Evaluation of Reagent Emplacement Techniques for Phosphate-based Treatment of the Uranium Contamination Source in the 300 Area

White Paper

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June 2010

Pacific Northwest
NATIONAL LABORATORY

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Summary

Persistent uranium contamination of groundwater under the 300 Area of the Hanford Site has been observed. The source of the uranium contamination resides in uranium deposits on sediments at the groundwater interface, and the contamination is mobilized when periodically wetted by fluctuations of Columbia River levels. Treatability work is ongoing to develop and apply phosphate-containing reagents to promote the formation of stable and insoluble uranium phosphate minerals (i.e., autunite) and other phosphate precipitates (di-calcium phosphate, apatite) to stabilize the uranium source. Technologies for applying phosphate-containing reagents by vertical percolation and lateral injection into sediments of the periodically wetted groundwater interface are being investigated.

This report is a preliminary evaluation of technologies for lateral injection. Lateral injection involves the pressurized introduction of a fluid reagent into the porous media of the vadose zone. Multiple fluid application techniques are possible and are considered in this evaluation: lateral injection with use of shear-thinning carrier liquid, lateral injection of foam, and lateral injection of mists or aerosols.

- Injecting liquid with a shear-thinning agent at the groundwater interface at high water elevation is the most mature of the prospective technologies. Properly deployed, lateral liquid injection is capable of contacting wetted vadose zone sediment at distances as great as 15 meters from each injection well. Xanthan gum is most likely to be used to facilitate the penetration of the reagent and prolong the contact time of the phosphate reagent after initial injection.

- Injecting foam mixtures of liquid and gas may permit sediment to be treated above the wetted zone and may permit vertical as well as lateral distribution of the reagent. Foam bubbles limit the volumetric density of phosphate delivery and may require high delivery pressures. However, delivery of foam technology is at an early stage. Continued research into foam transport and behavior is suggested, particularly relating to reducing apparent elevated viscosity behavior and decreasing deployment pressures that restrict foam application distances.

- Liquid mist injection applies liquid reagent in aerosol form. To date, only limited proprietary implementation of this delivery technique has been conducted. The principal practitioner of mist injection has indicated that superior application distances from the injection well are achievable. However, actual confirmation of performance and deployment range is not yet available. The technology may require proprietary licensing. Minimal laboratory testing of the technique has been conducted.

All of the technologies are limited in their capability to transport phosphate reagent into sediment contaminated with uranium. If the targeted zone is restricted to sediment periodically wetted by seasonal water table rises, then injecting liquid solutions with sheer-thinning fluids is the best of the three technologies. Should ongoing efforts to apply phosphate reagent solutions via vertical infiltration from the ground surface prove to be unsuccessful, pilot testing of liquid injection via a vertical well is recommended. Such testing of liquid reagent with a shear-thinning additive should be conducted to synchronize with the annual spring-early summer rise in aquifer levels to maximize lateral spreading of phosphate reagent into sediments within the periodically rewetted zone.

Contents

1.0   Introduction

This white paper is being provided in preparation for testing carrier mechanisms for transporting phosphate reagents to remedy mobile uranium deposits that provide a continuing source of uranium to the groundwater in the 300 Area. Carrier techniques are described that apply to the lower vadose zone affected by groundwater level fluctuations and, to a lesser extent, the vadose zone.

2.0   Statement of the Problem

Dissolved uranium has persisted in a large groundwater plume with relatively stable dimensions and concentrations beneath the 300 Area of the Hanford Site for many years. This persistent plume of uranium contamination continues despite the cessation of liquid waste discharges since the mid 1980s as well as removal of contaminated soil from former discharge ponds and trenches. During this same period, groundwater velocities through the aquifer have been relatively high with observed tracer and plume drift observations indicating velocities as high as 50 ft/day. The present conceptual model for the situation attributes the observed uranium in groundwater to an ongoing release of mobile uranium from sediment in the periodically rewetted zone, i.e., the portion of the subsurface that is within the range of water table variations that occur seasonally and, to some extent, daily, because of changes in river level.

