Factors Affecting Hydraulic Conductivity of High pH, High Silica Groundwater at the Former

Occidental Chemical Corporation Facility

Christina Urbanczyk

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Mark Benjamin

Gregory Korshin

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Abstract

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Christina Urbanczyk

Chair of the Supervisory Committee:
Professor Mark Benjamin
Department of Civil and Environmental Engineering

Pollution of water and sediments in and along the Port of Tacoma, WA, has resulted from the historic discharge of chlorinated solvents and caustic materials from the former Occidental Chemical Corporation (OCC) Facility. A pump-and-treat (P&T) system is in operation, yet the extraction of contaminated groundwater with elevated pH is being avoided because doing so has previously fouled well screens. This study used batch and column tests to identify factors that affect hydraulic conductivity of OCC site soil in response to high pH groundwater.

High pH groundwater at the OCC site has elevated concentrations of Si and Al. These constituents dissolved from OCC site soil historically, though whether dissolution is still active in the OCC subsurface remains to be ascertained. It is however clear that precipitation of Si-based solids causes the soil to plug, reducing hydraulic conductivity. Soil plugging is due to the interactions between the soil and Si and Al in the groundwater, though Al has a greater effect.

This study shows that Darcy velocity of groundwater and specific groundwater-soil interactions have the largest impacts on hydraulic conductivity of OCC site soil when high pH, high Si groundwater passes through it. When the Darcy velocity exceeds a specific threshold, hydraulic conductivity reduces over time, though soil plugging does not occur below this threshold. OCC site soil that has been exposed to high pH, high Si groundwater also has a higher Darcy velocity

threshold for soil plugging than soil that has not been exposed to this groundwater. Therefore, P&T efforts can be designed to explore options that may ultimately enable long-term extraction and ex-situ treatment of high pH, high Si groundwater.

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Table of Abbreviations

bgs	Below ground surface
cis-1,2-DCE	cis-1,2-dichloroethylene
CRA	Conestoga-Rovers & Associates
DC	Direct Current
DI	Deionized
DNAPL	Dense Non-Aqueous Phase Liquids
DOC	Dissolved Organic Carbon
HRT	Hydraulic Retention Time
GAC	Granular Activated Carbon
gpd	gallons per day
gpm	gallons per minute
ICP-MS	Inductively Coupled Plasma Mass Spectrometer
ID	Inner Diameter
ISE	Ion Selective electrode
m	Mass
M	Molar (mol/l)
MSL	Mean Sea Level
NA	Not Available
ND	Not Detected

OCC	Occidental Chemical Corporation
ORP	Oxidation-Reduction Potential
P&T	Pump and Treat
PCE	Tetrachloroethylene
PE	Polyethylene
PES	Poly Ether Sulfone
PP	Polypropylene
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
RCRA	Resource Conservation and Recovery
RTD	Residence Time Distribution
TCE	Trichloroethylene
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
UW	University of Washington
V	Volume
VC	Vinyl Chloride
VOC	Volatile Organic Compound

1 Introduction

Pollution of water and sediments in and along the Hylebos Waterway and the outer Commencement Bay in the Port of Tacoma, WA, has resulted from the historic discharge of contaminants from various parties. The Waterway is part of the Commencement Bay Nearshore/Tideflats Superfund site, which the US Environmental Protection Agency (USEPA) placed on the Superfund National Priorities List in 1983 (USEPA 2015a). The former Occidental Chemical Corporation (OCC) is one of the parties held responsible for the cleanup of this Superfund site due to discharge of contaminants that has resulted in elevated concentrations of volatile organic compounds (VOCs) and elevated pH both on and off-site.

Cleanup of the Commencement Bay Nearshore/Tideflats Superfund site is underway in order to promote a healthy marine environment and protect people from eating contaminated seafood from Commencement Bay (USEPA 2015a). The OCC site has a pump-and-treat (P&T) system in operation to remove VOCs and reduce the pH of contaminated groundwater to prevent further contamination of the Hylebos Waterway. However, difficulties have been encountered during the extraction of high pH groundwater that also has elevated Si concentrations (up to three orders of magnitude higher than those typical for natural environments). Pumping this groundwater has resulted in the plugging of extraction well screens and the aquifer in the immediate vicinity of the well screens (USEPA 2004).

This study was conducted to address the overlying research question: How does hydraulic conductivity change as a function of various system parameters when high pH, high Si groundwater passes through soil at the OCC site? To accomplish this, the groundwater and soils at the OCC site were initially characterized to identify specific factors that may cause changes in hydraulic conductivity. Groundwater with elevated pH and VOC concentrations at the site also has extremely high concentrations of Si and Al, so batch experiments were then completed to investigate the precipitation and dissolution of Si-based solids, which could alter

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the hydraulic conductivity of the soil. These initial experiments provided background to identify parameters, including Darcy velocity, column media, and concentrations of constituents in column feed, that should be varied during column tests to address the overlying research question. By understanding what factors significantly alter hydraulic conductivity of high pH, high Si groundwater during column tests, efforts can potentially be made to enable long-term extraction of this groundwater at the OCC site.

2   Background

2.1   Site Characterization

2.1.1   Groundwater Contamination Sources and Transport

The former OCC facility is located along the Hylebos Waterway and comprises properties at 605 and 709 Alexander Avenue, Tacoma, WA (Figure 2-1). The site encompasses approximately 37 acres, and groundwater and sediment at and surrounding the site have been contaminated primarily in response to historic operation of the OCC facility. OCC manufactured chlorinated solvents from 1947 to 1973, and products of this production included chlorine gas, caustic soda, bleach, trichloroethylene (TCE) and tetrachloroethylene (PCE) (USEPA 2004). Improper disposal of products manufactured at the site resulted in contamination of groundwater, soil and sediment by VOCs and elevated pH. Based on a review of facility operation and the extent of contamination, the USEPA (2004) presumed that caustic material was released during processing, transport, storage or disposal, while chlorinated solvents were likely released from former settling pond areas used for effluent from TCE and PCE processing activities. Both the caustic materials and VOCs, which are likely dense non-aqueous phase liquids (DNAPL), have high densities relative to that of water, which has resulted in plumes with elevated pH and VOC concentrations at depths over 100 ft. These plumes have migrated to areas outside of the OCC site, including into and under the Hylebos Waterway (USEPA 2004).

Figure 2-1. Location of the former OCC (Oxy) site, adjacent to the Hylebos and Blair Waterways in the Port of Tacoma, WA (Williams 2012).

Elevated VOC and pH plumes are widespread both horizontally and vertically at the OCC site. VOC concentrations well exceed permit levels, though some degradation of parent compounds has occurred in-situ. The primary breakdown products of TCE and PCE are cis-1,2-dichloroethylene (cis-1,2-DCE) and vinyl chloride (VC). The transport of various VOCs has resulted in extensive contamination on and off-site, with VOC concentrations orders of magnitude higher than permit limits. As of 2004, TCE concentrations in some wells stabilized at over 100 mg/l, and it is believed that persistent, elevated concentrations are a result of the DNAPL present that is continuously dissolving into the groundwater (USEPA 2004). As of 2011, some areas of the plumes had VC concentrations that exceeded 100 mg/l (Figure 2-2) (Williams 2012). Groundwater under the site also has pH values that exceed 13, and is migrating beneath and into the Hylebos Waterway (CRA 2011).

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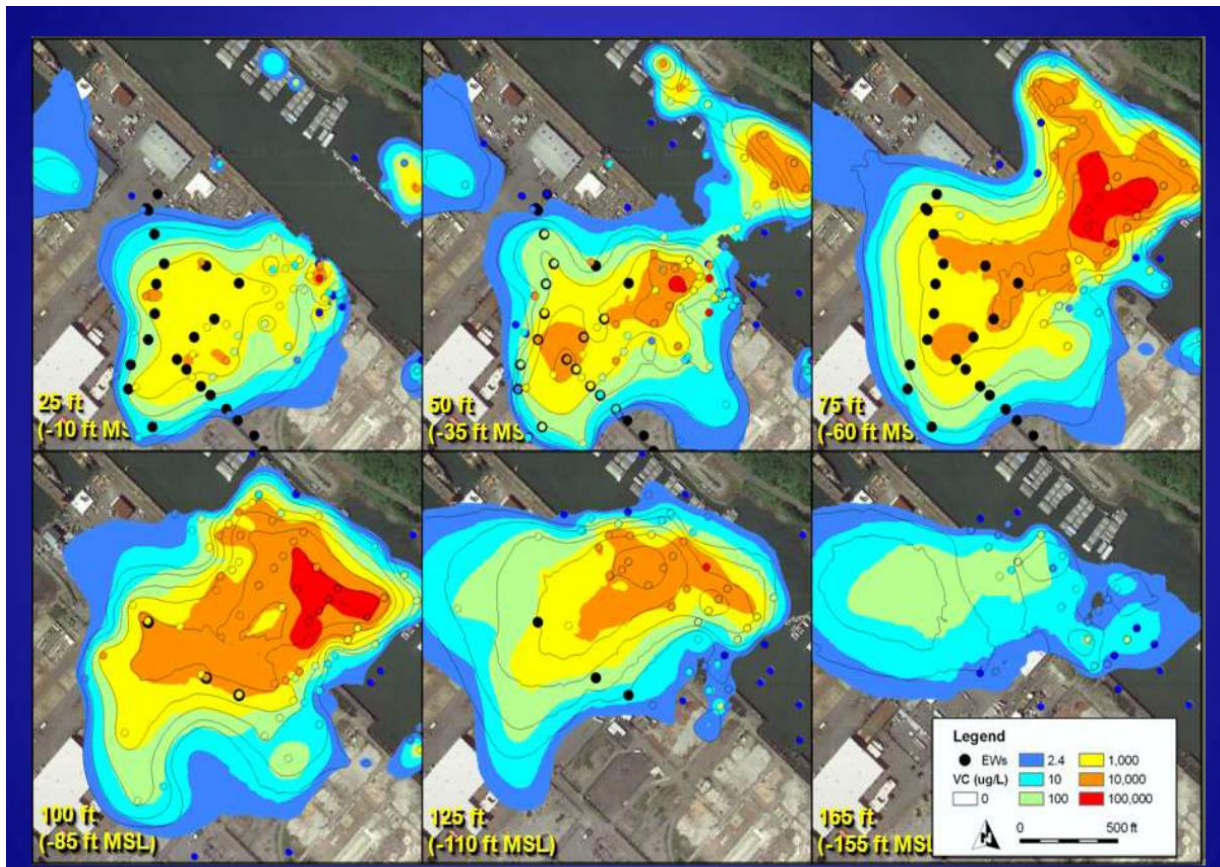
Figure 2-2. VC contours at various depths on and off-site at the OCC facility; off-site transport is causing VC to leach into the Hylebos Waterway (Williams 2012).

Elevated pH at the site has caused persistent and challenging complications with the extraction and treatment of the groundwater. The caustic material that was historically released from the site increased sodium hydroxide in the groundwater, which has resulted in the dissolution of metals and Si. Most notably, the hydroxide ions reacted with silicon-based materials (notably sand) to release silicate ions. The silicate ions and the hydroxyl ions still remaining in the groundwater contribute to the alkalinity of the soil and groundwater. The pH of the groundwater remains elevated though lower pH groundwater continues to dilute the source (UW SOW 2014). The release of silicate ions from the sandy aquifer has also caused extremely high concentrations of Si to be present in the groundwater; concentrations of Si at the OCC site are up to three orders of magnitude higher than typical dissolved Si concentrations found in nature

(Fetter 2001). Areas of elevated pH and Si concentrations therefore often coincide, especially at greater depths.

2.1.2 Ongoing Groundwater Treatment

Cleanup of the OCC site is ongoing to protect the primary receptor, the Hylebos Waterway. The USEPA's Resource Conservation and Recovery Act (RCRA) program initially was used as the framework for the management of remediation efforts before oversight was transferred to the WA Department of Ecology in 1998. The USEPA Superfund Program is also interested in the site because the Hylebos Waterway is part of the designated Commencement Bay Nearshore/Tideflats Superfund site (USEPA 2004). The primary goals of the cleanup include promoting a healthy marine environment and protecting people from eating contaminated seafood from Commencement Bay (USEPA 2015a).

OCC retains environmental liability for cleanup of the site though the facility is no longer in operation. A P&T system has been in place since 1994. In this system, 35 wells in three branches were initially designed and placed into operation. Due to early fouling of extraction well screens in the vicinity of the high pH plume, operation of the pumping system was revised and restricted to 25 wells extracting groundwater with a pH less than 9.5. Therefore, extraction and treatment of contaminated groundwater with a pH above 9.5 is being avoided, and this groundwater continues to migrate off-site. As of 2004, the extraction system pumped 105 to 110 gallons per minute (gpm), and less than 5 gpm was reinjected in wells adjacent to the Hylebos Waterway to maintain a level of at least 2.5 ft above mean sea level (MSL) in the wells (USEPA 2004). The injection system was designed to establish a barrier between the high pH plume and the Waterway, though fouling of the injection wells has caused operation of the injection system to cease almost entirely.

Contaminated groundwater at the OCC site is treated in a system that has a capacity of 200 gpm. Extracted groundwater is initially routed into settling tanks to allow solids to settle out. The

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groundwater then passes through air strippers, and the air is routed into a catalytic oxidizer while groundwater passes through granular activated carbon (GAC) beds (USEPA 2004). It is anticipated that, if the high pH groundwater was extracted, Si would precipitate from solution in response to lowering the pH to satisfy the discharge criteria. There is no doubt that Si precipitation would severely foul the treatment system. Therefore, if high pH groundwater is extracted in the future, the bulk pH would need to be lowered and the precipitated Si removed prior to treating the groundwater with the current P&T system. The P&T system was designed to include a filter press and sludge dryer with a capacity of 13 tons/day. This system was originally designed to treat backwash, but it could also be used for the handling these precipitated solids (USEPA 2004).

2.1.3 Hydrogeology

The hydrogeology of the site has affected contaminant transport and fate. The OCC property lies within the Puget Sound Lowland, which extends throughout Washington State and British Columbia (Figure 2-3). The site is within the Puyallup River Valley, a basin characterized by geologic units from four glacial advances and retreats (Vaccaro et al 1998). The geology of the OCC site is comprised of a shallow subsurface with a thick sequence of fluvial deltaic deposits, underlain by less permeable Vashon Till which acts as a lower confining layer. The fluvial deposits consist of sand and silty sand with discontinuous lenses of clayey silt, silt, and silty sand, with a horizontal hydraulic conductivity that is expected to range between 0.3 and 30 ft/day (CRA 2011).
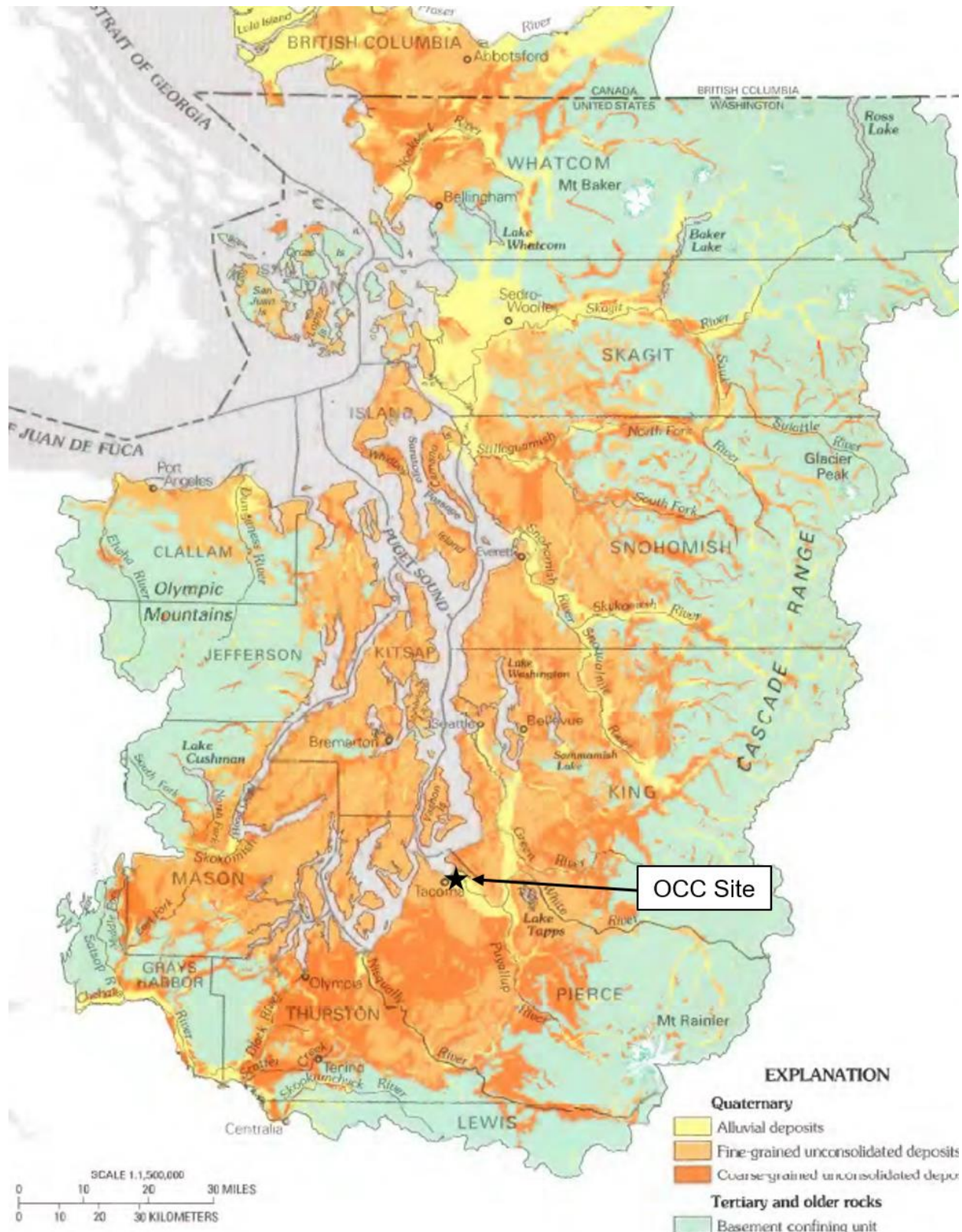
Figure 2-3. Geology of the Puget Sound Lowland with the location of the OCC site shown (Jones 1999).

Localized flow regimes are common in the Puyallup River Valley due to the discontinuous and heterogeneous nature of the geologic units, though regional flow regimes are also present (Vaccaro et al 1998). Groundwater flow at the OCC site in the upper 50 ft of the aquifer is dominated by limited surface recharge because the site is mostly covered by asphalt and concrete. This upper region of flow creates a divide parallel to the Hylebos Waterway when pumping is off-line, such that flow east of the divide discharges into the Hylebos Waterway and flow west of the divide discharges into the Blair Waterway. However, groundwater extraction has caused the flow divide to shift toward the Blair Waterway, causing more groundwater to flow toward the Hylebos Waterway. A majority of the flow into the Hylebos Waterway occurs from discharge of local groundwater in the shallow surface. Groundwater flow in the 50 to 100 ft depth range is controlled by regional flow that is recharged from precipitation in the northern highlands. Regional flow at these depths generally flows west into Puget Sound, though pumping at the site also causes groundwater to flow upward (CRA 2011).

Groundwater flow at the site is also influenced by tidal fluctuations and density-dependent plumes, introducing additional complexity into the treatment of the contaminated groundwater (USEPA 2004). Tidal fluctuations at the site cause a transient groundwater zone that mixes with the Hylebos Waterway both vertically and horizontally. This results in tidal dispersion of contaminants in groundwater in the immediate vicinity of the Hylebos Waterway. Tidal dispersion is reportedly the primary attenuation mechanism at locations along Commencement Bay. Transport of contaminated groundwater is also influenced by the density-dependent plumes. The density of the contaminated groundwater is higher than the densities of both fresh and salt water, so the plume migrates vertically downward and has resulted in contamination at great depths below the site and the Hylebos Waterway (CRA 2011).

2.2 Dissolution and Precipitation of Silica

Si is one of the dominant elements in soils, aquatic systems and other niches of the environment. Despite its abundance, dissolved Si concentrations normally do not exceed a few dozen mg/L, and extraordinarily high concentrations of Si in OCC groundwater are indicative of unusually aggressive properties of effluents released at the OCC site and the propensity of OCC soils to react with them. Extremely high concentrations of dissolved Si and Al measured in contaminated groundwater at the OCC site have heightened the need to understand factors controlling dissolution and precipitation of Si and Si-complexes, chemical processes that may alter hydraulic conductivity when passing high pH, high Si groundwater through OCC site soil. Though there is great complexity associated with the aquatic chemistry of Si and the wide range of complexes and solid phases that can be formed, factors that significantly affect Si precipitation and dissolution include pH, presence of Al, hardness cations and background salts, and the presence of organic matter. Additional factors that affect the physiochemical properties of Si include temperature, time available for precipitation, and mode and intensity of mixing (Krznaric et al 1997).

