Sustainable Remediation of Radionuclides By a Common Sense Approach to Enhanced Attenuation – 16441

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ABSTRACT

Development of *in situ* and relatively passive remedies for treatment of groundwater contaminated by metals and radionuclides is becoming more important because of the difficulty and cost – both to the environment and financially -- of removing these types of contaminants from the subsurface by pump-and-treat or excavation. *In situ* technologies rely on reactions that tend to remove contaminants from groundwater by partitioning them to solid phases in the aquifer. Monitored natural attenuation (MNA) relies solely on natural reactions to achieve remedial goals. Enhanced attenuation (EA) uses engineered approaches to supplement remediation when MNA is not sufficient to meet remedial goals. Both approaches leave contaminants in the subsurface and require a high burden of proof that contaminants will not be mobilized and become a risk in the future.

Proof of the sustained effectiveness of an EA remedy is made much easier by strategic design. In multi-contaminant plumes, it is important to prioritize contaminants according to the risk they pose, with the recognition that one remedy rarely treats all contaminants. The goal for the engineered portion of the remedy should be maximum risk reduction with minimal engineering. Natural attenuation or negotiated alternate concentration levels will often allow low risk contaminants to go untreated. Whenever possible, the remedy should be consistent with the geochemical evolution of the waste site, insuring that the treated immobilized contaminants are likely to remain relatively immobile for long time frames. Finally, use what nature provides geologically, hydrologically, geochemically, or microbiologically in the remedy design.

One of the impediments faced by waste site managers in implementing EA remedies is paralysis by perceived complexity. There are things that must be known to design an effective EA remedy, but there is always the temptation to know everything to eliminate the possibility of failure. Furthermore, there are plenty of people warning of failure if all is not known and they are usually willing to help the design team know all, for a price. Yet, the price of trying to eliminate all risk is never implementing an innovative remedy. All parties involved -- scientists/engineers, waste site managers, regulators and stakeholders must assume some degree of risk to deploy an EA remedy. If all parties are to assume some risk, then trust built through close communication from the start is required.

The U.S. Department of Energy Office of Environmental Management has funded an applied field research initiative for several years focused, in part, on developing EA remedies for metals and radionuclides using these guiding principles. This approach to EA remedies grew out of developing and deploying a remediation strategy to

replace a pump-and-treat system at the F-Area Seepage Basins on the Savannah River Site. The pump-and-treat system was energy intensive, produced several thousand cubic feet of solid radioactive waste per year, and cost $ 1 million per month to operate. The EA remedy that replaced the pump-and-treat is energy efficient, produces no waste, and costs approximately $1 million per year to maintain.

At the F-Area Seepage Basins approximately 7 billion liters of low level radioactive waste solutions were disposed in three unlined basins resulting in contaminated groundwater containing various radionuclides and other contaminants. The primary contaminants of concern are tritium, strontium-90, uranium, and iodine-129. Other key features of the contaminant plume are its acidic nature with pH values as low as 3.2, its vertical stratification in the water table aquifer, and the tendency of the most contaminated portions to follow troughs in the top of the clay separating the upper aquifer zone from the lower aquifer zone. The geology was exploited by installing a funnel-and-gate system into the clay with the barrier portion blocking contaminant flow paths in the troughs in the clay. This forces the most contaminated water to flow through the gates where it encounters an *in situ* treatment zone created by periodic injections of alkaline solution. The flux of tritium has been reduced significantly by the barrier walls. Strontium-90 and uranium are treated by enhanced sorption in the circumneutral pH treatment zone, consistent with natural geochemical evolution of the waste site from acidic to more neutral pH.

An additional *in situ* treatment zone was created upgradient of the one of the gates to treat iodine-129. Sub-micrometer diameter silver chloride particles were injected into the aquifer by direct push methods to create the treatment zone. In the laboratory and in a field pilot test the poorly soluble silver chloride particles reacted with iodide to form much less soluble silver iodide. Evaluation of the effectiveness of the silver chloride is ongoing.

