

RECLAMATION

Managing Water in the West

Feasibility of In Situ, Passive Groundwater Treatment to Reduce Selenium Impacts from Reclamation Projects

**Research and Development Office
Science and Technology Program
(Final Report) ST-2017-7113-01**



**U.S. Department of the Interior
Bureau of Reclamation
Research and Development Office**

February 2018

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Western Colorado Area Office

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Feasibility of In Situ, Passive Groundwater Treatment to Reduce Selenium Impacts from Reclamation Projects

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Executive Summary

Irrigation induced groundwater flow, as a source of selenium mobilization and movement into surface water is known, and assumed to be appreciable. However, mechanisms for directly reducing the selenium concentration of this source have not been widely investigated. Unlike treating a point source, agricultural seepage is more diffuse and can occur anywhere along the length of a stream. As documented at several Reclamation projects, high selenium concentrations can adversely impact fish and waterfowl.

The purpose of this scoping report is two-fold:

1. Perform a literature search of existing and emerging technologies with the goal of identifying an economical method to perform passive, in-situ removal of selenium from irrigation-induced groundwater.
2. In the event that a promising method was identified for further evaluation, identify and assess locations best suited for a potential pilot project.

Two types of reactive media, Zero-Valent Iron (ZVI) and Apatite, show some potential for the long-term, in-situ removal of selenium from groundwater. ZVI, which is a by-product of cast-iron machining, is readily available in the commercial market. It produces a low oxidation potential in the water, which then sequesters selenium into a less soluble form. Apatite is a natural calcium phosphate mineral that has the ability to sequester many different types of elements into its molecular structure via isomorphic substitution. Apatite minerals are very stable and for the most part, insoluble in water. It's been successfully used for the removal of uranium and other metals from groundwater.

Of the methods reviewed, three types of passive, in-situ media installation stand out as having the most promise: conventional Permeable Reactive Barriers (PRBs), Deep Aquifer Remediation Tools (DARTs) and Injectable PRBs. Conventional PRBs are an engineered zone of reactive media that is installed below ground to intercept groundwater flow. A DART consists of an inner core of reactive barrier material and four flexible wings to help direct the ground water flow through the barrier material. DARTs are installed in non-pumping wells. A series of DART wells can be used to capture and treat a plume of contaminated groundwater. The reactive material in a DART can be easily removed and replaced. Injectable PRBs are installed by pumping a fluidized media into the ground via small wells. Unlike conventional PRBs, they don't require the sometimes costly excavation and fill.

Six sites, located in the Lower Gunnison River Basin near the town of Montrose, Colorado, were selected as potential candidate locations for implementation of a future demonstration project. Proximity of active monitoring wells and surface water features that would act to receive treated water, as well as information on hydraulic conductivity and groundwater selenium concentration were used in site selections.

Geochemical modeling, using pH-REdox-Equilibrium (PHREEQC), was also conducted to understand the efficacy of using ZVI to passively remove selenium from the shallow groundwater at four of the six candidate sites. Initial model results indicate that ZVI would effectively remove dissolved selenium from water and immobilize it as elemental selenium. The initial results also indicated that there was a need to conduct further geochemical modeling to evaluate gas generation and to estimate the mass of precipitate generated during these reactions, as this is implicated in plugging of the ZVI.

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Introduction

Reducing the amount of selenium making its way to surface water has been the focus of many studies and projects. Irrigation-induced groundwater as a source of selenium to surface water is known, and assumed to be appreciable; however, mechanisms for reducing the effects of this particular source have not been widely investigated. Unlike a point source, such as occurs in mining and industrial areas, agricultural groundwater's contribution to surface water is often more diffuse and can occur anywhere along the length of a stream. As documented near several Reclamation projects, high selenium concentrations can adversely impact fish and waterfowl (Kovak, 2004) (Walker, 2010).

Several industry sectors, universities, and government agencies have developed and/or demonstrated various technologies to remove selenium from water with mixed results. Several reports are available that summarize the results of those efforts, including but not limited to CH2M HILL 2010, California DWR 2004, Salton Sea SCH Project 2010, and EPA 2014.

Previous Reclamation Science and Technology Program (S & T) projects, number 394, "Evaluation of Passive Bioreactors to Reduce Selenium Impacts from Reclamation Projects" and number 4414, "Passive Selenium Bioreactor--Pilot-scale Testing" demonstrated the use of passive bioreactors on surface-water. S & T project number 6623, "Understanding Effects of Recharge and Dissolved Nitrate on Selenium and Salinity Mobilization Using Geochemical Modeling and Laboratory Testing" studied the physical and chemical processes that control selenium mobilization and transport (Mast, 2014).

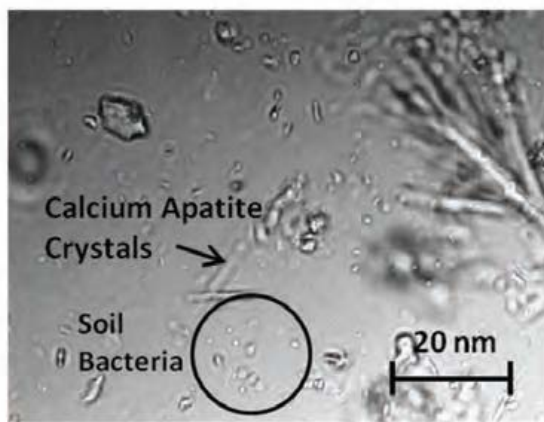
With the goal of finding an economical method to perform passive, in-situ removal of selenium from irrigation-induced groundwater, Reclamation's Western Colorado Area Office (WCAO), in partnership with the US Geological Survey, conducted a scoping study to research these available technologies. In the event that a promising method was identified for further evaluation, a second goal was to identify and assess locations best suited for a potential pilot project. Several locations within an existing, local groundwater study area were identified for assessment.

Methods Identified from Literature Search

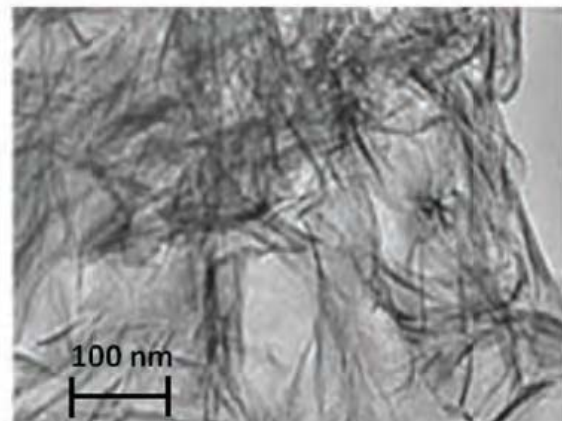
Several types of reactive media have been investigated during past studies of groundwater contaminant remediation, particularly around old mining sites. Many of the studies have focused on the removal of uranium, but the removal of many associated inorganic constituents, including selenium, have been noted and/or studied as well. Of all the currently available media reviewed during this scoping effort none stood out as being able to work in all environments. However, Zero-Valent Iron (ZVI) and Apatite both show promise and are the subject of several current, mining area remediation studies.

ZVI, which is by-product of cast-iron machining, is readily available in the commercial market. It produces a low oxidation potential in the water, which then sequesters selenium into a less soluble form. Due to the potential for mineral precipitation, the lifespan of ZVI varies considerably depending on the chemical makeup of the water. Lab column studies are recommended to determine its suitability for use in a particular area (Naftz, Morrison, Fuller, & Davis, 2003).

Apatite (fig. 1) is a natural calcium phosphate mineral that has the ability to sequester elements into its molecular structure via isomorphous substitution. Apatite minerals are very stable and for the most part, insoluble in water. It's been used successfully for the removal of uranium and other metals from groundwater. Although selenium will be sequestered into pure apatite, research indicates that carbonated apatite would immobilize selenium more efficiently (Moore & Stewart, 2014).



