_2O_3 + 2H^+ + H_2O = 2Fe(OH)_2^+$

Depending on the redox conditions, the ferric iron may be reduced to ferrous iron by the reaction:

$Fe(OH)_2^+ + 2H^+ + e^- = Fe^{+2} + 2H_2O$ log K = 18.70

The negative log of the electron activity (pE) in this system can then be described by:

$$pE = 18.70 + \log \frac{Fe(OH)_2^+}{Fe^{+2}} - 2pH$$

The variable pE is similar to Eh in that it describes the potential for oxidation or reduction in a system. The higher the pE of a system, the greater the tendency toward oxidation. Thus, in this method of estimation, the ratio of dissolved ferric to ferrous iron describes the redox conditions of the system. However, only total iron is measured in groundwater at F-Area. To obtain the ratio of ferric to ferrous iron, the system is assumed to be in equilibrium with a solid ferric iron phase that is present in the aquifer. The solubility of this phase can be calculated to provide the ferric iron concentration. The ferrous iron concentration is the difference between the ferric iron concentration and the total iron measurement. Figure 1 shows an iron speciation diagram with estimates of pE derived by this method. The closed triangles and circles were estimated based on the solubility of amorphous ferric hydroxide [$Fe(OH)_3$] and the open triangles and circles were estimated based on the solubility of hematite (Fe_2O_3). The difference is a reflection of the much higher solubility of the amorphous phase, which leads to a higher ferric to ferrous ratio. These two trends represent a reasonable range of redox conditions in the F-Area water table aquifer and are consistent with the few measurements of redox potential that have been made (open and closed green squares in Figure 1).

^{129}I and ^{99}Tc Concentrations in F-Area Groundwater

Figure 2 shows concentrations of ^{129}I and ^{99}Tc plotted against each other for the FSB wells since January 2001. The Underground Injection Control (UIC) limits of 60 pCi/L for ^{129}I and 170 pCi/L for ^{99}Tc are also shown. The ^{129}I concentrations range up to 539 pCi/L, nearly nine times the UIC limit. The maximum ^{99}Tc concentration is 208 pCi/L and is the only ^{99}Tc measurement that exceeds the UIC limit. This suggests that finding a remedy for ^{129}I contamination may be more beneficial than finding one for ^{99}Tc. This is important because many of the potential remedies are effective at treating one but not both of the contaminants.

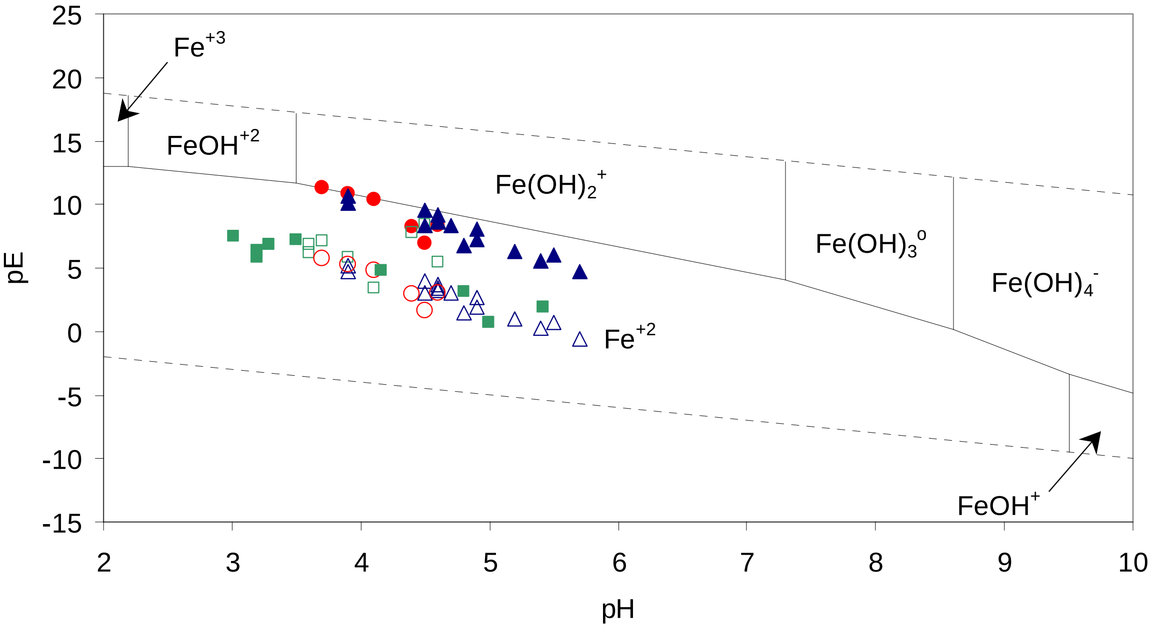

Figure 1: Speciation diagram for aqueous iron species. Triangles and circles were calculated by the method described in text (open symbols assume hematite as controlling phase, closed symbols assume amorphous ferric hydroxide as controlling phase). Squares are measured redox potential values (open are FBI well series; closed from Boltz et al., 1994).

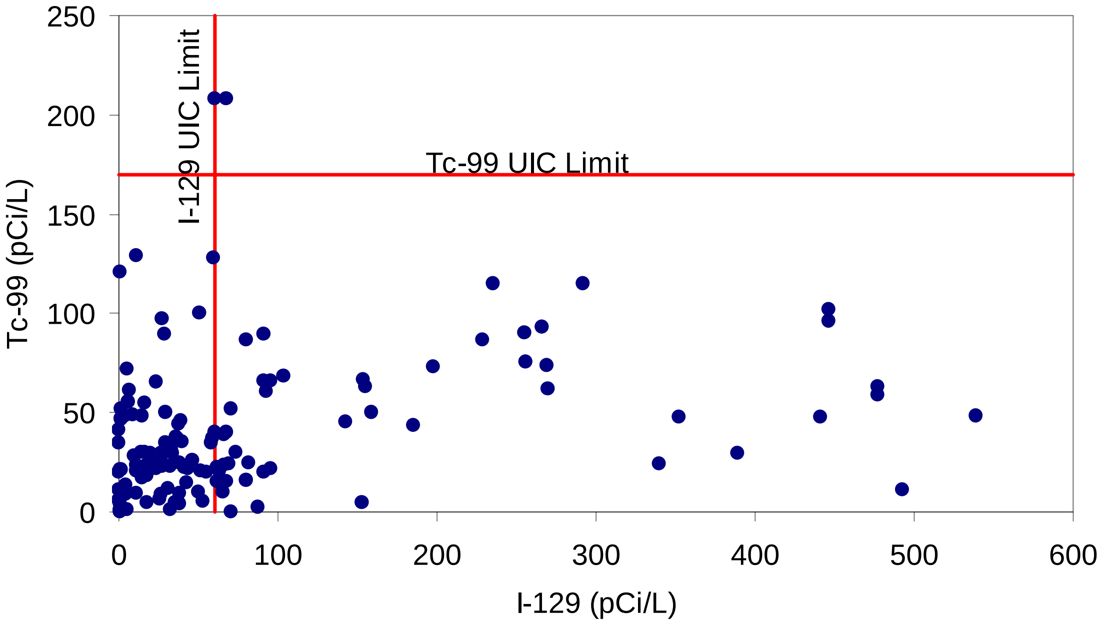

Figure 2: Analyses of ^{99}Tc and ^{129}I from FSB well series since January 2001. Red lines show UIC limit for ^{129}I (60 pCi/L) and ^{99}Tc (170 pCi/L).

Iodine Chemistry

The chemistry of iodine is complicated because of the multiple oxidation states and the multiple physical states in which it can exist. Valence states of –1, 0, +1, +3, +4, +5, and +7 are known and all except +4 form stable compounds. At conditions typical of groundwater, the –1, 0, and +5 states prevail. Figure 3 shows the pE-pH fields in which these predominate as iodide(I^-), diiodine(I_2), and iodate(IO_3^-). At the conditions in F-Area groundwater, iodide is expected to be prevalent.

Iodide forms insoluble salts with copper(I), silver(I), gold(I), and mercury. It also forms strong aqueous complexes with a number of metals. In some cases, this can significantly enhance the solubility of metals. For example, attempts to precipitate mercury by addition of iodide would not be successful. Even though mercury iodide is quite insoluble, the aqueous complexes HgI^+, HgI_2^o, HgI_3^-, and HgI_4^- would keep mercury in solution.

At acidic and moderately oxidizing conditions iodide will convert to diiodine. The only solid phase that diiodine forms is metallic iodine with a solubility of about 340 mg/L. Diiodine is also relatively volatile. Table 2 shows the vapor pressures of some common contaminants and diiodine at 20°C. The vapor pressure of diiodine is between those of volatile organic solvents and mercury.

Table 2: Vapor pressures of selected contaminants.

Contaminant	**Vapor Pressure @ 20 °C (atm.)**
Trichloroethylene	$8x10^{-2}$
Perchloroethylene	$2x10^{-2}$
Diiodine	$3x10^{-4}$
Mercury	$2x10^{-6}$

The most oxidized form of iodine found in groundwater is iodate. The salts of iodate with common metals are all soluble beyond acceptable environmental levels. The only remediation benefit of converting iodide to iodate is a tendency for iodate to adsorb more strongly to soils (Ticknor and Cho, 1990).