2.2.1 Effect of pH

The pH of groundwater at the OCC site, which ranges from circumneutral to >13, controls the solubility of Si and its dominant dissolved forms. Si is commonly found in nature as quartz, SiO_2 (Gasteiger 1992). The solubility of SiO_2 depends strongly on its crystalline form and solution pH (Figure 2-4). Note that a saturation index below zero indicates that the solution is undersaturated, while an index greater than zero indicates a supersaturated solution. The dissolution reaction of SiO_2 is often described by Equation 1 (House and Hickinbotham 1992).
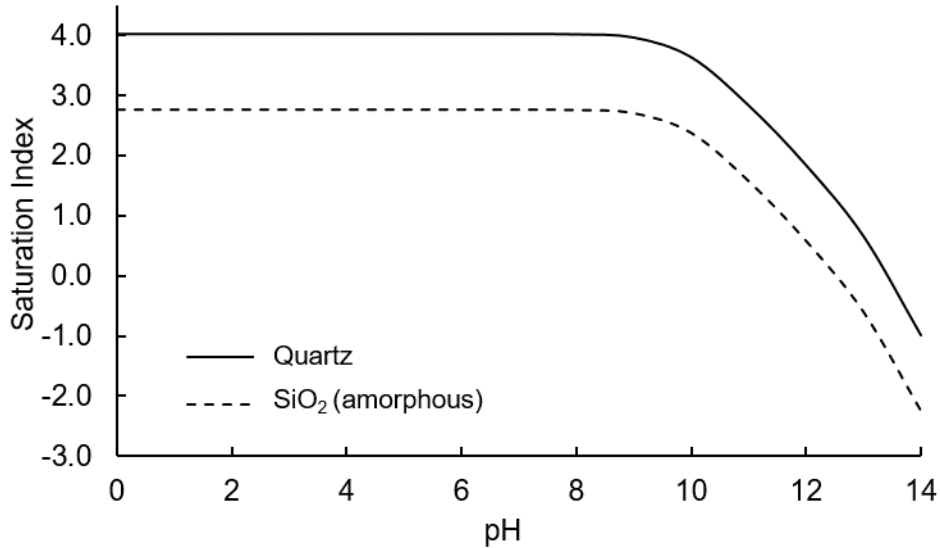
Figure 2-4. Saturation indices for quartz and amorphous Si as a function of pH for a 1 molal Si solution at 25°C. (Image generated using Visual Minteq software.)

$$SiO_2 + 2H_2O \rightarrow H_4SiO_4 \qquad \text{Equation 1}$$

Dissolved Si is commonly found in environmental aquatic systems as silicic acid, H_4SiO_4, which is a weak acid that can dissociate multiple hydrogen ions based on the pH of the aqueous solution. The dominant acid/base reactions are described by Equations 2 and 3, with the associated pK_a values indicated on the right of each equation (Gasteiger et al 1992) (Benjamin 2014). The pK_a values for the relevant acid/base reactions indicate that H_4SiO_4 is the dominant species in solutions with lower pH values (pH < 9.84). The deprotonated species, $H_3SiO_4^-$, is dominant at pH values between 9.84 and 13.2, and at even higher pH values (pH>13.2), $H_2SiO_4^{2-}$ is the dominant dissolved Si species (Figure 2-5). In aqueous solutions supersaturated with Si, the growth of silicates via polymerization can occur, leading to dissolved Si concentrations higher than that predicted by consideration of only monomers (Amjad and Zuhl 2010).

$$H_4SiO_4 \rightarrow H_3SiO_4^- + H^+ \qquad pKa_1 = 9.84 \qquad \text{Equation 2}$$
$$H_3SiO_4^- \rightarrow H_2SiO_4^{2-} + H^+ \qquad pKa_2 = 13.2 \qquad \text{Equation 3}$$

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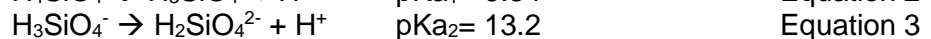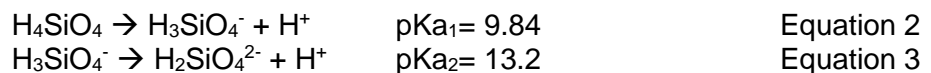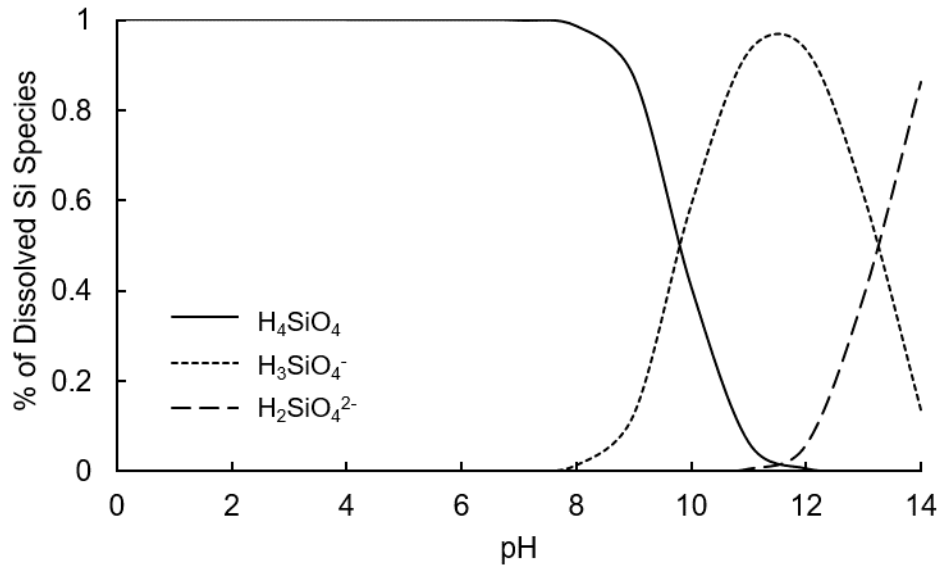
Figure 2-5. Dependence of dissolved Si speciation on pH. (Speciation data generated using Visual Minteq software.)

2.2.2   Effect of Aluminum and Salts

The high concentration of Al and salts such as sodium chloride and carbonate in high pH, high Si groundwater may affect dissolution of Si-based minerals and precipitation of Si-complexes at the OCC site. The presence of Al species directly impacts the solubility of Si and composition of precipitates formed. In aqueous solutions with a pH greater than 8 to 9 and a total Al concentration below 0.1 mol/l, the predominant Al species is the aluminate ion, $Al(OH)_4^-$. The tetrahedral structure of $Al(OH)_4^-$ resembles that of silicate ions. This stereochemical similarity promotes reactions between Al and Si to form aluminosilicates (Gasteiger et al 1992). Aluminosilicates are a group of minerals in which some Si^{4+} ions in silicates are replaced by Al^{3+} and other common cations such as sodium.

The physiochemical properties of aluminosilicates depend on the initial chemical composition and distribution of alkali cations and/or organic templates (Krznaric et al 1997). Gasteiger et al (1992) determined that the solubility of aluminosilicates increases with pH and decreases with ionic strength, with the effect of pH on solubility being stronger than that of the solution salt concentration. Gorrepati et al (2010) observed that chlorides of several representative cations accelerate particle formation and growth rates of Si polymorphs in the following order:

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AlCl$_3$>CaCl$_2$>MgCl$_2$>NaCl>CsCl>no salt. However, results from that study indicated that in the absence of specific interactions (e.g., formation of binary Si-Al solutes and solids), ionic strength has a larger effect on Si polymerization than cation identity.

The effects of Al and ionic strength on the dissolution kinetics of SiO$_2$ have been well documented. Specifically, the presence of Al(OH)$_4^-$ has been reported to depress the dissolution rate of Si by up to 85% (Bickmore et al 2006). On the other hand, the presence of background inert salt (e.g., NaCl) reportedly enhances dissolution rates. Dove (1999) observed that the dissolution rate of SiO$_2$ increases in the presence of hardness cations and Na$^+$ in the following order: Ba^{2+}>Ca^{2+}=Na$^+$> Mg^{2+}. Icenhower and Dove (2000) further determined that the introduction of 0.05 molal Na$^+$ increased the dissolution rate of amorphous Si by 21x as compared to a solution without appreciable salt.

2.2.3   Effect of Organic Matter

There are high concentrations of dissolved organic matter (DOM) in some of the high pH groundwater at the OCC site. Effects of DOM on the solubility of Si have not been well-defined due to the complex natures of both DOM and Si polymorphs.   However, it has been observed that the solubility of SiO$_2$ and Si polymorphs increases in aqueous solutions and soils rich in organic matter. Bennet and Siegel (1987) observed that organic compounds associated with DOM increased solubility of SiO$_2$ in a natural water, and Si was posited to be complexed and mobilized by organics. Humic acid, which frequently is the dominant fraction of DOM, has also been observed to increase the solubility of aluminosilicates. Specifically, humic acid slows polymerization of Al and Si at low temperatures, such that aluminosilicate gel formation decreases with the presence of humic acid (Rouff et al 2011).

2.2.4   Case Study: Hanford, WA

The Hanford Nuclear Site is a 586 mi^2 site located in southeastern Washington that served as a plutonium production facility for nuclear weapons for more than forty years. The site is

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designated as a Superfund site due to the massive contamination that occurred from operation of the facility (USEPA 2015b). The site discharged radioactive waste to 177 underground storage tanks, and a significant number of these tanks leaked, releasing waste fluids into the subsurface. Of particular interest is the high pH waste that contains high concentrations of Al and Na, which has reacted to dissolve Si naturally present in the subsurface as well as caused precipitation of secondary minerals (Mashal et al 2005). Major characteristics of the waste released at the Hanford site are similar to those in the high pH, high Si groundwater in some of the wells at the OCC site. Because the Hanford site is relatively well-studied, results from experiments performed on simulated waste from this site may provide insight into the chemical reactions occurring in the OCC site subsurface.

Studies using simulated waste from the Hanford site have indicated that both precipitation and dissolution occur when this waste comes into contact with site soils. Qafoku et al (2004) performed column tests with silty sand from the Hanford site and the injection of alkaline simulated waste. Results from this study indicated that Al in the simulated waste has a dual effect on the dissolution and precipitation of mineral phases. Specifically, Al decreased the OH$^-$ concentrations through the formation of aluminate ions which are the dominant Al species in high pH solutions, so base-promoted mineral dissolution decreased in the presence of Al. Dissolution of Si and other minerals was minimized due to the formation of secondary minerals that fully covered soil particles. This finding was supported by Mashal et al (2005). The Qafoku et al (2004) study also determined that the rate of Si dissolution increases with pH and decreases with contact time.

Additional column tests were conducted by Wang and Um (2012) to investigate changes in porosity in response to reactions associated with injection of simulated waste into quartz sand. Column porosity increased by up to 40.3% when Al was not included in the alkaline simulated

waste feed. However, when Al was included in the feed, the porosity decreased by 26.5% due to the formation of a secondary mineral phase on the media surfaces (Wang and Um 2012).

Experiments performed to understand subsurface reactions at the Hanford site may help to identify the nature and extent of the reactions potentially occurring in the OCC site subsurface. Specifically, these studies indicate that both dissolution and precipitation may occur at the OCC site. Si dissolution from the aquifer media depends on pH and Al concentration, yet precipitation of secondary minerals occurs simultaneously to inhibit further dissolution of Si and decrease the media porosity. The extent of these dual reactions may be of importance for the extraction of contaminated groundwater at the OCC site.

2.3   Research by the UW Group

Problems associated with the extraction of high pH groundwater were observed soon after the P&T system at the OCC site went into operation in 1994. The UW is involved in this project to assist with remediation of the OCC site. Major objectives of the UW study include the following (UW SOW 2014):

1. Analyzing metal partitioning between groundwater and aquifer soils

2. Investigating how high pH, high Si groundwater can be treated ex-situ or used to potentially create an in-situ hydraulic barrier

3. Understanding factors that contribute to changes in hydraulic conductivity of high pH, high Si groundwater to potentially identify ways to enable extraction

To satisfy the third objective of the UW study, this study was conducted to better understand the effect of high pH, high Si groundwater on hydraulic conductivity of OCC site soils under various conditions. The unique properties of the groundwater and soil were initially identified to determine what characteristics may potentially cause changes in hydraulic conductivity. The chemical processes that may alter hydraulic conductivity, notably the dissolution and

precipitation of Si, were studied with batch experiments, and significant parameters that affect these processes were then varied in column tests. Broad conclusions can be drawn from reproducible trends from column tests, and these results may potentially enable long-term extraction of this groundwater at the OCC site.

The first two tasks have been completed by the UW group. Of most significance for this study are results on ex-situ processing of Si from high pH, high Si groundwater. Pandya (2015) determined that, if high pH, high Si groundwater is extracted, precipitated solids could be treated by dewatering and gentle drying at ca. 30°C to yield approximately 16% (by volume of groundwater) dried solids. Therefore, if results from this study enable extraction of high pH, high Si groundwater, this method can be applied to reduce the volume and weight of the voluminous Si precipitate, which will significantly reduce the cost to treat this groundwater.

3   Methods and Materials

3.1   Overview of Groundwater and Soil Core Samples

Groundwater and soil core samples used in the experiments were collected at the former OCC facility by an outside party. All samples were initially collected in July and August, 2014, though groundwater samples from Well 7 were also collected at two later dates, December 11, 2014 and May 22, 2015.

Soil core samples were collected from boreholes within the vicinity of Wells 46C, 82 and 83C at depths of up to 150 ft below ground surface (bgs), though only subsamples from Well 46C (47 ft bgs) and Well 83C (103 ft and 128 ft bgs) were used in this study (Figure 3-1). Well 83C is within the vicinity of the high pH, VOC, and Si plume, so soil and groundwater samples collected from this area are considered 'affected' in this report (Table 3-1). Well 82 is also within the contamination plume but farther away from the source, so this area is 'affected' but to a lesser extent in terms of Si and VOC concentrations. Because Well 46C is the farthest of the three wells from the source of contamination, and consequently has circumneutral pH and relatively low VOC concentrations, groundwater samples and soil cores from that well were considered to be relatively 'unaffected'.
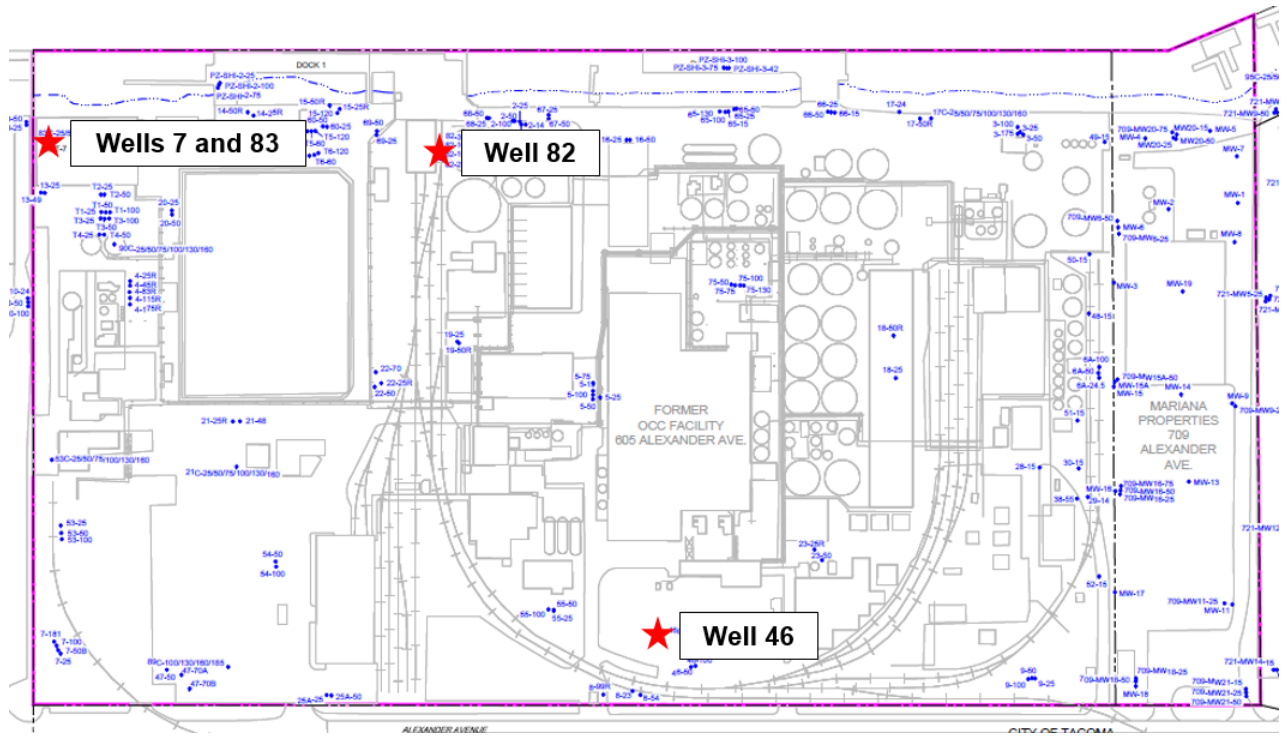
Figure 3-1. Plan view of OCC site with wells designated in which soil cores and groundwater samples were collected for use in this study.

Table 3-1. pH of OCC site solids/pore water used in this study.

Solids/Pore Water	pH[a]
46C-47	8.5
83C-103	9.1[b]
83C-128	10.3[b]

[a] Data collected in the field upon extraction of groundwater.

[b] Value measured in the lab would likely be higher.

Groundwater samples were collected from Wells 7, 46C, 82 and 83C. Well 7 is approximately 5 ft away from Well 83C, so it is also considered to be 'affected' by the high pH, VOC, Si plume (Table 3-2). Well 7 is screened from 122 ft to 132 ft bgs, so groundwater samples from this well were collected at this depth. Groundwater samples from Wells 46C-130, 83C-100, 83C-130, 82-30, and 82-100 were also used in this study.

Table 3-2. pH, ORP, and total VOCs in OCC site groundwater used in this study.

Groundwater	pH[a]	ORP (mV)[a]	Total VOCs (ppm) [b]
7	11.5	−493	NA
83C-100	10.3	−321	88.17
83C-130	13.1	−583	9.59
46C-130	7.5	−294	3.61E-03
82-30	13.1	-532	NA
82-100	13.5	−598	9.50E-04

NA Not Available

[a] Data collected in the field upon extraction of groundwater

[b] Data measured by outside party from samples collected in July and August, 2012

Groundwater and soil core samples were transferred to the UW laboratory after collection, and soil core samples and most groundwater samples were stored in the dark at ≤ 4 ◦C until use.

3.2 Column Test Set Up

Column tests were performed to explore the effect of high pH, high Si groundwater on hydraulic conductivity under various conditions. These columns were packed with 'affected' and 'unaffected' soils from the OCC site. Groundwater was injected into the column, and the trans-column pressure, and the pH, oxidation-reduction potential (ORP), and Br⁻ concentration of the column effluent were measured during these tests. Trans-column pressure measurements were used to determine the hydraulic conductivity of the media.

3.2.1 Hardware

Column tests were conducted using one experimental setup for the duration of the study (Figure 3-2). Feed was injected into columns via one peristaltic pump (Cole Parmer) or two connected in parallel when higher flows were tested. When one or both pumps were operated near their maximum speeds, a pulsation dampener (Cole Parmer) was connected between the pumps and column to remove hydraulic shock and vibration and enhance reliability of test results.
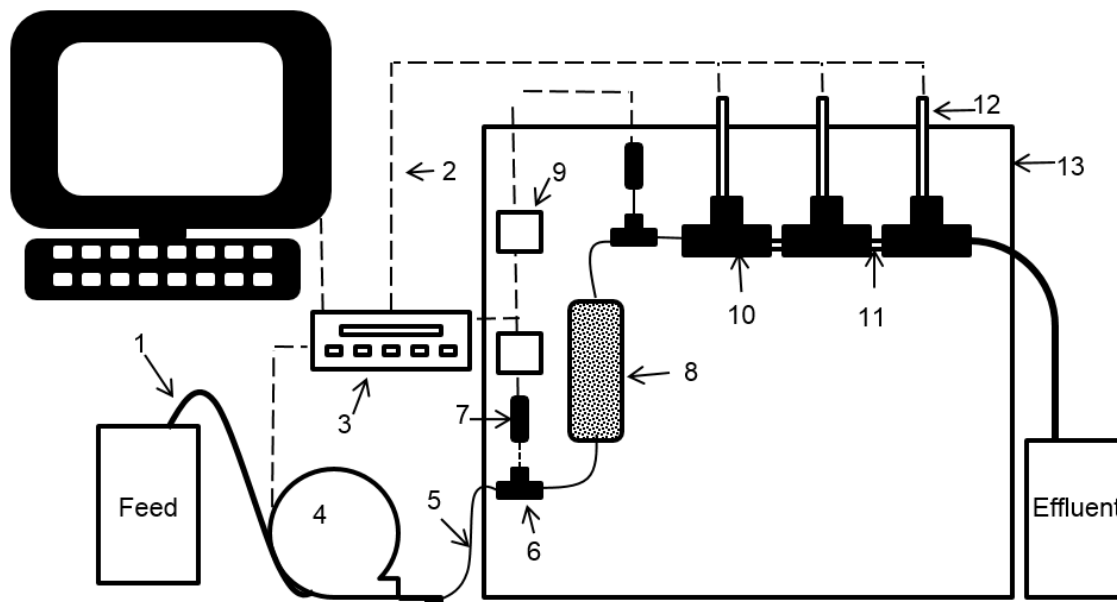
Figure 3-2. Schematic of column test set up. Labels are for the following equipment: 1. Masterflex Tygon pump tubing (Cole Parmer); 2. Electrical inputs/outputs Agilent Unit; 3. 20-channel Agilent Data Acquisition/Switch Unit (Model 34970A, Agilent Technologies); 4. Masterflex L/S Series Precision pump, peristaltic (Cole Parmer); 5. PTFE column tubing (Kontes Chromaflex); 6. PVDF compression tube fitting, tee (McMaster-Carr); 7. Pressure transducer with output up to 100 mV (PX302 Series, Omega Engineering, Inc.); 8. 4.8 cm ID, 15 cm long glass column (Kontes Chromaflex); 9. 7.5 W external power supply (Omega Engineering, Inc.); 10. PP three-way tees (McMaster-Carr); 11. PE tubing (McMaster-Carr); 12. Various electrodes (Cole Parmer); 13. Wooden board used to hold equipment upright

Pump tubing was connected to the polytetrafluoroethylene (PTFE) column tubing (Kontes

Chromaflex) and secured to the end of the column with a flangeless fitting. The glass column

(Kontes Chromaflex) used in experiments had a 4.8-cm inner diameter (ID) and was 15 cm long

with 20-µm PTFE bed supports on both ends.