Soil Bacteria forming Calcium Apatite



Calcium Apatite Crystals Formed in Soil

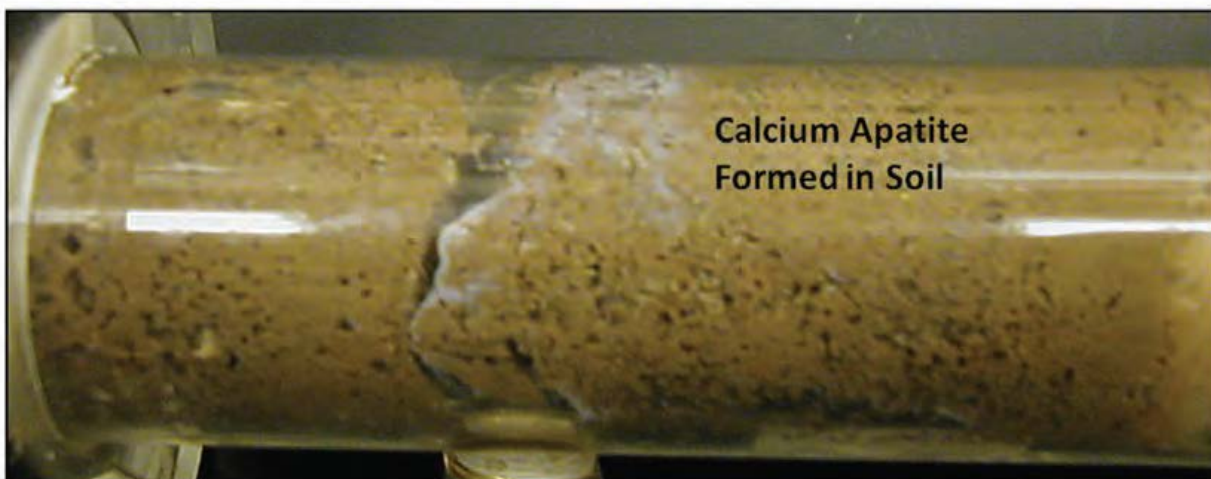


Figure 1. Calcium apatite formed in a soil column experiment. (Sandia National Laboratories & AECOM)

Methods of passive, in-situ media installation were also investigated, and of the methods reviewed, three techniques stood out as having promise: conventional Permeable Reactive Barriers (PRBs), Deep Aquifer Remediation Tools (DARTs), and Injectable PRBs.

PRBs are an engineered zone of reactive media that is installed below ground to intercept groundwater flow. Typically it requires extensive excavation to install the PRB “wall” and any needed, non-permeable funnel walls used to channel the groundwater flow toward the PRB (figs. 2-3). Although limited to shallow treatment depths (< 21 meters), and the requirement for excavation to remove or replace, PRBs have been successfully used in many areas.

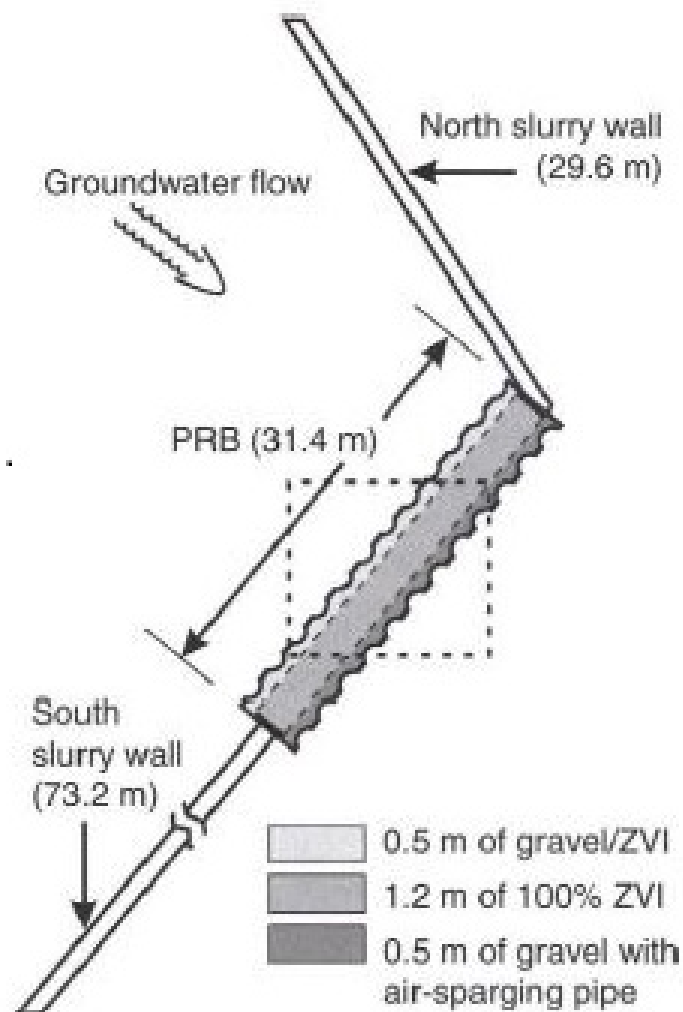


Figure 2. Diagram of permeable reactive barrier and slurry wall design. (US Department of Energy [DOE])



Figure 3. Permeable reactive barrier and slurry wall construction prior to reactive material emplacement. (DOE)

DARTs (figs. 5-6) can be installed in existing, non-pumping wells and treat water at greater depths than PRBs. Each DART consists of an inner core of reactive barrier material and four flexible wings to help direct the flow of ground water through the barrier material. A series of DART wells (fig. 4) can be used to capture and treat a plume of contaminated groundwater. Each well will have a capture zone of approximately two times the inside diameter of the well if the barrier material has an engineered hydraulic conductivity (K) of 50 to 200 times that of the aquifer (Naftz & Davis, 1999). Unlike buried PRBs, the reactive material in a DART can be easily removed and replaced.

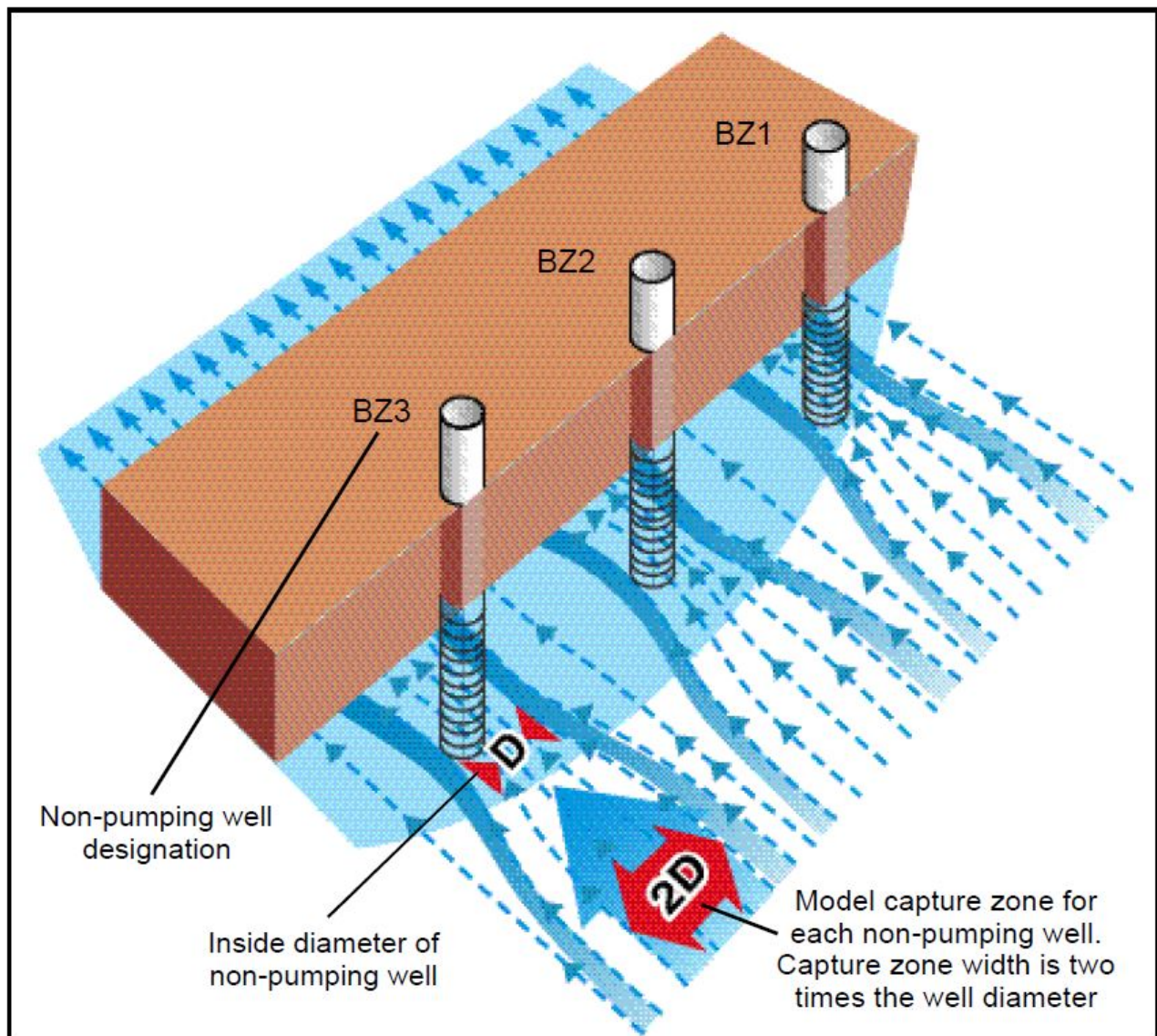


Figure 4. Schematic diagram showing non-pumping wells containing DARTs and modeled contaminant capture zones, Fry Canyon, Utah.