INTRODUCTION

In situ attenuation-based remedies are one way to contribute to green and sustainable remediation of radionuclides. The Interstate Technology and Regulatory Council defined green and sustainable remediation as:

"site-specific employment of products, processes, technologies, and procedures that mitigate contaminant risk to receptors while making decisions that are cognizant of balancing community goals, economic impacts, and environmental effect" [1]

Traditional remediation methods for radionuclides involve extraction of the contaminants from the subsurface by excavation or pump-and-treat. These mitigate risk to receptors, but are often inconsistent with green and sustainable remediation objectives. Table 1 lists the three considerations of GSR – community goals, economic impacts, and environmental effect – and some of the issues related to excavation and pump-and-treat. Positive aspects are in green with plus signs, negative aspects are in yellow with negative signs. Other than mitigating risk to receptors, the primary positive aspect of excavation and pump-and-treat is local job creation. Excavation jobs are likely to be short term. Jobs created by pump-and-treat may last for decades because even weak sorption of radionuclides to mineral surfaces can make the remediation a long-term endeavor. The positives must be balanced with the negatives – cost, generation of radioactive solid waste, and carbon footprint – compounded by the long life-cycle of a pump-and-treat system. At some sites excavation or pump-and-treat are the appropriate remedy, but at many more, a passive GSR remedy is desirable. Hence, the environmental community is searching for alternative remediation strategies that are more consistent with GSR considerations.

TABLE I: Comparison of Excavation and Pump-and-Treat in Relation to GSR Considerations.

GSR Considerations	**Excavation**	**Pump-and-Treat**
Community Goals	+mitigate risk to receptors	+mitigate risk to receptors
	+short term job creation	+long-term job creation
	-safety issues regarding packaging and trucking radioactive soil through communities	
Economic Impacts	-potentially expensive (depending on depth and size of plume)	-expensive over life-cycle (high initial costs, operating costs over decades)
Environmental Effect	-generation of radioactive solid waste	-generation of radioactive solid waste
	-potential for high carbon footprint	-high carbon footprint over life-cycle
	-potential for spread of wind-blown contamination or use of large amounts of water to minimize wind-blown dust	

Strategically designed attenuation-based remedies for groundwater contaminated with radionuclides can achieve all of the GSR objectives. Attenuation-based remedies are those that rely on *in situ* processes to retard the migration of contaminants to "mitigate contaminant risk to receptors". Monitored natural attenuation (MNA) relies solely on natural processes, whereas enhanced attenuation (EA) uses engineered processes to assist the natural attenuation. The attenuation processes for radionuclides can be both physical and chemical. Physical processes include dilution, dispersion, and the engineered processes of blocking or diverting the migration path or reducing the hydraulic driving force for migration. Chemical processes for radionuclide attenuation include the partitioning of contaminant from the aqueous to the solid phase by adsorption, absorption, or precipitation, as well as radioactive decay. The partitioning of contaminant to the solid phase can involve microbial reactions, particularly when redox transitions are required. With the exception of radioactive decay to stable low-risk daughters, all of these attenuation processes result in radionuclides being left in the ground rather than being extracted or degraded.

The fact that radionuclides are left in the subsurface by attenuation-based remediation strategies means extra effort must be expended to prove that risks to receptors will be mitigated for long periods of time. Partitioning of radionuclides to the solid phase is not irreversible and the concern is that risk reduction is only delayed until attenuation processes are reversed. Thus, it must be proven to the satisfaction of regulators and stakeholders that complete reversal of attenuation processes is unlikely and that release of radionuclides from treatment zones will be at rates slow enough to mitigate the risks.