Pressure transducers (PX302 Series, Omega Engineering, Inc.) with outputs up to 100 mV each

were located upstream and downstream of the column with polyvinylidene fluoride (PVDF)

compression tees (McMaster-Carr) to measure the pressure drop across the column. Each

transducer was wired to an external 7.5 W power supply (Omega Engineering, Inc.), which was

connected to a 20-channel Agilent Data Acquisition/Switch Unit (Model 34970A, Agilent

Technologies). The ORP electrode, pH electrode and Br⁻ ion selective electrode (ISE) (Cole

Parmer) were individually connected to a 10 V amplifier (Kwest Engineering) to reduce noise

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from their respective readings. Connections from the amplifier were wired to the Agilent unit for continuous data monitoring.

Ports were located downstream of the column to house various electrodes used in the tests (ORP, pH, Br⁻ ISE) for continuous data monitoring. These ports were assembled by connecting polypropylene (PP) three-way tees (McMaster-Carr) together with crack-resistant polyethylene (PE) tubing (McMaster-Carr), so an electrode could be secured in a tee with a compression fitting.

3.2.2 Data Acquisition Software

Data from the pressure transducers and other sensors (e.g., Br ISE, pH and ORP electrodes) were transmitted to the Agilent unit, which continuously monitored and recorded signals from the channels in use. The direct current readings from the electrodes and pressure transducers are proportional to the respective values, and these relationships were determined through calibrations. The Br⁻ ISE and pH electrode were calibrated prior to each test with standards. Calibration of the ORP electrode was completed according to the instructions provided by the manufacturer, which included adding crystals of quinhydrone to saturated pH buffers (one at pH 4 and the other at pH 7).

Column tests were controlled in two ways. Initially, the software included with the Agilent unit was used to record data from the electrodes and transducers multiple times per minute, and the pumps were controlled manually. Approximately halfway into the study, a software program that had the capability of receiving and recording data from the Agilent unit, as well as controlling pump settings, was completed by Kwest Engineering. External electrical connections between the peristaltic pump and the Agilent unit allowed the pump to be automatically shut off when the pressure across the column reached a user-specified threshold.

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3.3 Chemicals and Consumables

3.3.1 Chemicals

Ultra-pure deionized (DI) water (18.2 MΩ-cm) (EMD Millipore) was used to prepare solutions

and rinse glassware and column hardware when necessary. 1 M NaOH (Fisher Scientific) or

NaOH pellets (Fisher Scientific) and 1 M (Fisher Scientific) or 12 M HCl (Macron Fine

Chemicals) were individually used to adjust the pH of solutions to a desired value. NaCl (EMD

Chemicals, Inc.) was usually used to prepare a solution with a similar density and pH to the

subsequent feed, herein referred to as a benign solution, for column tests. However, $NaNO_3$

(Sigma Aldrich) was used in place of NaCl to prepare a benign solution when tracer tests were

conducted due to Cl^- interferences with the Br^- measurements that utilized a Br^- ISE. $AlCl_3*H_2O$

(Fisher Scientific), Na_2SiO_3 (Sigma Aldrich), and humic acid (Sigma Aldrich), either individually

or together, were used to prepare synthetic groundwater solutions. pH buffer solutions of 4, 7,

10, (Fisher Scientific) and 12.45 (Ricca Chemical Company) were used to calibrate electrodes

prior to use. The Br^- standards for the Br^- ISE calibration were prepared using NaBr (Sigma

Aldrich). Calibration standards (Ultra Scientific) for Inductively Coupled Plasma Mass

Spectrometer (ICP-MS) analyses were prepared using ICP-MS grade analytical standards. The

ORP electrode was calibrated using crystals of quinhydrone (Sigma Aldrich) to saturate pH

buffers. Trace-metal-grade HNO_3 (Fisher Scientific) and EPA Method 6020a internal standard

solution (Ultra Scientific) were incorporated into both diluted samples and standards for ICP-MS

analyses. A 1000 ppm organic carbon standard (Integra Chemical Company) was used to

prepare standards for TOC analyses.

3.3.2 Glassware and Consumables

Samples from experiments and column tests were collected in PP test tubes which were also

used in the preparation of samples and standards for ICP-MS and TOC analyses. Pipettes and

tips of various sizes were used to withdraw samples when needed. Polyethersulfone (PES)

filters (0.45μm) (VWR International) were attached to 10-ml Luer-Lok tip disposable syringes

(Becton, Dickinson & Company) to filter samples to prepare them for ICP-MS and TOC analyses.

Glass columns and other glassware were soaked in 20% HNO3 for one to three hours prior to rinsing at least three times with DI water.

3.4 Analytical Instruments

An Inductively Coupled Plasma Mass Spectrometer (ICP-MS) (PerkinElmer Elan DRC-e) was used to determine concentrations of analytes of interest for this study, notably those of Si and Al.

The Agilent Data Acquisition/Switch Unit (Model 34970A, Agilent Technologies) was used for continuous data monitoring of various parameters during column tests.

An advanced electrochemical multimeter (Orion™ Versa Star) was used with the high-pH electrode (Model 5994-23, Cole Parmer) to record the pH of solutions in tests other than the column tests. Similarly to usage with the Agilent unit, the pH electrode was calibrated using buffers at pH 4, 7, 10, and 12.45 prior to use with this instrument.

Total Organic Carbon (TOC) was measured using a Sievers 900 Portable Total Organic Carbon TOC Analyzer (General Electric).

3.5 Experimental Methods
3.5.1 Column Tests
3.5.1.1 Preparation

Columns were freshly packed for each test using a wet-packing method. Each end of the column was packed with glass wool and 3-mm glass beads. Initially, glass beads were placed on the bottom of the column and then saturated glass wool was placed on top of the beads in an even layer. Columns were then packed by repeatedly adding small aliquots of column media (50 to 70 g) along with 10 to 20 mL of DI water per aliquot. After the addition of each soil aliquot and DI water, a metal dowel was used to break up soil clumps. Saturated glass wool and then

glass beads were placed on top of the soil, and the column was tightly closed. Bed supports for the column were replaced when necessary.

The pH electrode was calibrated using standard 4, 7, 10, and 12.45 pH buffer solutions prior to each test. The Br⁻ ISE was also calibrated prior to each column test using standard solutions with Br⁻ concentrations between 10^{-6} and 10^{-1} *M.*

All solutions and groundwater used in column tests were allowed to equilibrate to room temperature prior to each experiment. Solutions other than groundwater used in one or more tests included various tracer, benign and synthetic groundwater solutions. The chemicals used to make up these solutions were described in the *Chemicals and Consumables* subsection.

3.5.1.2 Operation

To begin a column test, a benign solution with a pH and density close to those of the subsequent feed was injected to establish a baseline pressure across the column. The desired groundwater from the site or a synthetic groundwater solution was then injected at the same flow rate. The flow rate was measured multiple times during tests to ensure constant flow at the desired rate, and the average value was used to calculate values such as Darcy velocity and number of bed volumes treated for each test. Effluent samples were collected intermittently in PP tubes.

3.5.1.3 Reproducibility

Inherent variabilities in column packing are inevitable primarily due to the heterogeneous nature of the soil used. Br⁻ was used as a tracer in initial tests to test for short circuiting by comparing theoretical and actual residence time distributions (RTDs). These results are presented in the *Results and Discussion* section of this paper.

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3.5.2 Porosity Measurement

Porosity of soils used in the column tests was measured using two methods, which yielded similar results. These porosity measurements were used to estimate hydraulic residence time (HRT) in column tests.

The first method was implemented during the wet packing of columns used for tests. The mass of water used to pack the column was determined by finding the difference in the mass of a bottle filled with DI water before and after packing, and this mass was converted to a volume using density. The total volume of the column was determined using the dimensions of the column, so porosity could be computed as:

Porosity= $V_{water\ used\ in\ wet\ packing}$/ V_{column}

The second method utilized three replicates of soil subsamples to determine average porosity:

1. Weigh three small beakers

2. Place approximately 20 to 30 ml of soil sample into each beaker

3. Saturate soil samples (avoid excess water/ponding)

4. Weigh beakers with saturated soil sample

$m_{sat.\ soil} = m_{beaker+sat.\ soil} - m_{beaker}$

5. Dry samples in oven at 110°C for at least three hours

6. Allow samples to cool and weight contents

$m_{dry\ soil} = m_{beaker+dry\ soil} - m_{beaker}$

$\Delta m_{water\ sat.\ in\ soil} = m_{sat.\ soil} - m_{dry\ soil}$

7. Weigh approximately 50 ml of water (3 replicates)

8. Oversaturate soil samples to soften contents

9. Use additional water to move all soil and water into a 100 ml graduated cylinder

10. Measure volume of contents in graduated cylinder (V_{tot})

11. Weigh remaining water

$m_{extra\ water\ used\ to\ get\ to\ known\ volume} = m_{added\ water} - \Delta m_{water\ sat.\ in\ soil}$

12. Convert $\Delta m_{water\ sat.\ in\ soil}$ and $m_{extra\ water}$ to $V_{water\ sat.\ in\ soil}$ and $V_{extra\ water}$, respectively

13. Compute V_{soil}

$V_{soil} = V_{tot} - (V_{water\ sat.\ in\ soil} + V_{extra\ water})$

14. Compute porosity

Porosity $= V_{water\ sat.\ in\ soil} / (V_{soil} + V_{water\ sat.\ in\ soil})$

3.5.3 Dissolution Experiments

The dissolution experiments were conducted at 25°C, 35°C, and 55°C. The measurements

were carried out according to the following steps:

1. Rinse 120 ml glass vials with DI three times and allow to dry completely

2. Wash three 10 ml aliquots of each media (Well 46-44.5 soil, Well 83-127 and sand) with

   DI water

3. Dry selected media with paper towel

4. Place each sample into a 15 ml weighing boat and flatten to ensure similar volume

5. Weigh each replicate of each media (roughly 20 g each)

6. Transfer media into vial with 110 ml of Well 82-30 groundwater, DI water adjusted to pH

   11.6 or 1 *M* NaOH

7. Pour 110 ml of Well 82-30 groundwater, high pH DI water, or 1 *M* NaOH into vial without

   media to use as a control

8. Keep capped vials in a dark area at the appropriate temperature (25°C, 35°C, or 55°C) for the duration of the experiment

9. Gently shake vials for 10 seconds every 2 to 3 days

10. Collect 1 ml of supernatant samples intermittently (usually weekly)

3.5.4 Batch Groundwater Blending Experiments

Batch blending experiments were carried out in two sets concerned with: 1) blending groundwater from two different sites at the OCC facility and 2) blending synthetic solutions with groundwater from Well 7.

The experiments with blended groundwater were conducted in plastic vials. The dominant groundwater in the blend was initially placed into the vial, followed by addition of the less dominant groundwater. Each vial was shaken for 10 seconds after the blending, and each sample was examined visually to determine whether precipitation occurred instantaneously, within 2 hours, or within 1 day.

Batch experiments with synthetic solutions and Well 7 groundwater were conducted to determine how various factors affect precipitation of Well 7 groundwater. It was determined that blended solutions containing more than 20% of high pH DI water resulted in precipitation within 1 day, so synthetic solutions were prepared to ensure that all blends had less than 20% of the synthetic solution. Aliquots of high pH synthetic solution (2.5 g/l Al, 250 g/l NaCl, and 5 g/l humic acid) were added to Well 7 groundwater held in plastic vials in quantities according to the desired blend. Each vial was shaken for 10 seconds after the blending, and each sample was examined visually to determine whether precipitation occurred instantaneously, within 2 hours, or within 1 day.

Supernatant samples were collected from all samples that had visible precipitation within 1 day. The blends were then diluted with 1 M NaOH to redissolve the solids, and samples were

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collected. The samples were prepared and analyzed using ICP-MS. The difference in Si and Al concentrations between the supernatant samples and the total sample was interpreted as the Si and Al concentrations in the solids that formed within the one day incubation period.

3.6 Analytical Methods

3.6.1 ICP-MS

Due to the high concentration of matrix elements present in groundwater samples, a method that accounted for matrix effects was developed. This method developed by Pandya (2015) allowed minimizing problems with instrument sensitivity and other performance parameters. This method utilized standards with concentrations ranging from 10 to 50 ppm Si and Ca and 10 to 100 ppb for other analytes, including Al, as well as a blank. To circumvent matrix effects, all groundwater samples were diluted by at least 800x, and all samples and standards were spiked with an internal standard. Previous ICP-MS runs indicated that Well 7 groundwater has significant background concentrations of all recommended internal standards aside from Ge, so Ge (74) was chosen as the internal standard. All samples and standards also included 1% HNO_3 and were filtered through a 0.45-µm PES filter to avoid potential clogging of the nebulizer units of the ICP-MS instrument.

The concentrations of analytes in samples were determined using conventional ICP-MS signal processing that quantifies intensity of each ion counts. A calibration curve for each analyte was developed by plotting net ion count intensity versus known standard concentration. The concentration of the analyte was calculated by taking the difference between the net intensity measured for the sample and the net intensity of the associated standard blank. This difference was then divided by the slope of the associated calibration curve and finally multiplied by the dilution factor applied in sample preparation to determine sample concentration.

3.6.2 TOC

A Sievers 900 Portable Total Organic Carbon TOC Analyzer (General Electric) was used to determine TOC concentrations. The analyzer had previously yielded reasonable results for

TOC concentrations below 10 ppm. Therefore, standards with TOC concentrations ranging from 3 to 10 ppm were prepared using a 1000 ppm TOC standard. The background TOC concentration in Well 82-30 groundwater used in the dissolution experiments was expected to be high, so samples were diluted by 40x to ensure that sample concentrations remained below 10 ppm. The total inorganic carbon (TIC) concentration was also expected to be high and possibly interfere with TOC measurements. To avoid this effect, all samples were initially acidified to pH < 4 with 1 *M* HCl and then aerated for 10 minutes to remove all dissolved CO_2. Samples were then filtered through a 0.45-μm PES filter and transferred to glass vials for analysis.

4 Results and Discussion

This research was performed to better understand the effect of high pH, high Si groundwater on hydraulic conductivity of OCC soil under various conditions. Initially, the groundwater and soil were characterized to identify what unique factors may cause changes in hydraulic conductivity and guide further research. The factors identified may undergo chemical processes in-situ, which were explored through experiments investigating batch dissolution and precipitation of Si and Si-complexes. The batch experiments assisted in identifying factors that significantly alter dissolution and precipitation, and these parameters were then varied during column tests to determine their individual effects on hydraulic conductivity when high pH, high Si groundwater passes through OCC site soil. Though intrinsic differences exist between column tests, by comparing reproducible trends from multiple column tests, broad conclusions can be drawn. Results from column tests were used to address the overall research goal of potentially enabling long-term extraction of high pH, high Si groundwater at the OCC site.

4.1 Characterization of Groundwater and Soils Used

Groundwater with a pH below 9.5 has been successfully extracted for decades at the OCC site, but there have been challenges with the extraction of high pH, high Si groundwater. This may be due to the properties of high pH, high Si groundwater, soil in the immediate vicinity, or a combination of the two.

4.1.1 Groundwater

Extracting high pH, high Si groundwater from Well 7 has resulted in fouling of well screens in the past, so this groundwater was primarily used for batch and column experiments. However, at times it was necessary to use other sources of groundwater, which are summarized with their key parameters in Table 4-1.

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Table 4-1. Selected parameters of OCC groundwater used in this study

Groundwater	pH	Si (g/L)	Al (mg/L)	Ca (mg/L)	TIC (mg/L)[a]	TOC (mg/L)[a]
7	11.7	48	540	405	NA	783
83C-100	10.2	0.11	ND	16	102	83
83C-130	11.6	36	340	560	2150	549
82-30	11.6	3.5	2.2	49	1673	56
82-100	11.7	23	78	350	5298	226
46C-130	8.1	ND	ND	330	238	13

NA Not Available

[a] Analyzed by School of Forestry, UW

Well 7 groundwater has the highest Si concentration of the groundwater used, followed by Wells 83C-130 and 82-100. These groundwater sources are therefore referred to as most 'affected' by the high pH plume, which caused extreme dissolution of Si. On the other hand, Well 46C-130 has a circumneutral pH and a Si concentration below detectable limits, so this groundwater is assumed to be relatively 'unaffected' by the high pH plume. The elevated pH and Si concentration in Wells 7, 83C-130 and 82-100 also correspond with relatively high Al and TOC concentrations. The visual appearances of all groundwater used are shown in Figure 4-1, where the groundwater sources that are more 'affected' by the high pH plume are darker due to their relatively high TOC concentrations.

Figure 4-1. Visual appearances of OCC site groundwater used in this study.

4.1.2 Soils

Soils from the OCC site were used to perform batch dissolution experiments and column tests in order to analyze the effect of groundwater on hydraulic conductivity. Soil 'unaffected' by the high pH plume, Well 46 at a depth of 47 ft, and soils 'affected' by the high pH plume, Well 83 at depths of 103 ft and 128 ft, were chosen for these tests. The pH measured in the field (previously reported in the *Methods and Materials* section) and porosity of the soils are presented in Table 4-2.

Table 4-2. Porosity and pH of OCC site solids/pore water used in this study.

Solids/Pore Water	pH[a]	Porosity
83C-128	10.3[b]	28.9%
83C-103	9.1[b]	30.2%
46C-47	8.5	31.8%

[a] Data collected in the field upon extraction of groundwater.

[b] Value measured in the lab would likely be higher.

4.1.3 Discussion of the Characterization of Groundwater and Soils Used

The composition of Well 7 groundwater, which is indicative of the most 'affected' groundwater, was used to run a simulation in Visual Minteq, a chemical equilibrium model. The model determined that 99.9% of Al and 99.8% of Si should precipitate from Well 7 groundwater at equilibrium at 20°C. It is possible that these supersaturated analytes remain in solution because TOC was not included in the input and the model only considers monomeric Si. The complexation of Si and Al with TOC, which is relatively high in Well 7 groundwater, as well as the formation of aluminosilicates, can increase the solubility of Al and Si. The relatively high Al and Si concentrations in Well 7 groundwater may contribute to changes in hydraulic conductivity of OCC site soil, so further research was conducted to better understand processes and factors that may control their individual or combined effects.

4.2 Batch Dissolution and Precipitation of Silica

Batch dissolution and precipitation experiments were performed to determine whether these chemical processes may significantly contribute to changes in hydraulic conductivity at the OCC site.

4.2.1 Batch Dissolution of Silica

Two batch dissolution experiments were conducted to better understand how Si, Al, and TOC concentrations became so high in 'affected' groundwater. The OCC facility historically released caustic materials into the subsurface, which increased the pH of the groundwater. Therefore, in the first batch dissolution experiment, soils from the OCC site were incubated with 1 *M* NaOH at 55°C to model an extreme historic scenario. In the second experiment, the same media were incubated with Well 82-30 groundwater, which has a high pH yet relatively low Si, Al and TOC concentrations, at 25°C, 35°C, and 55°C. Supernatant samples were taken from all samples at various intervals, usually weekly, for analysis.