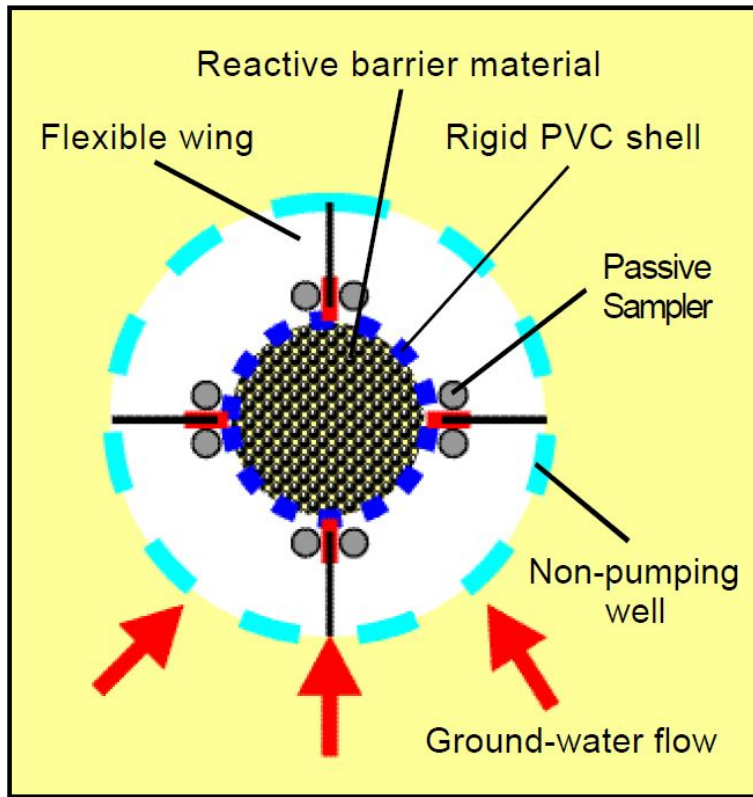


Figure 5. Schematic diagram of a Deep Aquifer Remediation Tool (DART).



Figure 6. Deployment of DART prototype into non-pumping well at Fry Canyon, Utah.

Injectable PRBs (fig. 7) don't require the sometimes costly, excavation and fill that's needed for conventional PRBs. Instead the reactive media is injected into the ground through the use of small wells (fig. 8). Media that has been used include micro- and nano-scale ZVI, as well as apatite mixtures. Advantages include: contaminant is kept below ground, installation can occur deep underground or below objects such as tanks, no or little operational expense is incurred, no removal and disposal is needed, and no waste stream is generated. Apatite appears to be the most versatile media for this type of installation, as it forms a continuous permeable reactive barrier on nano-sized apatite crystals that do not decrease soil porosity (Sandia National Laboratories & AECOM, 2017).

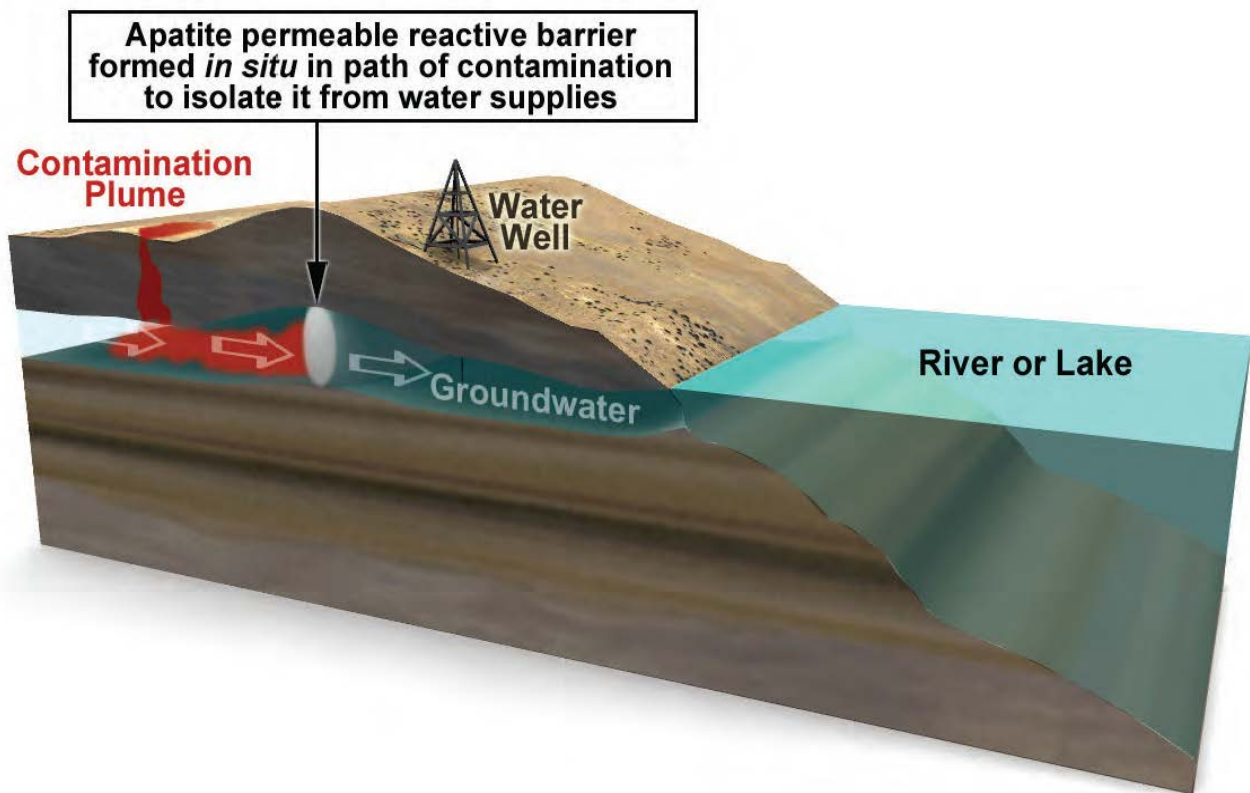


Figure 7. Schematic of formation of a modified apatite permeable reactive barrier using an aqueous solution of reagents and phosphate. (Sandia National Laboratories & AECOM)



Figure 8. Injecting apatite solution at DOE remediation site near Rifle, Colorado, November 2017.

Based on the literature research and site visits, the most promising methods that may warrant further research or testing are the DART and injectable PRB techniques, in conjunction with either ZVI or apatite reactive media.

Candidate sites

A second goal of this scoping study was to identify local areas best suited for a potential demonstration project. Potential locations were identified based on an understanding of groundwater gradients, hydraulic conductivities, estimated groundwater velocities, and saturated thickness of the aquifer. This information was assessed along with known groundwater-selenium-concentration data which had been collected as part of previous investigations. By targeting an area where groundwater has high selenium concentrations and using our understanding of groundwater flow, an ideal demonstration site could potentially be identified where groundwater could be intercepted just prior to entering a surface water. This would allow

us to more easily test and monitor selenium removal from groundwater, in the event that promising selenium removal techniques were identified in the literature search.

Located within the east side of the Bureau of Reclamation Uncompahgre Project, an existing, local groundwater study area was chosen for assessment. The Uncompahgre Project is located on the western slope of the Rocky Mountains in the Lower Gunnison River Basin of west-central Colorado. Project lands surround the town of Montrose and extend 34 miles north along both sides of the Uncompahgre River to Delta, Colorado. Groundwater's contribution to surface water occurs throughout the study area. Previously the USGS, in conjunction with a Reclamation drill crew, installed a 30 well network in this area in order to assess the near surface geology and aquifer properties, as well as, to monitor the occurrence of selenium and other groundwater quality constituents. The USGS continues to monitor and maintain this groundwater network. All of the potential study sites initially identified for assessment are located adjacent to at least one of these active monitoring wells. Hydraulic conductivities for aquifers on the east side of the Uncompahgre River range from 0.06 feet to 100 feet per day (median 4 feet per day, mean 10 feet per day) and indicate that groundwater flowpaths are highly variable. In addition to the variability in flowpaths, selenium concentrations observed in groundwater on the east side of the Uncompahgre River are also variable, and range from less than detection to 4,000 micrograms per liter (median 14 micrograms per liter, mean 300 micrograms per liter). Despite this variability in selenium concentrations in groundwater, groundwater is an appreciable source of selenium to surface water. Selenium concentrations in surface water can increase to 345 micrograms per liter (Loutsenhizer Arroyo) during the non-irrigation season when the majority of flow in surface water is from groundwater. The effects of dilution by fresh irrigation water masque the inputs of groundwater during the irrigation season (selenium concentration range from 14 micrograms per liter to 91 micrograms per liter at Loutsenhizer Arroyo), however, groundwater contributes to surface water throughout the year (Thomas, McMahon, & Arnold, 2018).