The isotopic chemistry of iodine may also be important to its remediation. Naturally occurring iodine exists almost exclusively as the non-radioactive isotope ^{127}I. Concentrations of ^{127}I in SRS groundwater are on the order of micrograms per liter compared to mass concentrations of ^{129}I that range from nanograms to micrograms per liter in contaminated groundwater. The chemical behavior of the two isotopes is identical and any process that removes ^{129}I also removes ^{127}I. This can be a detriment to ion exchange and other remediation systems, but can also be beneficial to clean-up efforts.

The complicated chemistry of iodine makes *in situ* remediation of ^{129}I challenging, but it also provides the opportunity to exploit multiple properties to design remediation strategies that are consistent with the overall goals at a site. The most promising properties to exploit are the low solubility of iodide in the presence of copper(I) and the volatility of diiodine.

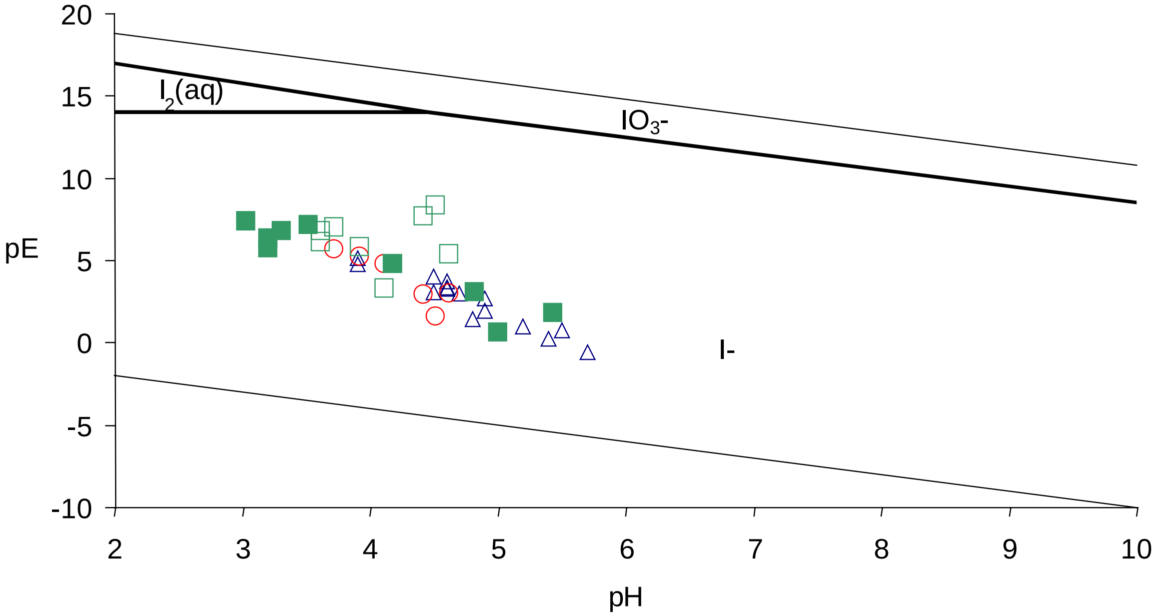

Figure 3: Speciation diagram for aqueous iodine species ([Itotal] = 3.6 ug/L). Squares are redox potential measurements (open squares are from FBI series; closed squares from Boltz et al., 1994). Circles are estimates from FBI well series and triangles from FSB well series using the redox estimation method discussed in text. Thin line shows limits of stability of water.

Potential ^{129}I Remediation Strategies

Precipitation

Summary of Method

Injection of reagents into the aquifer can cause iodide salts to precipitate, removing ^{129}I from groundwater. Addition of univalent copper [Cu(I)] would be effective and the most likely potential reagent to be acceptable to regulators. This process can be enhanced by addition of non-radioactive ^{127}I to expand the stability field of copper iodide and force its precipitation.

Uncertainties

- Kinetics of CuI precipitation
- Rate of ^{129}I release to groundwater with changing aquifer conditions
- Regulatory acceptance

Technical Basis

The fact that iodide forms insoluble salts with some metals suggests that precipitation may be a viable remediation strategy for ^{129}I. However, three of the four metals that could be used for this purpose have significant problems. Gold iodide is insoluble ($K_{sp} = 1.5\times10^{-14}$), but the cost of using gold would be prohibitive. Silver and mercury iodides are also insoluble ($K_{sp} = 8.1\times10^{-17}$ (AgI) and 2.3×10^{-29} (HgI_2)), but both are considered hazardous metals and would not be appropriate for injection into an aquifer. Thus, univalent copper is the most promising counterion for precipitation of iodide by the reaction:

$$Cu^+ + I^- = CuI \qquad K_{sp} = 3.5\times10^{-12}$$

The saturation curve for CuI is presented in Figure 4 as the concentration of iodide versus the concentration of Cu^+. At concentrations above the saturation curve, CuI is oversaturated and may precipitate. The data (squares) show concentrations of ^{129}I and copper in wells FBI-7, -9, -11, and –14. During the last two years, these wells have exhibited the highest ^{129}I and copper concentrations in the FBI well series. Under current conditions, F-Area groundwater is well below saturation with CuI. This is true even when concentrations of natural ^{127}I are considered. Addition of copper to bring the groundwater to saturation is constrained by the Maximum Concentration Limit (MCL) for copper of 1.3 mg/L. However, saturation can be achieved by addition of ^{127}I or a combination of both copper and ^{127}I without violating the MCL for copper.

The method of adding a common naturally occurring isotope to force precipitation of a radioactive isotope of the same atomic number has been termed autoprecipitation. This may be useful for several radioactive contaminants and is currently under study at SRTC for ^{90}Sr and ^{129}I. To force precipitation of ^{129}I, it can be incorporated as a co-precipitate in salts dominated by ^{127}I. Because the chemical behavior of the two isotopes is identical, ^{129}I is incorporated into ^{127}I salts at the same ratio as occurs in the groundwater. Thus, if 0.5 mg/L ^{127}I is added to a groundwater that contains 100 pCi/L (3.9×10^{-4} mg/L) ^{129}I, the radioactive isotope will co-precipitate with the non-radioactive isotope at an ^{129}I/^{127}I ratio of 7.8×10^{-4}. It is beneficial to optimize the amount of ^{127}I added to obtain the maximum ^{129}I/^{127}I ratio while ensuring that precipitation of ^{129}I will be sufficient to achieve the ^{129}I concentration goal.

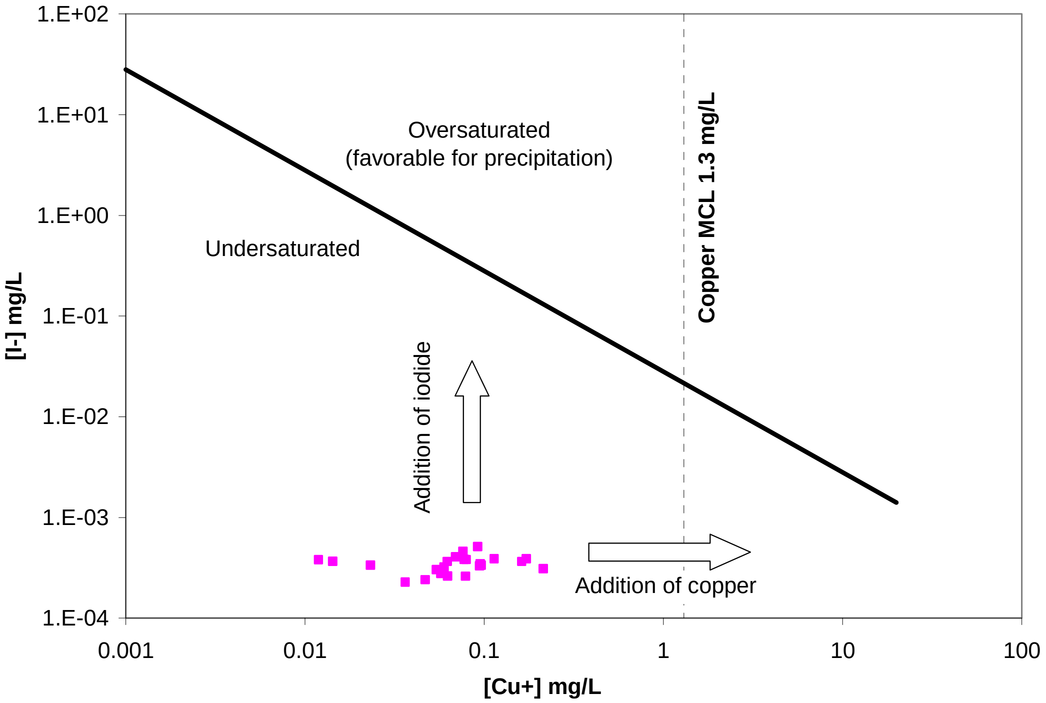

Figure 4: Saturation curve for CuI. Squares show measurements of copper and ^{129}I in FBI well series.