The first batch experiment was conducted by incubating 1 *M* NaOH (pH 13.8) with two OCC site soils and sand as a model reference at 55°C. The OCC soils included 'unaffected' soil from Well 46C-47 and 'affected' soil from Well 83C-128. Dissolution of the three media types visually appeared to have occurred within one week of incubation based on the color of the supernatant and the formation of a second, lighter solid phase (Figure 4-2). ICP-MS analyses of supernatant samples determined that there was a significant release of Si from OCC site soils over time, with more dissolution occurring from 'affected' Well 83C-128 soil than 'unaffected' Well 46C-47 soil and insignificant dissolution from sand (Figure 4-3). Al also dissolved significantly from OCC soils within three days of incubation. However, after this initial spike, Al concentrations significantly decreased in all samples after two weeks of incubation (Figure 4-4).
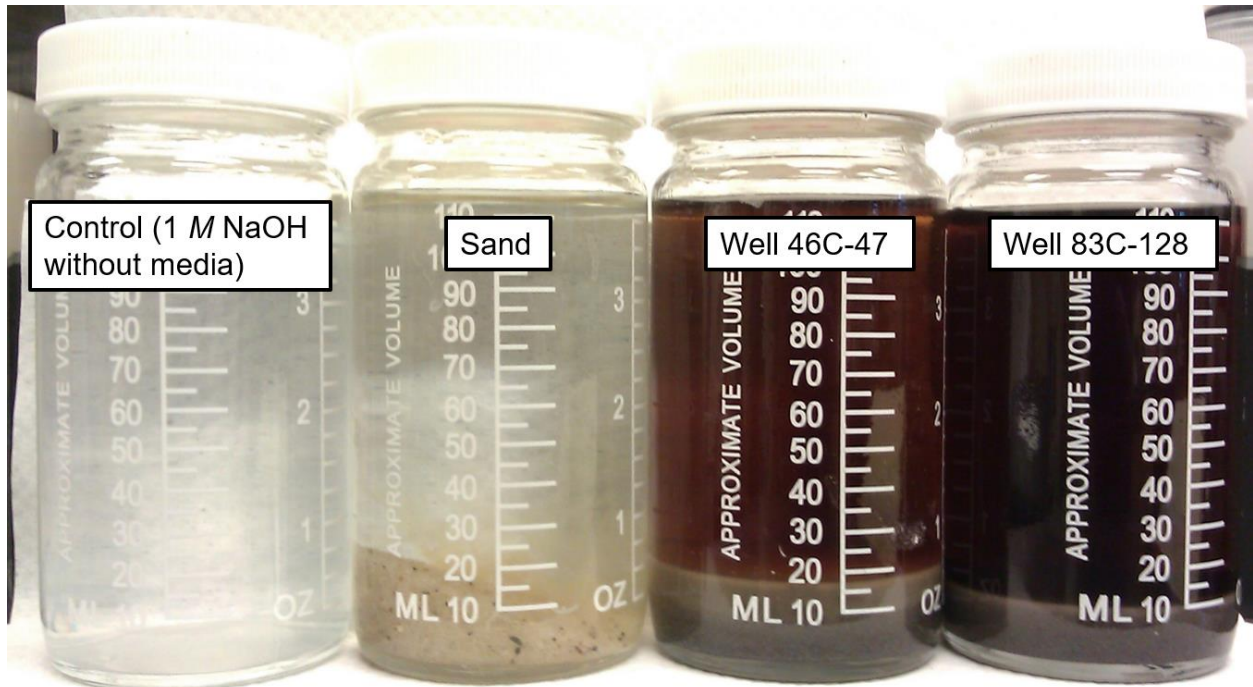
Figure 4-2. Visual appearances of samples in contact with 1 M NaOH at 55°C after one week of incubation.
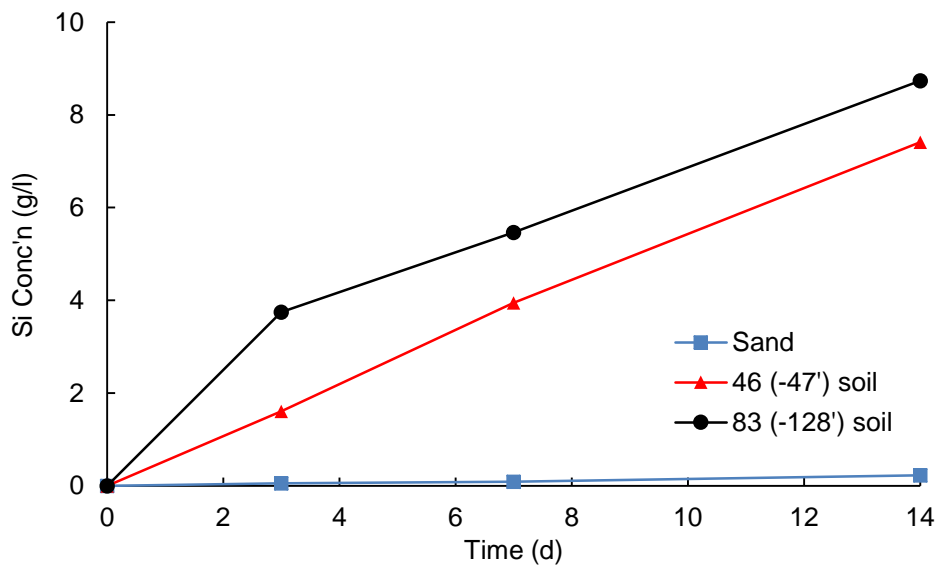
Figure 4-3. Si dissolution from sand, Well 46C-47, and Well 83C-128 in contact with 1 M NaOH incubated at 55°C.
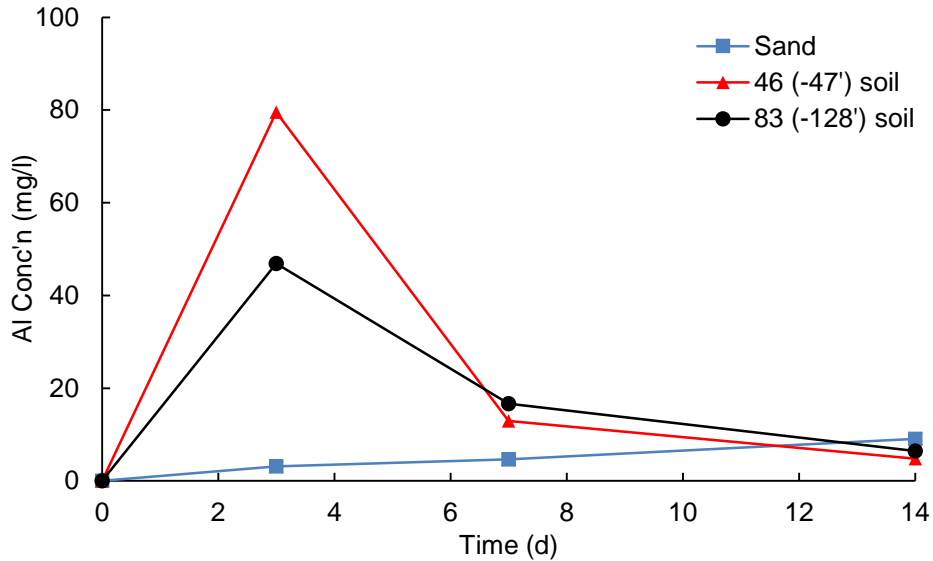
Figure 4-4. Al dissolution from sand, Well 46C-47, and Well 83C-128 in contact with 1 M NaOH incubated at 55°C.

The second batch dissolution experiment was conducted by incubating the same media used in the previous dissolution experiment in Well 82-30 groundwater at various temperatures. Well 82-30 groundwater from the OCC site was used to determine whether dissolution processes are continuing in the subsurface and may potentially alter hydraulic conductivity. Similar to the previous dissolution experiment, it was evident within one week of incubation that release of Al and Si from OCC site soils was occurring simultaneously with changes of the color of the supernatant (Figure 4-5). This color change was presumed to be associated with the dissolution of organic matter from the soils, so DOC was analyzed in samples incubated for one week and four weeks. DOC was released from OCC soils over time, with more DOC dissolution occurring from 'affected' Well 83C-128 soil than 'unaffected' Well 46C-47 soil and with increasing incubation temperature (Figure 4-6). Si did not significantly dissolve from sand or Well 46C-47 soil, and there was solely an immediate release of approximately 1.5 g/l Si from Well 83C-128 soil. Some Al dissolved from OCC soils, with more dissolving from 'affected' Well 83C-128 soil than from 'unaffected' Well 46C-47 soil, and none dissolving from sand (Figure 4-7, Figure 4-8).

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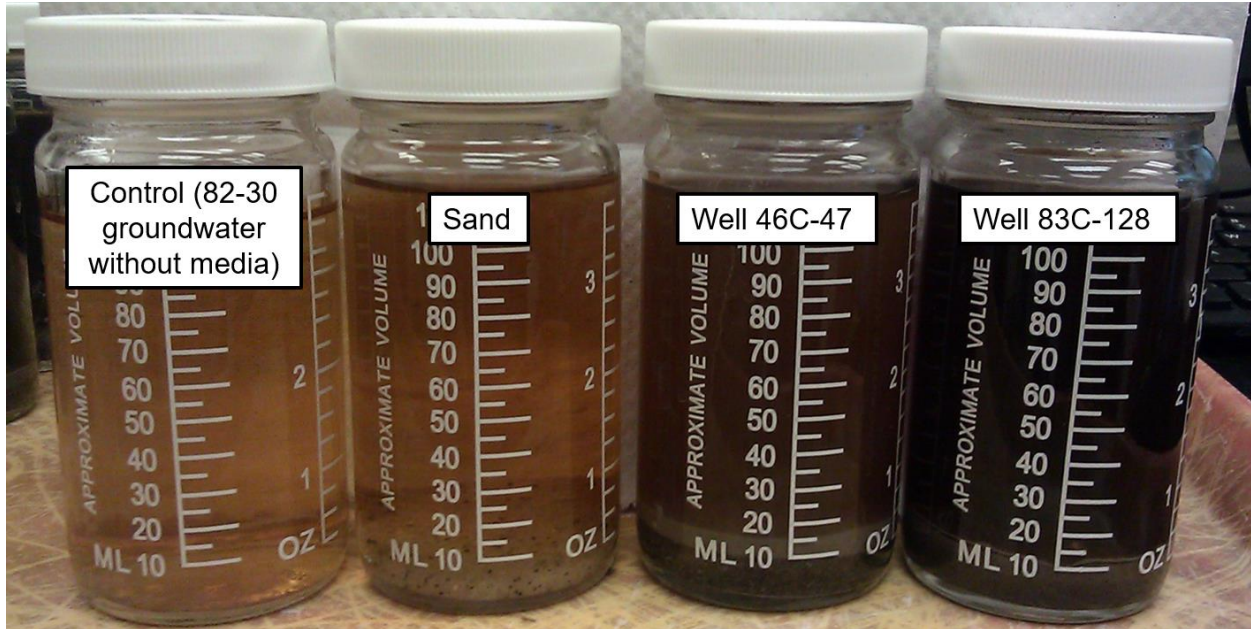
Figure 4-5. Visual appearances of samples in contact with Well 82-30 groundwater at 55°C after one week of incubation.
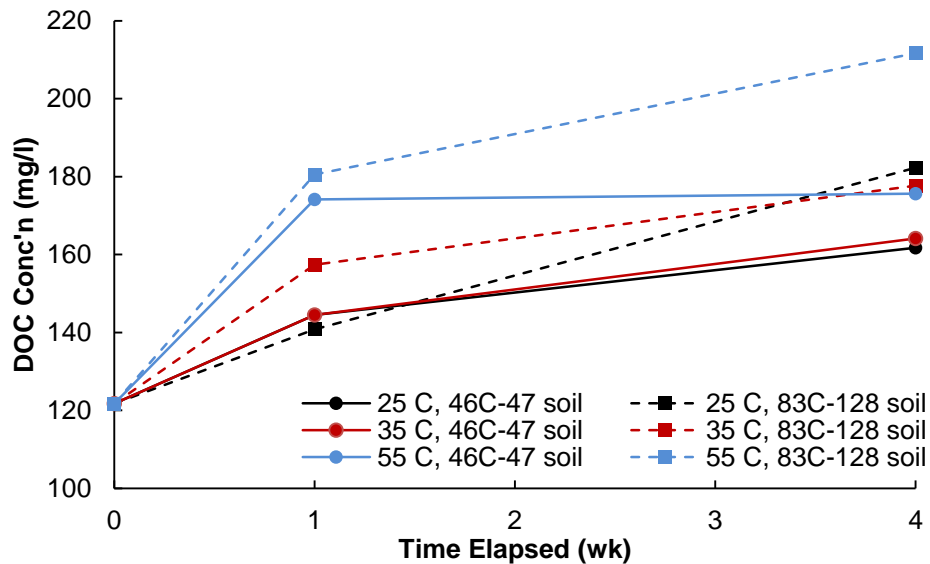
Figure 4-6. DOC release from Well 46C-47 and Well 83C-128 soils in contact with Well 82-30 groundwater and incubated at various temperatures.
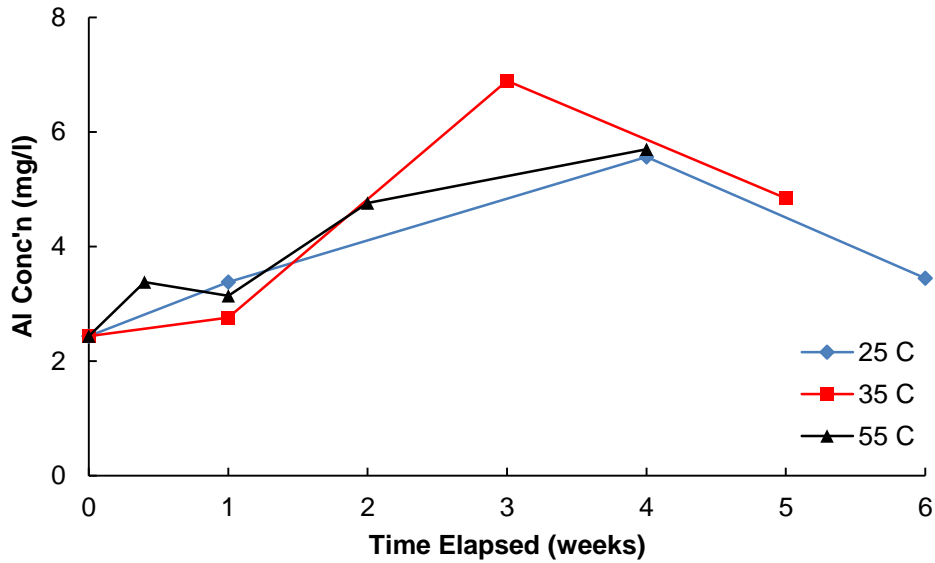
Figure 4-7. Al dissolution over time from Well 46C-47 soil in contact with Well 82-30 groundwater incubated at various temperatures.
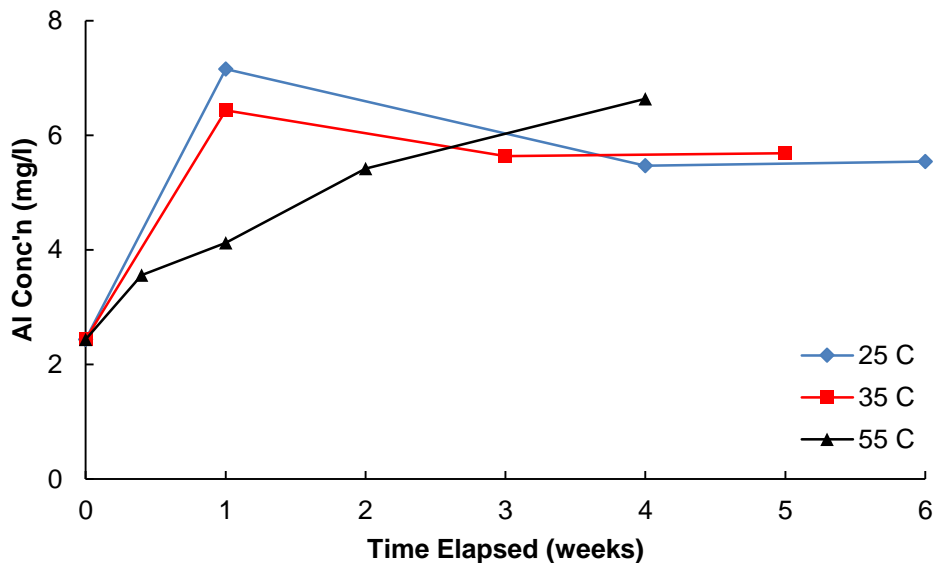
Figure 4-8. Al dissolution over time from Well 83C-128 soil in contact with Well 82-30 groundwater incubated at various temperatures.

4.2.2 Discussion of Batch Dissolution of Silica

The first batch dissolution experiment (1 *M* NaOH incubated with OCC site soils at 55°C)

assisted in better understanding how the Si, Al, and TOC concentrations became so high in

some OCC site groundwater. Significant Si concentrations were released from OCC site soil,

and more so from soil 'affected' by the high pH plume than soil 'unaffected' by the plume, when

exposed to a solution with an elevated pH and temperature. The 'affected' soil may undergo

enhanced Si dissolution due to specific properties of the soil (e.g., changes of intrinsic properties of its solids due to their long-term interactions with hydroxyl ions), possible enhancement of metal release caused by or associated with TOC co-release, or its previous exposure to groundwater containing high levels of Si. Therefore, it is anticipated that if the high pH plume migrates through this 'unaffected' soil at an elevated temperature, less Si, though still a significant amount, will dissolve. The TOC dissolution that occurs simultaneously with that of the other elements of interest for this study will likely aid in keeping elevated Si concentrations dissolved in the groundwater. The heightened Al concentrations in high pH, high Si groundwater are also a result of exposure to a solution with an elevated pH and temperature. However, the reason for the non-monotonic behavior of dissolved Al is unknown, though Al may have dissolved and then precipitated with Si to form a secondary lighter solid phase that was observed one week after incubation. The cause of this outcome may help to explain the role of Al in controlling Si release and precipitation.

The second batch dissolution experiment (Well 82-30 groundwater incubated with OCC soils at 25°C, 35°C, and 55°C) indicated that dissolution of Si and Al is currently not significant in the subsurface at the OCC site. Al and TOC dissolution was more prominent at 55°C than at lower temperatures. The measured temperature of groundwater at the site is below 25°C. Dissolution of Si, Al, and TOC from samples incubated at 25°C was much lower than that at higher temperatures, so the current rate of dissolution of these constituents is probably far lower than from the initial release of extremely caustic solutions at elevated temperatures. Therefore, this chemical dissolution of the soils in the area of initial releases of chlor-alkali effluents is not likely to significantly alter hydraulic conductivity of OCC site soil at present.

4.2.3 Batch Precipitation of Silica

Batch precipitation experiments were performed to identify what factors may induce in-situ precipitation of Si and potentially alter hydraulic conductivity of OCC soil. Well 7 groundwater

was largely used for these experiments because this groundwater has the highest Si, Al and TOC concentrations and has caused difficulties with extraction. In some experiments, additional groundwater sources were blended at various ratios. Precipitation was observed visually, and if precipitation occurred within one day after mixing, supernatant samples were extracted for subsequent analysis. The composition of the supernatant samples was used to infer the composition of the precipitates formed.

4.2.3.1 Acid Addition

Initially the pH of Well 7 groundwater was lowered with 12 *M* HCl to provide a baseline for Si precipitation. If the acid was added relatively quickly, Si precipitated instantly and formed a voluminous gel that prevented further stirring of the groundwater. Therefore, acid was added extremely slowly, in which case the small flocs that formed allowed further stirring (Figure 4-9). Acid was added until the pH of Well 7 groundwater was 9.7, at which point essentially all of the dissolved Si had precipitated. Supernatant samples were taken at various increments when the pH was lowered, and ICP-MS analysis indicated that all the Al and Ca in Well 7 groundwater also precipitated. Minimal amounts of Al, Ca, and Si precipitated until the pH was lowered below 11. Relationships between pH and the log concentrations of Al, Ca, and Si for pH <11 are shown in Figure 4-10. The precipitates formed at pH 9.7 were made up of 96.5% Si, 1.6% Al, and 1.9% Ca by mass, assuming these were the only metals in the precipitate.
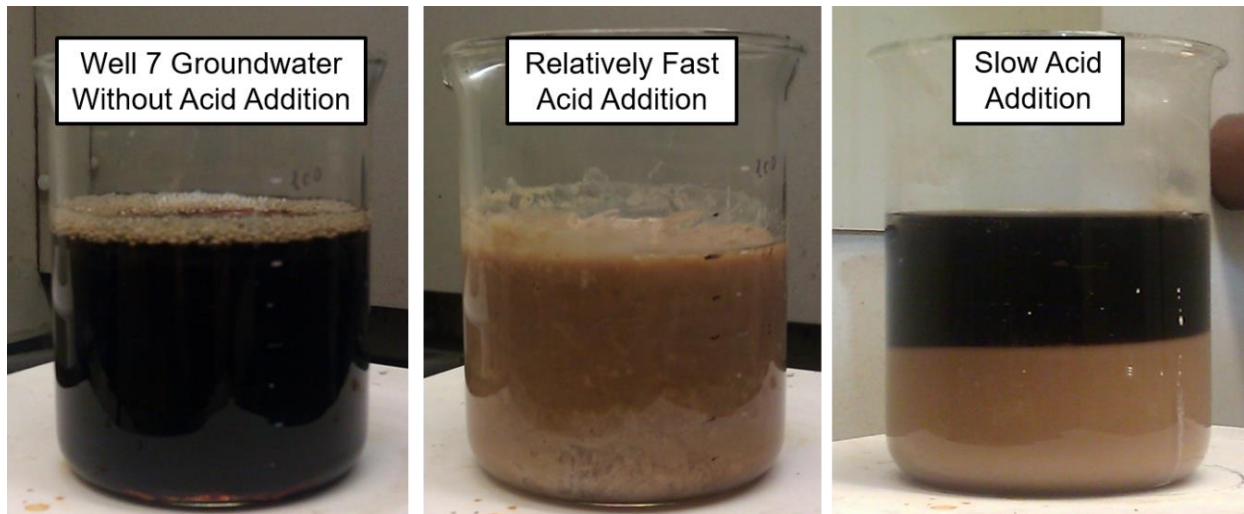
Figure 4-9. Precipitation of Si from Well 7 groundwater from relatively fast and slow acid additions.
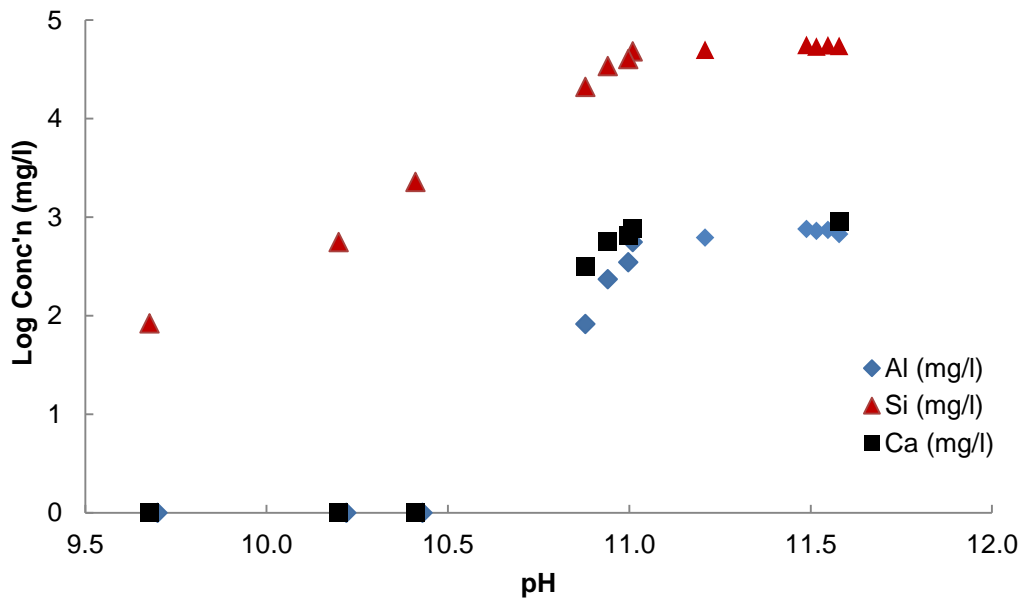
Figure 4-10. Log-scale representation of changes of concentrations of Al, Si, and Ca in Well 7 groundwater as a function of pH.

4.2.3.2   Dilution

The effect of dilution on precipitation of Si from Well 7 groundwater was explored by diluting the groundwater with high pH DI water (pH 12.5). Well 7 groundwater was diluted with this high pH DI water at 10% increments by volume from 50% to 90% Well 7 groundwater. Precipitation did not occur within the first couple of hours after mixing but was visually observed in 50% to 70% Well 7 groundwater samples within one day. Precipitation did not occur in samples composed of

80% and 90% Well 7 groundwater. It is possible that an unidentified constituent present in Well 7 groundwater or slow formation of nucleation/precipitation active centers kept supersaturated Si and Al in solution, and dilution of this constituent by more than 20% resulted in precipitation. The precipitates formed in these conditions appeared to be small flocs and did not resemble the voluminous precipitate formed from lowering the pH of Well 7 groundwater. The precipitates in the various DI/Well 7 groundwater blends were largely made up of Si with trace amounts of Al and Ca. The mass fraction of Si in the major metals in the solids decreased while the fraction of Al increased with increasing dilution of Well 7 groundwater (Table 4-3).