Previous remediation and treatability studies have determined that the most effective remedy is to apply phosphate-containing reagents to promote the formation of stable and insoluble uranium phosphate minerals (i.e., autunite) and other phosphate precipitates (dicalcium phosphate, apatiete) that adsorb uranium and are a long-term phosphate source to form autunite. Although phosphate emplacement appears to be effective in laboratory experiments, field-scale emplacement into a large volume of uranium-contaminated sediments is challenging. A previous treatability test employing the application of polyphosphate directly to groundwater with the intent of inducing uranium stabilization and providing long-term treatment capacity within the aquifer was not effective. High groundwater velocities and poor mixing of sequential application of multiple reagents limited the success of this approach within the aquifer. Also, applying aqueous phosphate solutions to groundwater poses limitations to the emplacement of phosphate mass in the periodically rewetted zone, which is a major source of uranium.

Subsequently, an effort to enable direct treatment of the sediments in the periodically rewetted zone is being pursued. Multiple routes of application are being considered: solution infiltration from the surface as well as lateral injection from multiple wells. This paper focuses on mechanisms to effect lateral transport into the periodically wetted sediment immediately above the nominal water table. Rather than attempt to immediately treat the entire vertical extent of the vadose zone, this study focuses on the proximate source of ongoing uranium contamination to the groundwater. This zone extends vertically to the limit of the observed seasonal upward groundwater excursion. The vertical extent of this seasonal wetting of the lower vadose zone varies over the site but is as great as 2 meters near the Columbia River. The initial remedial focus upon this periodically wetted zone is made because it is the immediate cause of ongoing groundwater contamination and because its proximity to groundwater provides the opportunity to use groundwater fluctuation to facilitate transport and application of phosphate reagent to the operative sediment source. Sediments above this zone containing uranium, particularly in areas beneath former disposal ponds and trenches, may be addressed later, depending upon the performance of remedial efforts in the periodically rewetted sediment zones.

Lateral injection involves the pressurized introduction of a fluid reagent into the porous media of the vadose zone. Multiple fluid forms are possible and are considered in this white paper: liquid or liquid-gas mixtures (i.e., foam, mists).

The result of the consideration is a recommended fluid reagent dispersal technology to be applied in pilot testing and modeling. The final objective is to develop an effective emplacement method for

delivering phosphate-containing reagent to stabilize uranium in periodically wetted vadose zone sediment at the 300 Area.

3.0   Characteristics of Uranium in 300 Area Sediments

From a geologic perspective, the sediment above the water table in the 300 Area consists principally of gravel-dominated deposits of coarse gravels and some laminated sands informally named as the Hanford formation. The sediment was deposited by cataclysmic glacial floods that inundated the Pasco Basin a number of times, as recently as 13,000 years ago. The gravel-dominated strata consist of coarse-grained sands and granule to boulder sized, clast-supported gravels. The gravels can have an open matrix structure with large pore spaces and very high permeability. The sand-dominated layers consist of fine to coarse-grained sand (Peterson et al. 2008). This unconsolidated, porous matrix may permit significant lateral transport of injected fluids. However, depending upon fluid density, heterogeneous horizontal permeability and dispersion in the vertical direction may constrain radial propagation and horizontal emplacement distances.

3.1   The Geochemistry of the Sediment

The geochemical origins of uncontaminated sediment form the context for understanding the chemical conditions observed in the contaminated sediment, which in turn controls the selection of geochemical processes one might employ to remedy the uranium contamination in the sediment. Background levels of uranium are observed even in uncontaminated sediments in the 300 Area. The Hanford formation sediment originates from the basaltic bedrock erosion and granitic lithic fragments. Total uranium analysis of uncontaminated sediment from background areas of the 300 area indicates that such sediment contains an average background uranium concentration of 1.5 to 5.1 mg/kg (Serne et al. 2002 and Zachara et al. 2007). The mineralogy of the sediment is principally quartz with lesser quantities of feldspar and hornblende. Sodium-rich feldspar (albite) appears to be more abundant than potassium-rich feldspar (orthoclase). The background uranium in the sediment appears to reside in discrete mineral grains of betafite, a uranium-calcium mineral, which is highly resistant to weathering (Zachara et al. 2007). Background uranium in the sediment is therefore distributed as discrete, stable betafite precipitates within the interiors of sediment grains. The average background aqueous uranium in Hanford groundwater is 2.6 µg/L (range 0.5 to 12.8 µg/L).