The redox chemistry of CuI presents a challenge to its use for autoprecipitation. The required univalent copper is easily oxidized to divalent copper or reduced to copper metal. Thus, the stability field of CuI is relatively small. Figure 5 shows the stability of CuI on a pE versus pH diagram for a solution containing 1 mg/L iodide and 0.1 mg/L total copper. The stability field extends over a narrow pE range, but is in the middle of the range of conditions expected for F-Area groundwater. Figure 6 shows that the solubility of CuI is dependent on redox conditions. As the system becomes either more oxidized or more reduced the solubility of CuI increases. Figure 6 also shows that the addition of iodide or copper can stabilize CuI over a wider range of redox conditions. Adding iodide increases the stability of CuI in both the oxidizing and reducing directions, but adding copper stabilizes CuI to more oxidizing conditions. Figure 5 reiterates this by showing an enlarged stability field for CuI at higher iodide (10 mg/L) and copper (1 mg/L) concentrations.

Redox Manipulation/Air Sparging

Summary of Method

If ^{129}I can be converted to diiodine (I_2), it can be purged from the groundwater by air sparging. This method would probably require addition of non-radioactive ^{127}I to expand the field in which diiodine is dominant and an oxidant to convert iodide to diiodine.

Uncertainties

- The best oxidant for conversion of iodide to diiodine without complete oxidation to iodate

- Henry's Law constant for diiodine
- Disposition of volatilized ^{129}I (collection, release to atmosphere, etc.)

Technical Basis

The volatility of diiodine may be exploited to remove ^{129}I from groundwater. This approach is commonly used to "mine" iodine from natural brines by oxidizing iodide to diiodine which is then stripped from the brine with air (Hills, 1956; Lauterbach and Ober, 1996). A similar approach may be viable for treatment of ^{129}I in F-Area groundwater.

Figure 7 shows the expected redox conditions of F-Area groundwater on a speciation diagram of iodine at a total iodine concentration of 3.6 ug/L. Diiodine is dominant at more oxidizing conditions than are prevalent at F-Area. In addition, at 3.6 ug/L total iodine, diiodine is stable only at pH below 4.45. Thus, direct oxidation of iodide in F-Area groundwater may not produce diiodine. Likewise, too vigorous an oxidation will convert iodide to iodate rather than diiodine.

One way to promote conversion of iodide to diiodine is to add ^{127}I to the system. The size of the diiodine field of dominance is dependent on the total concentration of iodine in the system. The dotted line in Figure 7 shows the expansion of this field by an increase in iodide concentration from 3.6 ug/L to 1000 ug/L. The pH at which diiodine is dominant increases to 5.67 and the pE decreases from 14.09 to 12.86. Addition of ^{127}I to F-Area groundwater would allow oxidation of iodide to diiodine under most conditions likely to be encountered, including those expected following base injection.

The choice of oxidant may be critical to success of an air sparging method for remediation of ^{129}I. The rate of oxidation must be sufficient to convert iodide to diiodine in a reasonable time and this conversion should be more rapid than the conversion of iodide to iodate. There is no definitive way of predicting these rates without experimental evidence. However, the thermodynamic driving force for a reaction is often a factor influencing the rate of reaction. For a particular oxidant, the difference in free energy of the reactions of 1 mole of iodide to diiodine and 1 mole of iodide to iodate may indicate promising oxidants. Table 3 shows several oxidants, the free energy of conversion to diiodine, and this value subtracted from the free energy of conversion to iodate. A positive difference means the oxidant will not convert iodide to iodate under the given conditions, but will convert iodide to diiodine. If the rate of reaction is sufficient, then this is the ideal oxidant. A negative difference means that conversion to iodate is thermodynamically favored over conversion to diiodine. A smaller difference is preferable because it means the driving forces for the two reactions are closer.

Table 3: Potential oxidants for conversion of iodide to diiodine. ΔGr shown for oxidation to diiodine. Free energy difference calculated by subtraction of free energy values for iodide to diiodine from free energy values for iodide to iodate reactions.

Oxidant	**ΔGr (kcal/mole)**	**Free Energy Difference (kcal/mole)**
$Fe(OH)_3$ (amorphous)	-8.15	+25.36
MnO_2 (pyrolusite)	-14.09	-4.39
O_2	-15.04	-9.12
O_3	-21.00	-38.90
ClO^-	-25.41	-60.98
H_2O_2	-26.39	-65.86

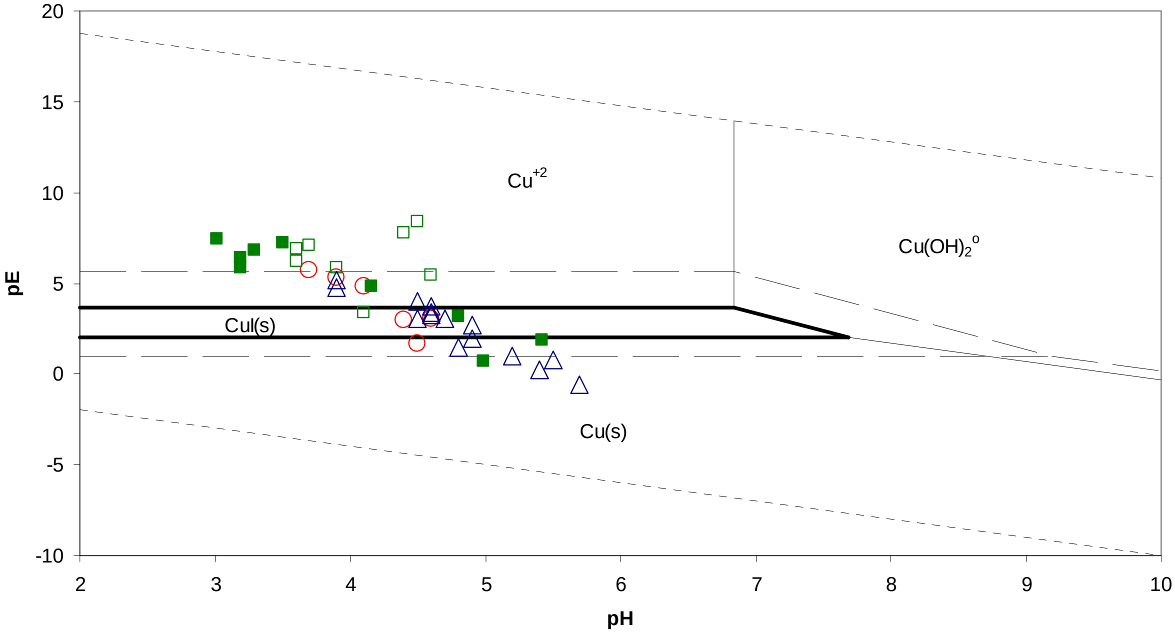

Figure 5: Speciation diagram for dissolved Cu(II) species and stability fields for solid CuI and copper metal ([I]=1 mg/L, [Cu]=0.1 mg/L). Dashed line shows expansion of CuI field at [I]=10 mg/L and [Cu]=1 mg/L. Squares are measurements of redox potential (open from FBI well series; closed from Boltz et al., 1994). Dotted line shows limits of the stability of water.

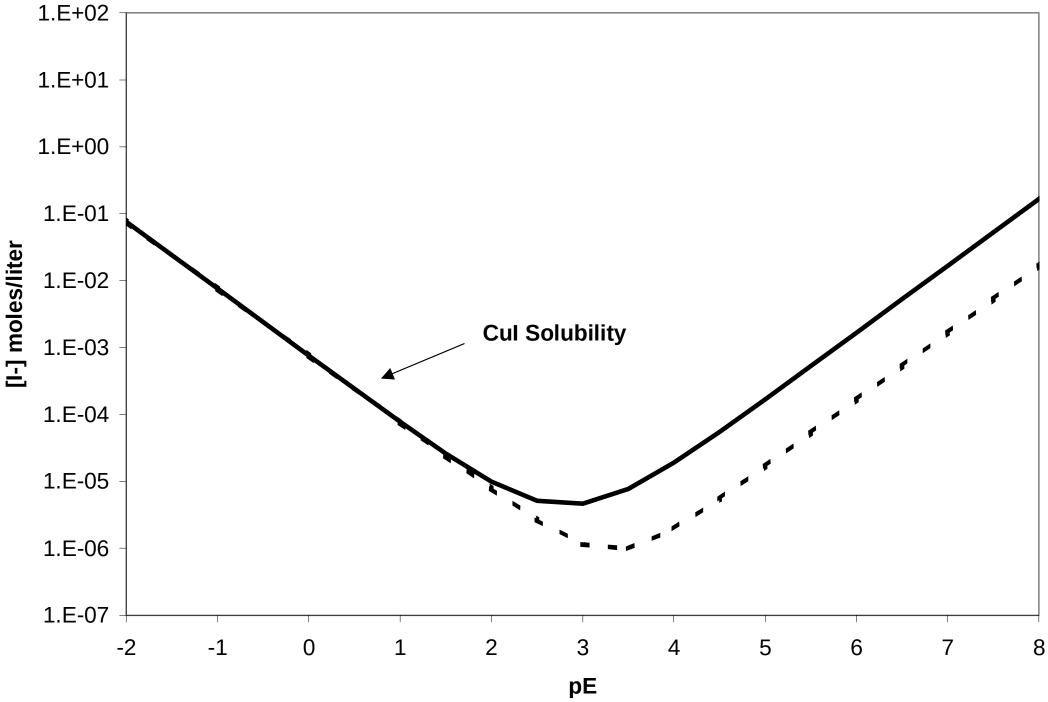

Figure 6: Solubility of CuI as iodide concentration versus pE. Solid line calculated at [Cu]=0.1 mg/L; dotted line calculated at [Cu]=1 mg/L.