Table 4-3. Mass fractions of Si, Al, and Ca in the major metals solids precipitated from diluting Well 7 groundwater with high pH DI water.

Blend	Mass Distribution of Metals in Solids		
	Si	Al	Ca
70% 7/30% DI	97.4%	1.2%	1.4%
60% 7/40% DI	96.5%	2.1%	1.4%
50% 7/50% DI	95.2%	3.4%	1.4%

Well 7 groundwater was also diluted by 'Si-free' Well 7 groundwater, prepared by slowly lowering the pH of the groundwater to 9.7 and then increasing the pH of the filtered supernatant to the initial pH, 11.7. Diluting raw Well 7 groundwater with 'Si-free' Well 7 groundwater at dilutions ranging from 0 to 100% did not result in precipitation within one day. Therefore, it is likely that the constituent keeping supersaturated concentrations of Si and Al in solution does not co-precipitate with these analytes.

4.2.3.3 Increasing Constituent Concentrations

The next experiments were conducted to identify the effects of increasing the concentrations of Al, TOC, and Na, in Well 7 groundwater. Because dilution of Well 7 groundwater by more than 20% results in precipitation, these batch experiments were performed at dilutions of less than

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20%. All synthetic solutions that were blended with Well 7 groundwater had a pH at or above 11.7 to ensure that changes in pH of the bulk solution were not responsible for inducing precipitation.

Well 7 groundwater was blended with a synthetic solution to determine the concentration of Al in Well 7 groundwater that causes precipitation. The 2.5 g/l Al solution was made by adding $AlCl_3*H_2O$ to DI water and increasing the pH to 12.6 with 1 M NaOH. Well 7 groundwater was mixed with the Al solution to yield samples with total Al concentrations of 695 mg/l, 790 mg/l, and 980 mg/l. There was visible precipitation within 10 minutes in the sample with 980 mg/l Al, and precipitation was observed in the 695 mg/l and 790 mg/l Al samples within one day. Thus, the addition of Al results in precipitation in Well 7 groundwater, and lower Al concentrations delay or decrease the rate of precipitation. The precipitates in these samples were hydrogels that comprised a majority of the sample volume. The mass fraction of Si in the major metals in the solids increased while the fraction of Al decreased with decreasing bulk Al concentration (Table 4-4).

The TOC concentration in Well 7 groundwater was increased by blending a TOC solution with Well 7 groundwater. The 2.5 g/l TOC solution adjusted to pH 12.1 was made by adding humic acid (assumed be 50% C) to DI water and increasing the pH with 1 M NaOH. The TOC solution and Well 7 groundwater were blended to yield samples with the following TOC concentrations: 0.87 g/l, 0.95 g/l, and 1.12 g/l. No precipitation was observed in the 0.87 g/l TOC sample, though small, flakey precipitates formed in samples with 0.95 g/l and 1.12 g/l TOC. The mass fractions of major metals in the solids formed in both the 0.95 g/l and 1.12 g/l TOC blends were similar to those determined for solids precipitated when acid was added to Well 7 groundwater (Table 4-4).

The effect of increasing the Na concentration of Well 7 groundwater was investigated by adding NaCl to the groundwater. Blends with a total Na concentration below 200 g/l did not result in

precipitation, though there was visible precipitation within one day in the sample with 250 g/l Na. The mass fractions of the major metals in the solids were similar to those in the TOC blends and from acid addition (Table 4-4).

Table 4-4. Mass fractions of Si, Al, and Ca in the major metals in solids precipitated from increasing constituent concentrations in Well 7 groundwater.

Blend	Mass Distribution of Metals in Solids		
	Si	Al	Ca
980 mg/l Al	87.7%	10.4%	1.8%
790 mg/l Al	93.0%	5.1%	1.9%
700 mg/l Al	97.8%	0.5%	1.7%
950 mg/l TOC	97.5%	1.1%	1.4%
1.1 g/l TOC	97.7%	1.0%	1.3%
250 g/l NaCl	96.9%	1.9%	1.2%

4.2.3.4 Blending OCC Site Groundwater

Precipitation may occur in-situ from the blending of different OCC site groundwaters, potentially affecting hydraulic conductivity of soil as a result. Therefore, batch precipitation experiments were conducted to identify the blending ratios of different OCC site groundwaters that induce precipitation. These results were also necessary to identify blended groundwater ratios that do not induce rapid precipitation for subsequent use of blends as feed for column tests.

An extreme case of blending groundwater at the OCC site was simulated by blending 'affected' Well 7 groundwater with 'unaffected' Well 46C-130 groundwater. Blends in which Well 7 groundwater was diluted by more than 5% with Well 46C-130 groundwater resulted in relatively rapid precipitation. Though blends ranging from 90% Well 7/10% 46C-130 to 50% Well 7/50% 46C-130 did not have a bulk pH below 11.7, precipitation still occurred likely due to localized pH changes from the addition of Well 46C-130 groundwater, which has a circumneutral pH. The compositions of the solids in all Well 7/46C-130 blends with visible precipitation were similar to

those determined for solids precipitated when acid was added to Well 7 groundwater (Table 4-5).

More plausible blends of groundwater that may be induced from pumping at the OCC site include Well 7 groundwater with Well 83C-100 groundwater, and Well 83C-100 groundwater with Well 82-100 groundwater. The extraction of Well 7 groundwater would likely cause vertical mixing with groundwater from above, for example Well 83C-100 groundwater. A blend with 75% Well 7/25% 83C-100 did not result in precipitation within one day, though precipitation occurred within one day for blends with 50% Well 7/50% 83C-100 and 25% Well 7/75% 83C-100. The bulk pH of the blends in which precipitation occurred was not lowered below 11.7, so precipitation may have been caused by the dilution of a constituent in Well 7 groundwater by more than 20%. The composition of the solids formed was similar to those for the Well 7/46C-130 blends (Table 4-5). Furthermore, Well 83C-100 groundwater needs to be extracted because it is highly contaminated with VOCs, and extraction of this groundwater will likely cause horizontal mixing with groundwater from Well 82-100. Blends with 90% 83C-100/10% 82-100 and 75% 83C-100/25% 82-100 resulted in precipitation within one day, though no precipitation was observed in a blend with 50% 83C-100/50% 82-100. Precipitation was likely induced in these samples by the lowering of bulk pH by 0.2 to 0.6 units. However, the solids had significantly less Si and more Ca than were present in solids generated by lowering the pH of Well 7 groundwater (Table 4-5).

Table 4-5. Mass fractions of Si, Al, and Ca in the major metals in the solids precipitated from blending OCC site groundwater.

Blend	Mass Distribution of Metals in Solids		
	Si	Al	Ca
90% 83-100/10% 82-100	85.9%	0.4%	13.7%
75% 83-100/25% 82-100	91.8%	0.0%	8.2%
90% 7/10% 46-130	95.4%	2.0%	2.7%
75% 7/25% 46-130	95.0%	2.4%	2.6%
50% 7/50% 46-130	94.5%	2.2%	3.3%
50% 7/50% 83-100	95.6%	2.2%	2.2%
25% 7/75% 83-100	94.4%	2.5%	3.1%

4.2.4 Discussion of Batch Precipitation of Silica

An extremely high concentration of Si is present in Well 7 groundwater, and precipitation of Si in-situ will likely lower hydraulic conductivity of OCC site soil. Precipitation of Si-based solids from Well 7 groundwater was affected by pH, rate of mixing/addition, dilution of Well 7 groundwater, and concentrations of constituents in the groundwater (Figure 4-11). The rate of precipitation and appearance of the solids formed also depend on these factors.

The specific compound(s) in Well 7 groundwater that keep relatively high Si and Al concentrations in solution are yet to be identified. However, the dilution of these unknown constituents by more than 20% results in precipitation within one day. The constituents do not co-precipitate out with Si.

Increasing Al, Na, and TOC concentrations in Well 7 groundwater results in precipitation. Precipitation induced by increasing Na above 200 g/l may be due to increasing ionic strength, though it is highly unlikely that the Na concentration in Well 7 groundwater will naturally exceed this concentration. Increasing the Al concentration also results in precipitation, which may be due to competition with Si for sites to bind with an unidentified constituent, supersaturation of Al, and/or formation of mixed Si/Al solid phases. On the other hand, the occurrence of precipitation

as a result of at increasing TOC concentrations may indicate that humic acid is not necessarily a major component in increasing Si and Al solubility in Well 7 groundwater. Increasing the concentration of humic acid may cause precipitation due to increasing ionic strength.

Blending OCC site groundwaters in certain ratios also induces precipitation. In some blends, such as Well 7/Well 46C-130 blends, precipitation might have been induced by localized lowering of pH. Though the bulk pH of Well 7/Well 83C-100 blends was not below the initial pH of Well 7 groundwater, precipitation occurred in some samples likely due to dilution of Well 7 groundwater by more than 20%. More gradual blending than what was tested in these experiments will likely occur in the field. This blending will be enhanced by extraction of contaminated groundwater which may result in localized precipitation.
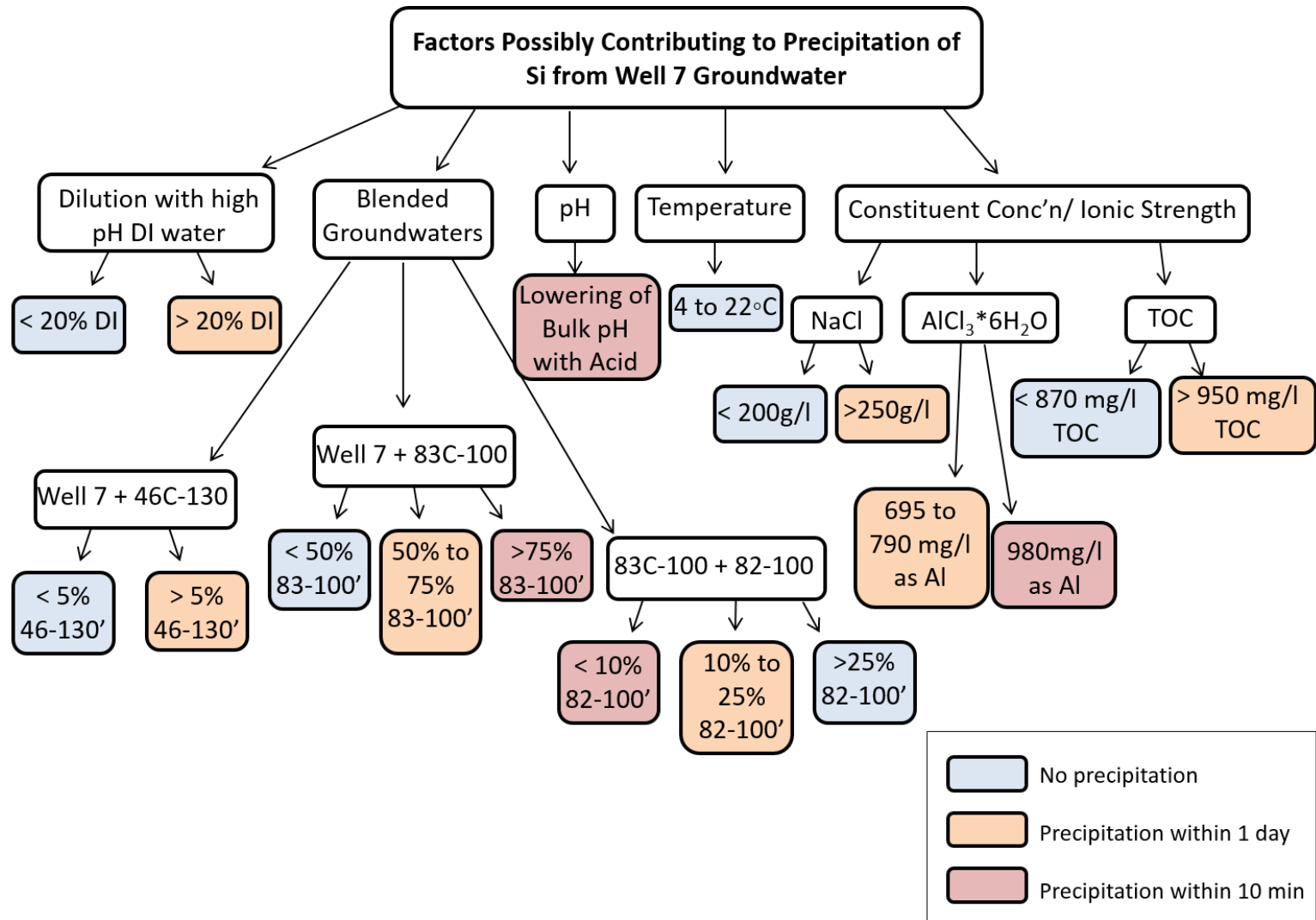
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Figure 4-11. Flow chart describing the occurrence and rate of precipitation of Si from Well 7 groundwater.

The precipitates formed from in-situ precipitation will alter hydraulic conductivity of soil to different degrees; more voluminous solids are expected to lower hydraulic conductivity more than less voluminous ones, other factors being equal. Si made up by far the largest mass fraction of major metals in all precipitates formed because the initial concentration was so high relative to Al and Ca concentrations. A majority of the precipitates have compositions similar to those formed from acid addition, though the appearance of these precipitates varied. Specifically, precipitates formed by additions of high pH DI water, TOC, and NaCl formed smaller flocs over a longer period of time than what was observed with fast and slow acid addition.

Based on the occurrence and rate of precipitation in these experiments, variations in chemical composition of Well 7 groundwater and blending of OCC site groundwater may plug soil due to formation of precipitates. Though lowering the pH of Well 7 groundwater with acid causes massive and instantaneous precipitation, this scenario is not necessarily likely to occur unless acid is injected into the subsurface. The pH of Well 7 groundwater may be lowered naturally in-situ due to blending with less contaminated groundwater, yet this would likely occur very gradually due to the relatively high alkalinity of Well 7 groundwater. Dilution of Well 7 groundwater by more than 20% also results in precipitation, yet dilution is likely to be more gradual and the rate of precipitation is slow. Therefore, factors that may potentially alter hydraulic conductivity of OCC site soil due to formation of solids, including the chemical composition of Well 7 groundwater and blending groundwater, were further explored using column tests.

4.3   Factors Affecting Hydraulic Conductivity

Column tests were performed to identify factors that affect hydraulic conductivity as a result of passing high pH, high Si groundwater through OCC site soil. Tests explored the effects of Darcy velocity, feed composition, column media, and groundwater blends on hydraulic resistance of

the soil. A baseline Darcy velocity of ≈7.1 ft/d (average linear velocity 23 ft/d) was chosen for early tests, and velocities over an order of magnitude higher were also investigated. A Darcy velocity of ≈47.2 ft/d corresponds to the extraction of ≈10,000 gallons per day (gpd) from a well with a 3 ft diameter and 10 ft screen height.

4.3.1   Column Test Reproducibility

Column experiments were subject to unavoidable variabilities due to several factors, including the heterogeneous nature of the soil, the age of soil and groundwater collected from the OCC site, and the use of complex solutions that required modified analytical procedures with reduced accuracy and precision. However, attempts to perform reasonably reproducible column tests were made by using a benign solution at the beginning of all tests and the use of a Br^- tracer to assess potential hydraulic short circuiting in initial tests.

Trans-column pressure was the key parameter measured in tests because it is inversely proportional to hydraulic conductivity of the column media. Hydraulic conductivity is related to the ratio of the pressure drop across the column to the Darcy velocity; an increase in this ratio corresponds to a decrease in hydraulic conductivity. The trans-column pressure readings detailed herein are representative solely of the hydraulic resistance across the column itself; these readings do not include the frictional losses and elevation head associated with the column test set-up. (The frictional losses for each test were calculated using a relationship between these losses and Darcy velocity, which is shown in Appendix A: Figure 7-1.)

In all tests, a benign solution, which is operationally defined as a solution with approximately the same pH and density as those of the subsequent feed, was injected for at least thirty minutes to establish a baseline trans-column pressure. The benign solution contained enough NaCl (4.3 M) and NaOH to adjust the density and pH of DI water to be similar to values in Well 7 groundwater (1.15 g/cm^3 and 11.7, respectively). A moderate correlation existed between trans-column pressure and Darcy velocity for injection of a benign solution into OCC site soil (R^2=0.670)

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(Appendix A: Figure 7-2). This relationship indicates that soil packing was reasonably reproducible amongst column tests but inherent differences existed. The effect of various system parameters on hydraulic conductivity was determined by comparing the trans-column pressure readings from the benign solution with those from the subsequent feed. Trends from tests examining specific system parameters were examined by conducting similar tests numerous times.

A Br⁻ tracer was used in initial tests to assess hydraulic short circuiting. A Br⁻ solution was injected as a step input into a column packed with OCC site soil, and effluent Br⁻ readings were used to develop an exit age distribution for a given test (Appendix A: Figure 7-3). The actual HRT was also calculated and compared with the theoretical HRT. These initial tests indicated that the difference between actual and theoretical HRTs was typically <10%, and the standard deviation about the mean residence time was commonly between 5 and 15% of the actual HRT. Therefore, though the column was determined not to be an ideal plug flow reactor, tracer tests indicated that the hydraulic short circuiting in the column was minimal.

4.3.2   Darcy Velocity

A major factor that affects the hydraulic conductivity of OCC site soil was determined to be Darcy velocity. The effects of Darcy velocity alone are discussed here, while combined effects of Darcy velocity with other system parameters are described in later sections.

In numerous column tests, Well 7 groundwater did not plug the OCC site soil at relatively low Darcy velocities, but it did so over time at relatively high Darcy velocities. The threshold for plugging by Well 7 groundwater is dependent on soil media (discussed in greater detail in the *Specific Soil Interactions* subsection), and for 'unaffected' Well 46C-47 soil, trans-column pressure was low and stable over time at a Darcy velocity of ≈7 ft/d. However, trans-column pressure increased within hours when Well 7 groundwater was injected into this soil at a Darcy velocity of ≈28 ft/d.

The column tests described above lasted a fixed amount of time, so the number of bed volumes of water injected increased with increasing Darcy velocity. Therefore, additional tests were conducted and compared after equal numbers of bed volumes had been exposed, rather than after equal elapsed time. In these tests, Well 7 groundwater was injected into Well 46C-47 soil for approximately 20 bed volumes at two different Darcy velocities—7 ft/d and 28 ft/d. Only the test at a Darcy velocity of 28 ft/d resulted in decreased hydraulic conductivity over time (Figure 4-12). Therefore, Darcy velocity, rather than the number of bed volumes exposed, affects hydraulic conductivity of OCC site soil.
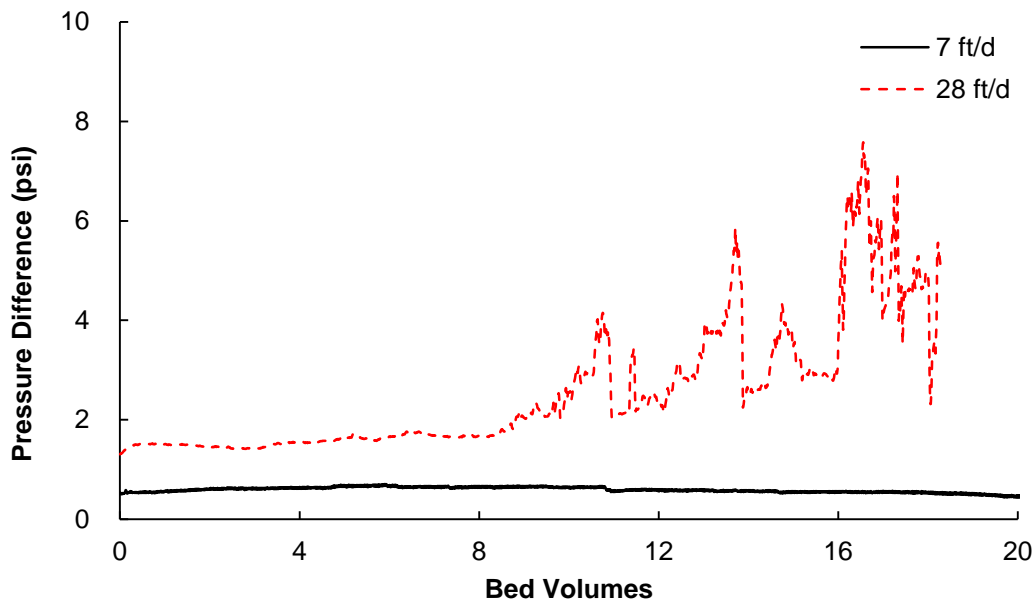

Figure 4-12. Pressure drop across column as a function of bed volumes for two tests, one conducted at a Darcy velocity of 7 ft/d and the other at 28 ft/d, when Well 7 groundwater is injected into Well 46C-47 soil.

To confirm that the plugging of the soil was caused by constituents in Well 7 groundwater and not solely the Darcy velocity, tests at a similar Darcy velocity were conducted with a benign solution as feed. In these tests, a benign solution (4.3 M NaCl adjusted to pH 11.7) and Well 7 groundwater were injected into a column packed with Well 46C-47 at a Darcy velocity of 28 ft/d in two separate tests, and sequentially in another test. The pressure across the column increased significantly within a few hours when the feed was Well 7 groundwater (Figure 4-13).