Six of the initially reviewed sites were selected as potential candidate locations to implement a potential, passive selenium removal demonstration project (fig. 9, table 1). Information on hydraulic conductivity and selenium concentration were used in site selection. For each candidate site, groundwater quality and hydraulic conductivity are associated with the monitoring well located at the site. The general direction of groundwater flow is indicated on each of the site maps (figs. 10-15) and was determined from a potentiometric map created for the area. On each of the site maps, the location of a nearby surface water feature is indicated and the approximate distance to that feature is provided in table 1. The purpose of identifying this surface water feature is to provide information with regard to site design where these features would act to receive water that had been processed by passive selenium removal. The goal is to not allow the treated water to interact in the shallow groundwater system but be conveyed to the nearby surface water feature.

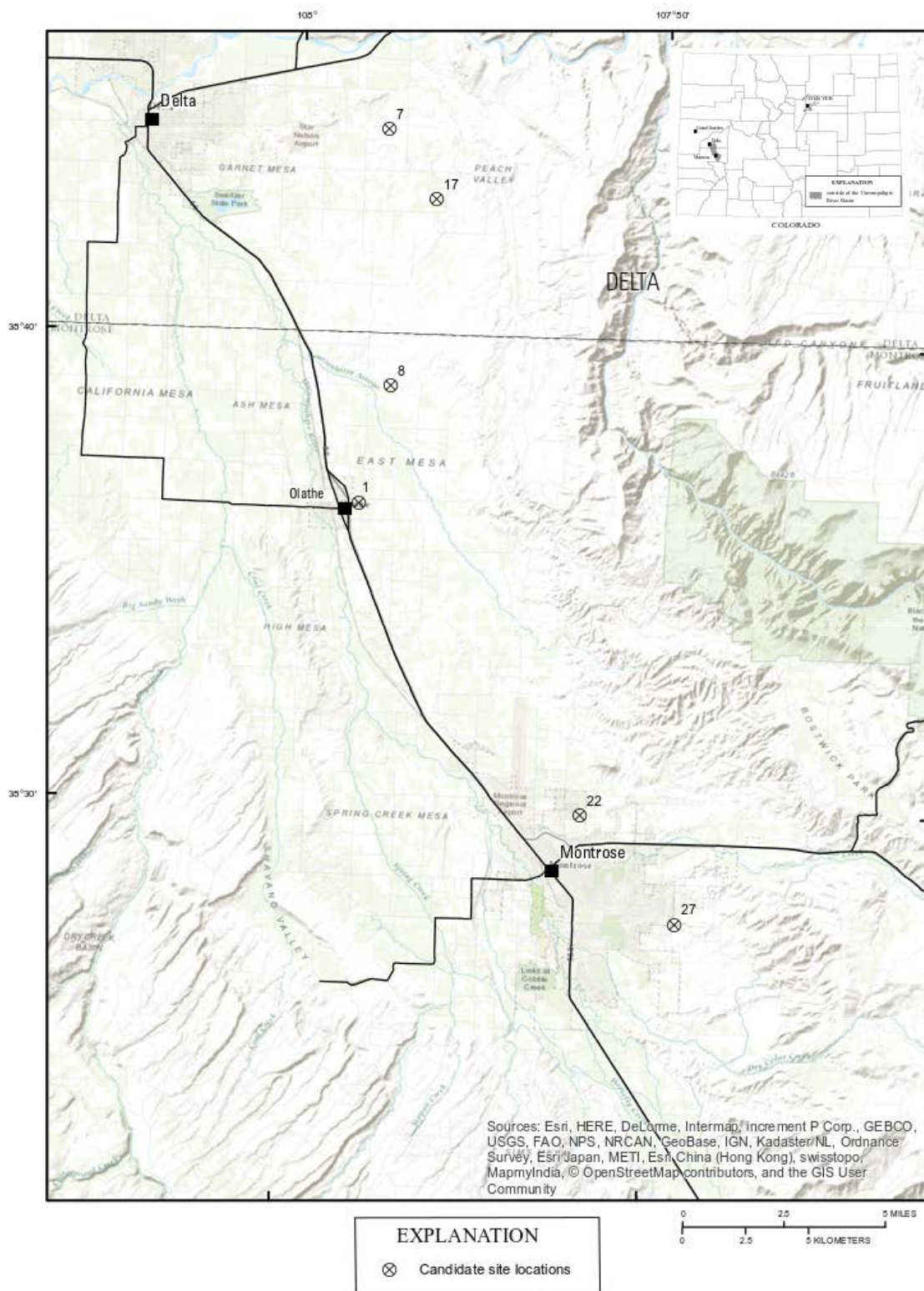


Figure 9. Location of candidate sites, lower Gunnison Basin, Colorado.

Table 1. Candidate sites for passive selenium removal in the lower Gunnison Basin, Colorado.

Site	Hydraulic conductivity (ft/day)	Selenium, micrograms per liter	Land ownership	Approximate distance to surface water feature
1	20	105	Private	300 feet
7	1	3,355	Federal	150 feet
8	5	506	Private	200 feet
17	10	88	Private	1500 feet
22	2	923	City of Montrose	250 feet
27	5	405	Private	25 feet

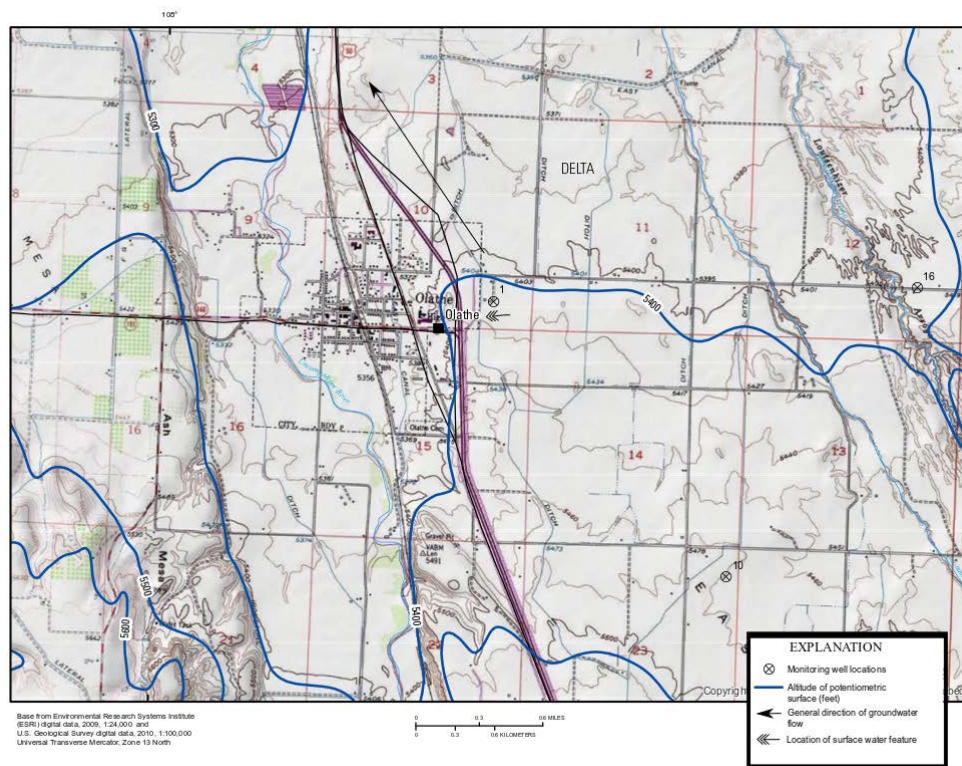


Figure 10. Site 1 located near Olathe, Colorado. General direction of groundwater flow and location of surface water feature indicated on figure.