The potential oxidants listed in Table 3 include solid, liquid, and gaseous amendments. Solid amorphous iron hydroxide is the only one that will oxidize iodide to diiodine, but not iodide to iodate. The mineral pyrolusite is also of potential interest because the driving forces for the two reactions are similar. The reactivity of these minerals with iodide is unknown. Similar phases exist in the F-Area aquifer, but apparently do not oxidize iodide. The reason for this is uncertain, but suggests that all potential oxidants should be considered.

Oxidation of iodide to diiodine allows dissolved diiodine to equilibrate with the vapor phase according to a simplified Henry's Law:

$$C_{vapor} = H' \times C_{dissolved}$$

Using consistent units of measurement, $C_{dissolved}$ is the aqueous concentration of diiodine (mass of iodine per volume of water), C_{vapor} is the concentration in the vapor phase (mass of iodine per volume of gas), and H' is the dimensionless Henry's Law constant. An approximation of the Henry's Law constant can be obtained from the solubility of diiodine and its vapor pressure (Lyman et al., 1982):

$$H' = \frac{Solubility}{Vapor\ pressure}$$

If the units of the solubility and the vapor pressure are the same, then a "dimensionless" Henry's Law constant (H') is obtained. Removal of diiodine by air sparging can be described by the equation:

$$\frac{C_{n'}}{C_o} = e^{-H'n'}$$

where n' is the ratio of the volume of air sparged to volume of water, Cn' is the concentration of diiodine at that ratio, and C_o is the initial concentration of diiodine. Solubility and vapor pressure data for diiodine were obtained from Hills (1956) and Lauterbach and Ober (1996) to estimate a dimensionless Henry's Law constant of 0.0125 at 25°C. The calculated sparging curve for diiodine is shown in Figure 8 with the curves for TCE and mercury shown for comparison. TCE and mercury have similar Henry's Law constants and are indistinguishable in this figure. Looney et al. (2001) have demonstrated the feasibility of air sparging as a remediation method for dissolved mercury. Mercury was removed at a rate easily achievable by conventional air strippers. The removal of diiodine would be less efficient and the use of a conventional high volume air stripper would probably not be suitable. However, *in situ* air stripping or unconventional surface air stripping techniques might be feasible. Figure 9 shows the calculated ^{129}I removal curve for an initial concentration of about 200 pCi/L. It indicates that to achieve the UIC limit of 60 pCi/L would require an air/water ratio of about 100.

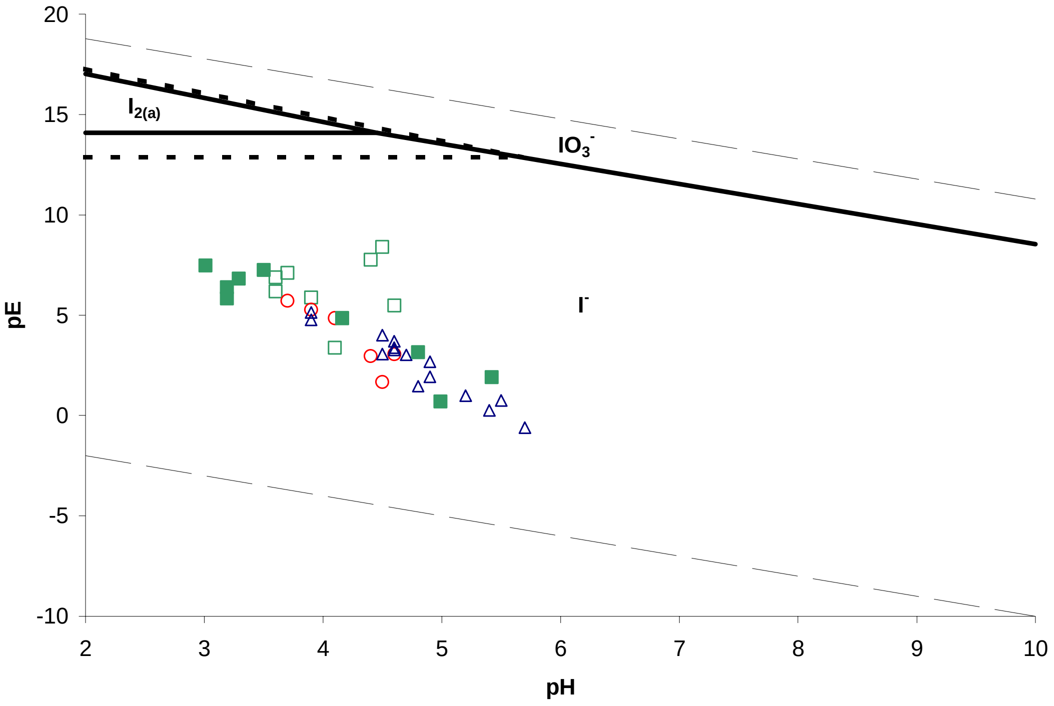

Figure 7: Iodine speciation diagram showing expansion of diiodine field (dotted line) by addition of ^{127}I to a total concentration of 1000 ug/L.

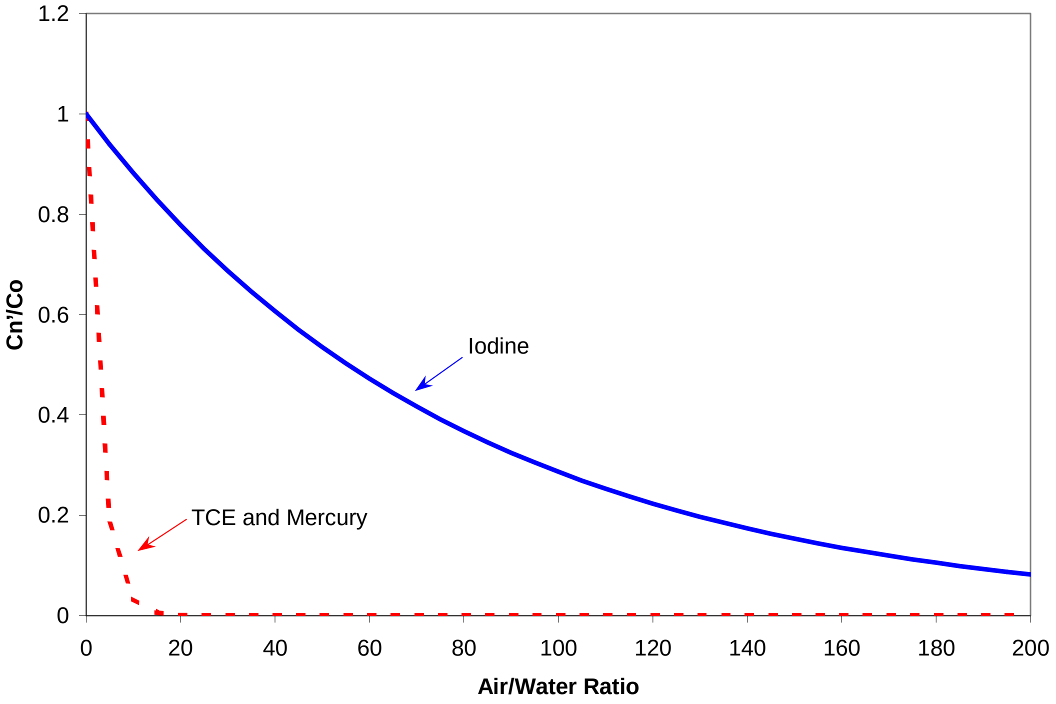

Figure 8: Iodine removal curve for air sparging (blue solid line) with indistinguishable TCE and mercury removal curves for comparison (red dotted line).