3.2   The Geochemistry of Uranium Contamination

As waste solutions have contacted the sediment, uranium contamination has been deposited on the surfaces of the sediment in a variety of forms, depending upon the chemical environment. The geochemistry of the uranium deposits on the sediments controls the mobility, the availability to contaminate groundwater, and ultimately the effectiveness of reagent application to induce the *in situ* stabilization and uranium remediation.

The subsurface movement of uranium released in waste streams is controlled by adsorption to the mineral substrate of the sediment and the dissolution/precipitation of uranium solids that are sorbed onto or incorporated into the sediment. Under oxidizing conditions present under the 300 Area, uranium is hexavalent [U(VI)] and exists as the uranyl ion (UO_2^{2+}) and its complexes with various ligands in aqueous phase. In the 300 Area, uranium sorbed to intragranular sediment particles is primarily characterized as uranyl silicates. The dissolution of deposited U(VI) from sediment appears to be promoted by aqueous bicarbonate (Liu et al. 2004) as a U-Ca-carbonate aqueous species form. The ionic

strength of groundwater controls the sorption/desorption of uranium from sediment because of competition for adsorption sites. Furthermore, since most U(VI) aqueous species are carbonate complexes, the carbonate concentration of the groundwater significantly influences the dissolved uranium concentration. There is greater U(VI) sorption and lower dissolved U concentrations in Columbia River water because of its lower carbonate concentrations than in the higher carbonate groundwater in the interior of the aquifer. The lower carbonate concentration Columbia River water results in greater U(VI) sorption and lower dissolved U concentrations relative to uranium behavior in higher carbonate groundwater in the interior of the aquifer. The form of the sorbed uranium affects its relative availability to dissolution and recontamination of groundwater. The relative stability of the sorbed form of uranium on sediment should be assessed when comparing remediation technologies for stabilizing uranium in sediments. Sorbed uranium forms range from easily exchangeable equilibrium sorption to more stable solid matrix carbonate surface precipitates to very stable phosphate uranium-phosphate mineral complexes (autunite and apatite) (Szecsody et al. 2010).

4.0   Candidate Emplacement Techniques

The cleanup goal is to attain a geochemically stable (i.e., low solubility in Hanford subsurface geochemical conditions) form of uranium. Phosphate-based reagents are preferred to stabilize uranium in the 300 area because of their comparatively stable and durable effect upon uranium, although other low solubility uranium mineral phases (i.e., vanadates) have been considered elsewhere. Consequently, this white paper reviews the application technologies available to disseminate and apply phosphate reagents to sediments contaminated with uranium deposits in the vadose zone of the 300 Area.

4.1   Liquid with Shear-Thinning Polymer

4.1.1   Description

Shear-thinning fluids are liquids that are generally aqueous solutions containing up to 2000 ppm of a polymer. The polymer is generally an organic polysaccharide compound. Examples of polymers used as shear-thinning fluids include xanthan gum, guar gum, or partially hydrolyzed poly acrylamide (PHPA). Inorganic viscosifiers, such as calcium-magnesium-oxide-hydroxide cationic compounds, do have shear-thinning properties. However, such inorganic additives may not be suitable for phosphate reagent transport because of interaction issues and their fragile nature at high shear stress.

A shear-thinning fluid exhibits non-Newtonian flow properties. At high velocities, where shear stress is high, the fluid viscosity is lower than under static conditions. For instance, when a shear-thinning fluid with a static viscosity of 100 cP is injected into a porous medium, its apparent viscosity may decrease to less than 10 cP during injection. This enables the reagent transport solution to be delivered into the formation at lower pressures compared to a viscous fluid that does not exhibit shear-thinning properties. When the injection ceases, the fluid viscosity increases to the static viscosity value and becomes recalcitrant to displacement by the surrounding groundwater. This property may increase the residence time of the injected reagents in the target zone.