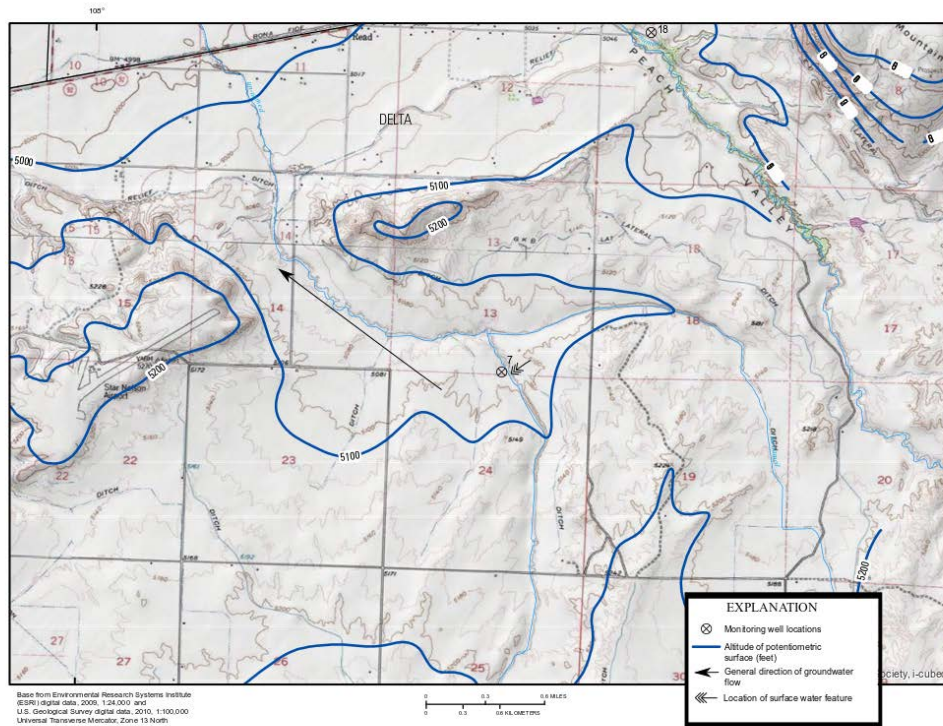


Figure 11. Site 7 located east of Delta, Colorado. General direction of groundwater flow and location of surface water feature indicated on figure.

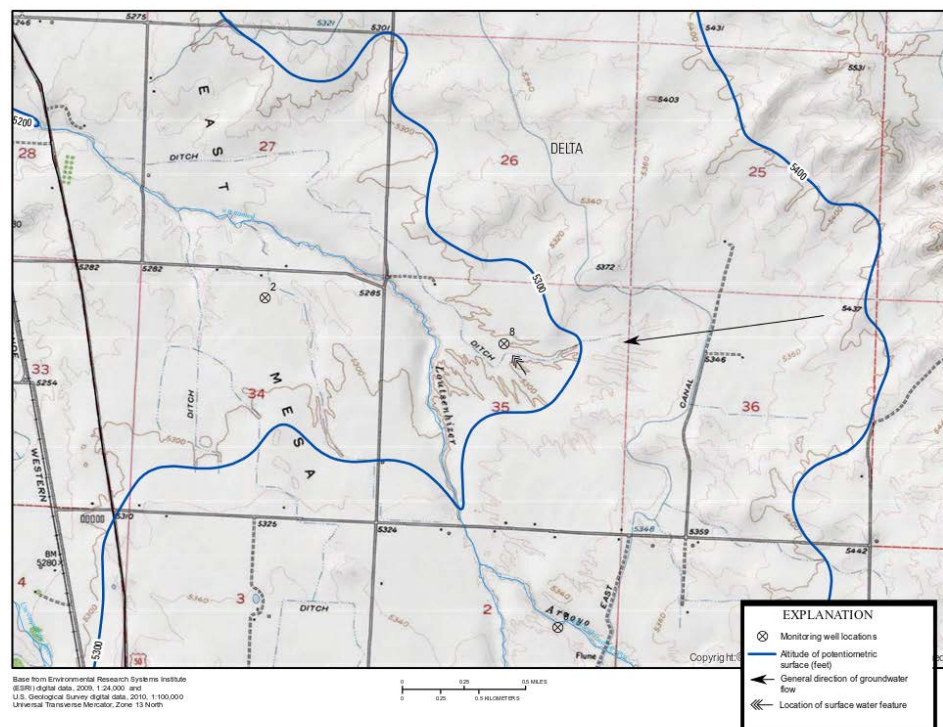


Figure 12. Site 8 located northeast of Olathe, Colorado. General direction of groundwater flow and location of surface water feature indicated on figure.

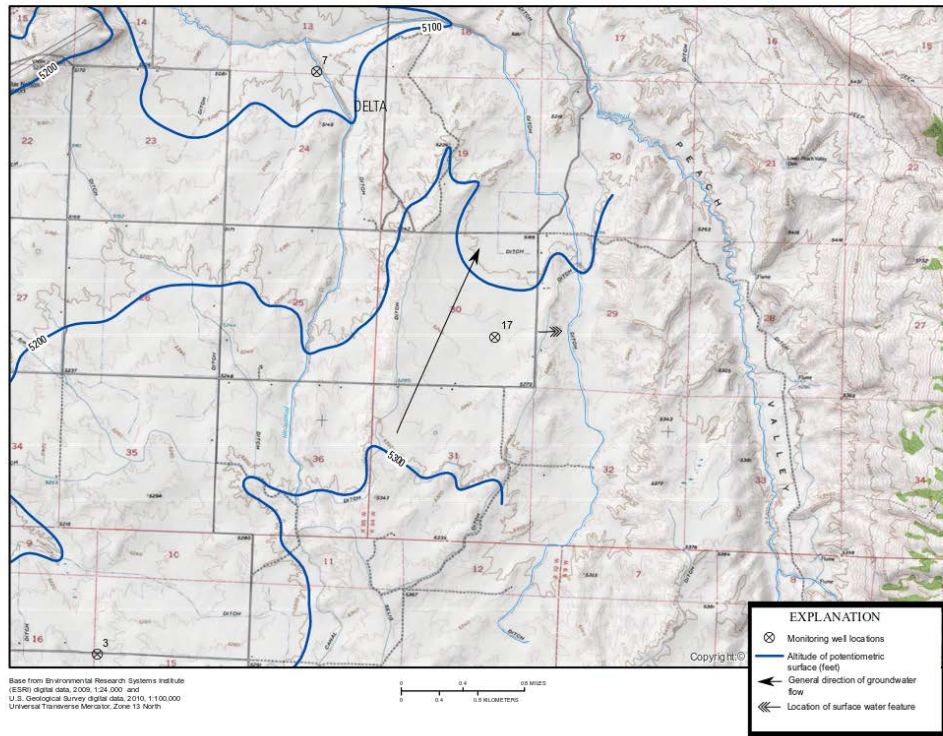


Figure 13. Site 17 located southeast of Delta, Colorado. General direction of groundwater flow and location of surface water feature indicated on figure.

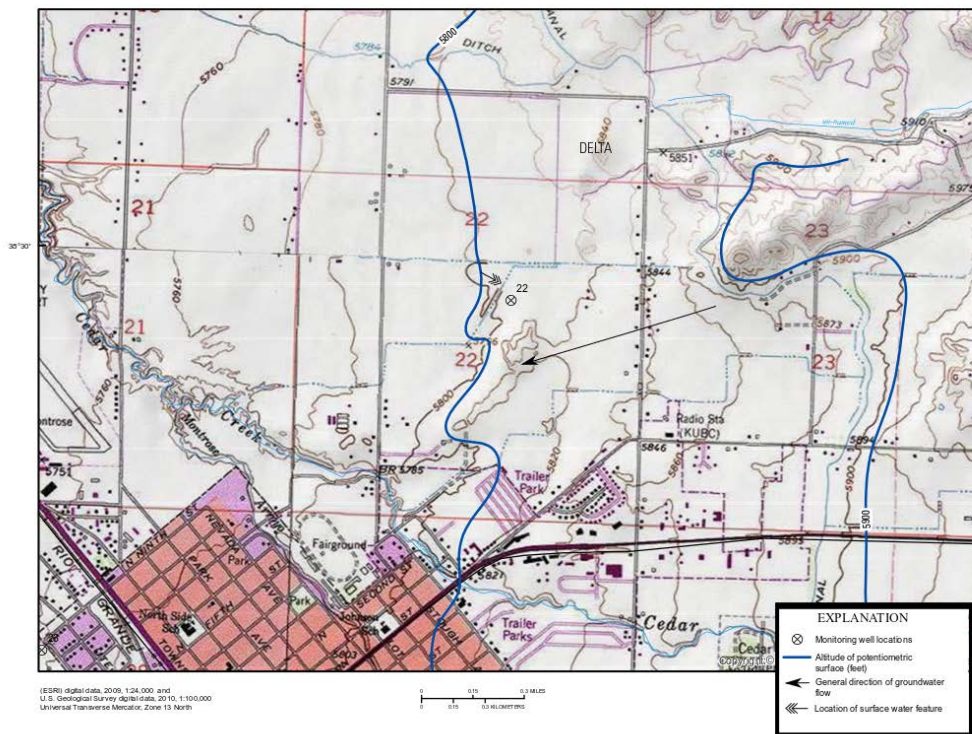


Figure 14. Site 22 located in Montrose, Colorado east of airport. General direction of groundwater flow and location of surface water feature indicated on figure.