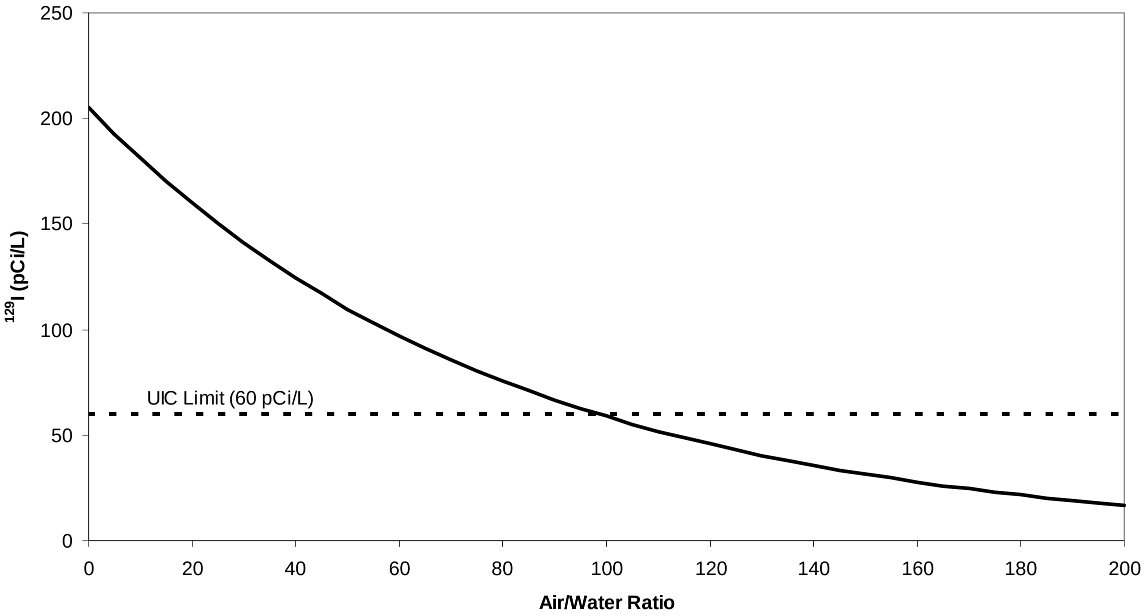

Figure 9: ^{129}I removal curve by air sparging for initial concentration of 205 pCi/L.

Solid Amendments

Summary of Method

Solid reactants to stabilize ^{129}I can be injected or emplaced in an aquifer as a permeable reactive barrier. Potentially useful solid amendments include amorphous ferric hydroxide or manganese dioxide to convert iodide to diiodine for air sparging and metallic copper to facilitate precipitation of copper iodide.

Uncertainties

- Engineering of emplacement
- Effect of coatings on reactivity
- For metallic copper – release of dissolved copper to groundwater
- For metallic copper – regulatory acceptance

Technical Basis

Solid amendments can be emplaced in an aquifer as slurries or as barrier walls. Both methods present greater engineering challenges than injection of liquid or gaseous amendments. Slurries require a carrier fluid to suspend the solid particles. The properties of this fluid control the mass of amendment and area of distribution that can be achieved per injection (Cantrell et al., 1997). In addition, viscous organic fluids are generally used to suspend reagent particles. The microbial degradation of these fluids introduces another variable that must be considered when designing a remediation. Installation of barrier walls generally requires trenching and backfilling the trench with solid amendment. Depth is a limiting factor for this approach, as is the ability to handle large volumes of radioactive soil and groundwater.

The advantage of solid amendments is that a greater mass of amendment can be emplaced per volume of aquifer. In theory, this equates to a longer period of reactivity for the amendment than is achievable with liquid or gaseous amendments. In reality, solid amendments can become coated with precipitates from the groundwater that reduce their reactivity. This requires that greater than stoichiometric quantities of amendment be used and may offset the advantage of the solid amendment.

Potential solid amendments for ^{129}I remediation include oxidants to facilitate air sparging, reactants that cause precipitation, and ion exchangers. The solid oxidants $Fe(OH)_3$ and MnO_2 are discussed above and would potentially oxidize iodide to diiodine to allow removal by air sparging. In a study of ^{129}I mobility in soils, Kaplan et al. (2000) found that iodine adsorbed appreciably to illite clay. They point out that the ^{129}I was easily desorbed by introduction of other halides. Thus, illite is not likely to be a useful amendment for ^{129}I. Brown (1997) and Vilensky et al. (2002) suggest that ion exchange resins can be placed in retrievable configurations in wells or walls. This may be useful, but would require long-term maintenance and disposal of waste associated with the resins.

Copper metal and mixtures of copper compounds are potentially the most useful solid amendments for remediation of ^{129}I by precipitation. Precipitation of CuI as a method of stabilizing ^{129}I in an aquifer is discussed above. Lefevre et al. (1999) demonstrated that a mixture of copper metal and the mineral azurite [$Cu_3(OH)_2(CO_3)_2$] causes precipitation of CuI. They suggested that such a mixture would be useful as a migration barrier around ^{129}I containing waste. Likewise, Balsey et al. (1996) found that the mineral chalcocite [Cu_2S] strongly adsorbed iodide. The strongest adsorption occurred at low pH (about 4), making chalcocite potentially useful for acidic groundwater. Mixtures of these relatively rare minerals might be useful for limited groundwater volumes, but would probably be too expensive for use at F-Area. Other mixtures could be designed that slowly release ^{127}I for reaction with copper metal and co-precipitation of ^{129}I.

Technetium Chemistry

Like iodine, 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 $TcO_2 \cdot nH_20$. Figure 10 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 $TcO(OH)^+$ and $TcO(OH)_2^o$. The data in Figure 10 show redox conditions in F-Area groundwater suggesting that conditions are close to the equal activity line between TcO_4^- and $TcO(OH)_2^o$. The ratio between $TcO(OH)_2^o$ and TcO_4^- can be calculated from the pE and pH data shown in Figure 10. Between pHs of 3.8 and 4.8 substantial concentrations of both TcO_4^- and $TcO(OH)_2^o$ may co-exist in the groundwater (Figure 11). At low pH technetium speciation is dominated by TcO_4^-, whereas $TcO(OH)_2^o$ dominates at high pH. This complicates ^{99}Tc remediation because various portions of the F-Area plume may be dominated by different species that respond differently to particular remediation methods. In the intermediate pH range both species may exist, further complicating remediation.

Potential ^{99}Tc Remediation Strategies

Redox Manipulation/Precipitation

Summary of Method

If total ^{99}Tc concentrations are high enough, reduction of Tc(VII) to Tc(IV) will cause precipitation of a hydrated technetium oxide phase. At lower ^{99}Tc concentrations, reduction removes ^{99}Tc from groundwater by enhancing sorption onto soil. Reduction can be accomplished chemically by injection of reagents or biologically by injection of nutrients to stimulate microbial reduction.

Uncertainties

- Mechanism of ^{99}Tc removal – precipitation or enhanced sorption
- Best reductant to use
- Ability to maintain reducing conditions – long-term stability

Technical Basis

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. The Natural and Accelerated Bioremediation (NABIR) program of DOE has funded several projects to microbially reduce technetium. Examples can be found on the NABIR website http://www.lbl.gov/NABIR.

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 12 the solubilities of TcO_2 and $TcO_2 \cdot 1.6H_2O$ are shown versus pH. Though the solubility of TcO_2 is much lower than the solubility of $TcO_2 \cdot 1.6H_2O$, TcO_2 does not precipitate readily at low temperatures. For example, Meyer and Arnold (1991) found that $TcO_2 \cdot 1.6H_2O$ was the stable stoichiometry of the solid phase precipitated by electrodeposition. This is consistent with other studies. The data in Figure 12, from FSB wells, indicate that concentrations of ^{99}Tc in F-Area groundwater are below the solubility of $TcO_2 \cdot 1.6H_2O$. Thus, reduction of technetium will not cause precipitation of $TcO_2 \cdot 1.6H_2O$ and is unlikely to result in precipitation of the less soluble TcO_2. Nevertheless, ^{99}Tc concentrations may decrease upon reduction to Tc(IV) because of enhanced sorption of the aqueous species $TcO(OH)^+$ and $TcO(OH)_2^o$ (Walton et al., 1986; Lieser and Bauscher, 1987; Liang et al., 1996).

Redox Manipulation and Co-precipitation

Summary of Method

Co-precipitation of ^{99}Tc after reduction from Tc(VII) to Tc(IV) may be a viable strategy for long-term stabilization. The method would require injection of one or two reagents to reduce technetium and force precipitation of the carrier phase.

Uncertainties

- Distribution coefficients of ^{99}Tc into appropriate carrier phases
- Kinetics of carrier phase precipitation
- Long-term stability of carrier phase
- Regulatory issues regarding tin

Technical Basis

A variant on redox manipulation and precipitation of technetium is to reduce technetium and co-precipitate it with a metal oxide, hydroxide, or other phase. This could involve addition of two reagents -- one to reduce technetium and one to force precipitation of the desired carrier phase. Ideally, though, the reductant would also be the primary cation in the desired phase and only one reagent would be required. Co-precipitation of reduced technetium may be particularly advantageous if the phase used to co-precipitate ^{99}Tc is stable at the natural post-treatment conditions of the aquifer. In this case, reducing conditions would not have to be maintained for long-term stabilization of ^{99}Tc.

