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Journal of Hazardous Materials 68 (1999) 125–153

**Journal of
Hazardous
Materials**

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Results of the reactant sand-fracking pilot test and implications for the in situ remediation of chlorinated VOCs and metals in deep and fractured bedrock aquifers

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Abstract

Permeable reactive barriers (PRBs), such as the Waterloo Funnel and Gate System, first implemented at Canadian Forces Borden facility in 1992, are a passive remediation technology capable of controlling the migration of, and treating contaminated groundwater in situ. Most of the PRBs installed to date have been shallow installations created by backfilling sheet-pile shored excavations with iron filing reactive media. More recently continuous trenchers [R. Puls, Installation of permeable reactive barriers using continuous trenching equipment, Proceedings of the RTDF Permeable Barriers Work Group, Virginia Beach, VA, September 1997] and Caissons [J. Vogan, Caisson installation of a pilot scale, permeable reactive barrier in situ treatment zone at the Sommersworth Landfill, NH, Presented to the RTDF Permeable Barriers Work Group, Alexandria, VA, April 1996], and vertical fracturing emplacements [G. Hocking, Vertical hydraulic fracture emplacement of permeable reactive barriers, Progress Report delivered to the Permeable Reactive Barriers Workgroup of the Remedial Technology Development Forum, Beaverton, OR, April 1998] have been used to create reactive barriers in soil. None of the prior methods are capable of adequately addressing groundwater contamination in deep and fractured bedrock aquifers. The purpose of the RSF pilot study was to install reactive media into an impacted bedrock aquifer, and to evaluate the effectiveness of in situ treatment of chlorinated volatile organic compounds (CVOCs) and metals in that type of aquifer. Three discrete fractures were identified and treated and were subjected to testing before and after treatment. Between 300 and 1700 lb. of 1 mm diameter reactive proppants were injected into each zone to facilitate treatment. Monitoring data obtained from adjacent observation wells verified that fracking fluids reached at least 42 ft from the treatment well following hydrofracturing. The concentrations of

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many of the CVOCs decreased up to 98% based on the results of pre- and post-RSF treatment analyses. Consistent with other research, concentrations of CVOCs were noted to decrease including trichloroethene (TCE), tetrachloroethene (PCE), 1,1,1-trichloroethane (1,1,1-TCA), 1,1-dichloroethane (1,1-DCA), and 1,1-dichloroethene (1,1-DCE) and increases were noted in concentrations of *cis*-1,2-dichloroethene (*cis*-1,2-DCE) and chloroform suggesting that the rate of transformation of the parent compounds to these daughter products is higher than the rate of destruction of the daughter products. The RSF pilot study demonstrated that: (1) zero valent iron foam proppants have the physical and chemical properties necessary to effectively treat CVOCs and metals in groundwater when inserted under high pressures into fractured bedrock. (2) Iron foam reactive media can be placed in bedrock using high pressure hydraulic fracturing equipment and polysaccharide viscosifiers. (3) The extent of the treatment can be monitored in situ using tracers and pressure transducers. (4) Well capacity is increased by improving hydraulic conductivity through hydraulic fracturing and proppant injection. The approximate cost of all of the effort expended in the pilot study was about US\$200,000. Full-scale implementations are projected to cost between US\$100,000 and US\$1,000,000 and would depend on site specific conditions such as the extent and level of impacted groundwater requiring treatment. This technology can potentially be implemented to create treatment zones for the passive treatment of CVOC and metal impacted groundwater in fractured rock aquifers offering a cost-effective alternative to a pump and treat forever scenario. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Permeable reactive barriers; Volatile organic compounds; Fractured bedrock aquifers

1. Introduction

The USEPA has determined that the restoration of deep and fractured bedrock aquifers is technically impracticable and containment is very expensive using conventional technologies such as groundwater pumping and above-ground treatment [30]. As described in the National Research Council's 1994 Report, Alternatives for Groundwater Cleanup [22], the best that groundwater pump and treat is capable of achieving is the containment of the dissolved phase plume at sites where dense nonaqueous phase liquids (DNAPLs) occur in fractured bedrock aquifers.

Conventional and proven groundwater remediation approaches which mostly focus on a combination of source control and hydrodynamic containment of the dissolved phase plume use pumping and above-ground treatment. The conventional approaches leave residual concentrations of contaminants in the aquifer that will continue to dissolve into the groundwater over long periods of time preventing aquifer restoration. Furthermore, the groundwater gradients induced by pumping can cause DNAPLs at rest to become mobilized, spreading contamination deep into an aquifer, and exacerbating the problem. Since restoration is technically infeasible and groundwater pump and treat requires expensive operations and maintenance, a goal was established to develop a passive in situ approach for containing and treating the impacted groundwater.

Permeable reactive barriers (PRB) and in situ treatment walls are a new class of passive in situ remediation treatment technologies that have been developed for passive containment and mitigation of groundwater impacted by a variety of compounds, including many chlorinated volatile organic compounds (CVOCs) [32]. Most of the PRB installed to date rely on the use of zero valent iron (ZVI) to affect reductive dehalogena-

tion of CVOCs and reduction/precipitation of dissolved metals. In comparison to pump and treat, passive treatment technologies such as PRBs potentially offer the advantages of low operations and maintenance costs coupled with comparable levels of risk reduction [34]. Although, various approaches have been developed for the installation of permeable reactive barriers in shallow to moderate depth aquifers composed of excavatable soils, until recently, no demonstrated methodology was available to address deep and fractured bedrock aquifers [1].

Reactant sand-fracking (RSF) is an innovative in situ groundwater remediation technology conceived to more effectively address CVOC and metal contaminated bedrock aquifers [19]. RSF uses hydraulic injection technology to emplace reactive proppants that contain zero valent metals into fractures within the contaminated aquifer, thereby affecting in situ treatment as the groundwater flows through the propped fractures. Unlike the granular iron filings used for many conventional PRBs, the RSF proppants are optimized for hydraulic injection and reactivity.

The hydraulic injection of proppants for reservoir and aquifer stimulation are well understood [15]. The application of these processes to in situ remediation of fractured bedrock is the innovation covered by this paper.

Batch and column tests of various reactive proppant designs were conducted in site-derived and synthetic groundwater's at the University of Waterloo, Ontario, Canada [5], USEPA Athens Lab [20] and the University of Arizona, Department of Civil and Environmental Engineering [7]. Cercofoam[®], iron foam proppants manufactured by Cercona of America, Dayton, OH were selected for use in RSF based on their superior reactivity and other properties such as high strength, low density, and roundness.

The RSF pilot study was conducted at a site located in Newbury Park, CA. A fractured volcanic bedrock aquifer underlies the closed RCRA facility which has been impacted by CVOCs and metals [predominantly trichloroethene (TCE) and hexavalent chromium compounds (Cr^{6+})] as a result of prior plating shop waste management practices, which included direct disposal to a leachfield. Historic concentrations of up to 180 mg/l TCE and 30 mg/l Cr^{6+} have been detected in monitoring wells installed adjacent a plating shop sump and leachfield [3]. TCE concentrations in the leachfield extraction well E-39A have averaged about 28 mg/l. Consistent with USEPA guidance, aquifers where CVOC/DNAPL compound concentrations exceed 1% of the solubility limit of that compound are likely to have DNAPL product and/or residuals present. Since 1% of the solubility limit of TCE is 13 mg/l, the USEPA, in its 1993 Statement of Basis (SB) for the Site [31], concluded that it is likely that residual DNAPLs are present at the Newbury Park Site, and that groundwater restoration would be technically infeasible using existing demonstrated remediation technologies. The SB included a provision for periodic reevaluation of the remediation systems performance and remediation technologies that could be potentially applied to remediation of the site's groundwater.

2. Site setting

The site is located at the foot of the Conejo Hills, in an area of low to moderate relief, located near the northwestern limit of the Santa Monica Mountains. Surface elevations at

the site, and its vicinity, range from roughly 600 to over 1000 ft above mean sea level (MSL). The Facility itself is located on a site that has been graded and is essentially flat. The northeast corner of the site adjoins the US 101 freeway and is roughly at the same grade.

2.1. Physical setting

2.1.1. Geological units

As noted in prior publications on the site [17,18], and as shown in Fig. 1, the facility is underlain by a thin veneer of unconsolidated alluvial and colluvial soils that overlie mafic to intermediate composition volcanic rocks of the Conejo Volcanic Series of Middle Miocene age. The soils are very thin or nonexistent over the western third of the site and thicken eastward across the site into the adjacent valley, to over 100 ft.

The bedded volcanics and sedimentary rocks are intruded by dikes and sills of mafic to intermediate composition. Many of the dikes that intrude high angle east–northeast trending structures, are fine-grained and display dense, chilled margins. Consequently, the dikes and sills are lower in permeability than the rocks they intrude, and serve as impediments to subsurface groundwater flow.