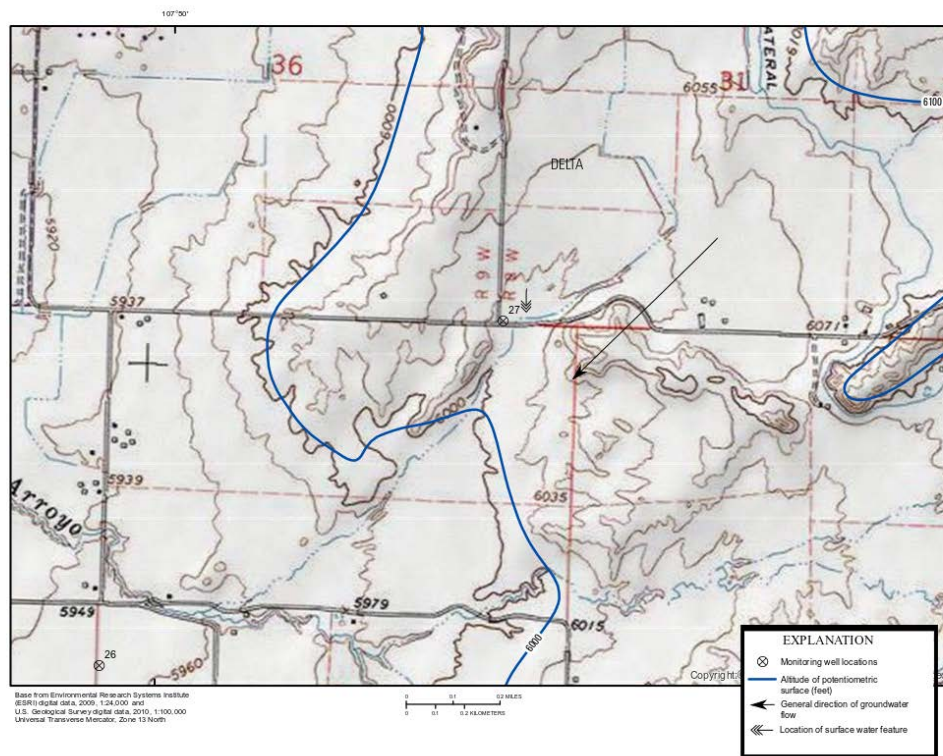
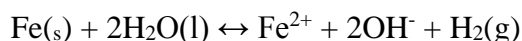


Figure 15. Site 27 located east of Montrose, Colorado. General direction of groundwater flow and location of surface water feature indicated on figure.

Preliminary geochemical modeling to address the feasibility of using zero valent iron (ZVI) to remove selenium from shallow groundwater in western Colorado

Geochemical modeling was conducted to understand the efficacy of using ZVI to passively remove selenium from shallow groundwater. The modeling was done by David Naftz, U.S. Geological Survey (USGS), who is one of the lead authors of “Handbook of Groundwater Remediation Using Permeable Reactive Barriers” (Naftz, Morrison, Fuller, & Davis, 2003) and a research hydrologist for the USGS.

Initial modeling used water-quality data collected at site 7 to evaluate ZVI removal of selenium. Anaerobic corrosion of iron causes an appreciable increase in pH where starting pH was 6.90 and ending pH was 10.55.



where s is solid, l is liquid, and g is gas

The hydrogen gas generated from this reaction would subsequently be consumed in additional reactions with sulfate and carbon dioxide which would result in mineral precipitation (plugging/reactive surface passivation) and the generation of gas bubbles which would have associated hydraulic impacts (e.g. reduce flow).

The geochemical modeling was done using pH-REdox-Equilibrium (PHREEQC) (Parkhurst & Appelo, 2013) to simulate the mineral precipitate and gas generation resulting from the anaerobic corrosion of metallic iron (fig. 16). Reaction-path modeling evaluated the potential for calcite, siderite, FeS, gypsum, and elemental selenium precipitation. Results for reaction-path modeling were plotted for each constituent where the x-axis is zero valent iron corrosion in mmoles per liter and the y-axis is the saturation index (SI) for each constituent where SI is a unitless value (fig. 17). Results of reaction-path modeling indicate that dissolved selenium in water would be reduced to elemental selenium and the solution would remain oversaturated with respect to elemental selenium (fig. 17). These initial model results indicate that ZVI would effectively remove dissolved selenium from water and immobilize it as elemental selenium. These initial results indicated that there was a need to conduct further geochemical modeling to maintain equilibrium with respect to calcite, siderite, and FeS after each reaction step. In addition, estimates could be made for the mass of precipitate generated during these reactions, as this is implicated in plugging of the ZVI, and to evaluate gas generation. In addition, the modeling should be repeated with other water chemistries.

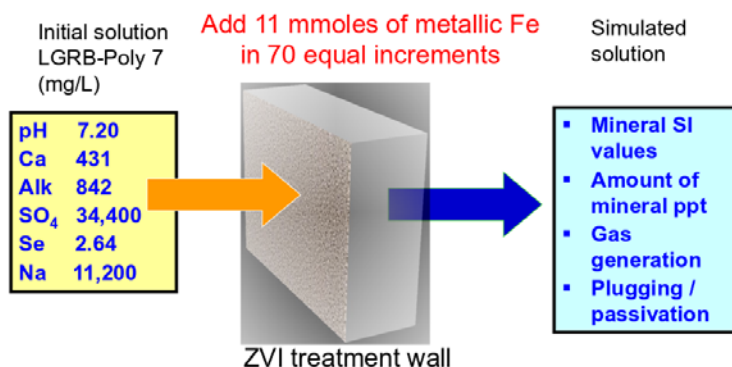


Figure 16. PHREEQC simulation of mineral precipitation and gas generation for candidate site 7 via anaerobic corrosion of metallic iron.

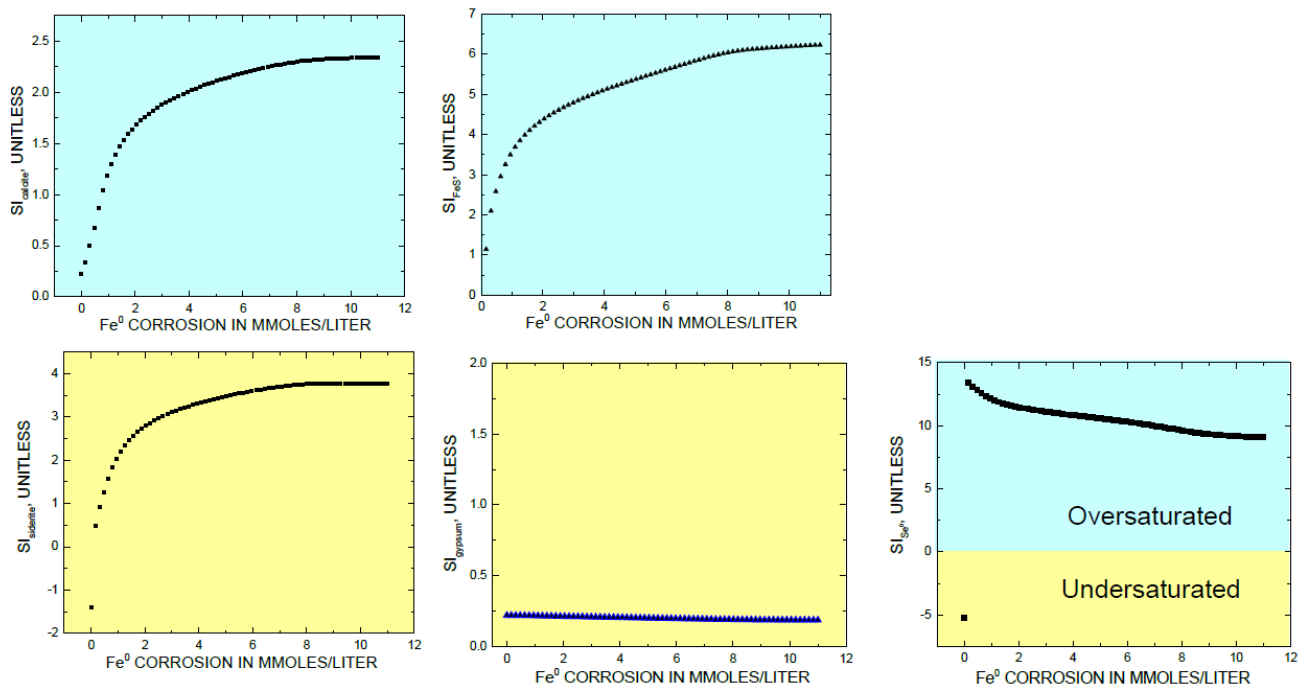


Figure 17. Reaction-path modeling results for calcite, siderite, FeS, gypsum, and Se⁰