4.1.2   History, Prior Literature

Much of the development and use of shear-thinning fluids in geotechnical settings originated in the petroleum drilling industry. Since the 1970s, organic polymer compounds, such as guar and xanthan gums, were experimented with in drilling muds to enhance density, rheology, and borehole stability. In the mid 1980s, synthetic polymers, such as partially hydrolyzed polyacrylamide (PHPA), were applied to drilling mud as a supplement to bentonite slurry to improve borehole stability. In the 1990s, vinyl polymers with propan-2-ylbenzene were applied to improve drilling mud properties. The polymer formulation is commercially available as SlurryPro® CDP^{tm} by KB International of Houston, TX. Typically vinyl polymers are applied to drilling slurries at concentrations ranging between 0.1 mass % to 0.18 mass %. Such polymers, when applied to aqueous solutions at concentrations $^1/_{10}$ lower than drilling mud concentrations, exhibit shear-thinning properties. However, recent test mixes of polyphosphate reagent with SlurryPro® vinyl polymers have shown the vinyl polymer to be incompatible with the polyphosphate. Guar and xanthan gums will most likely be used with polyphosphate reagents. Guar gum viscosity properties are stable only in the pH 5 to 7 range. Guar gum also tends to polymerize in the

presence of aqueous calcium. Preliminary experiments with guar gum[a] show that the guar gum shear thinning behavior is not effective in pH 8, high-calcium Hanford groundwater.

4.1.3 Application

A shear-thinning fluid is formulated by onsite mixing of water with a polymer, such as xanthan gum, at a concentration typically varying between 0.01 mass % to 1 mass %, depending on the application. Preliminary experiments in Hanford groundwater used 1500- and 2000-ppm xanthan gum. The reagent is also mixed into the solution before injection. The reagent with the carrier solution is applied via well points or wells into the desired subsurface zone under pressure. Injection rates are modulated using information from anticipated flow volume, back pressure measurements, and possibly pressure measurements at nearby wells. The application of the shear-thinning fluid is primarily focused on injection to the uppermost volume of the groundwater at or near the water table. The application would be timed to coincide with the high water table for injection into the periodically wetted vadose zone while it is saturated. A phosphate reagent would be delivered with the shear-thinning fluid to treat the sediments. Because the injected fluid would have a high viscosity after injection, the reagent would be held in contact with the sediments for an extended period of time, even after the water table drops. Direct injection into unsaturated sediments over a large radius is not feasible, though some mounding effects in the immediate vicinity of saturated zone injection will occur.

4.1.4 Estimate of Delivery Efficiency

Delivery efficiency of phosphate reagent is a function of the reagent concentration in the carrier liquid and the range of the carrier liquid propagation from the injection well. The delivery efficiency is controlled by the amount of reagent capable of being dissolved and transported in the carrier liquid. The solubility limit of the polyphosphate compounds sets the upper bound maximum concentration capable of being deployed. Presently, a solution composed of 47 mM (6.6 g/L) sodium orthophosphate and 1.75 mM (0.76 g/L) sodium tripolyphosphate formulated to provide 1000 mg/L polyphosphate is contemplated. Compared to foam or aerosol delivery, liquid can deliver far more polyphosphate mass per volume of carrier fluid applied, although the presence of high ionic strength water does cause some down-gradient uranium mobilization during the phosphate precipitation. The aqueous reagent in a foam or mist volume is inherently diluted by the foam gas or the small-droplet volume of mist in the sediment void volume.

The maximum range for fluid transport from the injection point will be a function of the injection pressure, effective fluid viscosity, the formation permeability and whether a less permeable confining layer limits downward gravitational flow. Based on similar efforts at other sites, a target injection radius of about 15 m is anticipated. Additional site-specific design and testing are required to evaluate actual delivery efficiency in this hydraulically complex process. The use of shear-thinning fluid will also facilitate advection of the aqueous phosphate solution into some low-permeability zones that contain higher uranium concentrations.