However, the pressure remained low and stable when the benign solution was injected in the separate test. In the test with sequential injections, the benign solution was first injected for six hours, followed by Well 7 groundwater for eight hours. No plugging occurred during injection of the benign solution, yet trans-column pressure began increasing within a few hours of Well 7 groundwater injection and continued throughout the remainder of the test (Figure 4-14). Therefore, these tests indicate that specific properties of Well 7 groundwater, excluding density, ionic strength and pH, cause plugging of OCC site soil when the water is injected at a relatively high Darcy velocity.
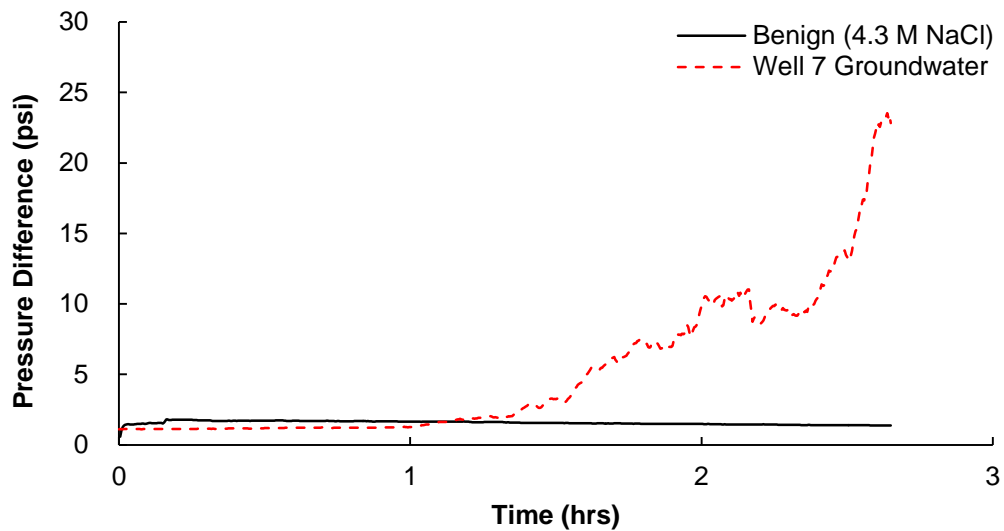

Figure 4-13. Pressure drop across the column as a function of feed injection into Well 46C-47 soil at a Darcy velocity of 28 ft/d.
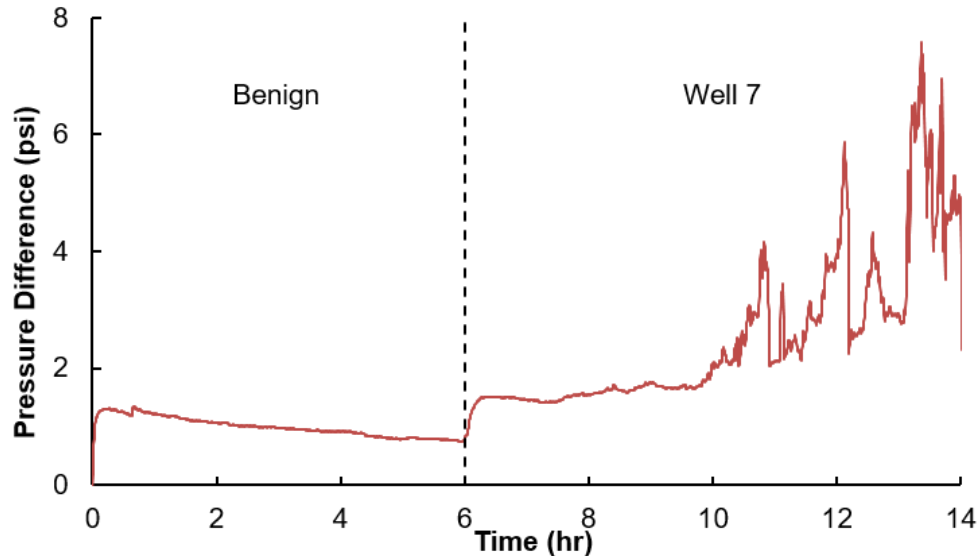
Figure 4-14. Pressure drop across the column when Well 7 groundwater is injected into Well 46C-47 soil at a Darcy velocity of 28 ft/d.

4.3.3 Discussion of Darcy Velocity

Early tests indicated that Well 7 groundwater plugs 'unaffected' OCC site soil when injected at a relatively high Darcy velocity (28 ft/d versus 7 ft/d). Though the onset and magnitude of plugging differed across column tests, the trend that trans-column pressure increases in response to Well 7 groundwater injection remains. This response is not related to bed volumes and is specific to the feed.

The dependence of hydraulic conductivity on Darcy velocity was an unexpected finding and has little precedence in technical literature. Darcy velocity may increase the rate of formation of Si-based solids but not the rate of dissolution. Regardless of the mechanism, this finding has important implications for the extraction of high pH, high Si groundwater at the OCC site. Additional column tests were therefore performed to better understand why this feed specifically plugs soil at relatively high Darcy velocities and what factors impact this response.

4.3.4 Constituents in Well 7 Groundwater

Column tests were conducted to identify key constituents in Well 7 groundwater that induced the change in hydraulic conductivity previously observed. Of the major constituents in Well 7 groundwater, Si was a likely candidate as a major contributor to plugging of the soil because it is

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virtually completely removed from Well 7 groundwater when the pH is lowered to <10, and the concentration of Si is magnitudes higher than other constituents in the groundwater. As was previously presented in *Batch Precipitation of Si* subsection, all of the Al in Well 7 groundwater also precipitates out with Si. The concentration of Al in Well 7 groundwater is relatively high, and Al is known to form complexes with Si, so this constituent was also considered to be a potential candidate. Therefore, the individual and combined effects of Si and Al on plugging of OCC site soil by Well 7 groundwater were explored in greater detail.

A column test was initially conducted to examine trans-column pressure in response to injection of an OCC site groundwater with relatively low Si and Al concentrations. Well 82-30 groundwater was used as the column feed because this groundwater has a similar pH to Well 7 groundwater (11.6) but Si and Al concentrations that are orders of magnitude lower than those in Well 7 groundwater (3.5 g/l and 2.2 mg/l, respectively). Well 82-30 groundwater was used as feed after injection of the benign solution, and these solutions were injected into Well 46C-47 soil at a Darcy velocity of 27 ft/d. The trans-column pressure increased immediately in response to injection of Well 82-30 groundwater yet then stabilized and did not continue to increase throughout the remainder of the test (Figure 4-15). The major differences in Si and Al in Wells 7 and 82-30 groundwater indicate that these constituents alone or together may contribute to plugging of OCC site soil at a relatively high Darcy velocity.
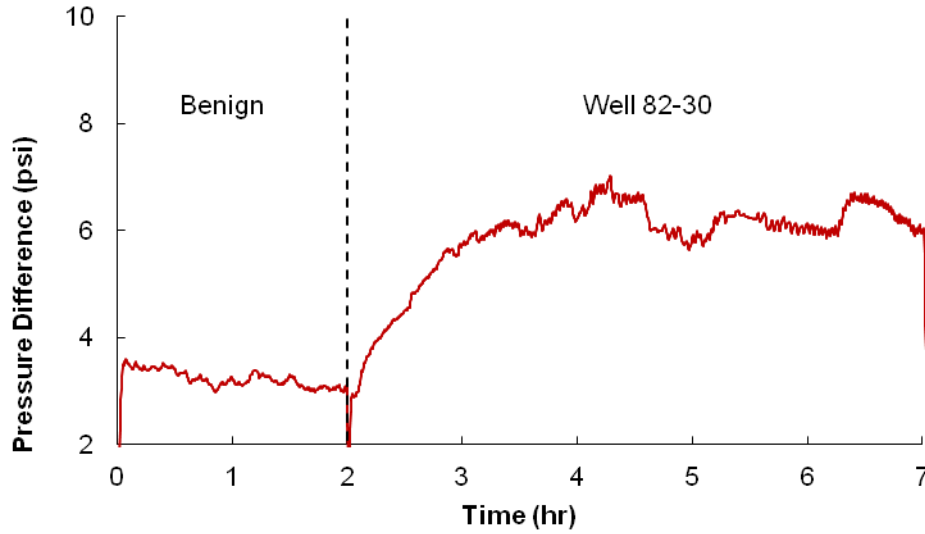
Figure 4-15. Pressure difference across the column when Well 82-30 groundwater was injected into Well 46C-47 at a Darcy velocity of 27 ft/d.

The combined effect of Si and Al from Well 7 groundwater was further explored by conducting a column test using unaltered Well 7 groundwater and 'Si-free' Well 7 groundwater. 'Si-free' Well 7 groundwater was prepared by lowering the pH of the groundwater <10, filtering out precipitated solids, and raising the pH back to ≈11.7. Therefore, 'Si-free' groundwater had approximately the same composition as unaltered Well 7 groundwater, except with major metals removed. The Darcy velocity and soil used in this column test were the same as those in the previous test, but the injection sequence of solutions was as follows: benign solution for two hours, 'Si-free' Well 7 groundwater for 5.5 hours, and then Well 7 groundwater for five hours. The trans-column pressure remained stable when 'Si-free' Well 7 groundwater was injected and then steadily increased as a response to injection of Well 7 groundwater (Figure 4-16). This test further indicates that the major metals in Well 7 groundwater, such as Si and Al, are primarily responsible for the decline in hydraulic conductivity at the relatively high Darcy velocity investigated.
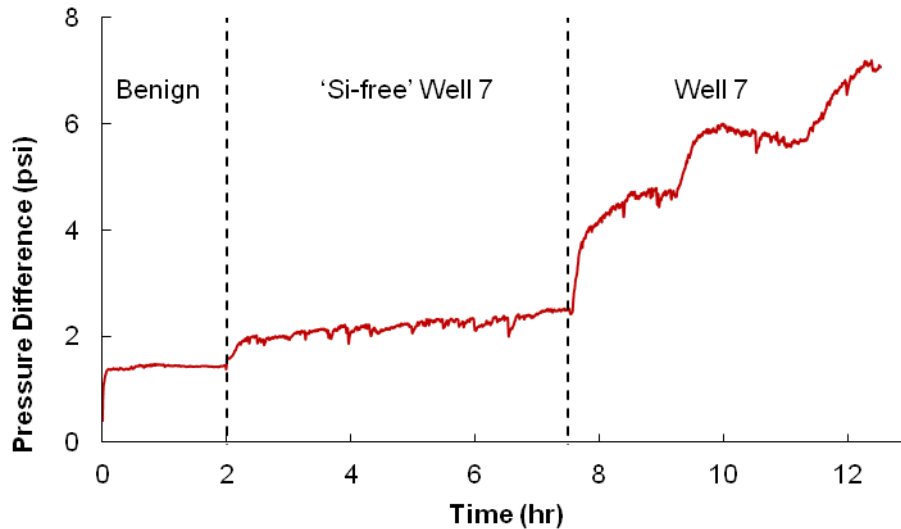
Figure 4-16. Pressure difference across the column when 'Si-free' Well 7 groundwater and Well 7 groundwater were injected into Well 46C-47 at a Darcy velocity of 27 ft/d.

An interesting result of these tests was that, even when hydraulic conductivity declined dramatically as a result of Well 7 groundwater injection, no significant declines in major constituent concentrations were detected. The differences between influent and effluent concentrations of major constituents measured from a handful of tests in which plugging occurred typically ranged between -6 to 15% (Appendix B: Figure 7-4). These differences can be real yet they can also be attributed to the decreased accuracy of the analytical method used to measure these concentrations, which required dilutions of at least 800x. However, this result could be obtained even if one or more of the major constituents were responsible for plugging of the soil, because precipitation of even an undetectably small amount of Si, for example, could generate enough solids to affect hydraulic conductivity.

Because no significant decline in Si and Al concentrations could be detected as water passed through the soil, column tests with synthetic solutions were used to investigate the individual and combined effects of Al and Si on hydraulic conductivity. Synthetic solutions at the pH of Well 7 groundwater were prepared containing 44 g/l Si and 600 mg/l Al either alone or in combination to isolate effects of these constituents on hydraulic conductivity. When the solution containing Si but no Al was injected into Well 46C-47 soil at a Darcy velocity of 27 ft/d, trans-

column pressure increased slightly but remained relatively stable throughout the duration of the test. However, when the solution with Al but no Si was injected in a separate test with similar system parameters, pressure increased rapidly. Injection of the synthetic solution with both Al and Si caused the trans-column pressure to also increase rapidly but over a longer duration (Figure 4-17). An additional test under similar system conditions was conducted by injecting the synthetic solutions sequentially to provide a direct comparison amongst the effect of specific synthetic solutions on hydraulic conductivity. During this test, trans-column pressure dramatically increased solely when column feed included Al (Figure 4-18). These column tests indicated that though Si may contribute to some soil plugging, Al plays a more critical role in the process.
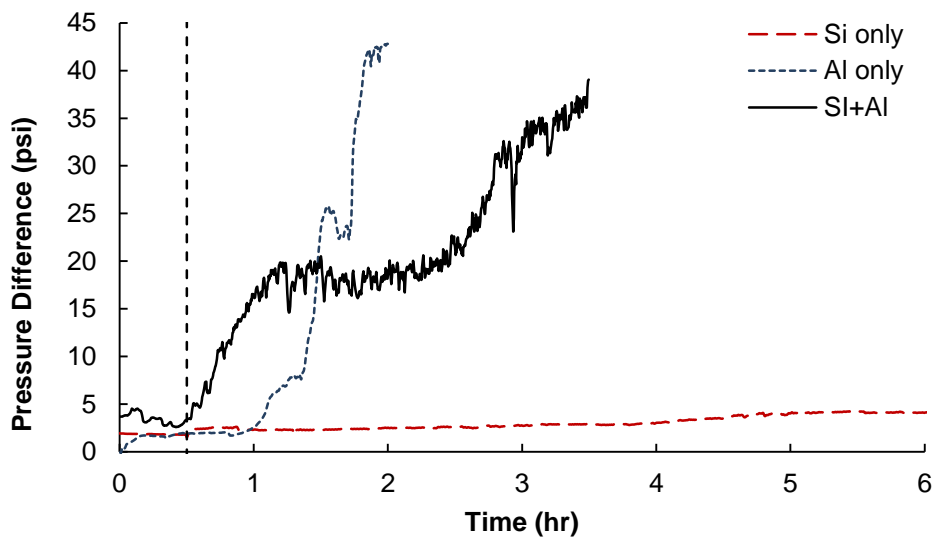

Figure 4-17. Trans-column pressure when Si only, Al only and Si+Al synthetic solutions were injected into a column packed with Well 46C-47 soil at an average Darcy velocity of 28 ft/d. The switch from a benign solution to a synthetic solution is shown with the vertical dashed line.
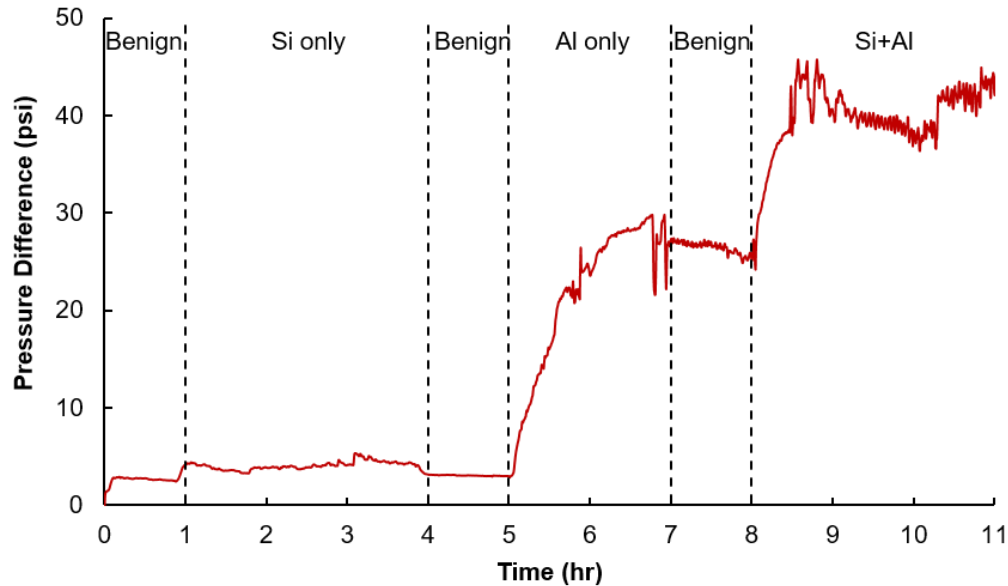
Figure 4-18. Trans-column pressure as a function of various synthetic solutions injected into Well 46C-47 soil at a Darcy velocity of 27 ft/d.

Well 7 groundwater has a high TOC concentration, so the effect of TOC added in the form of commercially available Aldrich humic acid on soil plugging was investigated. The previous test with sequential injections of synthetic solutions was repeated, yet now containing 100 mg/l humic acid. The results indicated that humic acid reduces soil plugging (Appendix B: Figure 7-5*).* To further explore this phenomenon, tests were conducted to specifically focus on the effect of humic acid on plugging from the Al synthetic solution. Two tests were performed by sequentially injecting the Al solution with humic acid and the Al only solution, one test with a humic acid concentration of 100 mg/l and the other with 500 mg/l. Both tests were conducted with a freshly packed column with soil from Well 46C-47, and the Darcy velocities for the test with 100 mg/l and the test with 500 mg/l humic acid were 26 and 28 ft/d, respectively. The test with the Al solution with 100 mg/l humic acid was also repeated with the order of the synthetic solutions reversed to ensure that injection order was not responsible for the outcome (Appendix B*:* Figure 7-6). Results from these tests indicated that the addition of humic acid reduced but did not completely prevent soil plugging which would have otherwise occurred from an Al only

solution (Figure 4-19). Increasing the concentration of humic acid in the Al synthetic solution was also not able to further mitigate soil plugging.
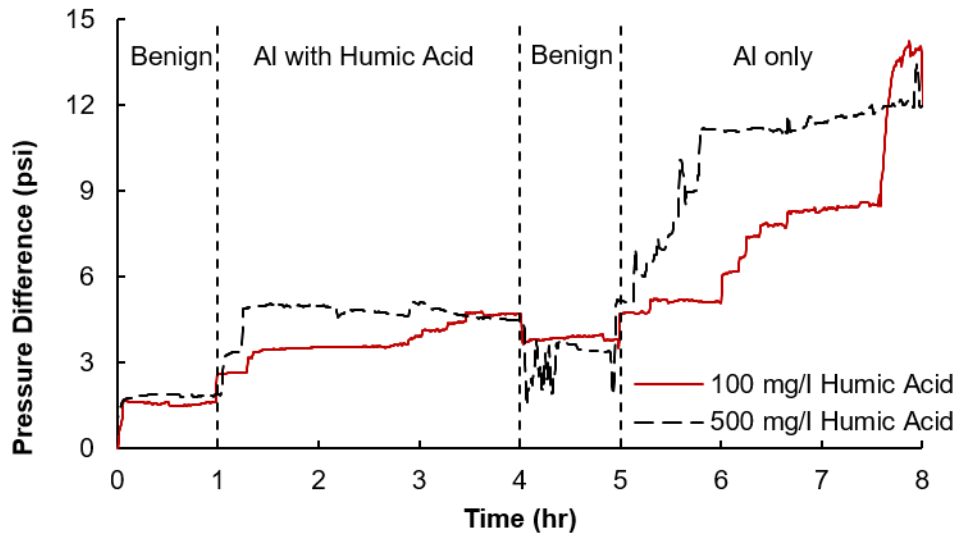

Figure 4-19. Trans-column pressure as a response to injection of Al solutions, with and without humic acid, into Well 46C-47 soil at an average Darcy velocity of 27 ft/d.

4.3.5 Discussion of Constituents in Well 7 Groundwater

Specific constituents in Well 7 groundwater are contributing to soil plugging when Well 7 groundwater is injected at a relatively high Darcy velocity. It was initially assumed that Si likely contributes most to soil plugging, but instead, column tests determined that Al plays a more critical role in the process. Al in Well 7 groundwater may react with Si present in the OCC site soil to form secondary minerals, or Al may precipitate in soil pores due to localized changes in pH. The presence of Si with Al slightly mitigated the plugging that occurred from the Al only solution, possibly because Si and Al form complexes that do not plug pores as readily. TOC also reduces, though does not prevent, the effect of Al on soil plugging. This may be due to complexation between TOC and Al which increases Al solubility. Therefore, the high concentration of TOC present in Well 7 groundwater might be helping to mitigate soil plugging during extraction efforts.

4.3.6 Specific Soil Interactions

The effect of Well 7 groundwater on hydraulic conductivity of various column media was investigated in this phase of the study. Previous column tests were conducted with Well 46C-47 soil, which is considered to be 'unaffected' by the high pH plume at the OCC site. These tests indicated that plugging of this 'unaffected' soil occurs when Well 7 groundwater is injected at a relatively high Darcy velocity (≈28 ft/d) and does not occur at a relatively low Darcy velocity (≈7 ft/d). Therefore, the next series of tests further explored the effect of both column media and Darcy velocity on hydraulic conductivity when Well 7 groundwater is injected.

Similar tests to those previously conducted with 'unaffected' Well 46C-47 soil were repeated with soil from 'affected' Well 83C-128 to explore differences between the two media. When Well 7 groundwater was injected into Well 83C-128 soil at a Darcy velocity of 80 ft/d for roughly 17 hours, the pressure remained stable throughout the test. On the other hand, injection of Well 7 groundwater into Well 46C-47 soil at a Darcy velocity 27 ft/d (approximately one-third the Darcy velocity in the Well 83C-128 soil test), the trans-column pressure increased rapidly over a few hours (Figure 4-20). These tests indicate that 'affected' soil is less prone to plugging than 'unaffected' soil when Well 7 groundwater is injected.
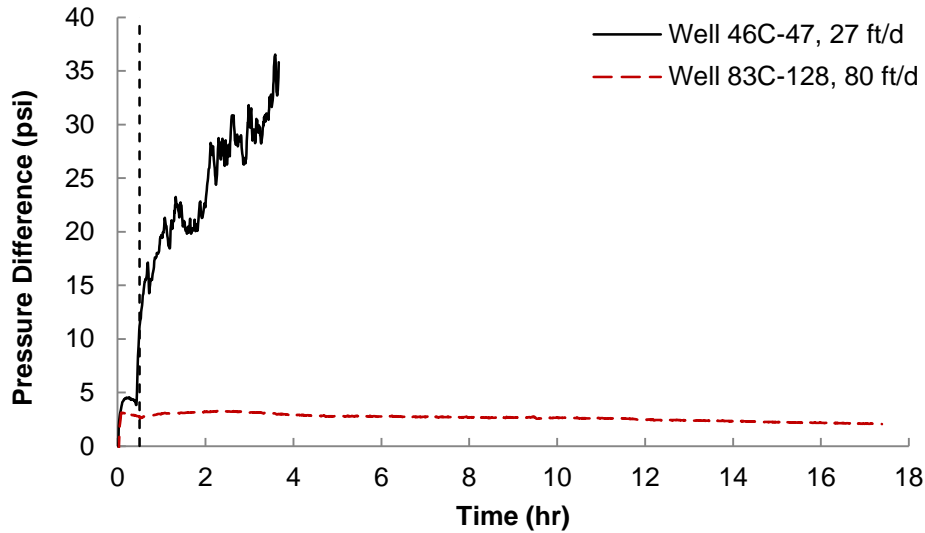
Figure 4-20. Pressure across the column as a function of soil type when Well 7 groundwater was injected. The vertical dashed line represents the switch from the benign solution to Well 7 groundwater.