The volcanic bedrock occurring in the shallow subsurface beneath the site is generally weathered and oxidized throughout its upper 30 to 50 ft of thickness. The weathered volcanic rocks are generally more fractured, friable, and porous than the unweathered volcanic rocks due to the effects of weathering removing soluble con-

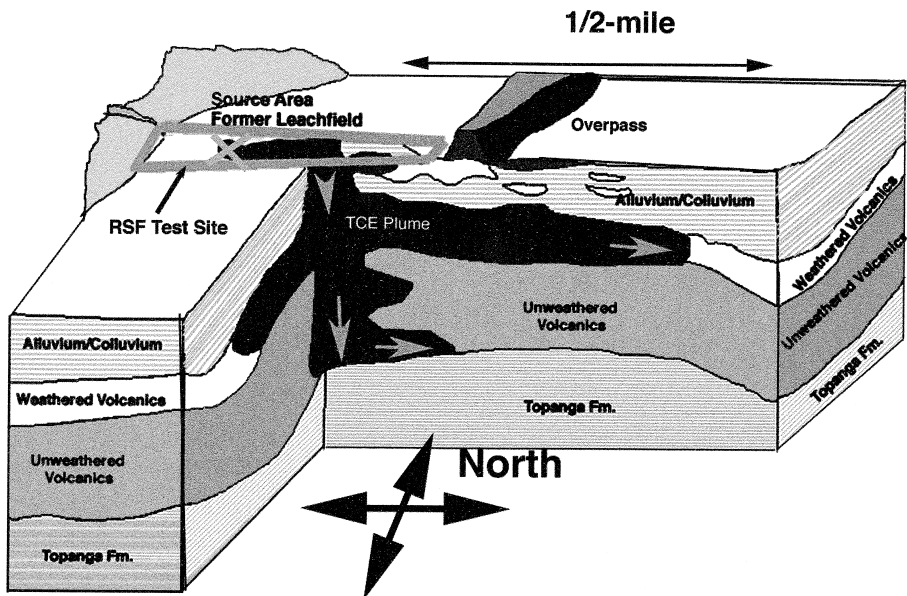


Fig. 1. Conceptual model of site hydrogeology and contaminant migration.

stituents and breaking down the mineral constituents of the rocks. Open fractures are common within the zone of weathering, but less abundant in the unweathered rocks. Based on drill-core logs, most of the aperture widths of the fractures vary from 0.01 to 0.1 in. Most of the fracture surfaces are semi-smooth to semi-rough, resulting in variable aperture widths.

The weathered volcanic rocks are generally red, yellow, orange, and brown, due to staining by iron oxide and hydroxide minerals. Dendritic manganese oxide coatings are also commonly present. The underlying unweathered volcanics are typically gray, blue, dark green, or black. Iron pyrite, serpentine and calcite commonly form vein-fracture fillings in the unweathered bedrock. The mafic volcanic rocks are commonly altered adjacent to veins. The occurrence of open fractures is less frequent in the unweathered zone. The rare open fractures noted in drill-cores, of the unweathered rock, show oxidized halos due to the penetration of oxygenated waters along the fracture conduits.

2.1.2. Structural geology

The site is located in the western Santa Monica Mountains of Southern California. The Santa Monica Mountains lie within the Transverse Ranges physiographic province [23]. The Transverse Ranges are an east–west trending structurally controlled belt of mountains and valleys. Northeasterly and northwesterly trending structural elements locally transect the east–west trending structural elements. The bedrock contains fracture systems with northeast–southwest, northwest–southeast, and east–west orientations. The northeast-trending fractures are often host to volcanic dikes or mineral fillings.

Structurally, the site is located near the axis of a westward plunging anticline [2]. At the site, bedding of the volcanic bedrock strikes in a northeasterly direction and dips in a northwesterly direction along the northern flank of the anticline.

2.2. Hydrogeology

Based on data collected from the extensive investigations of the site to date, the uppermost groundwater occurs beneath the site at depths ranging from between 10 and 50 ft below the ground surface (bgs). Historically, the highest water levels and the steepest groundwater gradients have been noted following heavy periods of rainfall.

Groundwater occurs within the two principal geologic units: alluvium and volcanic bedrock. The volcanic bedrock can be further subdivided into weathered and unweathered zones based on differing hydrogeologic properties. Heterogeneity's in the fractured bedrock aquifer have affected groundwater flow, resulting in an anisotropic flow regime. A conceptual model of the site hydrogeology and contaminant migration is shown in Fig. 1.

2.3. Groundwater geochemistry

The historical data for TCE and Cr concentrations in well E-39A show that TCE concentrations in well E-39A have been as high as 83,000 $\mu\text{g}/\text{l}$ and total chromium concentrations have been as high as 8400 $\mu\text{g}/\text{l}$. Chemical testing conducted in August 1997, verified that the total chromium is present as the hexavalent species. Well E-39A

was a groundwater extraction well until April 1997. It is now used as an observation well.

As illustrated in Fig. 1 the TCE plume is irregularly distributed [17,18] and these irregularities, or lobes, of the plume, are considered the manifestation of anisotropic flow conditions within the Conejo Volcanics aquifer. The irregular configuration of the plume suggests that localized microgradients, oriented at an angle to the main gradient, occur in the aquifer because of anisotropic conditions. The anisotropic flow conditions may be due to the presence of low permeability zones in the aquifer that act as impediments to the groundwater flow. As a result of these impediments to groundwater flow, microgradients could be induced that result in a divergence of flow. This occurrence could explain the formation of southerly, northerly and an easterly directed lobes of the plume.

Based on the quarterly monitoring data [4] the groundwater can be characterized as an oxygenated groundwater enriched in anions having the following characteristics:

- pH of 6.5 to 7.5
- Total dissolved solids: 700 mg/l
- Nitrate: 45 mg/l
- Sulfate: 70 mg/l
- Chloride: 120 mg/l
- Dissolved oxygen (DO): 5–15 mg/l

This chemistry was considered acceptable for sustaining a reductive dehalogenation reaction without causing excessive pore clogging due to mineral precipitation.

3. Technology overview

The use of zero valent metals to dechlorinate chlorinated compounds was originally investigated and patented by Sweeny and Fischer [29] for use as industrial wastewater treatment process for reductive dechlorination of chlorinated pesticides. Japanese researchers further evaluated the use of zero valent metals for wastewater treatment in the 1980s. In 1990, researchers at the University of Waterloo, rediscovered the effects of reductive dechlorination, due to the corrosion of zero valent metals, during research conducted to evaluate interactions of various well-casing materials with CVOCs present in groundwater. The potential importance for groundwater remediation was realized, and in late 1992, the first PRB was constructed at Canadian Forces Borden, Ontario. The 1.5-m thick reaction gate contained 21% granular iron mixed with 79% sand. Influent TCE and PCE concentrations of about 200 and 60 mg/l, respectively, were reduced about 90% through reactions occurring within the gate [9]. A stepwise dechlorination process appeared to be evident for some of the CVOCs, and daughter products such as *cis*-1,2-dichloroethene and vinyl chloride (VC), appeared and were mostly degraded within the reactive zone [10].

A majority of the PRBs installed to date have been Funnel and Gate designs [28]. The low permeability 'Funnel' is used to channel groundwater flow into the high permeability, reactive 'Gate'. In many cases multiple gates with intervening funnels have been

used to more optimally accommodate groundwater flux. Funnel and gate systems are effective where aquifer conductivity is low to moderate and groundwater flow rates are relatively slow. In areas where aquifer conductivity is high and/or plume widths are relatively narrow it may be more advantageous to implement the reactive ‘Gate’ without any flow constricting funnels. One such implementation was completed at the Elizabeth City North Carolina Coast Guard Station [25]. In general, commercial ZVI, a waste byproduct of the automobile manufacturing industry, has been the reactive media of choice due to price and availability. Other reactive media have been evaluated, especially for use with radionuclides and mixed waste [13,21].

Various investigators have conducted research on the reaction mechanisms and the relative effectiveness of ZVI reactive media. Important conclusions identified include:

- Commercial iron containing impurities such as graphite are more reactive than pure iron.
- The reactivity of iron media is proportional to the available reactive surface area.
- Passivation of reactive sites and shut down of the reductive dechlorination reaction occurs when pHs are allowed to rise in solution.
- If the pH of the solution is buffered, as is the case in many natural systems, passivation of reactive sites is not significant.
- Both stepwise dechlorination and instantaneous hydrogenolysis appear to be occurring.
- The instantaneous hydrogenolysis reaction becomes the predominant reaction pathway in bimetallic systems where a second metal such as palladium, nickel or copper is coated on the iron (Fernando, 1995) [11,24,27].

A variety of construction methods have been developed for installing PRBs in soils:

- Sheet pile shored trenching [9]
- Caisson [33]
- Slurry stabilized trenching [12]
- Vibrating beam [16]
- Jetting [16]
- Vertical fracturing [14]
- Chemical modification [8]

Few of the construction methods tested to date are potentially applicable to deep or fractured rock environments.

4. Process description

This report summarizes existing information, laboratory and field procedures, results, discusses the achievement of project objectives, and provides conclusions pertinent to the testing of RSF at the Newbury Park Site. The purpose of the pilot test was to evaluate the effectiveness of RSF to simultaneously improve hydraulic conductivity, and conduct in situ treatment of a TCE and hexavalent chromium impacted fractured bedrock aquifer. The scope of work conducted to accomplish this included:

- Development of reactive proppants
- Bench scale testing of reactive proppants

- Preparation of borehole including drilling a new borehole
- Pre-injection testing:
 - ⇒ Surface geophysics-seismic refraction and resistivity surveys
 - ⇒ Borehole geophysics-induction, caliper and acoustic televiewer
 - ⇒ Borehole camera log
 - ⇒ Discrete chemical analysis of groundwater from identified fracture zones
 - ⇒ Packer permeability testing
- Evaluation of data and selection of three fractures/test intervals
- Pre-test hydraulic fracturing the formation
- RSF injection
- Post-injection testing:
 - ⇒ Surface geophysics-resistivity survey
 - ⇒ Borehole geophysics-induction, caliper and acoustic televiewer
 - ⇒ Discrete chemical analysis of groundwater from identified fracture zones
 - ⇒ Packer permeability testing
 - ⇒ Extraction well installation
 - ⇒ Post-injection well development and pump testing
 - ⇒ Anti-biofouling well treatment and redevelopment

Now that the feasibility of the injection process has been demonstrated, it seems feasible that larger scale remediation systems could be installed using overlapping zones of treatment.

5. Reactive media development and testing

Hydraulic fracturing technology was originally developed for use in the enhancement of hydrocarbon and geothermal production. To achieve hydrofracturing, high pressure fluids are injected into consolidated materials. The high pressure fracking fluids are confined to limited areas of the borehole by inflatable devices called packers. When hydrofracturing occurs pressures drop rapidly and flow-rates increase dramatically. To maintain aperture openings and create sustainable increases in production, propping materials called proppants are injected into the fractures. A wide variety of materials are used for proppants ranging from natural sand to ceramic or glass beads [15]. For use in RSF it was decided to evaluate if proppants could be coated by or constructed of reactive media.