(a) Preliminary experiments conducted by L. Zhong in 2010 showed that the shear thinning behavior of guar gum is not effective in Hanford groundwater, due to its high calcium concentrations and high pH (~pH 8).

4.1.5   Unknowns

Until site-specific testing is conducted, the actual radial distance of effective contact of phosphate reagent within periodically rewetted zone in the 300 Area is unknown. Testing needs to include selection of the shear-thinning agent (e.g., xanthan gum, guar gum), compatibility of the fluid with the phosphate reagent, and impacts of the fluid on uranium-phosphate geochemistry (i.e., uranium mobilization). Field testing is needed to evaluate the effectiveness and implementability, including items such as sediment contact and reaction extent.

4.1.6   Advantages

Preparation, mixing, and application of shear-thinning fluid uses conventional fluid handling equipment and injection well technology. Because the carrier fluid is undiluted by gas or air, more concentrated (relative to foam or mist technologies) reagent concentrations can be applied. If the application is suitably timed at high groundwater levels, the reagent application may be maximized to contact sediments in the periodically wetted sediment zone near the water table. Potentially, the reagent can be distributed over a large radial distance (e.g., 15 m) from an injection well. Shear-thinning fluids have been shown to facilitate penetration and reagent delivery in low-permeability zones in heterogeneous sediment systems (Zhong et al. 2008).

4.1.7   Disadvantages

Because the carrier fluid is an aqueous liquid, contact into non-wetted sediment above the water table is limited. Hydraulic mounding effects in the vicinity of the injection well are limited by the formation permeability. Therefore, the timing of the injection relative to the fluctuating groundwater table is critical to optimize contact with the periodically rewetted sediments. Although the extent is unknown, it is likely that uranium-sugar solution complexes will form, thus increasing uranium aqueous solubility. Consequently, there may be a short-term increase in uranium mobilization until the xanthan gum is completely degraded and advected downgradient.

4.1.8   Assessment and Recommendations

Presently, fluid injection of a phosphate reagent in a solution with a shear-thinning agent is judged to be better than the other two primary delivery technologies to periodically wetted sediments. The single phase form of the all-liquid technology is capable of transporting far more reagent per volume of carrier fluid compared to other methods, which are diluted considerably by gas or air in the delivery medium. In addition, if the targeted treatment zone is focused on the lowermost sediments that are periodically wetted, fluid injection synchronized with seasonal water lever excursions likely offers a superior application range laterally from a vertical injection well.

Recommendations for further consideration of direct injection of shear-thinning fluid include:

1. Verify compatibility of phosphate reagent with selected shear-thinning agent (i.e., demonstrate compatibility with xanthan gum).

2. Evaluate effects of shear-thinning fluid on uranium-phosphate geochemistry as well as uranium solution speciation and adsorption and understand the influence of breakdown products on uranium concentration.

3. Define formulation of carrier solution.

4. Select pilot test location.

5. Prepare and approve test plan.

6. Install adequate monitoring equipment for pilot test.

7. Conduct and analyze results of pilot test application.

4.2 Foam

4.2.1 Description

Foam is a colloidal dispersion in which a gas is dispersed in a continuous liquid phase. Foam is observed as a liquid encapsulating many small gas bubbles. In persistent liquid foams, bubble dimensions are referred to as having dimensions, when in fact, the bubbles are polyhedral and not spherical. In most observed liquid foams, bubble sizes usually exceed diameters greater than 10 µm and may be larger than 1000 µm. Foam stability is not necessarily a function of bubble size, although there may be an optimum size for a particular foam type. It is common but generally inappropriate to characterize a foam in terms of a specific bubble size because most foams exhibit a distribution of bubble sizes. Surfactants are used as foaming agents to reduce surface tension of the foaming liquid when dispersed gas is entrained into the fluid to form multiple bubbles. For subsurface applications, aqueous surfactant foam is generated by either simultaneous injection of gas and liquid or by pulsating injection of alternating slugs of liquid and gas into porous media. Foam formation is a dynamic process, and the resulting liquid foam is thermodynamically unstable. Capillary-suction and gas diffusion are two principal mechanisms of foam destruction (Kosvscek and Rakde 1994). As a carrier vehicle for propagating polyphosphate reagent, the polyphosphate is dissolved into the liquid solution before foam is generated.