The U.S. Environmental Protection Agency (USEPA) released guidance on MNA of metals and radionuclides in 2007 [2] that supports the recently released Office of Solid Waste and Emergency Response Directive on use of MNA for inorganic contaminants [3]. These documents use a phased approach for demonstrating that MNA is a viable remedy for inorganic contaminants. Table 2 shows the four phases

TABLE II: Phases in Demonstrating MNA of Inorganic Compounds [3]

Phase I	**Phase II**	**Phase III**	**Phase IV**
Demonstrate plume stability	Determine mechanism and rate of attenuation	Determine system capacity and stability	Design performance monitoring plan and identify alternative remedy

of evidence. For MNA, these are characterization guidelines, but for EA, they can be used as design guidelines. Nevertheless, they show the type of information required to demonstrate that radionuclides treated by an EA process will remain attenuated.

Within this framework the degree of proof will be flexible depending on the risk. Figure 1 shows one conception of how the burden of proof might change depending on characteristics of the contaminant and the site. The highest burden of proof should be on relatively mobile radionuclides with long half-lives and relatively high toxicity. An example that fits into this category is I-129 with a half-life of 1.6×10^7 years. An example of a radionuclide that would have a lower burden of proof of effective long-term attenuation is Cs-137. It has a relatively short half-life of 30.2 years, but in most groundwater systems has a high retardation factor, and thus a longer travel time to receptors.

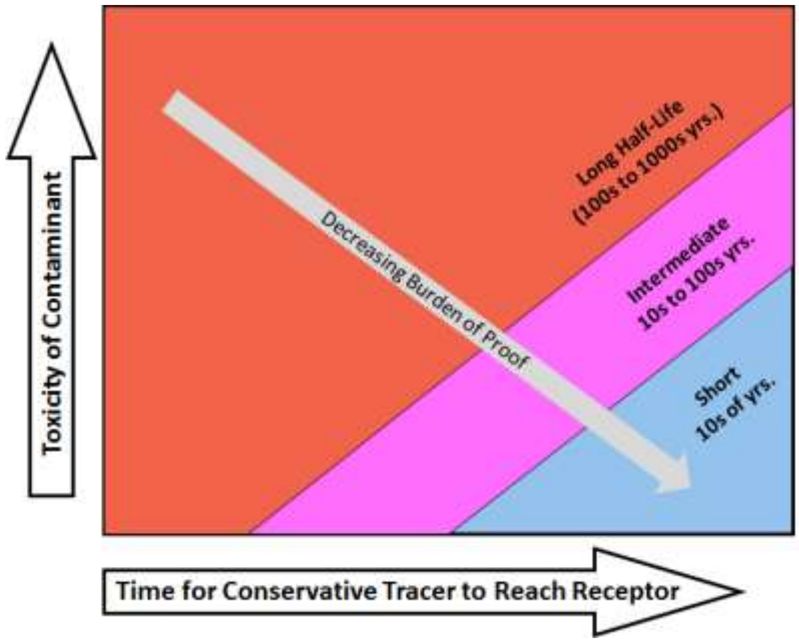

Figure 1: Relative Burden of Proof of Long-Term Effectiveness of EA Remedies

Strategic design of EA remedies build in much of the burden of proof of effectiveness and longevity. This makes it easier to get from concept to deployment. Savannah River National Laboratory and the Savannah River Site have been working in this area for two decades and have achieved multiple successful deployments of EA technologies for radionuclides in groundwater. The remainder of this paper summarizes the approach to developing EA remedies that has evolved over this time.