Additional modeling was conducted using other groundwater chemistries to further understand how ZVI would perform in removing dissolved selenium from groundwater along with other

related reactions (fig. 18 – 21). One of the modeling exercises evaluated the changes in specific conductance as water is reacted with ZVI with implication to salinity reduction (fig.18).

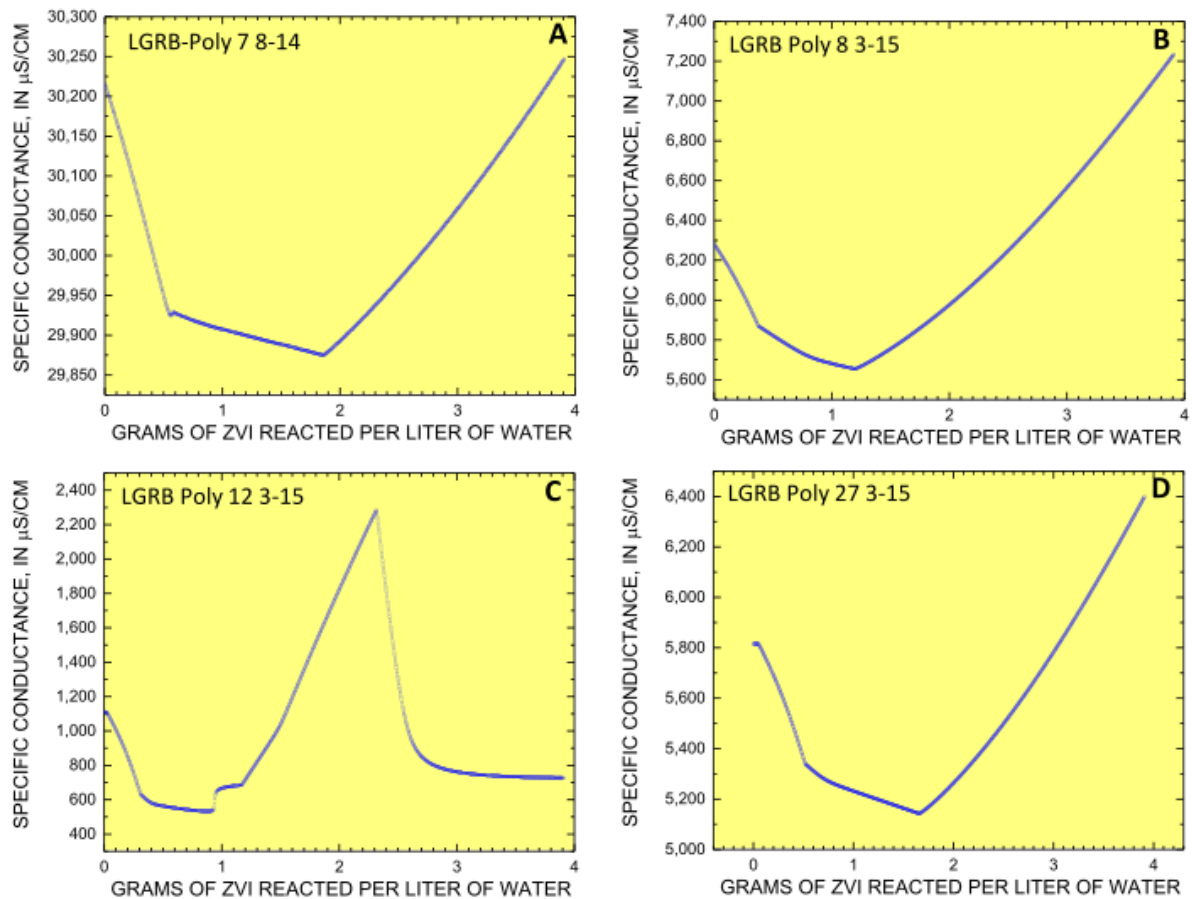


Figure 18. Simulated changes in specific conductance as a function of incremental reaction of zero-valent iron with ground water from monitoring wells (A) Site 7; (B) Site 8; (C) Site 12; and (D) Site 27.

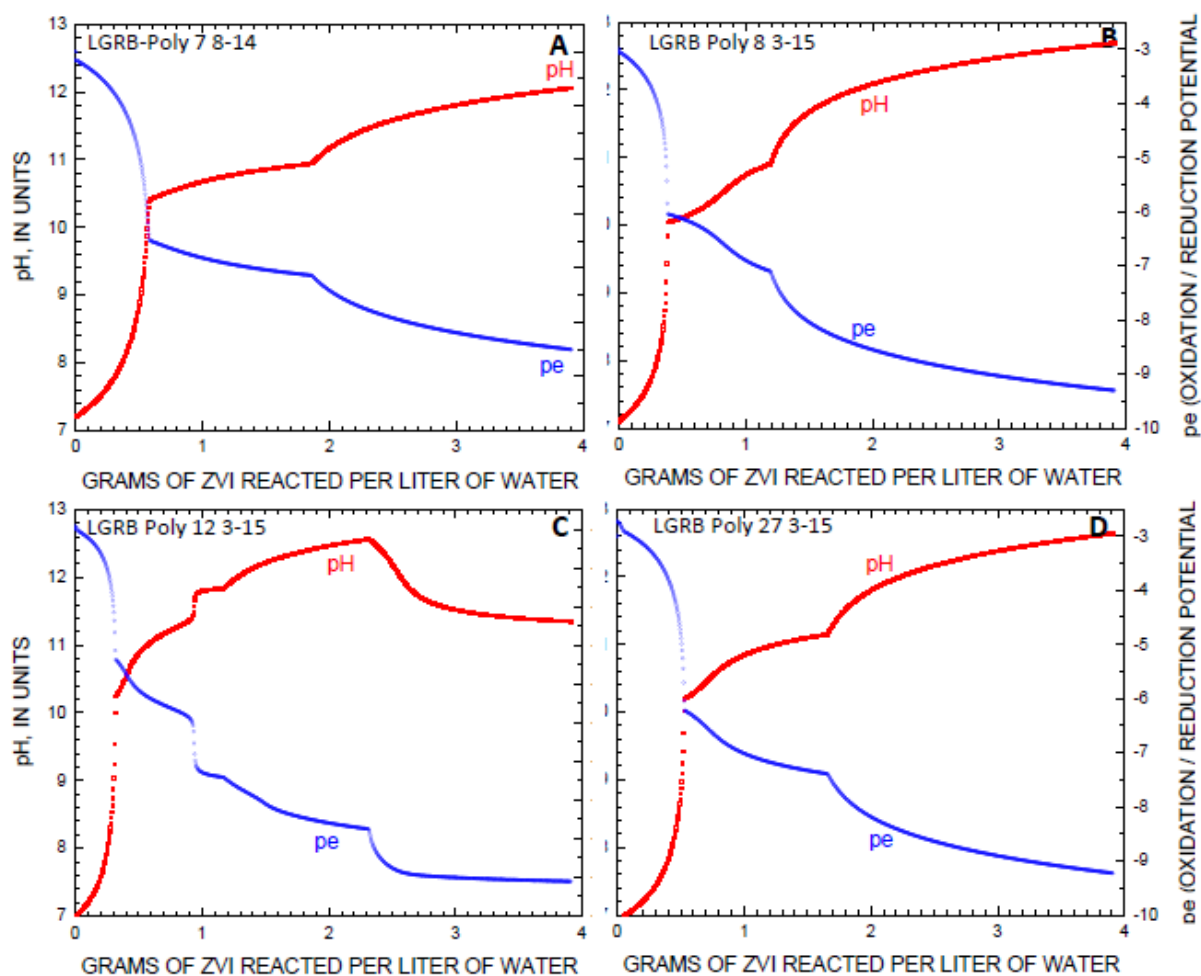


Figure 19. Simulated changes in solution pH and pe as a function of incremental reaction of zero-valent iron with ground water from monitoring wells (A) Site 7; (B) Site 8; (C) Site 12; and (D) Site 27.