Early research by University of Waterloo researchers identified that zero valent metals such as aluminum, iron and zinc can cause the abiotic reductive dechlorination of CVOC. Due to the potential toxicity of aluminum, most of EMCON's proppant design efforts focused on the use of zinc and iron. A schematic drawing portraying the reductive dehalogenation decay series is provided in Fig. 2.

5.1. Conceptual design

The reactive media needed to meet the criteria of weight, strength, roundness and reactivity. Proppants used for hydrofracturing must be light weight enough to minimize

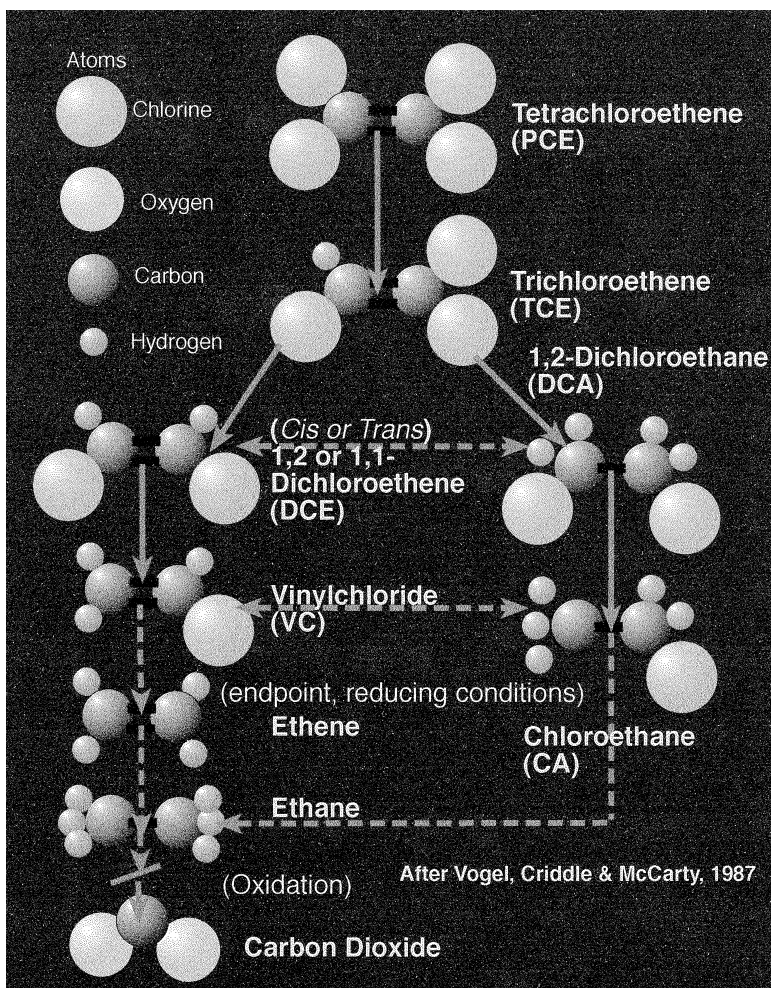


Fig. 2. Reductive dehalogenation decay series.e

the viscosity of the fracking fluids. Iron filings, although theoretically usable for hydrofracturing applications, are dense enough to require high viscosity cross-linked polymers for hydraulic injection. By creating light weight reactive proppants, the need for cross-linked viscosifiers is avoided. In addition, by using spherical proppants, it is easier to suspend, pump and inject them into the formation. Hence, other advantages of the use of reactive proppants over iron filings are the superior suspension and delivery properties. In addition it is estimated that the regular size and distribution of pore spaces between the proppants will provide higher hydraulic conductivity than the irregular pore spaces found in iron filings.

Another important proppant design factor is strength. Commercial proppants need to be strong enough to withstand pressures of many tons per square inch (approximately 1

psi/ft of overlying rock). For purposes of the RSF treatment the reactive proppants needed to withstand pressures of a few hundred pounds per square inch. Initially, light weight commercial proppants were coated with reactive coatings. Eventually, it was decided to create sand-sized pellets composed entirely of the reactive media but with internal porosity (iron Cercofoam[®]), so the ultimate bulk density would be the equivalent of natural sand.

5.2. Zinc coated proppants

Teleflex's Sermatec division, of Limerick, PA, conducted zinc coating by a proprietary method. Aluminosilicate proppant cores were selected because of their superior strength and adhesion properties. The proppant size used was 12–20 mesh. The coated

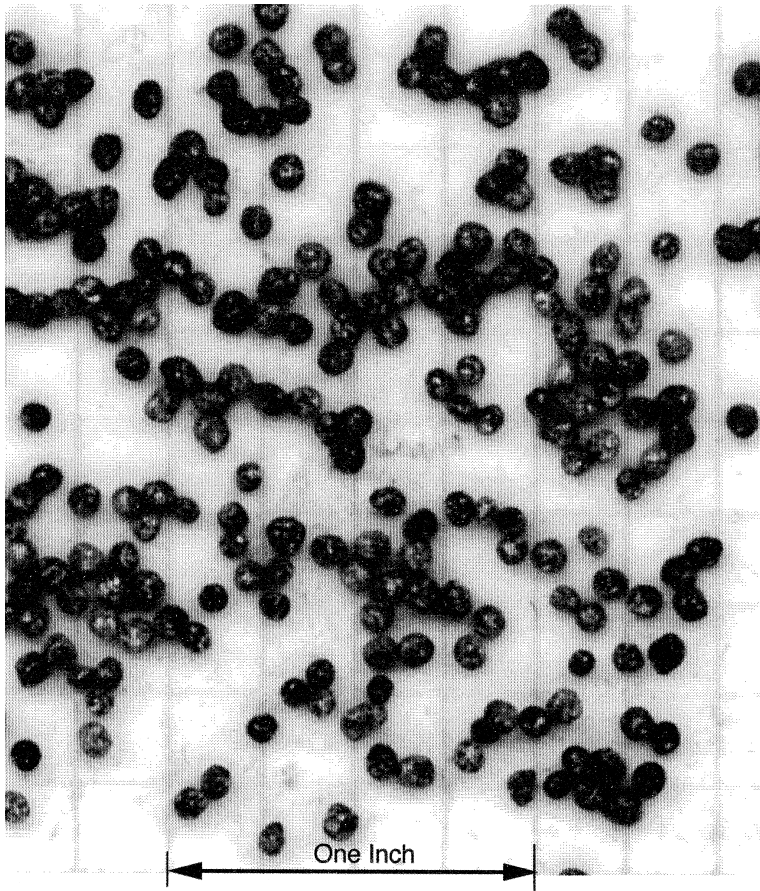


Fig. 3. Zinc-coated proppants.

proppants, shown in Fig. 3 were approximately 1 mm in diameter, and had coatings of zinc, and/or aluminum, and/or iron a few thousandths of an inch thick.

5.2.1. Waterloo test results

Batch and column tests were conducted at the Institute for Groundwater Research at the University of Waterloo, Ontario, Canada [5]. Batch tests were used to evaluate the effectiveness of various metal alloys coatings. The selected proppant coating contained more than 90% zinc by weight. The reactive media were packed in a 50 cm long column and site groundwater was pumped upward through the column. A logarithmically spaced array of sampling ports were used to obtain spatially distributed groundwater samples. Over a 90% decrease in TCE concentrations were noted by reaction of the high concentration groundwater during a 1.3 day residence time within the reactive media. Although this initial reaction rate was acceptable, the reactivity of the media decreased

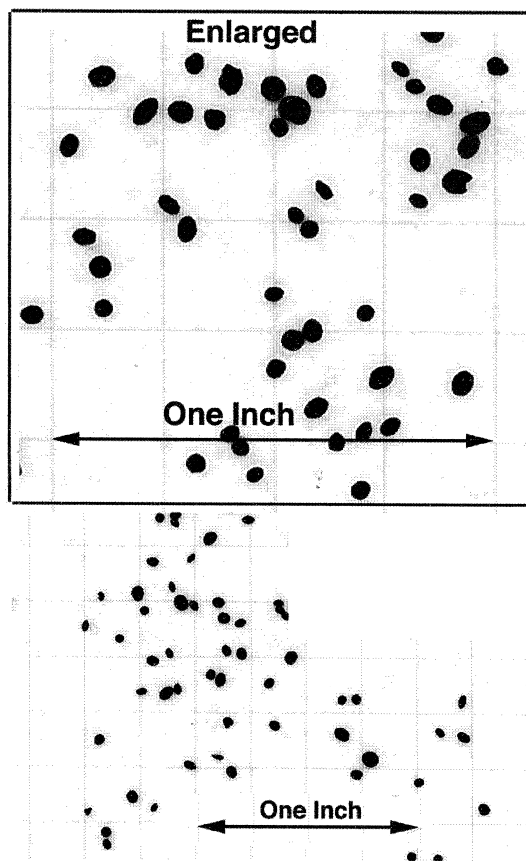


Fig. 4. Iron cercofoam proppants.

with time, and after a brief unscheduled shutdown, dropped below the 90% reactivity objective, resulting in a reevaluation of the design of the reactive media.

5.2.2. USEPA Athens test results

Three week-long batch tests were conducted at the US EPA Athens lab to determine if the zinc coated proppants or prototype iron foam pellets should be submitted for column testing [20]. Approximately a 90% reduction in TCE concentrations occurred during the 1 week batch test using the Cercona pellet proppants, with significantly less effect noted in the concurrent batch using the zinc coated materials. Based on this testing, the iron foam pellets proppant, were selected as the more reactive media, and it was decided to proceed with the development of iron Cercofoam[®] proppants.

5.2.3. Iron foam proppants

Iron Cercofoam[®], a patented product of Cercona of America, Dayton, OH, is a foamed iron product that is fired in a reducing atmosphere to prevent oxidation. The material is pelletized and fired in a reducing atmosphere rotary kiln to enable manufacture to design specifications and prevent oxidation. The resulting material, shown in Fig. 4, is lightweight ($< 3 \text{ g/cm}^3$), hard, and spherical enough for use as proppants.