DISCUSSION

The SRNL approach to developing EA remedies is demonstrated by relating a case study, groundwater associated with the F-Area Seepage Basins, to each major element of the approach and how it applied to the case study. It is considered an approach because individual steps for EA remedy development are not specified. Instead, guidelines for considering an EA remedy at a site are provided. Much of the approach was defined by the remediation team for the case study site as the remediation evolved. It wasn't until the basics of the EA remedy were in place that the general applicability of the approach to other sites with radionuclide contamination in groundwater was realized. The fundamental tenets of the approach are:

- Engage regulators and stakeholders early in the process of EA remedy development
- Keep the conceptual model as simple as possible
- Stay consistent with geochemical evolution where possible
- Maintain a holistic view of the remedy

Case Study: The F-Area Seepage Basins Groundwater

The F-Area Seepage Basins consist of three unlined, earthen surface impoundments used to dispose effluents from the F-Area Separations facility. From 1955 through 1988, these unlined basins received approximately 7.1 billion liters of low-level waste solutions originating from the processing of uranium slugs and irradiated fuel. The effluents were acidic low activity waste containing a wide variety of radionuclides and dissolved metals [4]. The wastewater was allowed to evaporate and to seep into the underlying soil. The purpose of the basins was to take advantage of the interaction with the basin soils to minimize the migration of contaminants to exposure points. Though the seepage basins essentially functioned as designed, the more mobile contaminants reached groundwater in sufficient concentrations to cause a contaminant plume requiring remediation.

A determination was made in 1986 that the basins be regulated under the Resource Conservation and Recovery Act (RCRA) as hazardous waste disposal facilities, and closure plans were initiated. Closure actions included dewatering, physical and chemical stabilization of the remaining sludge, and isolation with a protective multilayer system to reduce rainwater infiltration. These actions were completed in 1991. Groundwater downgradient of the basin was contaminated with several constituents including Sr-90, uranium isotopes, I-129, Tc-99, Cs-137, and tritium. Other constituents such as Pb and Cd sporadically exceed regulatory standards in various monitoring wells. In addition, the groundwater remains acidic, with pH as low as 3.2 near the basins, increasing to 5-6 at the fringes of the plume.

SRS designed and installed a pump-treat-and-reinjection system in 1997 that coupled a water treatment unit with upgradient reinjection. The system was designed to trap untreatable tritium in a continuous loop by extracting groundwater from downgradient, removing contaminants other than tritium from the water, and re-injecting the treated water upgradient of the seepage basins. The water treatment system consisted of precipitation/flocculation, reverse osmosis, and ion exchange. The pump-and-treat system operated as designed, but had significant drawbacks; most notably, it was expensive to operate and resulted in the production of large amounts of radioactive solid waste. As a result, SRS sought another more efficient way to treat the groundwater contaminant plume. Operation of the water treatment unit began in 1997 and was suspended in 2003.

The pump-and-treat system was replaced in 2004 by a hybrid funnel-and-gate system installed approximately 300 meters from the stream (Figure 2). The purpose of the funnel-and-gate is to slow migration of contaminated groundwater and to funnel contaminated water through *in situ* treatment zones at the gates. The subsurface barrier portions of the funnel-and-gate were installed across the entire thickness of the water table aquifer and tied into a clay layer separating the upper aquifer zone from a lower aquifer zone. An alkaline solution is periodically injected into the gates to create an elevated pH treatment zone. The frequency of injection is approximately once every 12-18 months. The treatment zones at the gates attenuate migration of uranium and Sr-90 by enhanced sorption. Tritium migration is slowed by the walls and additional decrease in tritium concentrations is achieved when the stratified plume mixes with less contaminated groundwater as it migrates up through the gates.