Additional column tests were conducted to determine the threshold for plugging of Well 83C-128 soil by Well 7 groundwater. This soil is representative of soil in the immediate proximity of Well 7, so further investigation into a Darcy velocity threshold that induces plugging may assist with extraction of Well 7 groundwater at the OCC site. Initial column tests involved injecting Well 7 groundwater into Well 83C-128 at Darcy velocities of 142 and 189 ft/d. The trans-column pressure rapidly increased in response to the injection of Well 7 groundwater in both tests, though more significant plugging occurred over time at the higher Darcy velocity (Appendix C: Figure 7-7*).* Therefore, in Darcy velocity was increased step-wise in the next test to determine the threshold at which Well 7 groundwater significantly alters the hydraulic conductivity of Well 83C-128 soil. Trans-column pressure increased linearly in response to increasing the Darcy velocity, and then began to significantly increase when the Darcy velocity was 104 ft/d (Figure 4-21). The pressure increased even more dramatically when the Darcy velocity was increased to 118 ft/d. Results from this test indicate that the threshold for plugging of Well 83C-128 soil by Well 7 groundwater is between 85 ft/d and 104 ft/d.
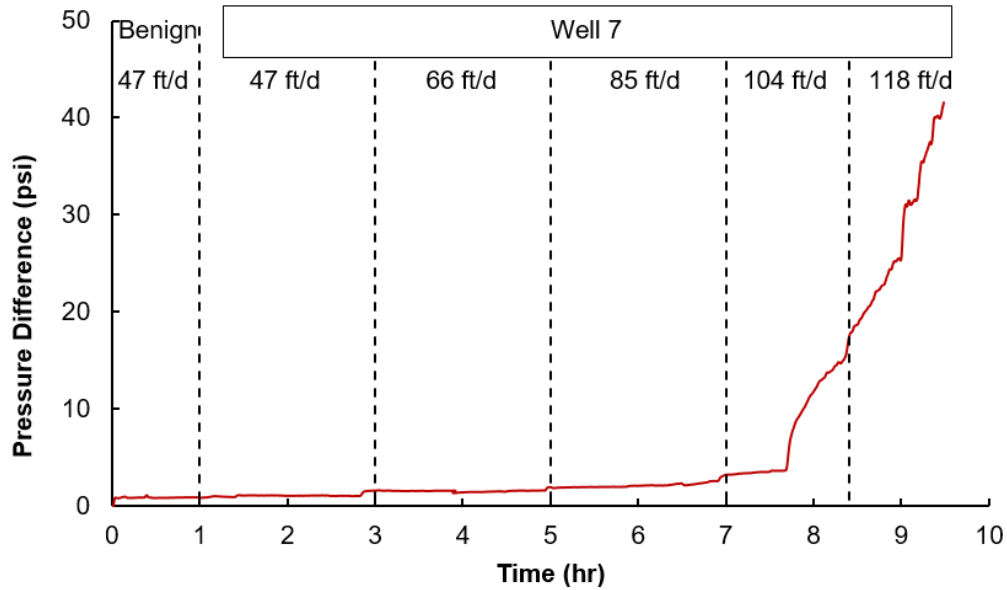
Figure 4-21. Pressure across column when Well 7 groundwater was injected into Well 83C-128 soil at various Darcy velocities.

Previous column tests indicated that plugging of OCC site soil in response to Well 7 groundwater injection is dependent on both the soil and Darcy velocity. The dependence on OCC site soil was explored by conducting column tests with sand as a model reference. Two tests were conducted, one each at Darcy velocities of 52 and 104 ft/d, by injecting Well 7 groundwater into the sand. The lower Darcy velocity is representative of a velocity in which 83C-128 does not plug when Well 7 groundwater is injected, though this soil plugs at the higher Darcy velocity investigated. Trans-column pressure remained low and stable throughout both tests, which lasted for six to eight hours (Appendix C: Figure 7-8). Therefore, plugging of column media is dependent on specific interactions between Well 7 groundwater and OCC site soil, rather than solely based on constituents in the groundwater.

4.3.7   Discussion of Specific Soil Interactions

Well 7 groundwater plugs soil 'affected' by the high pH plume less readily than soil that has not been exposed to the plume. Specifically, Well 7 groundwater plugs 'unaffected' soil at a Darcy velocity of 27 ft/d, yet injection of Well 7 groundwater into 'affected' soil at approximately three times that Darcy velocity (80 ft/d) does not reduce hydraulic conductivity of the soil. 'Unaffected'

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soil may plug more readily because this media was not previously exposed to this groundwater. Well 7 groundwater may reduce hydraulic conductivity of this soil due to localized pH changes that cause precipitation of constituents in the groundwater and/or because less Si has dissolved from this soil, which is contributing to the formation of secondary minerals on particle surfaces. 'Affected' soil is less prone to plugging in response to Well 7 groundwater injection because the soil was previously in contact and is likely in equilibrium with the groundwater. Therefore, additional reactions that may occur from passing Well 7 groundwater through the soil would occur more slowly if at all.

Extraction of Well 7 groundwater at the OCC site will likely be from a point source (e.g., Well 7) rather than capturing the plume elsewhere. Though there are differences in groundwater flow in the field versus in the test columns, a Darcy velocity threshold for plugging of 'affected' soil was determined to provide a general guideline for appropriate extraction rates from Well 7. Darcy velocities between 84 and 104 ft/d resulted in reduced hydraulic conductivity of 'affected' soil in column tests over time, which is equivalent to an extraction rate of 5000 to 6100 gpd from the existing geometry of Well 7 (assuming the open surface area is 50%). It is likely that this range will not correspond exactly to the threshold for soil plugging during Well 7 groundwater extraction at the OCC site, but it emphasizes the fact that pumping efforts should begin at a low pumping rate and slowly increase until a threshold is determined.

4.3.8   Groundwater Blends

Extraction of groundwater at the OCC site will likely result in heightened blending of groundwater from nearby wells. The impact of this blending on hydraulic conductivity of soil was investigated with column tests to better understand how extraction efforts may be affected and potentially improved. The following groundwater blends were injected as feed into columns with soil from the OCC site: Wells 7 and 46C-130, Wells 7 and 83C-100, and Wells 83C-100 and 82-100. Most blends were injected into a column packed with 'unaffected' soil and one packed with

'affected' soil. For each soil type, two tests were performed at different Darcy velocities, 47 or 52 ft/d and 95 ft/d.

4.3.8.1   Wells 7 and 46C-130

Groundwater from Wells 7 and 46C-130 were blended for a series of column tests. This blend represents an extreme scenario that would likely not occur at the OCC site due to the large distance between the two wells. Groundwaters from these wells have very different properties as well; Well 7 groundwater has a high pH and VOC, Si and Al concentrations, while Well 46C-130 groundwater has a low pH, low VOC concentrations, and undetectable Si and Al concentrations. As was described previously in the *Batch Precipitation of Si* subsection, Well 7/46C-130 blends with >5% Well 7 groundwater resulted in precipitation. Therefore, the following blends were injected into the column for one hour each after initial injection of a benign solution: 100% Well 7, 99% Well 7/1% 46C-130, 98% Well 7/46C-130, 97% Well 7/3% 46C-130, and 95% Well 7/5% 46C-130.

Because all injected blends were largely comprised of Well 7 groundwater, the effect on the hydraulic conductivity of both 'affected' and 'unaffected' soils was similar to that previously determined from pure Well 7 groundwater injection. Injection of the blends into 'unaffected' Well 46C-47 soil at the Darcy velocities of 52 and 95 ft/d both resulted in soil plugging within a few hours, with more rapid plugging occurring during the test with the higher Darcy velocity (Figure 4-22). When the blends were injected into 'affected' Well 83C-128 soil at a Darcy velocity of 95 ft/d, significant plugging occurred within two hours. However, trans-column pressure remained low and stable in response to injection of the blends at a Darcy velocity of 52 ft/d (Figure 4-23).
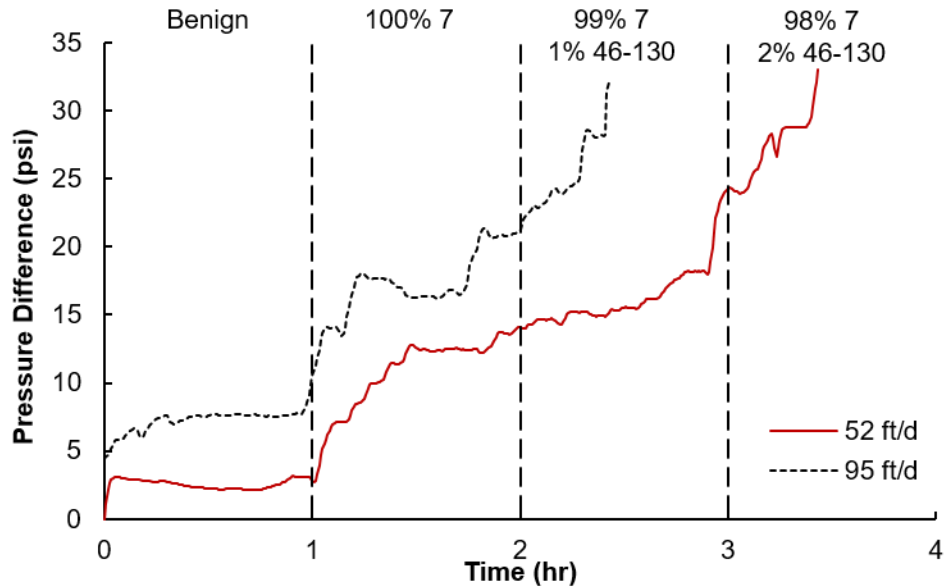
Figure 4-22. Pressure across column when blends of Well 7 and Well 46C-130 were injected into 'unaffected' Well 46C-47 soil at Darcy velocities of 52 and 95 ft/d.
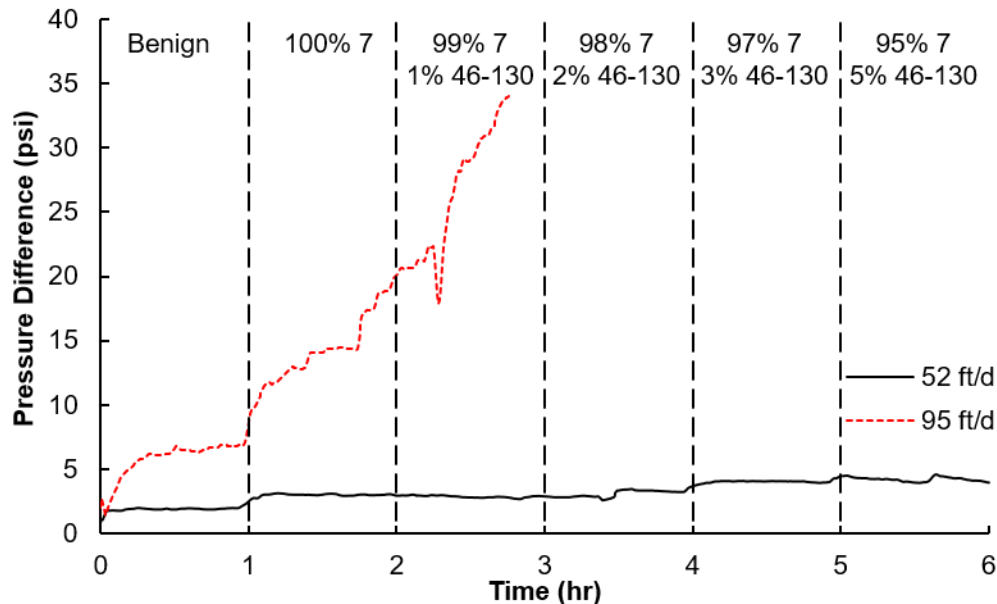

Figure 4-23. Pressure across column when blends of Well 7 and Well 46C-130 were injected into 'affected' Well 83C-128 soil at Darcy velocities of 52 and 95 ft/d.

4.3.8.2   Wells 7 and 83C-100

Blends of groundwater from Wells 7 and 83C-100 may occur due to vertical mixing, which would

likely be heightened as a result of extraction activities at the OCC site. Well 83-100 has a lower

pH than Well 7 (10.2 versus 11.7), relatively low Si and Al concentrations, and relatively high

VOC concentrations. Blends with ≥75% Well 7 were previously determined not to cause

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precipitation within a few hours, so the following blends were injected into the columns for one hour each after initial injection of a benign solution: 100% Well 7, 98% Well 7/2% 83C-100, 95% Well 7/5% 83C-100, 90% Well 7/10% 83C-100, and 80% Well 7/20% 83C-100. A larger range of blends was used for these column tests due the higher dilutions of Well 7 groundwater possible without causing rapid precipitation.

Injection of the blends into 'unaffected' soil at both 52 and 95 ft/d resulted in soil plugging; significant plugging occurred within 1.5 hours at the higher Darcy velocity and within 4 hours at the lower Darcy velocity (Figure 4-24). When the blends were injected into 'affected' soil, plugging occurred only at the higher Darcy velocity and within four hours; trans-column pressure remained low and stable when the blends were at the lower Darcy velocity (Figure 4-25). Plugging was less rapid when the blends were injected into the different soils at the same higher Darcy velocity because 'affected' soil is less prone to plugging when Well 7 dominant groundwater is injected.
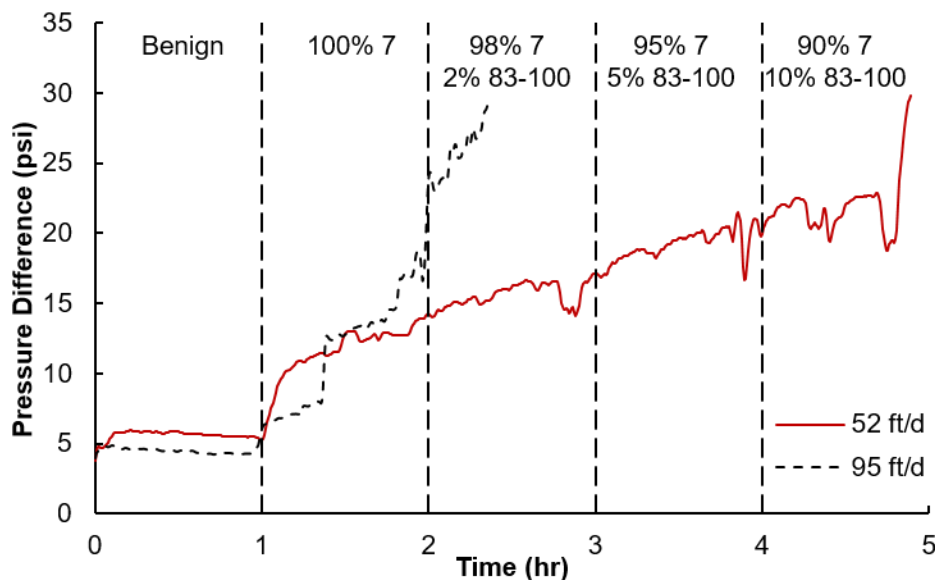

Figure 4-24. Pressure across column when blends of Well 7 and Well 83C-100 were injected into 'unaffected' Well 46C-47 soil at Darcy velocities of 52 and 95 ft/d.
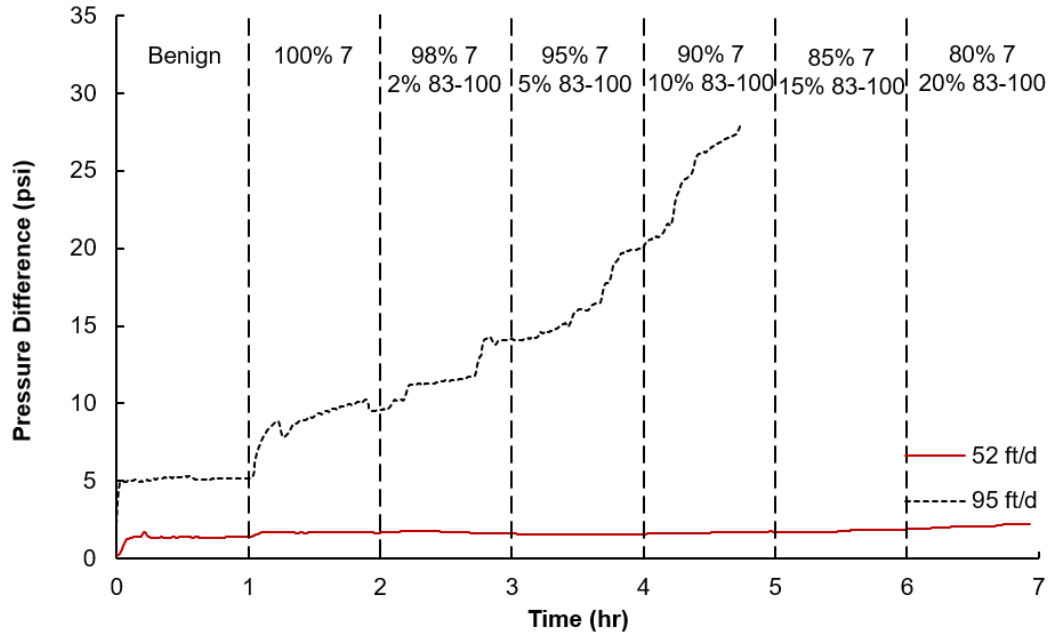
Figure 4-25. Pressure across column when blends of Well 7 and Well 83C-100 were injected into 'affected' Well 83C-128 soil at Darcy velocities of 52 and 95 ft/d.

4.3.8.3 Wells 83C-100 and 82-100

Blends of Well 83C-100 and Well 82-100 groundwater may result from horizontal mixing. Groundwater from Well 82-100 has a higher pH than Well 83C-100 groundwater (11.7 versus 10.2) as well as Si and Al concentrations at least two orders of magnitude higher than in Well 83C-100 groundwater. Blends with ≥75% 83C-100 resulted in precipitation within a few hours, so the following blends were injected for one hour each after initial injection of a benign solution: 100% 83C-100, 70% 83C-100/30% 82-100, 60% 83C-100/40% 82-100, and 50% 83C-100/50% 82-100.

Column tests were conducted by injecting Well 83C-100/82-100 blends into a column packed with 'affected' soil from Well 83C-103 at two Darcy velocities, 47 and 95 ft/d. Tests were only performed with Well 83C-103 soil, which is affected by the high pH plume and is within the immediate vicinity of Well 83C-100 groundwater, due to a shortage of Well 83C-100 groundwater. Trans-column pressure remained relatively low during both tests, yet pressure increased more during the test conducted at the higher Darcy velocity (Figure 4-26). The gradual increase in trans-column pressure over time likely occurred because blends had more

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Well 82-100 groundwater by volume, which is more 'affected' by the high pH plume than Well 83C-100 groundwater.
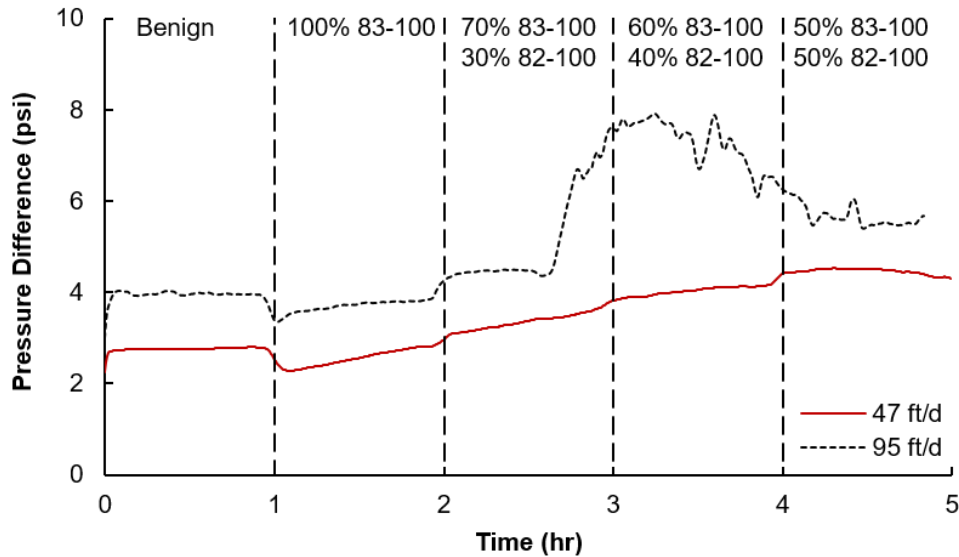

Figure 4-26. Pressure across column when blends of Well 83C-100 and Well 82-100 were injected into 'affected' Well 83C-103 soil at Darcy velocities of 47 and 95 ft/d.

4.3.9 Discussion of Groundwater Blends

Blends of groundwater from different wells at the OCC site were injected into columns packed with 'affected' and 'unaffected' soils at two different Darcy velocities. These tests were performed to better understand the effect of blending, which is likely heightened as a result of extraction activities, on hydraulic conductivity of soil.

Pressure increases across the column as a response to injection of the Well 7/46C-130 and Well 7/83C-100 blends were reasonably predictable based on the findings from previous tests. Specifically, plugging occurred when these blends were injected into 'unaffected' soil at both Darcy velocities investigated, 52 and 95 ft/d. Plugging of soil generally occurred in previous tests when pure Well 7 groundwater was injected into 'unaffected' soil at a Darcy velocity as low as 27 ft/d, and Well 7 groundwater made up a majority of the Well 7/46C-130 and Well 7/83-100 blends by volume. When the Well7/46C-130 and Well 7/83-100 blends were injected into 'affected' soil at the same Darcy velocities, soil plugging only occurred at the higher velocity.