5.2.4. University of Arizona test results

A column test using the Cercofoam proppants was conducted at the University of Arizona, Department of Civil and Environmental Engineering under the direction of Dr. James Farrell [6]. Fig. 5 summarizes some of the column test results. The reactive media were packed in a 50 cm long column. Site groundwater containing about 35 mg/l of TCE, less than 1 mg/l of PCE and about 5 mg/l total chrome was sparged with TCE and PCE vapor to near saturation, and pumped upward through the column. Influent concentrations of TCE were about 800 mg/l (significantly higher than site groundwater). Over the first 30 days, about a 90% decrease in TCE concentrations were noted by reaction of the groundwater during a 2-day residence time within the reactive media.

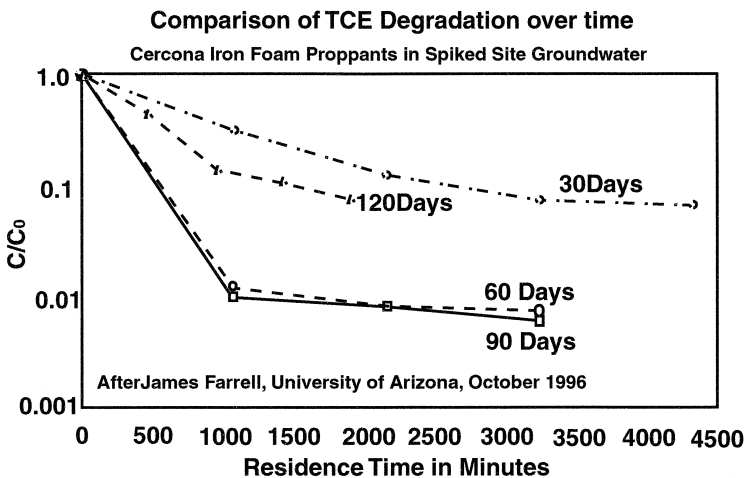


Fig. 5. Column-test results.

The reaction rate was noted to decrease slightly through time due to assumed partial passivation of the media. Between 30 and 60 days, the reactivity of the media increased with time and about 99% of the TCE was being broken down within the column. PCE breakdown remained steady. Dr. Farrell concluded that biological degradation became established within the column, resulting in the higher rate of breakdown of TCE than PCE. Analysis of column effluent was also conducted to verify if total and/or hexavalent chrome was attenuated in the column, due to reduction and precipitation and/or adsorption. Chromium was not detected in the effluent.

The major reaction products for TCE and PCE degradation are the nonchlorinated hydrocarbons ethane and ethene. Less than 2% of the TCE and PCE degradation lead to chlorinated byproducts. Based on gas chromatographic retention times, the chlorinated byproducts include three dichloroethene (DCE) isomers (1,1-; *cis*- and *trans*-1,2-), VC, and one unknown compound. Purge and trap analysis of one interim sample indicated that VC was present at a concentration of 50 ppb in the column effluent. Although this concentration exceeded the Federal drinking water standard, VC production accounts for only 0.012% of the total TCE and PCE disappearance, and if the influent concentrations were not spiked to such high levels, the VC concentration would not be measurable. Therefore, the anticipated production of VC under natural groundwater conditions is likely to be a few parts per billion at most, and given the oxidizing conditions of the aquifer outside of the zone of treatment, VC is not expected to persist or present a health hazard.

The initial porosity measured in the column was about 60%. After 250 days of operation the measured porosity had decreased by 50%. The decrease in porosity is considered to be due to precipitation of minerals such as iron carbonate and the formation of plaques due to biological activity. Flow-rates remained fairly constant due to the fact that hydrogen gas production, which was prolific early in the column test, had decreased. For this reason the decrease in porosity due to precipitation, was offset by the decrease in gas-filled porosity as hydrogen gas generation decreased. Furthermore, the decrease in porosity in a laboratory column test is not considered representative of in situ processes where a greater buffering capacity is afforded by bedrock groundwater interactions. The flow through test has now been discontinued following two years of testing during which reactivity and flow was sustained at acceptable levels.

6. RSF test methods and results

The RSF pretreatment tests included the following: borehole geophysics, surface geophysics, discrete groundwater sampling, packer permeability testing, and selection of RSF treatment zones. Most of the procedures used in the above tests will be discussed along with the results of the testing.

6.1. Borehole E-39B drilling

Boring E-39B, was drilled approximately 19 ft north of well E-39A for use in the RSF test. Boring E-39B to a total depth of 101 ft bgs was advanced using 8-in. diameter

air-rotary percussion drilling equipment. A 10-in. temporary PVC conductor casing was driven through the soil zone to the bedrock contact at 5 ft bgs to minimize soil slough, which could result in borehole obstruction.

Soil types encountered consisted of sandy clay to silty sand to approximately 5 ft bgs. From 5 to approximately 40 ft bgs, weathered bedrock consisting of brown to gray, friable to hard, weathered andesitic volcanic rock was encountered. From approximately 40 to 101 ft bgs, bedrock consisting of gray to locally purple, hard to very hard, unweathered andesitic volcanic rock was encountered. The weathered samples obtained were commonly iron oxide stained and unweathered bedrock often displayed green mineral alteration. The observation of iron oxide FeO staining and green mineral alteration became less common with increasing depth. Flowing groundwater was not encountered during drilling, although minor signs of groundwater (i.e., slight moisture changes) were observed in airlifted cuttings at depths of 85 and 95 ft bgs. This is despite the fact that static groundwater was observed at a depth of 28 ft bgs in adjacent wells.

Within 28 h after the completion of drilling, groundwater had entered the boring and a water level was measured at a depth of 88.25 ft bgs. This constituted a water level rise of only 12.75 ft or the equivalent of a 1.1-gallons-per-hour (gph) groundwater recharge rate, consistent with the very low hydraulic conductivity of the unweathered bedrock.

6.2. RSF testing

The RSF tests consisted of borehole geophysics, surface geophysics, discrete groundwater sampling/parameter determination, and packer permeability testing. The results were used in the selection of the RSF treatment zones and confirmation of the effectiveness of the treatments.

6.2.1. Borehole geophysics

Geophysical logging runs using video, caliper, induction/gamma, and acoustic televiewer (ATV) methods were performed to a total depth of approximately 100 ft bgs in boring E-39B. A composite geophysical log is presented to document the pretreatment and post-treatment conditions in Figs. 6 and 7, respectively.

6.2.1.1. Video camera log. Boring E-39B was video logged to a total depth of approximately 90 ft bgs using a Laval 1 5/8" diameter, black and white, downhole video camera. Geologic and hydrogeologic features observed during the logging runs were noted on the video recording by audio dubbing the feature and its depth. Although the video log did reveal some of the textural changes associated with lithologic variations and fracture occurrence. The low rate of seepage along the fractures in boring E-39B limited video log usefulness for this pilot study.

6.2.1.2. Caliper log. A caliper log of boring E-39B was performed from a depth of approximately 100 ft to the ground surface using a caliper logging probe. The caliper log was used to determine areas of borehole diameter change due to weathering, fracturing, the presence of resistant layers, and areas where treatments had emerged into the borehole.

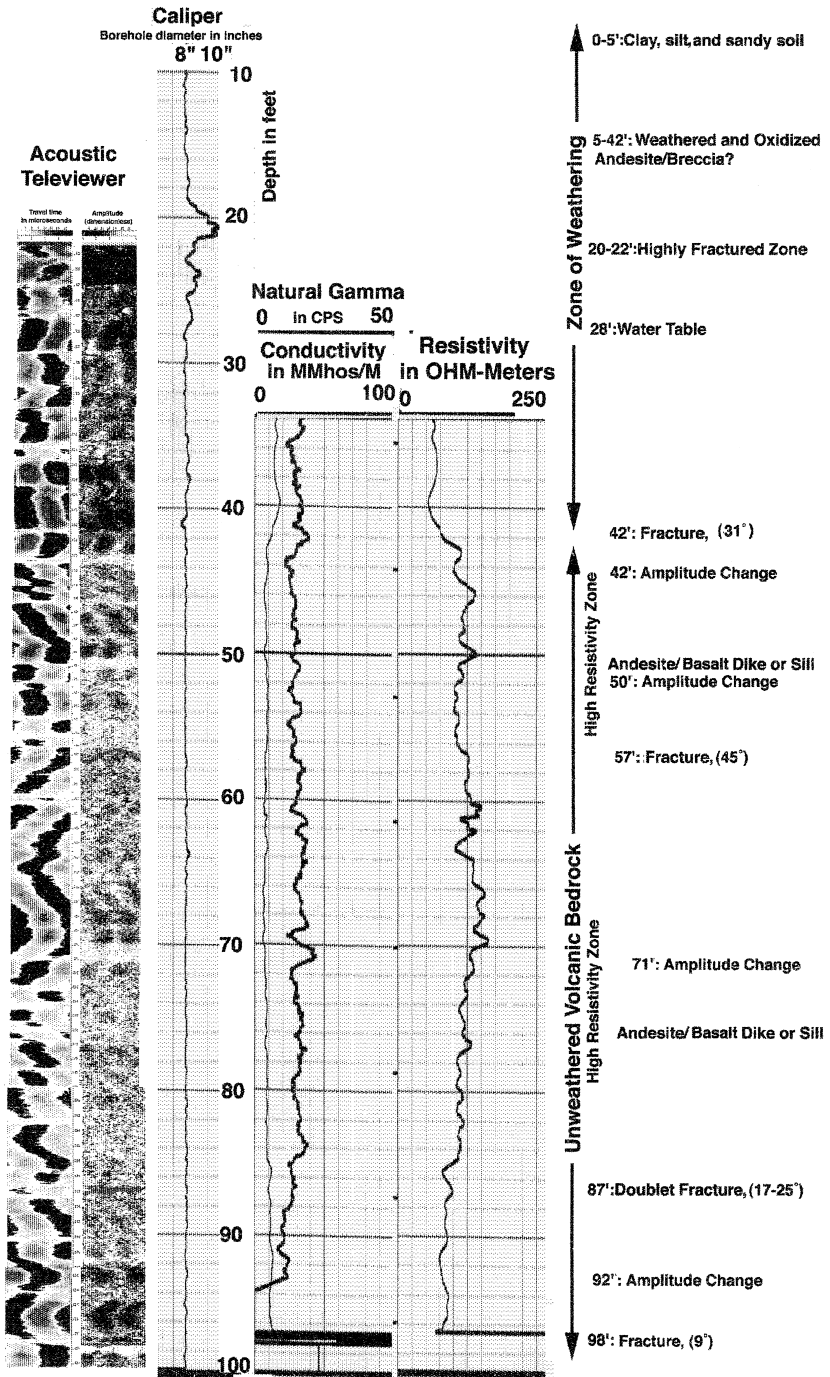


Fig. 6. Pre-RSF geophysical logs.