A minor or trace element is incorporated into a precipitating phase according to the relation:

$$D \times \frac{m_{tr}}{m_p} = \frac{X_{tr}}{X_p}$$

where m_{tr} and m_p are the molalities of the trace and primary cation, X_{tr} and X_p are the mole fractions of the trace and primary cations in the solid, and D is the distribution coefficient. The distribution coefficient is related to properties of the respective cations and their pure solid phases. For example, the distribution coefficient for a trace element in calcite is related to the ratio of the solubility products of pure calcite and the pure trace carbonate (Rimstidt, 1998). Charge on the cation and the radius of the cation in the solid phase are important as well.

Figure 13 illustrates the removal of ^{99}Tc by co-precipitation from groundwater with an initial concentration of 200 pCi/L. Curves for distribution coefficients ranging from 0.05 to 5 are shown. Even at a low distribution coefficient (e.g. 0.05) sufficient ^{99}Tc can be removed from groundwater to achieve the UIC limit, but much more solid must be precipitated than for higher distribution coefficients. For a distribution coefficient of five, $4x10^{-6}$ moles must be precipitated compared to $1x10^{-4}$ moles for a distribution coefficient of 0.05.

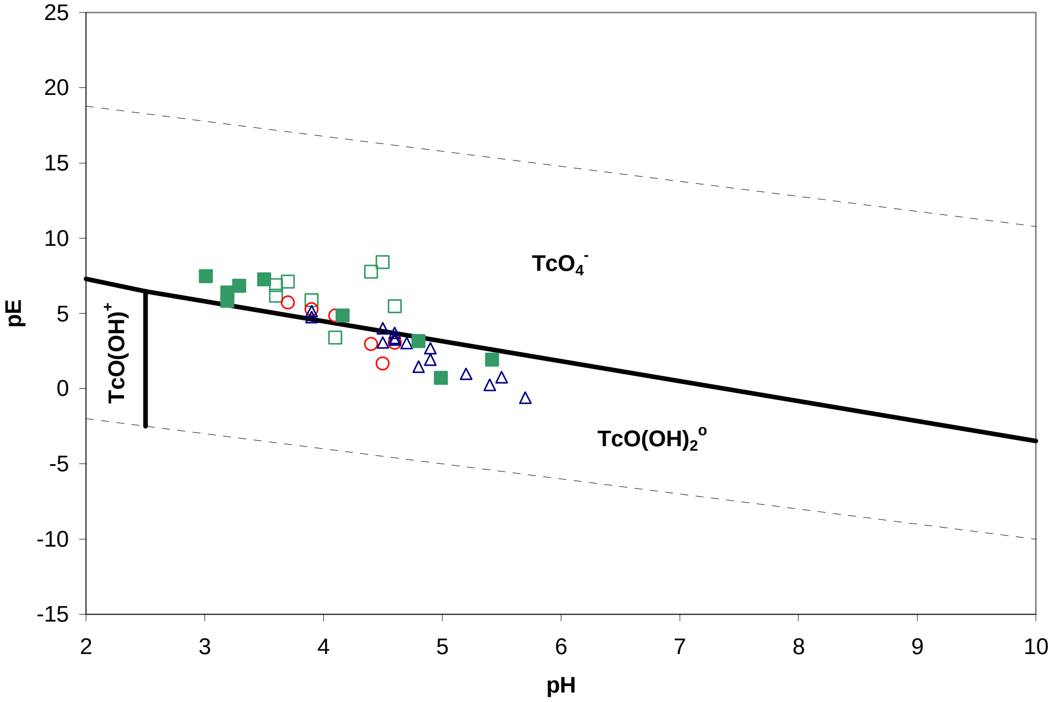

Figure 10: Speciation diagram for technetium. Squares are measurements of redox potential (open from FBI well series; closed from Boltz et al., 1994). Triangles and circles are estimates from [Fe] and pH of FBI wells (circles) and FSB wells (triangles). Dotted line shows limits of the stability of water.

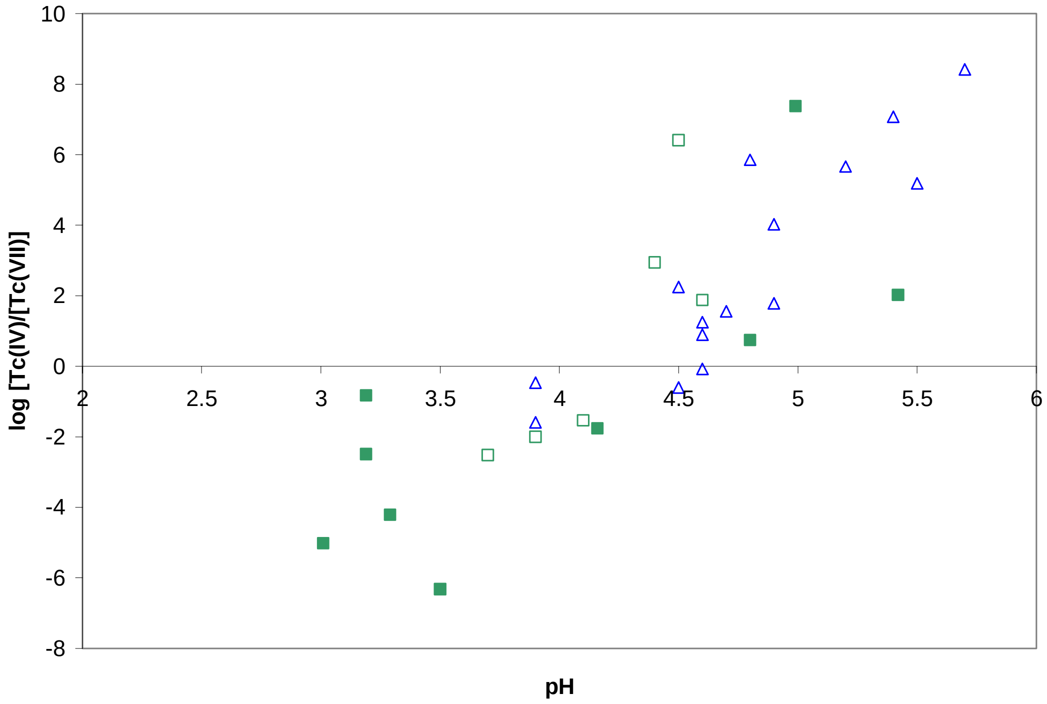

Figure 11: Ratio of reduced to oxidized technetium versus pH in F-Area aquifer. Squares are measurements of redox potential (open from FBI well series; closed from Boltz et al., 1994). Triangles are estimates from [Fe] and pH of FSB wells.

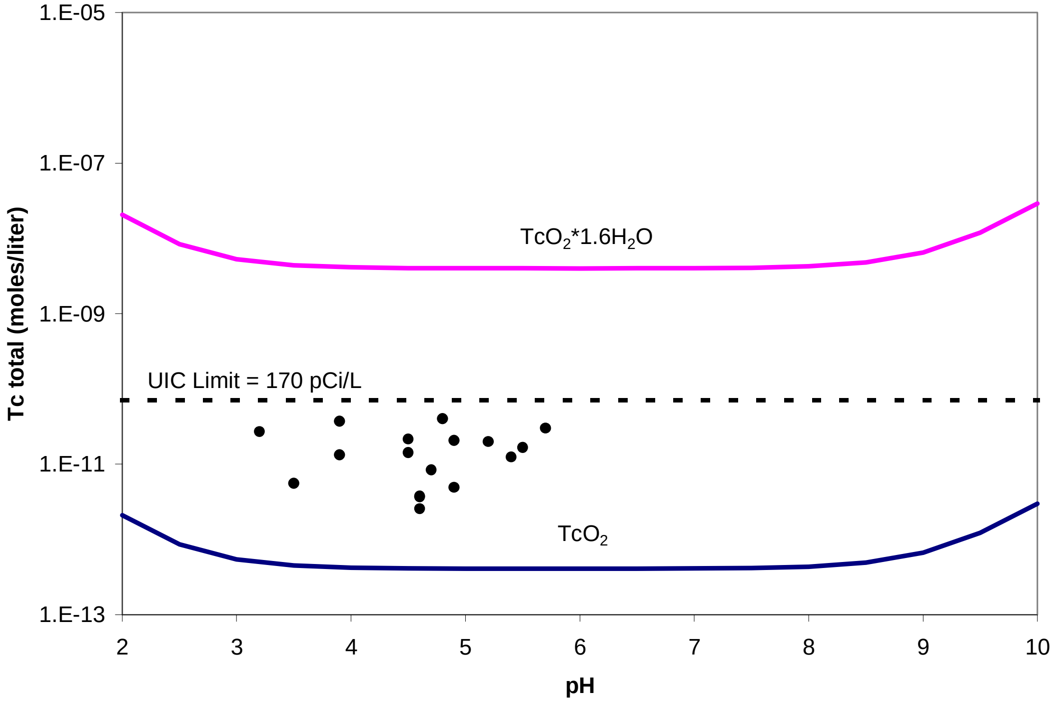

Figure 12: Solubility curves for the phases $TcO_2 \cdot 1.6H_2O$ and TcO_2. Data are concentrations of ^{99}Tc from FSB wells.