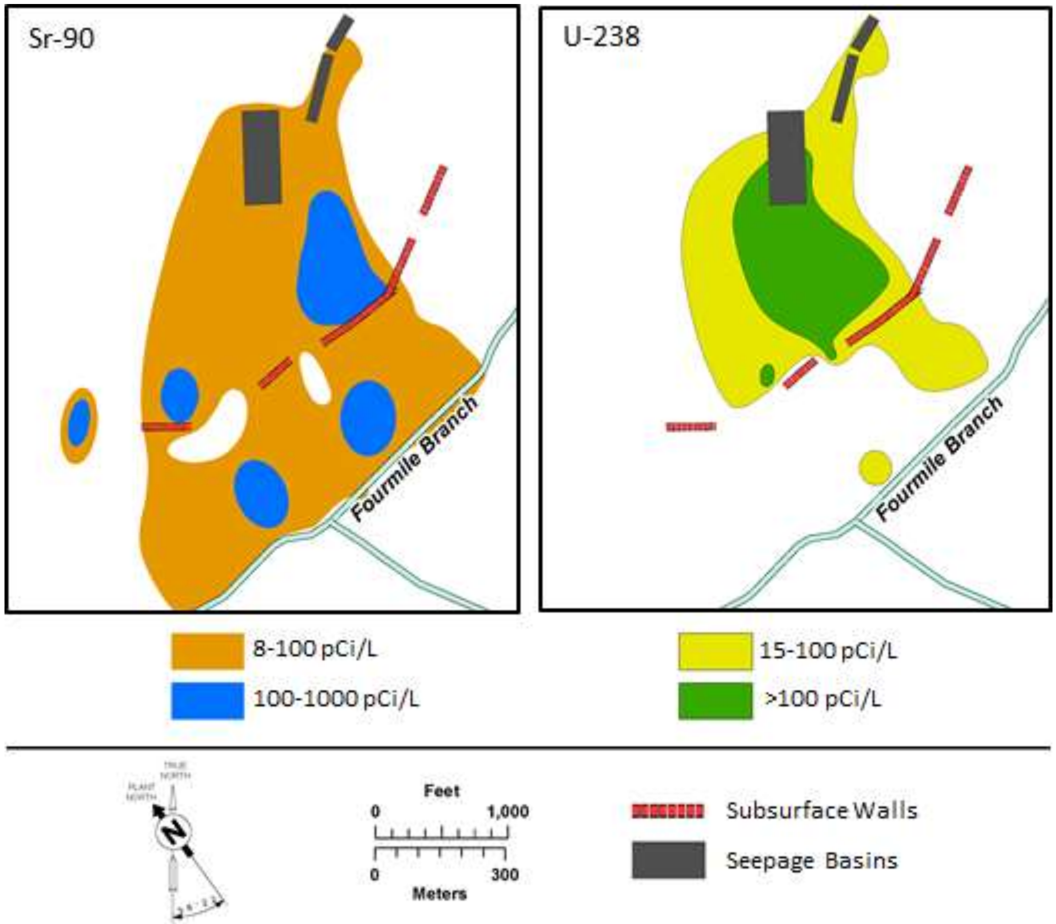

Figure 2: Map of Sr-90 and Uranium Concentrations at the F-Area Seepage Basins from 2011 Data.

Monitoring of the performance of the funnel-and-gate with base injection indicates that it has functioned as designed. Analysis of subsurface cores collected downgradient of the middle gate shows that an elevated pH treatment zone has been established. Monitoring of groundwater indicates that tritium flux has been reduced to target levels and regulatory limits on concentrations of Sr-90 and uranium have been achieved downgradient of the treatment system.

A pilot study was initiated in 2009 to evaluate sequestration of dissolved I-129 by the injection of silver chloride particles. Contaminant I-129 and natural I-127 react with the silver chloride to form insoluble silver iodide, removing I-129 from groundwater. In 2011, a modification to the RCRA permit was approved to deploy silver chloride technology at the middle gate as part of the corrective action. An additional application of silver chloride was done in 2015. Effectiveness of the silver chloride technology is still being evaluated.

An Approach to EA Remedy Development for Radionuclides

Engage regulators and stakeholders early in the process of EA remedy development

The most important aspect of developing EA remedies for a site is to engage regulators and stakeholders early in the process. Requesting approval for an EA remedy that will leave radionuclides in the subsurface is asking regulators and stakeholders to take a risk. They cannot be expected to take that risk if they have not been part of the process of developing the remedy. In fact, all parties involved in developing an EA remedy are taking a risk. The scientists and engineers involved risk reputation and, potentially, future funding. The site manager or owner takes a financial risk. So, it is imperative that all parties build trust through open and honest communication.