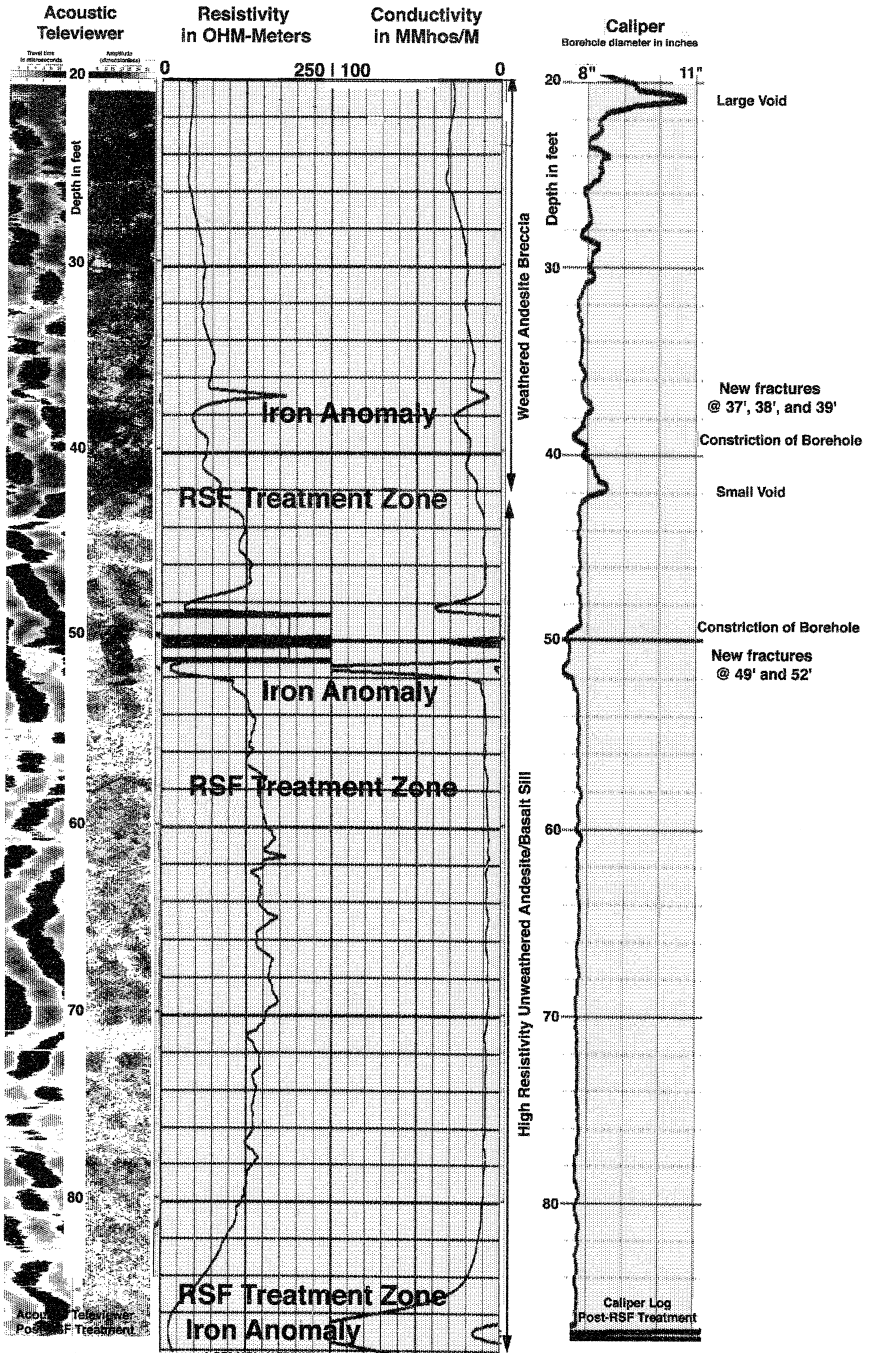


Fig. 7. Post-RSF geophysical logs.

6.2.1.3. Induction / gamma log. A combination induction/gamma log was performed on boring E-39B from the ground surface to a total depth of 95 ft bgs using an induction conductivity/natural gamma logging probe. Significant variations in both conductivity and resistivity were noted to correlate with lithologic changes, variations in weathering and the existence of fracturing. The post-treatment testing showed the existence of iron related induction log anomalies that coincide spatially with the zones treated. The gamma log was uniformly low in the pre-testing so it was not used in the post-testing program.

6.2.1.4. Acoustic televiewer log. An ATV log was performed on boring E-39B to a total depth of 99.25 ft bgs using a borehole televiewer logging probe. Due to the lack of groundwater in boring E-39B, the boring was filled to approximately 17.5 ft bgs with an estimated 440 gal of city tap water prior to running this log.

The acoustic log is useful in locating fractures and fracture zones in an aquifer where groundwater flow may be concentrated in various rock formations (Driscoll, 1986). The ATV log produces a continuous core-like image of the borehole, which is recorded in an electronic file that can be processed later to determine fracture orientation including both azimuth and inclination. Several fracture zones were identified in the borehole that were candidates for RSF treatment including 42, 57, 87 and 98 ft zones. The post-test ATV logs demonstrated that the treatments were emplaced and that some new fractures were created as a result of the treatment. The 98 ft zone was not treated due to lack of sufficient borehole below the zone to enable seating of the lower packer, and therefore no comparison was made.

6.2.2. Discrete groundwater sampling and testing

Before the RSF treatments, four discrete groundwater samples at 42, 57, 87, and 98 ft depths were collected from boring E-39B adjacent to existing fracture(s) using the SimulProbe™ Aquifiler. Following the RSF treatments, discrete samples were again collected at 42, 57 and 87 ft depths for comparison to the pretreatment results.

The Aquifiler was outfitted with a YSI 600 XL water quality probe inside the canister in order to collect in situ water quality parameters during the sampling. During sampling, a YSI 600 probe and surface datalogger were used to collect in situ measurements of the water quality parameters: temperature, specific conductance, pH, oxidation reduction potential (ORP), DO, and depth. The pre- and post-test YSI parameters are compared graphically in Fig. 8. Several striking contrasts are notable including the significant change of ORP to as much as -600 mV and the decrease of DO to nearly the detection limit following the treatment. These data support the effective creation of conditions favorable for reductive dehalogenation to occur in the aquifer following the treatment.

A tap water sample was also obtained for analysis to evaluate what compounds may have been introduced into the borehole along with the water used to fill the boreholes for the ATV log. Although, the tap water contained significantly lower levels of TDS and anions, significant concentrations of trihalomethanes and chloroform were also present that were generally not observed in the natural groundwater.

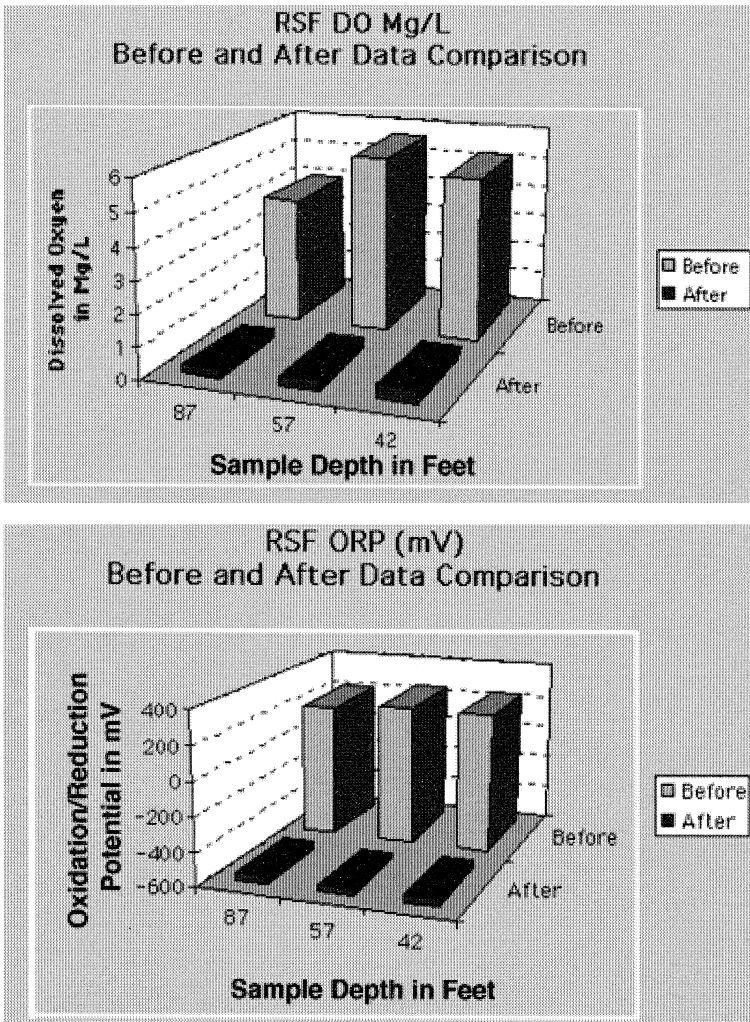


Fig. 8. Graph of YSI probe in situ parameter data.