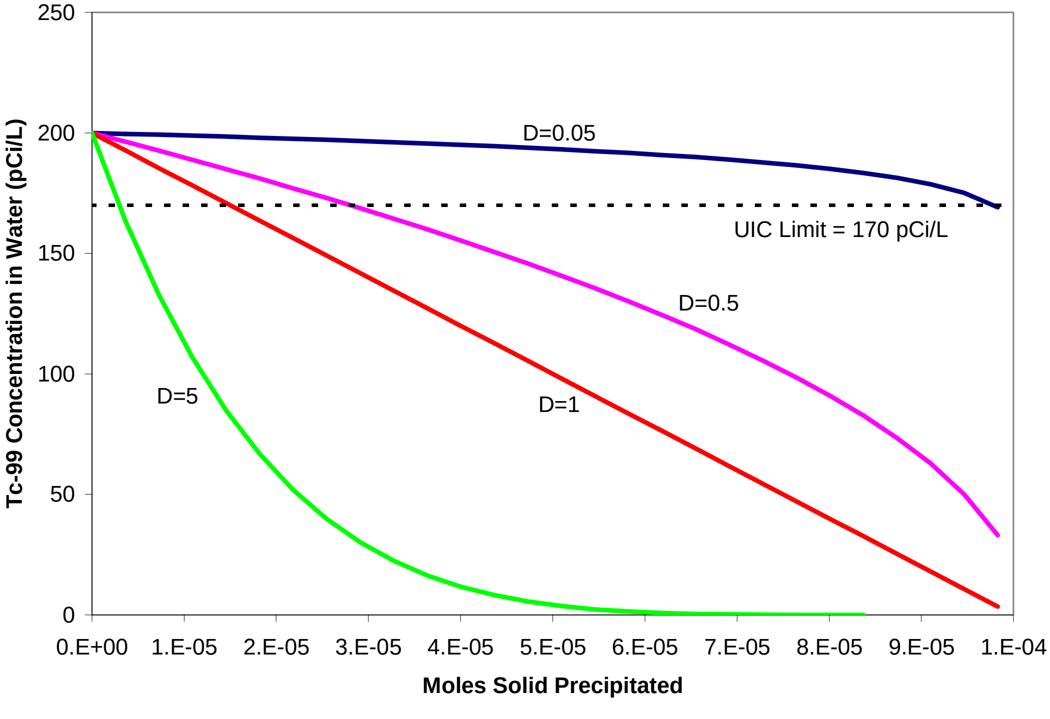

Figure 13: Removal of ^{99}Tc from groundwater by co-precipitation in a phase with different distribution coefficients. Initial ^{99}Tc concentration of 200 pCi/L.

Stannous tin [Sn(II)] is a potential reductant for Tc(VII) that precipitates as a potential carrier (SnO_2) as it oxidizes. The reaction below is thermodynamically favorable and Sn(II) has been used to reduce Tc(VII) in the laboratory (Yoshihara, 1996).

$$1.5Sn^{+2} + TcO_4^- + 2H^+ + 2H_2O = TcO(OH)_2^o + 1.5SnO_{2(s)} + 4H^+ \qquad \log K = 34.26$$

The cations in TcO_2 and SnO_2 have the same charge and hydrolyze to similar species in water (Séby et al., 2001). This suggests the possibility that Tc(IV) might preferentially partition into SnO_2 as technetium is reduced and SnO_2 is precipitated. If this is the case, a remediation strategy might consist of injection of stannous chloride into the aquifer to reduce and co-precipitate ^{99}Tc. An advantage of co-precipitating with SnO_2 is that this phase is stable at natural aquifer conditions. A collateral benefit of this approach is that it may assist in removal of mercury from the groundwater. Looney et al. (2001) demonstrated that mercury reduced by stannous chloride to Hg^o could be purged from groundwater by air sparging.

Solid Amendments

Summary of Method

Solid reactants to stabilize ^{99}Tc can be injected or emplaced in an aquifer as a permeable reactive barrier. Potentially useful solid amendments include activated carbon, zero-valent iron, and zero-valent copper.

Uncertainties

- Engineering of emplacement
- Interfering reactions
- For zero-valent iron and copper – effect on nitrate
- For zero-valent iron and copper – release of iron or copper to groundwater
- Effects of coating of particles

Technical Basis

Solid amendments for ^{99}Tc remediation are designed to either reduce Tc(VII) to Tc(IV) or adsorb the pertechnetate (TcO_4-) anion. Gu et al. (1996) found that activated carbon was an effective adsorbent for TcO_4- over a wide range of pH. The range of Kd values for the activated carbon exceeded 10^4 ml/g. Zero-valent iron is the primary reductive solid amendment that has been considered for ^{99}Tc remediation. Liang et al. (1996) demonstrated rapid removal of ^{99}Tc from groundwater by reduction to Tc(IV) in the presence of zero-valent iron. They concluded that the decrease in ^{99}Tc concentrations was the result of sorption of Tc(IV) aqueous species rather than precipitation or co-precipitation. Korte et al (1997) also reported effective removal of ^{99}Tc from groundwater by zero-valent iron, but concluded that reductive precipitation was the primary removal mechanism. In F-Area groundwater the concentrations of ^{99}Tc are below the solubility of $TcO_2 \cdot 1.6H_2O$, so the removal mechanism would have to be sorption onto iron hydroxides in the soil or coating the iron particles (Walton et al., 1986; Lieser and Bauscher, 1987).

Zero-valent copper may also be useful for ^{99}Tc removal from groundwater. The removal of ^{99}Tc would occur in the same way it does with zero-valent iron -- reduction of Tc(VII) to Tc(IV) and sorption of Tc(IV) aqueous species to the copper or soil particles. Zero-valent copper has advantages over zero-valent iron. The reducing potential of copper is sufficient to reduce technetium, but is not low enough to reduce water. In contrast, iron does reduce water resulting in hydrogen gas production and an equilibrium pH that typically exceeds nine. Production of hydrogen gas can reduce permeability by trapping gas bubbles in pore throats (Liang et al., 1996) and by stimulation of microbial growth. Use of copper as a reductant would avoid these problems and result in an equilibrium pH between 5 and 6. Another important advantage is that copper could be used in conjunction with remediation of ^{129}I. Under the correct conditions, the presence of metallic copper would promote precipitation of CuI, as well as reduction of Tc(VII) to Tc(IV).

The two main disadvantages of using zero-valent copper are the cost of copper and the potential release of dissolved copper to the aquifer. As long as the concentration of chloride in the groundwater exceeds 1 mg/L, the concentration of copper should not exceed 0.26 mg/L because of the low solubility of CuCl:

$CuCl_{(s)} = Cu^{+} + Cl^{-}$ log K = -9.94

This would minimize the potential for copper concentrations to exceed the primary drinking water standard of 1.3 mg/L.

A thorough understanding of the reactions involved would be required for cost effective use of copper in an aquifer. Zero-valent iron is inexpensive enough that large excesses can be emplaced and still be cost effective. The excesses tend to counter poor distribution in an aquifer, preferential pathways in a barrier wall, and decreased reactivity of particles due to coating. These issues would be the same for particles of copper injected into an aquifer or a copper barrier wall, but using an excess of copper would not be cost effective. Thus, optimization of the amount of copper used would be important, as would innovative emplacement methods to ensure efficient copper reaction.

A potentially viable method for emplacing copper in an aquifer is electrodeposition. This method is commonly used in the plating and electronics industries to deposit a carefully controlled coating of copper on objects. To achieve this, the object is placed in a solution containing dissolved copper and connected to the cathode of an electrical cell. Copper in solution is reduced at the cathode and deposited on the object. If sufficient current can be carried by soil particles they may act as a cathode some distance away from an electrode placed in an aquifer. Dissolved copper injected into this soil may then be deposited as thin films on the soil particles. These films would be highly reactive and easily re-deposited when exhausted. If this were feasible, it would maximize the efficient use of copper for ^{99}Tc remediation. A variant on this method would be to electrodeposit copper coatings on zero-valent iron particles in a permeable barrier wall. Groundwater in the wall would be monitored to determine when re-deposition was necessary. For example, an increase in pH would indicate that the copper was exhausted and the iron was becoming the primary reactant.

Conclusions

The methods of ^{129}I and ^{99}Tc remediation presented here vary in approach, but all involve emplacement of reagents in the aquifer. This can present challenges that range from regulatory issues to engineering of emplacement. Evaluation of these methods must consider these various challenges. For example, reaction with copper may be very effective at removing ^{129}I from groundwater, but is likely to require substantial proof that regulatory limits for copper will not be exceeded. Likewise, potential for collateral damage to the environment must be considered. Groundwater associated with the F-Area Seepage Basins discharges to a seepline and stream. Reagents injected into the groundwater or products of reaction with solid amendments may adversely affect this surface water. In particular, the technologies to reduce ^{99}Tc have the potential for undesirable consequences to surface water. Reducing agents that discharge into surface water will increase the chemical oxygen demand and be potentially harmful to wildlife supported by these wetlands. In most cases this can be avoided by careful design and placement of the amendments, but is still a factor that must be considered.