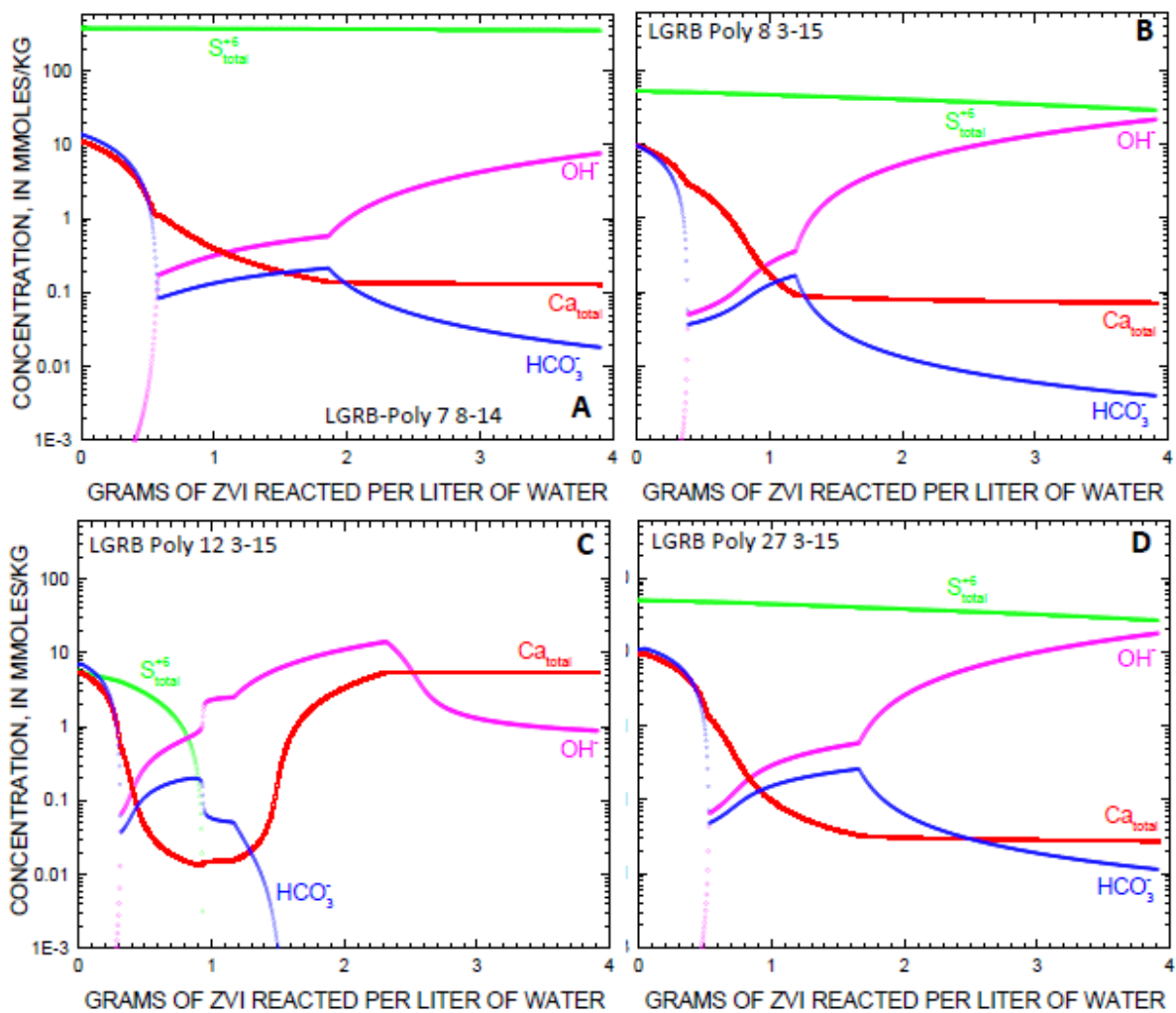


Figure 20. Simulated changes in solution concentration of S^{6+} , OH^- , Ca total, and HCO_3^- as a function of incremental reaction of zero-valent iron with ground water from monitoring wells (A) Site 7; (B) Site 8; (C) Site 12; and (D) Site 27.

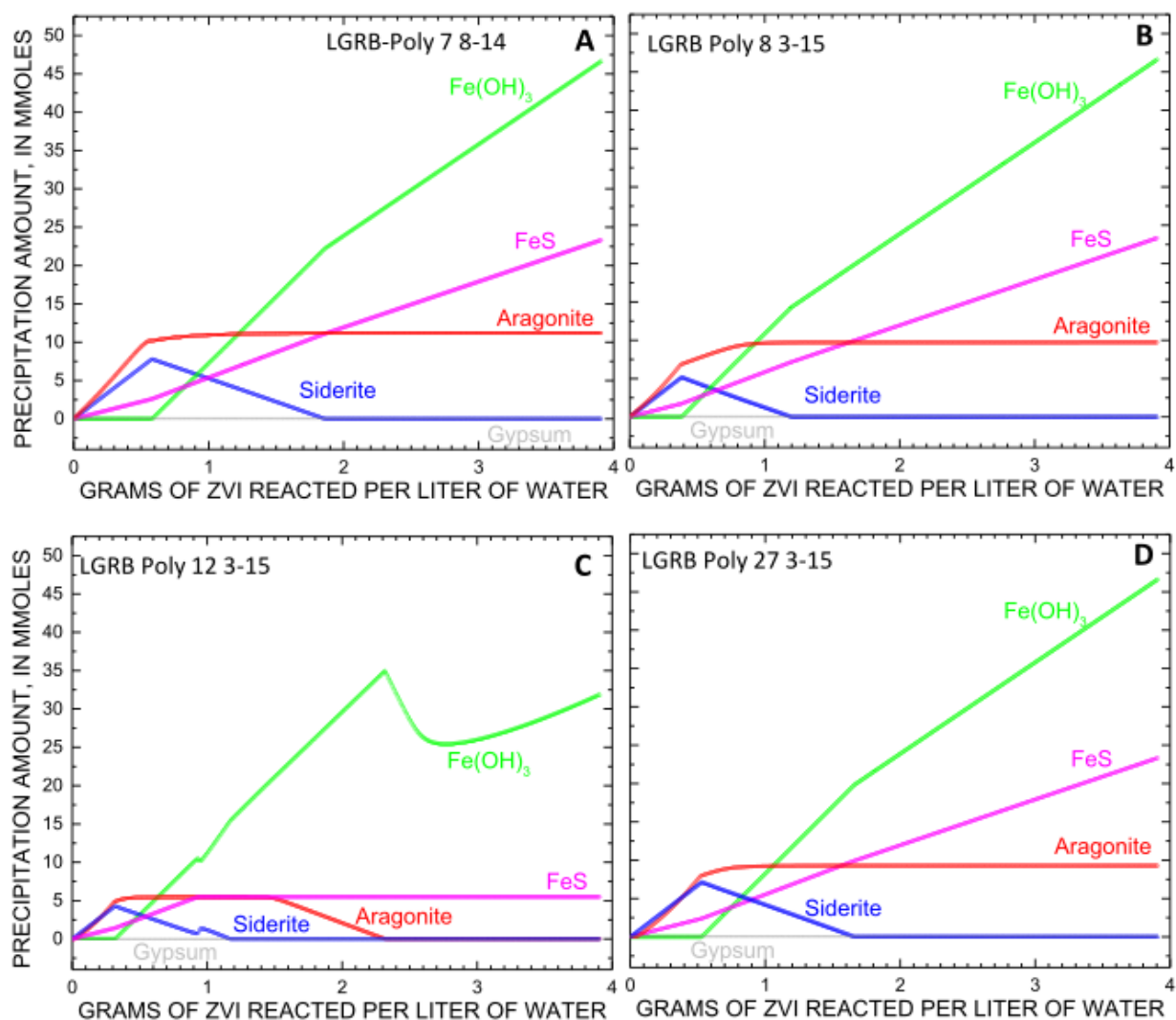


Figure 21. Simulated changes in mineral precipitation as a function of incremental reaction of zero-valent iron with ground water from monitoring wells (A) Site 7; (B) Site 8; (C) Site 12; and (D) Site 27.

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