The water samples were transported to a laboratory and analyzed for the following: halogenated VOCs by USEPA Method 8010, total dissolved chromium by USEPA Method 6010A, general minerals by USEPA Method 600, and bromide by USEPA Method 300. The pre- and post-treatment CVOC data are summarized in Fig. 9. The general mineral and anion parameter analyses included alkalinity, bicarbonate, carbonate, hydroxide, bromide, chloride, conductivity, fluoride, hardness, nitrate, pH, sulfate, and total dissolved solids. The metals analyzed for included calcium, chromium, copper, iron, magnesium, manganese, potassium, sodium, and zinc. Comparisons of pre- and post-treatment metals and general minerals data are provided in Figs. 10 and 11. The data suggest that the reactions occurring in association with the treatment decreased

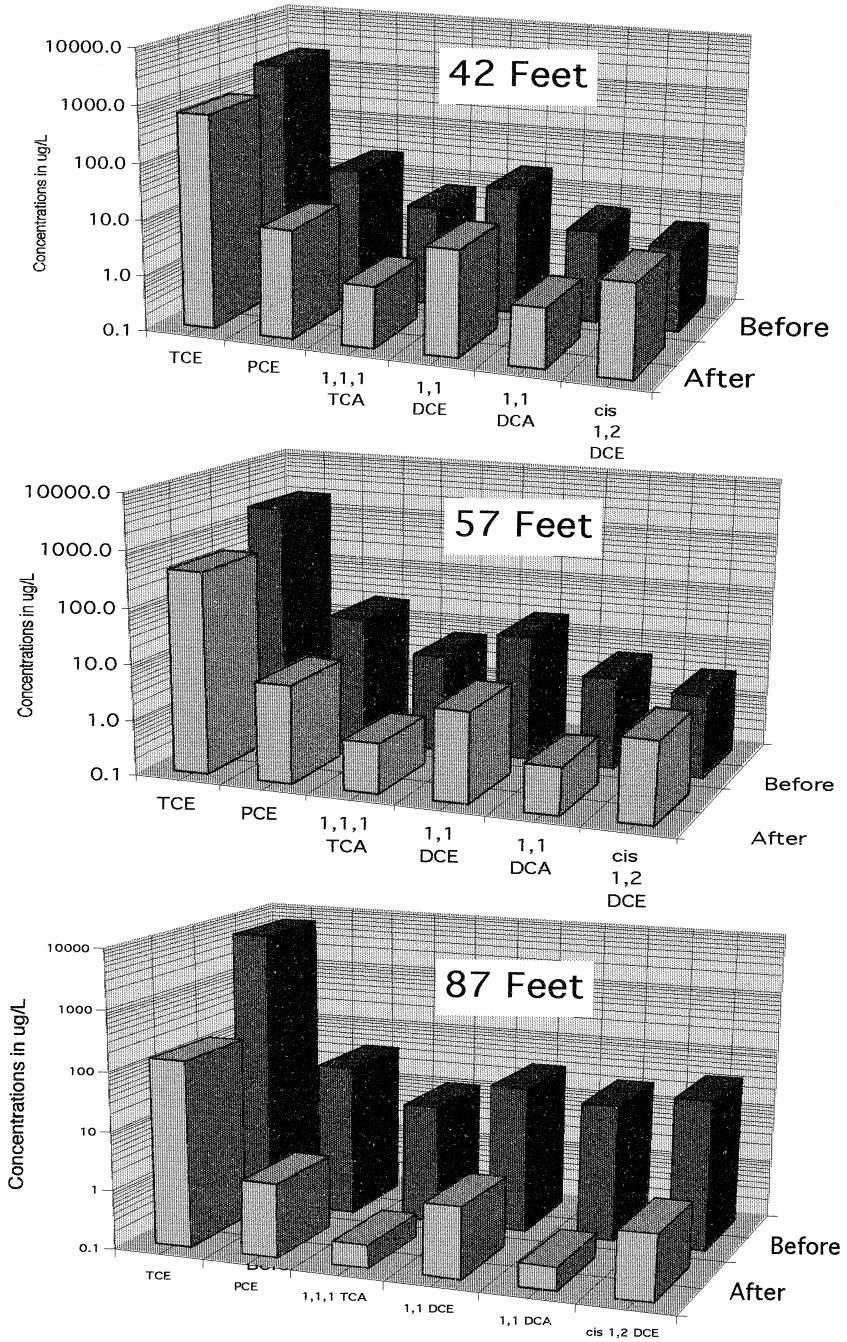


Fig. 9. Comparison of before and after VOC concentrations RSF pilot test.

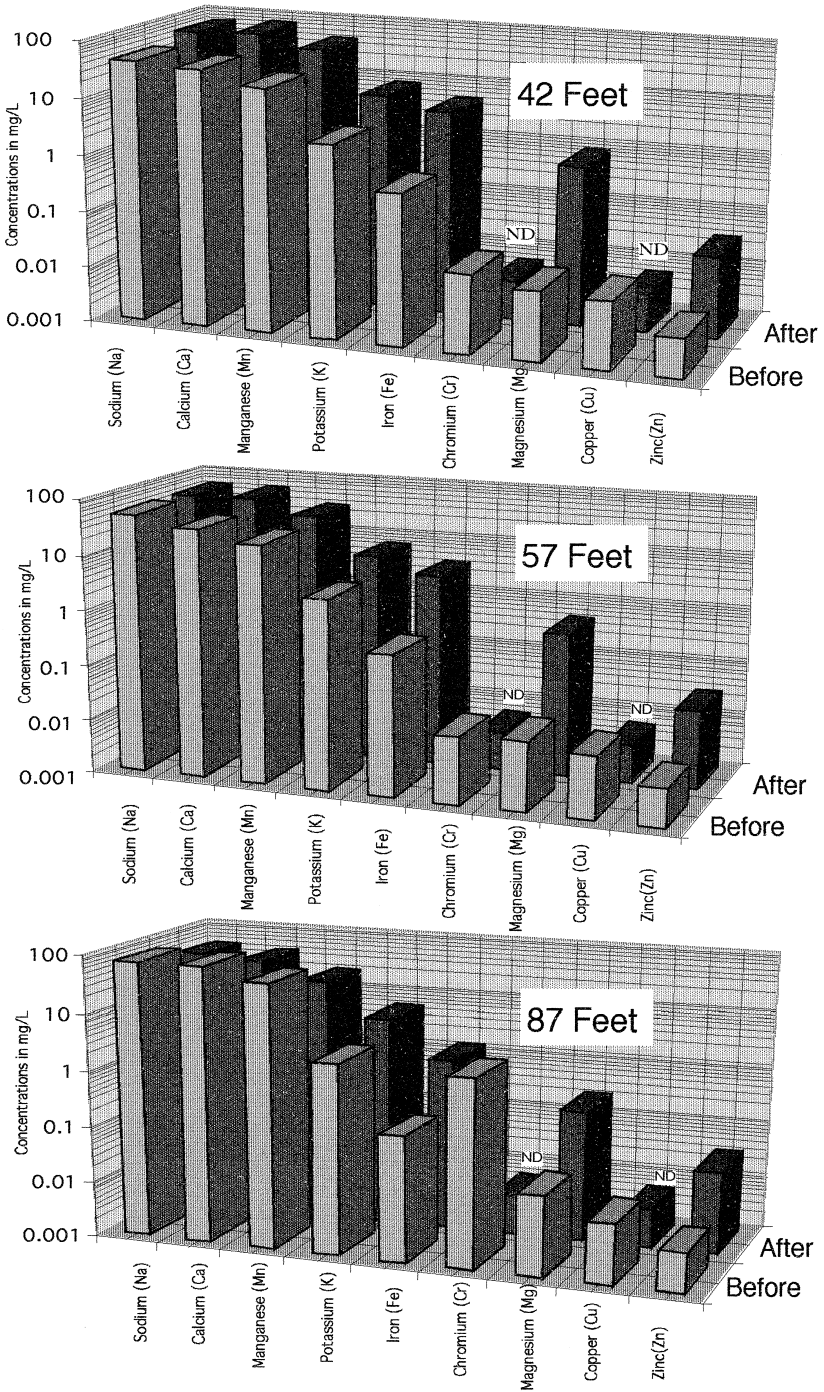


Fig. 10. Comparison of before and after metals data RSF pilot test.