Another consideration in evaluating these methods is their compatibility with base injection. Methods requiring only emplacement of dissolved amendments are most compatible with base injection because the amendment can be injected with the base solutions and no additional infrastructure is needed. Emplacement of solid amendment slurries requires more injection wells and perhaps different mixing and injection equipment. Solid amendment barrier walls require the most installation effort and thus are least compatible with base injection. The compatibility of air sparging for ^{129}I is intermediate. Reagents to oxidize iodide can be injected with base solutions, but some additional infrastructure is required to purge the diiodine from the groundwater.

One final consideration is the disposition of the contaminant after treatment. Air sparging of ^{129}I removes the contaminant from the aquifer and allows it to be collected for safe disposal. All the other methods presented here stabilize the contaminant in place in the aquifer. This requires confidence that the phases involved will be stable over the long-term and will keep concentrations below regulatory limits. In the short-term, the effect of transferring contaminant mass from the groundwater to the solid phase is minimal, because most of the contaminant mass is already on the solid phase. For example, at a Kd value of 1 ml/g, 89% of the contaminant mass is on the solid phase and only 11% is in the groundwater. Therefore, stabilization can decrease concentration of a contaminant in groundwater substantially while increasing the concentration in the solid phase only slightly.

Table 4 summarizes the potential remediation methods presented here with an assessment of each of the considerations discussed above. These are potential for regulatory issues, potential for collateral damage, and compatibility with base injection. The numerical qualifiers indicate the relative concern associated with each of these methods for these issues. It must be emphasized that the numerical qualifiers indicate relative factors among the methods presented in this paper. For example, the 3 listed for the potential for reducing technologies to cause collateral damage means that these methods have the highest potential among the methods presented here. It does not mean that they will cause collateral damage. Likewise, for the copper technologies, the 3 listed for potential for regulatory issues does not mean these will be unacceptable to regulators. It means that regulators may require more bench-scale work for these methods than other methods to prove that copper will not exceed regulatory limits.

Table 4: Summary of methods of *in situ* remediation of ^{129}I and ^{99}Tc.

	Method	**Technical Uncertainties**	**Potential for Regulatory Issues**	**Potential for Collateral Damage**	**Compatibility with Base Injection**
^{129}I	Precipitation of CuI	• Kinetics of CuI precipitation • Future ^{129}I release	3 – Cu in aquifer	2 – Cu in surface water	1
	Redox Manipulation/ Air Sparging	• Best oxidant • Henry's Law constant for diiodine	1 – Disposition of purged ^{129}I	1	2
	Solid Cu Amendments	• Engineering of Emplacement • Effect of Coatings	3 – Cu in aquifer	2 – Cu in surface water	3
^{99}Tc	Reduction/ Precipitation or Enhanced Sorption	• Mechanism of Tc stabilization • Best reductant • Long-term stability	1	3 – reducing conditions in surface water	1
	Reduction/ Co-precipitation	• Distribution coefficient for Tc • Kinetics of carrier phase precipitation • Long-term stability of carrier phase	2 – Sn in aquifer	3 – reducing conditions in surface water	1
	Solid Amendments	• Engineering of emplacement • Effect of coatings • Effect on nitrate	2 – fewer issues with Fe than Cu	2 – Reducing conditions in surface water (worse for Fe than Cu)	3

1 – least potential for regulatory issues; least potential for collateral damage; most compatible with base injection

2 – intermediate potential for regulatory issues; intermediate potential for collateral damage; requires some additional infrastructure

3 – most potential for regulatory issues; most potential for collateral damage; least compatible with base injection

References

Amonette J. E., Szecsody J. E., Schaef H. T., Templeton J. C., Gorby Y. A., and Fruchter J. S. (1994) Abiotic Reduction of Aquifer Materials by Dithionite: A Promising In-Situ Remediation Technology. PNL-SA-24505. Pacific Northwest National Laboratory, Richland WA.

Balsley S. D., Brady P. V., Krumhansl J. L., and Anderson H. L. (1996) Iodide Retention by Metal Sulfide Surfaces: Cinnabar and Chalcocite. *Environmental Science and Technology* **30**(10), 3025-3027.

Boltz D. R., Johnson W. H., and Serkiz S. M. (1994) Analytical Results, Database Management, and Quality Assurance for Analysis of Soil and Groundwater Samples Collected by Cone Penetrometer from the F and H Area Seepage Basins (U). WSRC-TR-94-0484. Westinghouse Savannah River Company, Aiken SC 29808.

Brown, G. (1997) Selective Sorption of Technetium from Groundwater. Proceedings of the Efficient Separations and Crosscutting Program 1997, Technical Exchange Meeting. PNNL-SA-28461. Gaithersburg MD.

Cantrell K. J., Kaplan D. I., and Gilmore T. J. (1997) Injection of Colloidal Fe^0 Particles in Sand with Shear-thinning Fluids. *Journal of Environmental Engineering* **123**(8), 786-791.

Cui D. and Eriksen T. E. (1996) Reduction of Pertechnetate by Ferrous Iron in Solution: Influence of Sorbed and Precipitated F(II). *Environmental Science and Technology* **30**(7), 2259-2262.

Gu B., Dowlen K. E., Liang L., and Clausen J. L. (1996) Efficient Separation and Recovery of Technetium-99 from Contaminated Groundwater. *Separations Technology* **6**, 123-132.

Hills G. J. (1956) The Physical and Chemical Properties of Iodine. In *Supplement to Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 2, pp. 826-856. Longmans, Green, and Co.

Kaplan D. I., Serne R. J., Parker K. E., and Kutnyakov I. V. (2000) Iodide Sorption to Subsurface Sediments and Illitic Minerals. *Environmental Science and Technology* **34**(3), 399-405.

Korte N. E., Liang L., Bu B., Muck M. T., Zutman J. L., Schlosser R. M., Siegrist R. L., Houk T. C., and Fernando Q. (1997) In Situ Treatment of Mixed Contaminants in Groundwater: Application of zero-valent iron and palladized iron for treatment of groundwater contaminated with trichloroethene and technetium-99. ORNL/TM-13530. Oak Ridge National Laboratory, Grand Junction CO.

Lauterbach A. and Ober G. (1996) Iodine and Iodine Compounds. In *Encyclopedia of Chemical Technology*, Vol. 14 (ed. Kirk-Othmer), pp. 709-737. John Wiley & Sons.

Lefèvre G., Alnot M., Ehrhardt J. J., and Bessière J. (1999) Uptake of Iodide by a Mixture of Metallic Copper and Cupric Compounds. *Environmental Science and Technology* **33**(10), 1732-1737.

Liang L., Gu B., and Yin X. (1996) Removal of Technetium-99 from Contaminated Groundwater with Sorbents and Reductive Materials. *Separations Technology* **6**, 111-122.

Lieser K. H. and Bauscher C. (1987) Technetium in the Hydrosphere and in the Geosphere. *Radiochimica Acta* **42**, 205-213.

Looney B. B., Denham M. E., and Vangelas K. M. (2002) Low Concentration Mercury Treatment Using Chemical Reduction and Air Stripping (U). WSRC-MS-2001-00388. Westinghouse Savannah River Company, Aiken SC 29808.

Lyman W. J., Reehl W. F., and Rosenblatt D. H. (1982) *Handbook of chemical property estimation methods : Environmental behavior of organic compounds*. McGraw-Hill.

Meyer R. E. and Arnold W. D. (1991) The Electrode Potential of the Tc(IV)-Tc(VII) Couple. *Radiochimica Acta* **55**, 19-22.

Rimstidt J. D., Balog A., and Webb J. (1998) Distribution of trace elements between carbonate minerals and aqueous solutions. *Geochimica et Cosmochimica Acta* **62**(11), 1851-1863.

Séby F., Potin-Gautier M., Giffaut E., and Donard O. F. X. (2001) A Critical Review of Thermodynamic Data for Inorganic Tin Species. *Geochimica et Cosmochimica Acta* **65**(18), 3041-3053.

Ticknor K. V. and Cho Y. H. (1990) Interaction of Iodide and Iodate with Granitic Fracture-Filling Minerals. *Journal of Radioanalytical and Nuclear Chemistry, Articles* **140**(1), 75-90.

Vilensky M. Y., Berkowitz B., and Warshawsky A. (2002) In Situ Remediation of Groundwater Contaminated by Heavy- and Transition-Metal Ions by Selective Ion-Exchange Methods. *Environmental Science and Technology* **36**(8), 1851-1855.

Walton F. B., Paquette J., Ross J. P. M., and Lawrence W. E. (1986) Tc(IV) and Tc(VII) Interactions with Iron Oxyhydroxides. *Nuclear Chemistry and Waste Management* **6**, 121-126.

Williams M. D., Vermeul V. R., Szecsody J. E., and Fruchter J. S. (2000) 100-D Area In Situ Redox Treatability Test for Chromate-Contaminated Groundwater. PNNL-13349. Pacific Northwest National Laboratory, Richland WA.

Yoshihara K. (1996) Technetium in the Environment. In *Technetium and Rhenium: Their Chemistry and Its Applications* (ed. K. Yoshihara and T. Omori), pp. 17-35. Springer.