4.2.2 History, Prior Literature

Liquid foams have been deployed in the petroleum industry to enhance oil recovery and improve drilling fluid performance since the 1950s. Foams intended for use in petroleum wells and in several near-well reservoir processes are pre-formed at the surface before injection. The foam generators used in petroleum well applications can be quite simple, involving mixing surfactant and gas streams at high flow velocities and ejecting the mixture through a nozzle or valve with a sudden pressure drop. Most of the previous literature concerning the use of foam in geotechnical situations comes from petroleum engineering. Foams have not yet been applied to field-scale dissemination of reagents to remediate sediment contamination.

4.2.3 Application

Formulating foam would consist of mixing a biodegradable anionic surfactant, such as sodium lauryl ether sulfate, with water and the desired polyphosphate reagent. The foam mixture would be produced at

a surfactant concentration on the order of 0.5 percent by mass. The foam would be generated by permeating the solution with air or nitrogen through a porous stainless steel plate with a 20-µm pore size. Other technologies that have greater longevity are available to create smaller bubbles. The foaming gas and surfactant flow rate are modulated to deliver foam with a foam quality (i.e., foam volumetric content) approximating 95 to 99 percent. Foam quality is the measure of the proportion of gas volume to total foam volume. The foam is conducted through piping, down the borehole, and into the targeted vadose zone sediment. The driving force of foam movement is differential pressure between the advancing foam front and the foam generator, and in some cases, air suction at some other well to direct foam movement. Assuming a generally uniform sediment, the overall foam mass propagates as enlarging spheroid-shaped mass with local bulbous extrusions into local sediment zones with relatively higher permeability. Laboratory studies (Zhong et al. 2010), indicate that multiple layers of phase fronts advance before the overall advancing foam mass. Initially, a gas front advances as bubbles break and reform. A gas tracer in some experiments has shown that the gas used to form the bubbles can move eight times faster than the foam front. A liquid front composed of almost entirely water forms in advance of the foam volume. The surfactant and phosphate reagent are not present in this liquid front. It is known that the phosphate lag is caused by adsorption. It is not known what controls the lag of the surfactant. This liquid front is formed where bubbles break at the periphery of the foam front, and liquid accumulates. Foam gas released from the bubble breakage forms a gas front that travels in advance of the liquid front and foam front. The foam flow exhibits a high effective viscosity relative to water. The bulk foam flow tends to exhibit a linear pressure distribution with respect to distance from the injection point. Foams with higher foam quality tend to result in lower injection pressures at fixed injection rates. The injection pressure for delivering a 98% foam quality with a phosphate reagent into an unsaturated sediment column is 11 times greater than injecting water to a similar sediment column. The influence of sediment permeability on the foam injection pressure is a function of the foam injection rate. Foam injection rates per injection well as high as 60 gallons per minute as pre-foam surfactant fluid are feasible.

4.2.4   Estimate of Delivery Efficiency

It is expected that polyphosphate reagent entrained with the liquid foam solution would contact, wet, and be deposited onto sediment contacted by the foam. The surface tension of the fluid contacting the sediment is reduced because the foam by nature contains a surfactant, thereby enhancing wetting of the sediment with the polyphosphate reagent. The delivery efficiency of the phosphate reagent in foam is a function of the reagent concentration in the foam, the quality of the foam, and the extent of foam propagation from the injection point. A polyphosphate concentration in foam solution, 12 mM phosphate-equivalent, similar to that specified for a shear-thinning fluid application scenario, would use a similar formula of polyphosphate specified for the fluid application. Because of foam gas, foam would contact contaminated sediment surfaces with a smaller amount of reagent per volume of foam compared to reagent per volume of liquid. However, if sufficient foam with sufficient phosphate is delivered to sediment to allow full stoichiometric reaction and uranium stabilization, the excess polyphosphate in the liquid contact would be no more efficient in stabilizing uranium in the sediment. Laboratory tests have indicated that the deployment range of foam is limited by the viscosity-induced pressure drop. In other words, at a distance determined by the formation and foam, very high pressures beyond equipment capabilities are observed that limit the range of foam deployment.