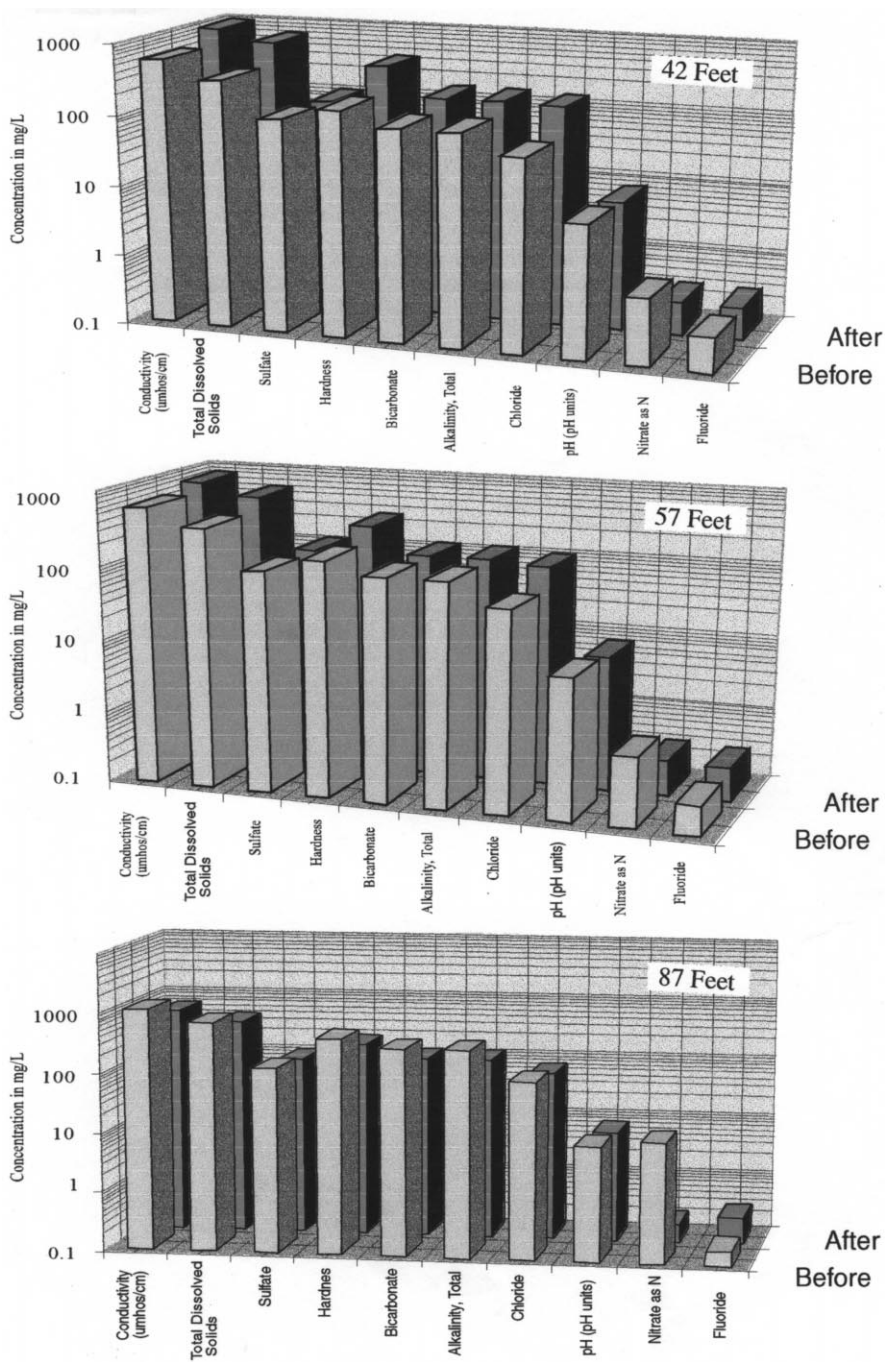


Fig. 11. Comparison of before and after general mineral data RSF pilot test.

nitrate, copper and chromium concentrations and caused an increase in iron, manganese and zinc.

6.2.3. Packer permeability testing

Prior to treatment packer permeability tests were performed on the fracture zones at 21, 42, 57, 87, and 98 ft bgs in boring E-39B using the general procedures outlined in the Earth Manual (USBR, 1974) and the Ground Water Manual (USBR, 1977). Prior to conducting the packer test, theoretical maximum value of excess head (H_{\max}) for each zone was calculated. The range of H_{\max} values for the test intervals was as follows: 42 ft zone (39 to 53 psi); 57 ft zone (49 to 68 psi); 87 ft zone (68 to 98 psi); and 98 ft zone (78 to 111 psi). A Tamm International 5.5 to 10 in. inflatable straddle packer assembly with a test zone length of 6 ft was used for testing the 42, 57, 87, and 98 ft zones. Nitrogen gas was used to inflate the packers.

The pressure data were then plotted against the flow data and compared with test graphs for evidence of problems such as leakage around packers, erosion of the test zone, and clogging of fissures. Once the data graphs indicated that the test results were of good quality, H_{\max} and the corresponding flow rate were used to calculate the hydraulic conductivity of the formation within the test zone. The range of pretreatment hydraulic conductivities was about 10^{-6} cm/s. The post-treatment hydraulic conductivity's were up to two orders of magnitude higher with values of up to 10^{-4} cm/s calculated for the 87 ft zone.

6.3. Hydraulic fracturing

Hydraulic proppant fracturing and gravel packing are common stimulation and stabilization treatments used during completion, testing, and exploitation of hydrocarbon reservoirs in the oil and gas exploration and production industry; they have been expanded for use in geothermal and groundwater extraction fields [15]. Natural sand or synthetic proppants of different types and grain sizes are used to support or prop the crack created in hydraulic fracturing to keep it open against the closure stress acting at depth and to maintain a highly conductive drainage path through the rock matrix for fluids entering the borehole/well. The primary purpose of gravel packing is to plug the perforation tunnels created by jetting action during hydraulic fracturing and to build a gravel mantle along the borehole wall in order to filter the fluids entering the wellbore and prevent formation sand from flowing into the wellbore. Hydraulic proppant fracturing and gravel packing can be used to enhance recovery of oil and gas, geothermal, or groundwater fluids from low-permeability and weakly-cemented to loose friable sandstones. The treatments have been demonstrated to improve flow rates and minimize influx of sand into the borehole, respectively.

Aquifer hydraulic fracturing is an emerging technology that uses hydraulic fracturing with or without proppants to stimulate groundwater flow through tight/fracture-flow dominated aquifers such as occur in crystalline rocks. To date most of the hydraulic fracturing applications have focused on improving fracture interconnection and increasing well efficiency. The techniques that are used for aquifer treatments are generally

smaller in scale than those of oil and gas and geothermal reservoir treatments, but usually are governed by the same physical and chemical constraints.

6.4. RSF treatment

The selected fracture zones (42, 57 and 87 ft) in boring E-39B underwent RSF treatment. The treatment was performed by the hydraulic fracturing contractor Northeast Water Production (NEWPI), Sterling, MA. The treatment phase included hydrofracturing equipment setup, pre-RSF hydrofracturing, mixing of fracking fluids, and RSF injection and monitoring. Procedures and results are provided below.

6.4.1. Pre-RSF hydro-frac

Before the RSF mixture was injected, a hydro-frac using clean water was performed on the three fracture zones at 42, 57, and 87 ft bgs. Packer, injection, and shut-in pressures were monitored periodically during each hydro-frac. Additionally, water levels in test boring E-39B and the two nearby observation wells (E-39A and E-1) were monitored periodically during the hydro-fracs.

Hydro-frac operations began by lowering the straddle packer assembly to the test zone, inflating the packers, and injecting clean water under high pressure into the isolated zone. The 87 ft zone was hydro-fractured first, followed by the 57 and 42 ft zones. The straddle packers were inflated to approximately 2000 psi using a pressurized propylene glycol and water mixture. Injection pressures of up to 900 psi were required to initiate the hydro-fracture for each of the three zones. The hydro-fracture was signaled by a rapid pressure buildup and low water acceptance rate followed by an instantaneous pressure drop and a moderate to high rate of water acceptance. Following the actual hydro-frac, the injection pressure decreased and the flow rates were increased to as high as the formation would accept. Approximately 700, 600, and 800 gal of clean water were injected into the 87, 57, and 42 ft zones, respectively during hydro-fracturing. The entire process for each zone was completed in less than 7 min.

6.4.2. Mixing of fracking fluids

For each RSF injection, approximately 1000 gal of water and Variflo QD guar gum viscosifier were mixed in order to achieve a fluid viscosity capable of suspending the iron foam reactive proppants. Contractor bench tests indicated that the injection fluid viscosity required would be equal to a Marsh funnel viscosity of 100 to 110 s. To ensure proper mixing, the guar gum viscosifier was incorporated into the water using a jet type mixer. The viscosity of the fluid was periodically checked during mixing with a Marsh funnel and stopwatch. After reaching the proper fluid viscosity, approximately one pint of QED-4 delayed action enzyme breaker was added to the viscosifier to accelerate the speed of guar breakdown. For each 1000 gal of fluid mixed, approximately 1000 lb. of iron foam proppants were added.

At the completion of the mixing, a conservative tracer, consisting of 8 lb. of potassium bromide (KBr) powder in 5 gal of water was added to the mix. In theory this amount of KBr equated to a bromide concentration of approximately 933 mg/l in the mix. An Orion 290A meter and TempHion™ probe with an ion selective electrode (ISE)

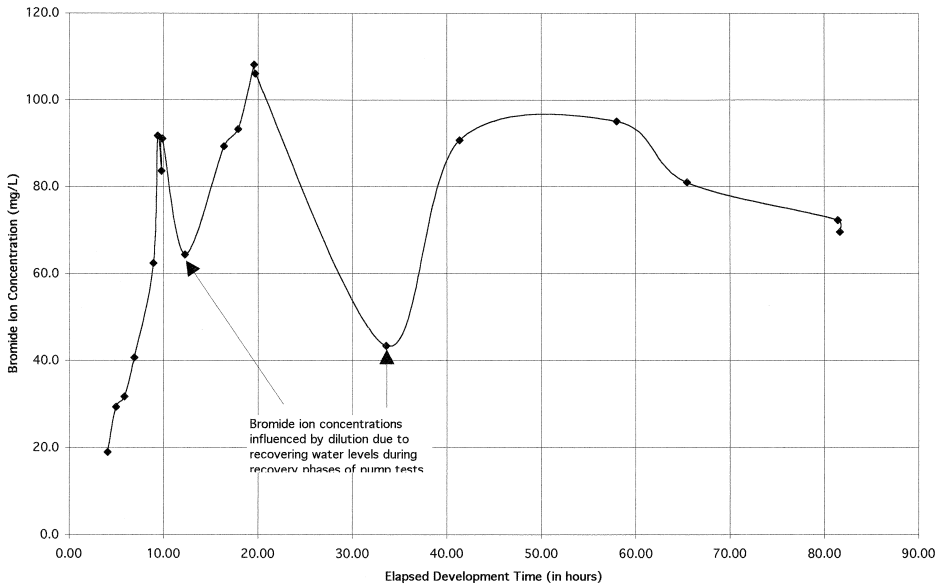


Fig. 12. Graph of bromide pump back data—well E-39B.

calibrated for bromide was used to field verify the concentration of Br^- in the injection batches (Instrumentation Northwest 1996). KBr was added to three of the four RSF batches injected into the 87 ft zone and to the single RSF batches injected into the 57 and 42 ft zones.

The bromide tracer breakthrough data was monitored in situ in the observation wells using the TempHion™ probes. Breakthrough was confirmed within several hours of the treatment, in well E-39A during the deep (87 ft) treatment and in well E-1 during the shallow (42 ft treatment).