Regulators and stakeholders were engaged 5 years prior to the approval to shut off the pump-and-treat system at the case study site and replace it with the funnel-and-gate system. Regulators and stakeholders were consulted prior to laboratory and field studies and were briefed on the results of these. The initial agreement for transition away from the pump-and-treat system was to keep the system on stand-by until regulators were satisfied that the new more passive system would adequately address the problem.

Keep the conceptual model as simple as possible

Much has been written and expressed about remediation systems that have failed because of overly simplistic conceptual models, and much of this is true. However, this should not lead to over complication of conceptual models in an effort to eliminate risk of a remedy failure. The cost of eliminating risk of failure by attempting to know everything about a site is never deploying an EA remedy. Radionuclides do have varied, and in some cases, complicated biological and geochemical behavior. Yet, it is important not to become paralyzed by the perceived complexity at a given site or a specific location within a site. It is better to build a conceptual model based on what is currently known about a site, begin considering EA remedies, and let the specific remedies under consideration guide further characterization. If there is evidence that processes or parameters are not important to success of a remedy, then significant resources should not be expended to refine understanding of these. If it turns out one of these is important, it should become apparent during laboratory and field tests of the remedy.

It may seem to be a paradox, but a multidisciplinary team is required to achieve an appropriately simple conceptual model. The key is that the members of the team must be candid about whether a process or parameter within their expertise is truly important or not.

There was a considerable amount known about the case study site because there had been some degree of environmental monitoring there since the 1960s. Early depictions of the contamination plume suggested that there were preferential pathways of contaminant migration, though these became less prominent as the plume matured. The acidic and aerobic nature of the groundwater was known, as were the stratigraphy, depositional environments, and mineralogy of the aquifer. Characterization for installation of the pump-and-treat system refined understanding of these, as well as provided measurements of hydrogeologic parameters. It was also known that the cationic contaminants were more mobile under the acidic conditions of the contaminated groundwater than at background pH values. A relatively robust conceptual model was built based on what was already known about the site.

The conceptual model, and the process of developing an EA remedy, was simplified by prioritizing contaminants to be treated. This is important at sites with multiple contaminants because EA remedies that rely on chemical or biological attenuation mechanisms cannot treat a suite of contaminants with a wide spectrum of chemical behaviors. Tritium, uranium, Sr-90, and I-129 were ranked as the highest priority for treatment, based on their concentrations relative to maximum concentration levels.

Another simplification of the conceptual model was the assumption that microbial processes were not important in controlling contaminant behavior throughout most of the aquifer. The assumption of minimal microbial influence on contaminant behavior was based on the acidity of the groundwater, the low organic carbon content of the aquifer sediments and groundwater, and the lack of any depletion of nitrate concentrations relative to tritium.

The simplifications of the conceptual model led to an EA remedy that combined containment to treat tritium with pH adjustment to treat Sr-90 and uranium. The focus of further characterization then became where to place the subsurface barriers and gates, the buffering capacity of the acidified aquifer, and the effects of injecting high pH fluids into an acidic aquifer. The latter two were answered by laboratory and field tests. The optimal location of the subsurface barriers was answered with geologic characterization by cone penetrometer. It was found that the preferential contaminant migration paths were along topographically low areas or “troughs” in the top of the clay that separates the upper and lower aquifer zones. The characterization also confirmed earlier observations that the plume was highly stratified, with the highest concentrations near the bottom of the aquifer moving along the top of the clay layer.

The subsurface barriers were placed across the troughs leaving the gates across the higher elevation portions of the clay. This placement of the barriers has the effect of controlling the release of contaminants from the troughs through the gates. The barriers have resulted in substantial reduction of tritium flux to the local stream and, together with the elevated pH treatment zones at the gates, have reduced downgradient uranium and Sr-90 concentrations to below MCLs.