4.2.5   Unknowns

Foam has yet to be deployed as a carrier of a remediation agent in vadose sediments. Until actual use in Hanford sediment is conducted, foam transport, stability, and effectiveness are unknown. Economic costs are not fully known. The influence of the presence of anionic surfactant on uranium solution speciation and adsorption are not known, although this is currently being investigated.

4.2.6   Advantages

The use of foam for delivery may provide a better control on the volume of fluids injected and the ability to contain the vertical and lateral migration of contaminant-laden liquids. Foam has the potential of being directed through unsaturated sediments by use of vacuum gradients (i.e., air extraction wells) and pressure gradients (i.e., injection wells). Foam may have an advantage in propagation range relative to liquid injection. Depending upon the stratigraphy and permeability of the receiving sediment, foam may be less susceptible to downward gravitational forces that limit propagation and could cause undesired or ineffectual drainage of reagent liquid into sediment beneath the target zone. Foam may be applied into zones above the water table and not rely upon groundwater for extended propagation beyond the injection well.

4.2.7   Disadvantages

Foam delivery of polyphosphate reagent has the inherent limitation of having only a small percentage of its volume, generally less than 5 percent depending upon the foam quality, available for conveying dissolved reagent, although preliminary experiments at higher phosphate concentrations suggest that some of this disadvantage may be mitigated. Consequently, a greater quantity of foam relative to a direct liquid application may be required to adequately contact a given volume of contaminated sediment. Foam delivery is limited by a very high pressure at the injection point that limits the distance of foam propagation, based on initial laboratory experiments with only one type of surfactant. This distance may be as constrained as 1.5 meters (5 feet). The use of alternate surfactants, additives to stabilize foam, and foam-generating devices are being investigated to produce smaller bubble size foams that are more stable with less pressure.

4.2.8   Assessment and Recommendations

The development of foam technology is currently at an early stage. Future developments of foam delivery technology may significantly improve this alternative. However, at this time, lateral application of phosphate to periodically wetted sediments using foam is judged to be inferior to liquid injection of a phosphate reagent in a solution with a shear-thinning agent. Foam, in the limited range of laboratory conditions tested thus far, appears to be limited by the excessive pressures required to push it out beyond a few feet into a formation. Foam does appear to have a superior application range into vadose zone sediment above the periodic wetted zone where liquid injection does not have the capability of using groundwater level changes and flow conveyance.

Continued research into foam transport and behavior is suggested, particularly relating to reducing apparent elevated viscosity behavior and decreasing deployment pressures that restrict foam application distances.

4.3   Liquid Mist

4.3.1   Description

Simultaneous injection of a liquid reagent with a pressurized gas into subsurface sediment or soil produces a mist or aerosol. The mist is released from a down-hole nozzle in a cylindrical pattern with a kinetic energy that imparts the fine liquid droplets with a velocity that aids in penetration into the formation. Compressed nitrogen or pressurized air is the gas generally employed in the mist production and application. A commercial geotechnical contractor, ARS Technologies, Inc. of Berkeley, CA, appears to claim this technology as a proprietary service. A cursory review of the patents suggests that the ARS patent is focused on application to pneumatic fracturing and enhanced reagent fluid delivery in *in situ* bioremediation applications.

4.3.2   History, Prior Literature

The injection of fluids as aerosol or fine liquid mist into the vadose zone appears to have limited applications historically. ARS Technologies issued a white paper documenting the injection of zero valent iron/reducing reagent in the 10- to 40-micron size range into groundwater below the water table at a Canadian military site to produce a reactive barrier wall (Tossell et al. 2007). However, no peer-reviewed publications of the application of aerosols to unsaturated soils have been found. ARS has not employed the method to inject reactive liquids into a vadose zone.