Bromide concentrations were also measured in the well development water at periodic intervals through the process (Fig. 12). Initially the KBr concentrations were noted to increase until a maximum was achieved which coincides with recovery of the center of mass of the slug of injected fluids. Thereafter the KBr concentrations were noted to decrease. These data were used to document recovery of the hydrofracturing fluids.

6.4.3. RSF injection and monitoring

Four separate RSF injections were performed in the 87 ft zone using approximately 3050 gal of viscosifier mixed with approximately 1900 lb. of proppants. Injection, packer, and shut-in pressures were periodically monitored during the RSF injections using in-line pressure gauges. Injection pressures up to 900 psi were attained during the four separate injections.

A single RSF injection was performed on the 57 ft zone using approximately 1000 gal of viscosifier mixed with approximately 1000 lb. of proppants and a single RSF injection was performed in the 42-ft zone using approximately 1000 gal of viscosifier

mixed with approximately 1000 lb. of proppants. Injection pressures up to 2500 psi were attained during the single injections.

Treatment of the 42 and 57 ft zones were significantly less effective than the 87 ft zone and the reason is considered to be the higher angles of the fractures at those depths.

6.4.4. Water level monitoring

Water levels in test boring E-39B and observation wells E-1 and E-39A were monitored continuously during the RSF injections and recovery periods. Pressure transducers were placed in boring E-39B and observation wells E-1 and E-39A at a depth of approximately 36 ft bgs. In addition to continuous monitoring, water levels were periodically monitored using a water level sounder and recorded in a field logbook. During all of the injections, water levels were noted to rise in the observation wells within minutes of the initiation of pumping.

6.4.5. Bromide tracer breakthrough monitoring

Field monitoring for the breakthrough of the bromide tracer solution was performed during the RSF injections. An Orion 290A meter and TempHion probes with ISEs calibrated for bromide were used in observation wells E-39A and E-1 to periodically measure the concentration of Br^- during the RSF injections. The probes were placed in wells E-1 and E-39A at depths of 38 and 40 ft bgs, respectively. Background measurements were collected in wells E-1 and E-39A in order to establish a baseline for determining when breakthrough occurred. Periodically during the injections, the Br^- concentration was measured and recorded in a field logbook. Breakthrough of the injection fluid was noted when the Br^- concentration began to increase above the baseline concentrations in the observation wells during the RSF injections. The most significant bromide breakthrough was observed in well E-39A during the 87 ft injection in E-39B. Significant breakthrough of bromide was also noted in E-1 during the 42 ft injection of E-39B. These data suggest that the radius of influence of the hydrofracturing fluids was as great as 42 ft during the test.

6.4.6. E-39B well installation and development

Following completion of the testing, boring E-39B was converted into a 100-ft deep groundwater extraction well. The well was constructed using 4-in. diameter, schedule 40 stainless steel wire-wrapped screen set from approximately 30 to 95 ft bgs and 4-in. diameter, schedule 80 PVC blank casing from 0 to 30 ft bgs. A 5-ft stainless steel sump was installed at the base of the well.

Well E-39B was developed, using bailing and pumping methods, of approximately 8200 gal of fluids. It is estimated that 7500 gal of water/fracking fluid was injected into the formation during RSF testing. A 5-ft length, 3-in. diameter stainless steel bailer was used to purge the first 55 gal of development water. After sufficient fine sand and silt were removed from the well, a Grundfos 3/4 hp submersible pump was lowered into the well and used to complete the well development. The fluids removed from the well during the development were contained in a 21,000-gal steel FRAC tank located on site. Groundwater quality parameters (pH, temperature, electrical conductivity) were periodically monitored using a HyDAC 910 meter during well development.

6.4.7. Aquifer testing

Aquifer testing was conducted on extraction well E-39B while it was being developed. Aquifer characteristics were assessed using step-drawdown and constant-discharge tests.

During the course of the pumping tests, bromide tracer recovery monitoring was performed in order to monitor the concentration of the bromide tracer injected as part of the RSF treatments. Periodically during the tests, a grab sample of the well discharge was collected in a 1000 ml graduated cylinder and the Br^- concentration was determined using a TempHion probe with bromide ISE and an Orion 290A meter. After the pump testing, mass balance was calculated to estimate the amount of bromide entrained fracking fluid that was recovered during well development/pump testing. Periodic bromide tracer recovery monitoring performed during aquifer testing indicates that the highest concentration of bromide (108 mg/l) and the center of the mass of bromide was recovered after approximately 18 h of pumping (see Fig. 12). The bromide concentrations measured at the beginning and end of the tracer recovery period were 18.9 and 70 mg/l, respectively. The total KBr mass recovered was about 7 lb. It is speculated that much of the bromide that was not recovered was adsorbed to iron. This is consistent with research that has documented iron adsorption of bromide in laboratory testing [26].

6.4.8. Fracking fluid management

Approximately 12,000 gal of produced groundwater, fracking fluid and washout water was collected in a Frac tank. Approximately 2000 gal of fracking fluid was processed through the facility groundwater treatment system in an 18-h period, at which time a microfiltration module became plugged and the treatment was discontinued. A finely divided black material was noted in the filtrate.

To evaluate the potential causes of plugging, the laboratory analyzed samples of the water for total organic carbon, total suspended solids, chemical and biochemical oxygen demand, and dissolved iron. The analysis confirmed that residual organic carbon, and chemical and biochemical oxygen demand remained elevated, and that dissolved iron was present. A bench test was conducted using the addition of hydrogen peroxide to affect oxidation (and hopefully breakdown) of the residual polysaccharide. The oxidation eliminated the black filtrate and resulted in the formation of a yellowish orange precipitate (iron oxy-hydroxide).

6.5. Continued monitoring

The RSF Workplan [3] called for ongoing monitoring of the treatment following the re-initiation of pumping of the extraction well. Due to concerns about residual polysaccharide in the groundwater, the planned pumping of well E-39B was delayed two months. Pumping at a rate of approximately 1.2 gpm was re-initiated and groundwater samples were obtained after 1 h and approximately 5 days of pumping, and thereafter about 1 month and 3 months. The 1-h sample showed a significant increase in the concentration of 1,2-DCE. The 5-day and 1-month samples showed a dramatic increase in 1,2-DCE and TCE concentrations to levels far in excess of pretreatment levels.

Shortly after the high concentrations were noted the pump impeller melted and the pump went out of service. It is thought that the pump was damaged by a combination of well biofouling and mobilization of a TCE DNAPL. The well was rehabilitated, a new chemical resistant pump installed and pumping resumed. Following rehabilitation, the well was once again sampled after several days of pumping. Concentrations had decreased more than an order of magnitude from the prior high concentrations.

6.5.1. Analytical results

The principal chemical of concern, TCE, was detected at a concentrations of 2900 $\mu\text{g}/\text{l}$ after 1 h of pumping and 52,000 $\mu\text{g}/\text{l}$ after 5 days of pumping. The value of 52,000 $\mu\text{g}/\text{l}$ is within the historical variability of concentrations detected in wells E-39A and E-1. These data suggest that much of the impacted groundwater entering the well after 5 days of pumping was from outside the zones which were treated and therefore, did not pass through the reactive media. TCE concentrations in well E-1 (total depth 38 ft) historically as high as 180,000 $\mu\text{g}/\text{l}$ suggest that pockets of residual TCE are present at shallower depths than reached by the RSF treatments that were installed at 42, 57 and 87 ft bgs.

PCE concentrations ranged from 40 to 175 $\mu\text{g}/\text{l}$.

The compounds 1,1-DCE and *cis*-1,2 DCE, common degradation products of TCE and PCE, were detected at concentrations ranging from 65 to 3630 $\mu\text{g}/\text{l}$.

The compound 1,1,1-TCA was detected in the latest sample at a concentration of 75 $\mu\text{g}/\text{l}$. The elevated concentrations of 1,1 DCE and *cis*-1,2 DCE are suggestive of their production due to the reductive dehalogenation breakdown of the parent compounds (TCA, PCE, and TCE). VC was not detected in the groundwater.

Iron was detected at a concentration of 5 mg/l in the 5-day sample, suggesting that iron is being liberated to the groundwater from the reactive media.

Chromium was not detected in both the 1-h and 5-day samples. These data suggest that the ferrous iron liberated by the reactive media is causing the reduction and precipitation of chromium. Chromium was however detected in later samples, however in all cases the concentrations were lower than pretreatment levels.

7. Conclusions

The RSF pilot study has provided a proof of concept of the technology by demonstrating the following.

- ZVI can be injected into a fractured bedrock aquifer at practically achievable pressures and costs. The approximate cost of this pilot study was about US\$200,000. Full-scale implementations are projected to cost between US\$100,000 and US\$1,000,000 and would depend on site specific conditions. This process can potentially be used to create in situ treatment zones in deep and fractured rock aquifers.

- Hydrodynamically efficient iron foam proppants provide the means for delivering sufficient ZVI to sustain the reductive dehalogenation and metallic reduction reactions.

- The reductive dehalogenation reaction is evidenced by
 - extremely negative oxidation reduction potential (> -500 mV)
 - disappearance of dissolved chromium, copper, oxygen, and nitrate
 - substantial reductions in concentrations of TCE, PCE, and 1,1-DCE.
- The occurrence of the corrosion reaction is supported by increases in the concentration of iron and zinc.
 - The iron foam proppants are capable of sustaining open fractures created by hydraulic fracturing, resulting in enhanced hydraulic conductivity and well production.
 - The effective radius of hydrofracturing achieved was at least 42 ft given the bromide breakthrough into observation well E-1.
 - The center of mass of the fracking fluids was recovered during well development given the bromide tracer concentration vs. time curve.
 - Dealing with fracking fluids containing a combination of contaminants and residual polysaccharide viscosifier may be problematic for certain groundwater treatment systems. Biofouling may occur, and antifoulant treatments may be required in certain cases. Commercially available products appear to be effective for this purpose.

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