The trial injection of silver chloride to treat I-129 was performed upgradient and near the gates. The field pilot study of this technology suggested that effective distribution of silver chloride particles in the treatment zone was the primary challenge to successful treatment. In this case, an additional layer of complexity may be beneficial to the conceptual model of I-129 remediation. Speciation analyses of I-129 suggest that in the acidic portions of the plume the dominant species of iodine is iodide, the species targeted by silver chloride, but the dominant species changes in other portions of the plume [5], [6].

Stay consistent with geochemical evolution where possible

EA remedies that are consistent with the geochemical evolution of a contaminant plume require a lower burden of proof that the attenuated contaminants are not subject to remobilization. A contaminant plume is a perturbation of the natural system. After the source is removed, the system will have a tendency to return toward the natural conditions. An acidified aquifer will eventually return to near the natural pH value. An aerobic aquifer made anaerobic by organic contaminants will eventually return to an aerobic system. EA remedies for radionuclides that are not consistent with the natural evolution of the aquifer require proof that the attenuation mechanisms will not be reversed as the aquifer returns to its natural conditions. This has been the main challenge to technologies that attenuate uranium and Tc-99 in aerobic aquifers by inducing anaerobic conditions. They must prove that as the aquifer returns to aerobic conditions, the uranium or Tc-99 will remain in a low mobility form.

Returning to the case study, one of the reasons that raising pH in the treatment zones in the gates was chosen to treat Sr-90 and uranium is that it is consistent with the natural geochemical evolution of the site. Eventually, the pH of groundwater at the site will return to a value near 5. At this pH the contaminants will remain attenuated.

Maintain a holistic view of the remedy

Considering the entire system from source to receptor is important in the design and implementation of EA remedies. EA remedies targeting one contaminant may increase mobility of another or release native toxic metals (e.g., arsenic). EA remedies deployed upgradient may affect downgradient portions of the system. Considering GSR objectives should also be part of a holistic view of an EA remedy.

The case study provides some examples of taking a holistic view of the remediation. It was recognized that installing a funnel-and-gate system would affect downgradient monitoring, in particular at seepline monitoring stations where groundwater crops out into wetlands. Walk-downs of the seepline have been done to investigate this and changes in monitoring locations have been made. Another example is the potential for silver chloride to kill microbes. In the location where it is deployed, microbial activity is compromised anyway. Nevertheless, silver is monitored near the deployment and concentrations are generally below detection limits. However, it is agreed that this technology will never be deployed in the wetlands where damage to microbial communities could severely impact the environment.

The remedy in the case study also meets several GSR objectives. The pump-and-treat system treated approximately 600 liters of contaminated groundwater per minute 24 hours a day and was expected to operate for 30 years. This was a much larger carbon footprint than the current system of injections every 12-18 months. The cost of operating the pump-and-treat system was approximately $1 million per month. The average cost of operating the current system is approximately $1 million per year. Finally, the current system produces no solid radioactive waste.

CONCLUSIONS

Enhanced attenuation (EA) remedies for radionuclide contaminated groundwater are generally consistent with the objectives of green and sustainable remediation. Through physical and/or chemical mechanisms, EA remedies limit the migration of radionuclides *in situ*. While EA remedies can be quite effective at achieving remedial goals, radionuclides are left in the subsurface post treatment. Hence, it must be demonstrated to the satisfaction of regulators and stakeholders that the attenuated radionuclides pose no future risk to receptors. Strategic design improves performance of remedies, attainment of regulatory objectives and acceptance by stakeholders.

This study presented an approach to designing EA remedies that the Savannah River National Laboratory and the Savannah River Site have used to deploy multiple successful EA remedies for radionuclides in environmental media. The tenets of the approach are:

- Engage regulators and stakeholders early in the process of EA remedy development;
- Keep the conceptual model as simple as possible;
- Stay consistent with geochemical evolution where possible; and
- Maintain a holistic view of the remedy.

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