4.3.3   Application

Forming an aerosol would require simultaneously applying high-pressure gas with liquid containing a polyphosphate reagent mixture in aqueous solution through one or more down-hole nozzle(s). A reagent solution similar to the 12 micromole polyphosphate mixture considered for the other delivery methods is feasible. Because the spray nozzle is susceptible to plugging, complete dissolution of reagent compounds to avoid suspended solids would be necessary. The nozzle at the end of the drill stem would be moved vertically across the targeted stratum to promote uniform distribution. Because of the high pressures used, care must be taken to avoid excessive long injections at any one level so as to prevent excessive mobilization of fines that could both erode the sediment and plug pore spaces.

4.3.4   Estimate of Delivery Efficiency

The ratio of liquid to propellant gas is a major factor to determining delivery efficiency. According to ARS Technology literature, fine mist injection of liquids in unconsolidated materials may penetrate up to 25 feet (7.6 meters), but this estimate has not been empirically confirmed. The injection equipment is capable of delivering up to 50 gallons per minute of liquid. Assuming maximum flow and penetration could be applied, aerosol injection could deliver polyphosphate reagent over a similar vertical profile and up to 67 percent greater radial distance than comparable foam application. In the vicinity of the water table, with the possible addition of a sheer reducing agent, aerosol injection could provide similar if not greater reagent delivery compared to a shear-reducing liquid application.

4.3.5   Unknowns

Actual field deployment of aerosol injection into vadose zone sediments at Hanford is required to determine actual sustainable application rates, penetration distances, and operating feasibility. It is not known whether aerosol delivery into vadose sediments is constrained to a single source contractor or whether alternate non-proprietary aerosol delivery is legally possible.

4.3.6   Advantages

A mist or aerosol injection may have an advantage over other carrier fluid deployment techniques regarding range of radial distance. However, actual testing of aerosol injection into unsaturated sediments is required to verify this alleged advantage. Mist injection does have the advantage that no additional chemicals (i.e., shear thinning fluid or surfactant) is used, thereby simplifying the chemistry of formulating and managing the phosphate reagent.

4.3.7   Disadvantages

Spray plugging may pose a problem with aerosol injection. Actual effective delivery distances using mist application have not yet been verified. The cost of application is unknown and may be subject to the apparent proprietary nature of the technology. Uranium mobilization and excess liquid infiltration into groundwater may be problematic as high-velocity spray may contribute to unmonitored over-application and erosion.

4.3.8   Assessment and Recommendations

Presently, lateral application of phosphate to periodically wetted sediments by high-pressure liquid spray is judged to be inferior to liquid injection. The effective range of contact that spray aerosols have in the laboratory does not agree with claims by ARS Technology, Inc. Actual field testing of aerosol injection in Hanford sediment is required, which could be accomplished in a large wedge-shaped system with many monitoring points that are currently being constructed for another project. Such testing should use a tracer in the injected fluid. Actual sampling and analysis of sediment exposed in the vicinity of the test injection location should be conducted to measure the effectiveness. Should such field testing indicate that deployment ranges exceed observed capabilities of other horizontal application technologies, liquid mist application may be considered for treating vadose sediment above the periodically wetted zone.

5.0 Conclusions

Three horizontal delivery technologies for lateral application of phosphate reagent to Hanford Formation sediments in the 300 Area have been considered. All of the technologies are limited in their capability to transport phosphate reagent into sediment contaminated with uranium. If the targeted zone is restricted to sediment periodically wetted by seasonal water table rises, then the injection of liquid solutions with shear-thinning fluids is the best of the three technologies. Should ongoing efforts to apply phosphate reagent solutions via vertical infiltration from the ground surface prove to be unsuccessful, then pilot testing of liquid injection via a vertical well is recommended. Such testing of liquid reagent with a shear-thinning additive should be conducted to synchronize with the annual spring-early summer rise in aquifer levels to maximize lateral spreading of phosphate reagent into sediments within the periodically rewetted zone.

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