This was also the outcome when pure Well 7 groundwater was injected into 'affected' soil in previous column tests. Therefore, when gradual blending of Well 7 groundwater is induced due to extraction from this well, it is likely that soil plugging will occur similarly to plugging that would otherwise occur with pure Well 7 groundwater.

Column tests with Wells 83C-100 and 82-100 groundwater blends solely investigated the effect of Darcy velocity on injection of blends into 'affected' soil due to a shortage of groundwater. The Well 83C-100/82-100 blends caused a slight increase in trans-column pressure over time, likely due to the increased volume of Well 82-100 groundwater in blends. However, the pressure increase was not dramatic, so the extraction of Well 83C-100 groundwater should not be as problematic as extraction of Well 7 groundwater; the threshold for the Darcy velocity that causes soil plugging is potentially higher for Well 83C-100 groundwater than for Well 7 groundwater. It is likely that the trans-column response to injection of these blends into 'unaffected' soil would be more drastic for both Darcy velocities investigated. However, extraction of Well 83C-100 groundwater would likely occur at the point source (Well 83C) rather than capturing this plume elsewhere, so results from tests with 'affected' soil are more applicable for extraction activities at the OCC site.

5 Conclusions and Recommendations

Due to difficulties associated with extracting high pH, high Si groundwater at the OCC site, pumping this groundwater has been avoided, allowing it to continue to contaminate soil, sediment, and surface water. To address and ultimately circumvent these difficulties, batch and column tests were performed to better understand the factors that affect hydraulic conductivity when high pH, high Si groundwater passes through OCC site soil. Results from this study can be used to assist in future P&T efforts by enabling long-term extraction of high pH, high Si groundwater at the OCC site.

High pH, high Si groundwater has unique characteristics that may reduce the hydraulic conductivity of OCC site soil. Well 7 groundwater in particular has extremely high Si concentrations and relatively elevated Al concentrations, both of which exceed equilibrium saturation levels at 20°C. These constituents may remain dissolved in Well 7 groundwater due to the elevated TOC concentrations, the presence the aluminosilicate and other complexes, the presence of other unidentified complexing agents, and/or or formation of colloidal particles not accounted for in calculations of chemical equilibria.

The precipitation of large amounts of Si-based solids from high pH, high Si groundwater likely affects hydraulic conductivity. Precipitation of Si is affected by a variety of factors, though dilution, groundwater blending and the lowering of pH are most relevant for P&T efforts. In-situ plugging of soils may also result from the blending of less contaminated groundwater with Well 7 groundwater. These factors are of heightened importance after high pH, high Si groundwater is extracted. Specifically, to avoid uncontrolled precipitation, it is critical that high pH, high Si groundwater not be blended with other groundwaters or otherwise diluted. It is also important that the pH of high pH, high Si groundwater is lowered in a highly controlled process to reduce the volume of the precipitate; acid should be added at an extremely slow rate while the groundwater is continuously stirred. Results found by Pandya (2015) on further reducing the

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volume of the precipitate should be followed thereafter to reduce costs associated with solids handling and disposal.

Factors that may reduce hydraulic conductivity were investigated in column tests. Results indicated that the following cause soil plugging: relatively high Darcy velocities, elevated Al concentrations, and specific soil interactions. These results, as well as additional findings, are summarized in Figure 5-1, which can be used as a tool to better understand factors that contribute to soil plugging. Soil plugging that resulted from elevated Al concentrations in Well 7 groundwater and the specific soil used in tests was primarily a function of Darcy velocity. That is, soil plugging occurred only at relatively high Darcy velocities, and the threshold for plugging was higher when Well 7 groundwater passed through 'affected' soil than 'unaffected' soil; the threshold for plugging of 'affected' Well 83C-128 soil by Well 7 groundwater was between 85 ft/d and 104 ft/d, which was over three times that for 'unaffected' Well 46C-47 soil. It was determined that this plugging was primarily due to elevated Al concentrations which may have formed secondary minerals with Si.

It is possible to control some of the factors that reduce hydraulic conductivity during pumping activities, and thereby possibly enable long-term extraction of Well 7 groundwater. Darcy velocity was the most significant factor that contributed to soil plugging, so it is essential that the Darcy velocity threshold for soil plugging be identified and not exceeded. The Darcy velocity threshold will likely be different in the field than that identified from column tests, so pumping should start at a low extraction rate and gradually increase until the pressure increases more than would be expected from increasing the flow rate. Well 7 groundwater should be extracted from Well 7, rather than attempting to capture that plume from an adjacent well. The 'affected' soil in the immediate proximity of Well 7 has a higher Darcy velocity threshold for plugging, so the extraction rate from this location can be higher without resulting in soil plugging.

Though there have been complex and unforeseen difficulties associated with the extraction of high pH, high Si groundwater at the OCC site, P&T efforts can be designed to potentially enable long-term extraction. Extraction of this groundwater will reduce contamination at and surrounding the site, decreasing harm to potential receptors.
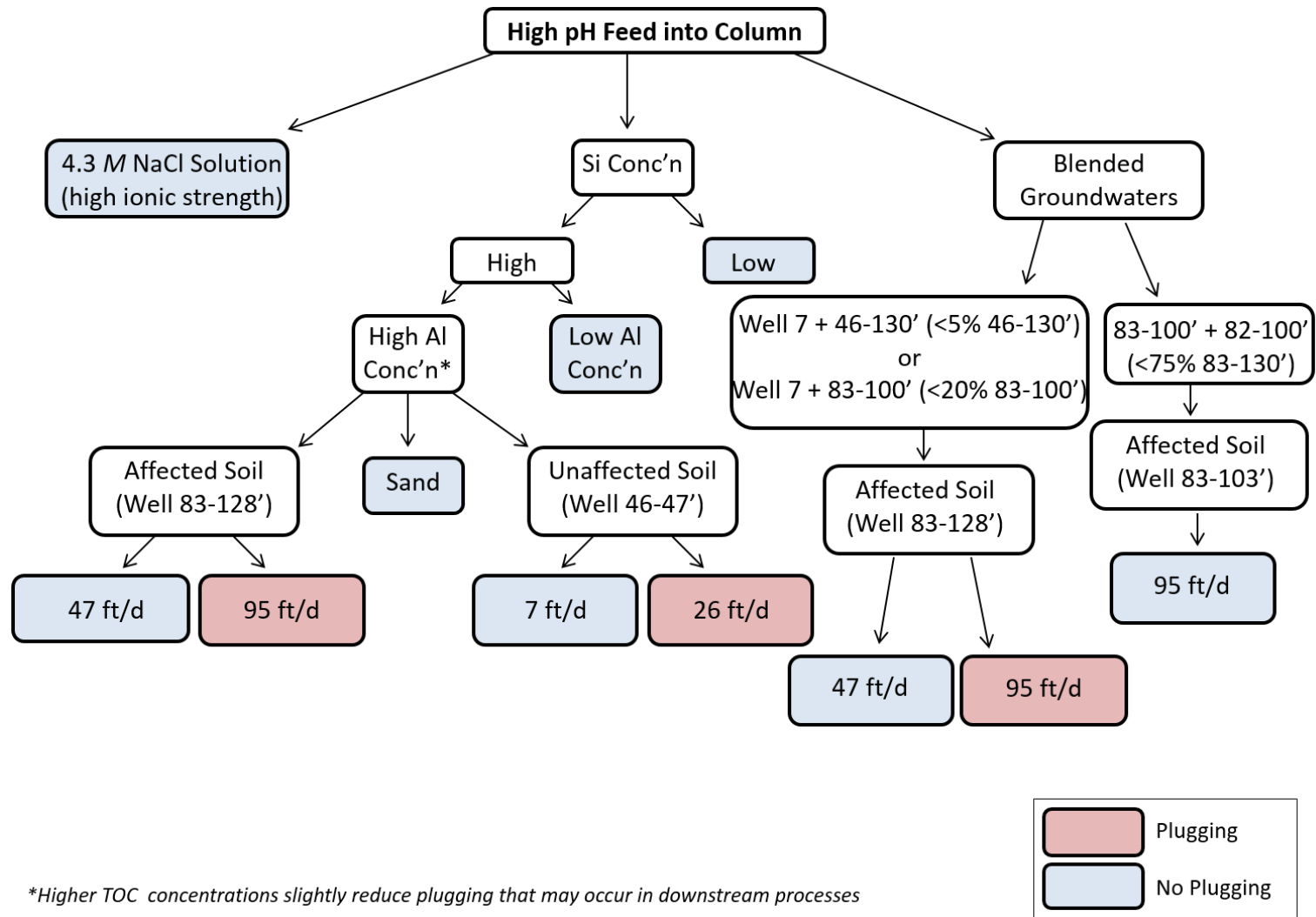
Figure 5-1. Factors that caused plugging of OCC site soil during column tests.

Higher TOC concentrations slightly reduce plugging that may occur in downstream processes

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7 Appendices

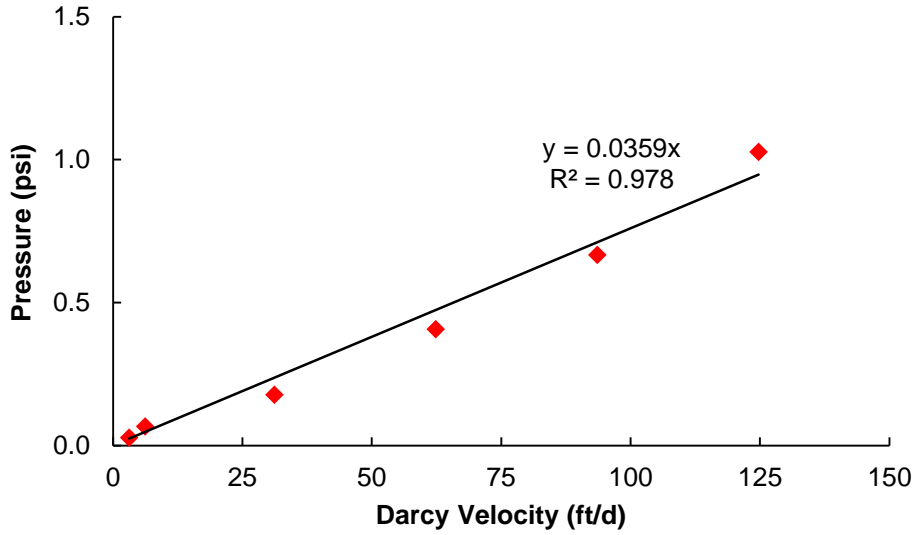## 7.1 Appendix A: Column Test Reproducibility

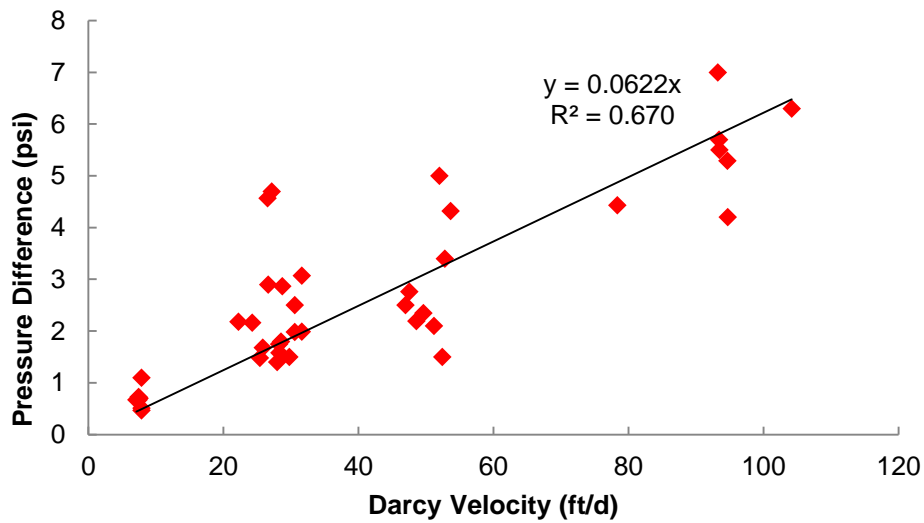Figure 7-1. Frictional losses due to column test apparatus.

Figure 7-2. Relationship between transcolumn pressure and Darcy velocity when 4.3 M NaCl adjusted to pH 11.7 was injected at the beginning of column tests.
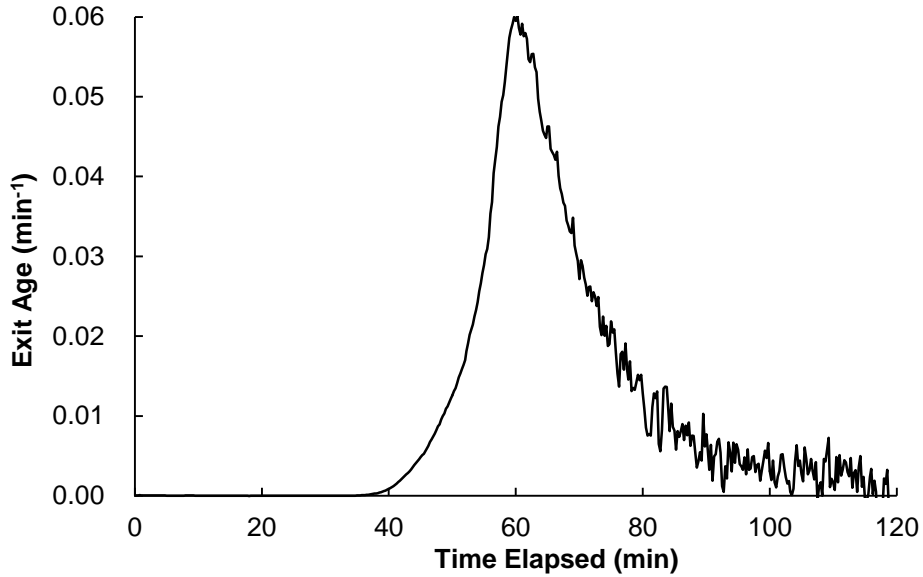
Figure 7-3. Exit age distribution for an initial tracer test with a step input. The actual and theoretical HRTs were 61 and 64 minutes, respectively, and the standard deviation about the actual HRT was 8.5 minutes.

7.2   Appendix B: Constituents in Well 7 Groundwater
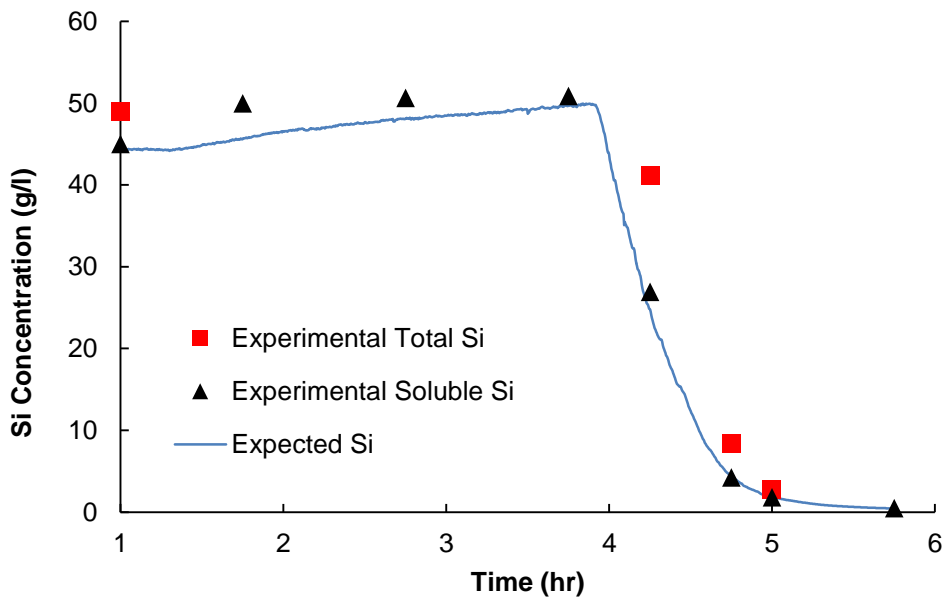
Figure 7-4. Measured Si concentrations in effluent versus expected Si (as determined by a Br-tracer) during a column test in which Well 7 groundwater was injected into Well 46-47 soil at a Darcy velocity of 27 ft/d.
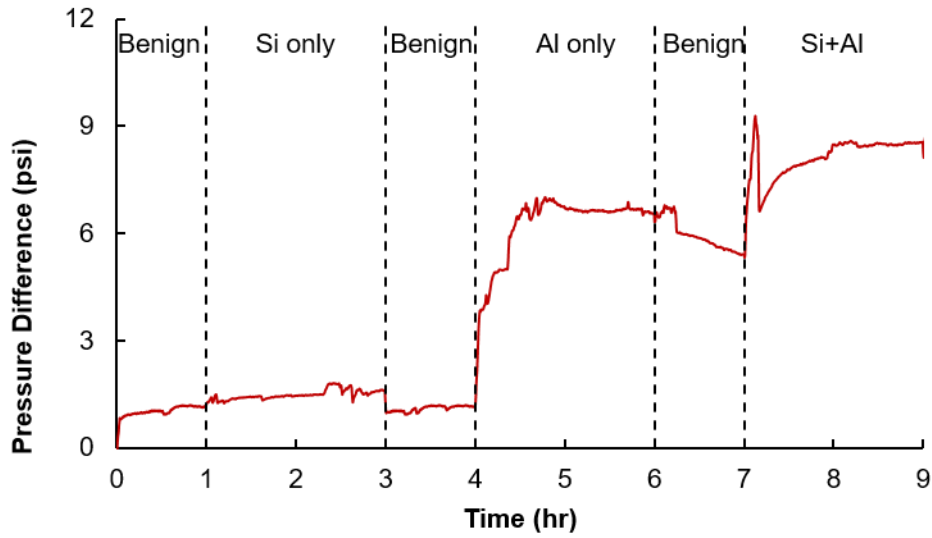
Figure 7-5. Transcolumn pressure as a function of various synthetic solutions, all with 100 mg/l humic acid, injected into Well 46C-47 soil at a Darcy velocity of 28 ft/d.
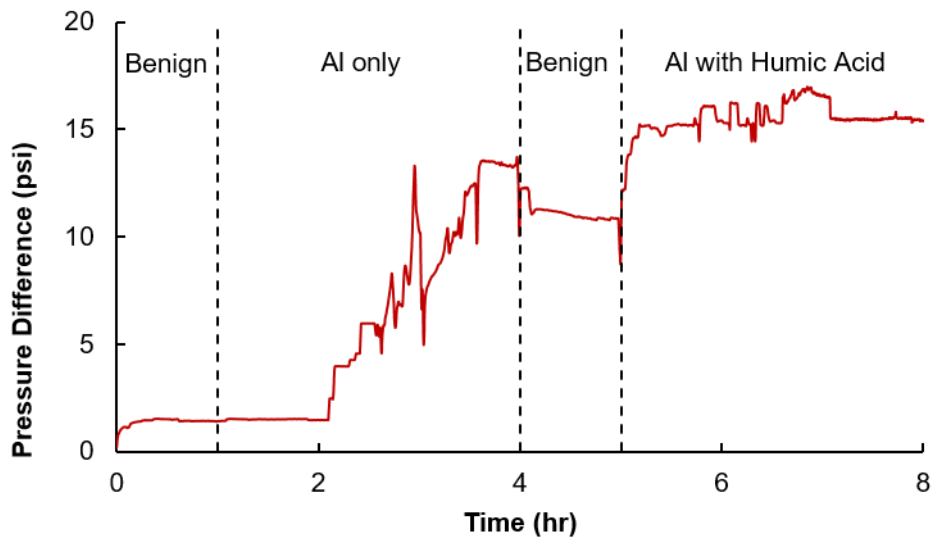

Figure 7-6. Transcolumn pressure as a response to injection of Al solutions, with and without 100 mg/l humic acid, into Well 46C-47 soil at an average Darcy velocity of 28 ft/d.
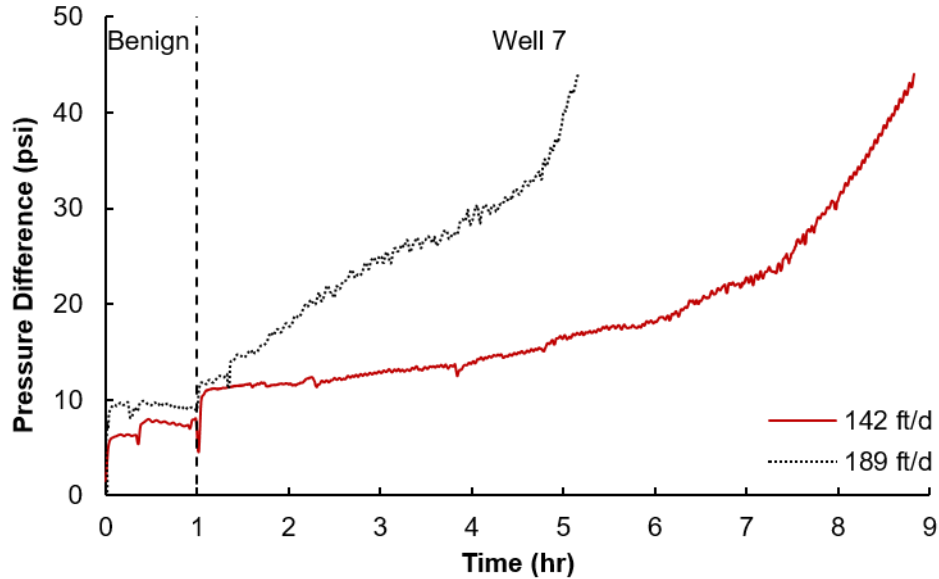
7.3   Appendix C: Specific Soil Interactions

Figure 7-7. Pressure across column when Well 7 groundwater was injected into Well 83C-128 soil at two Darcy velocities, 142 and 189 ft/d.
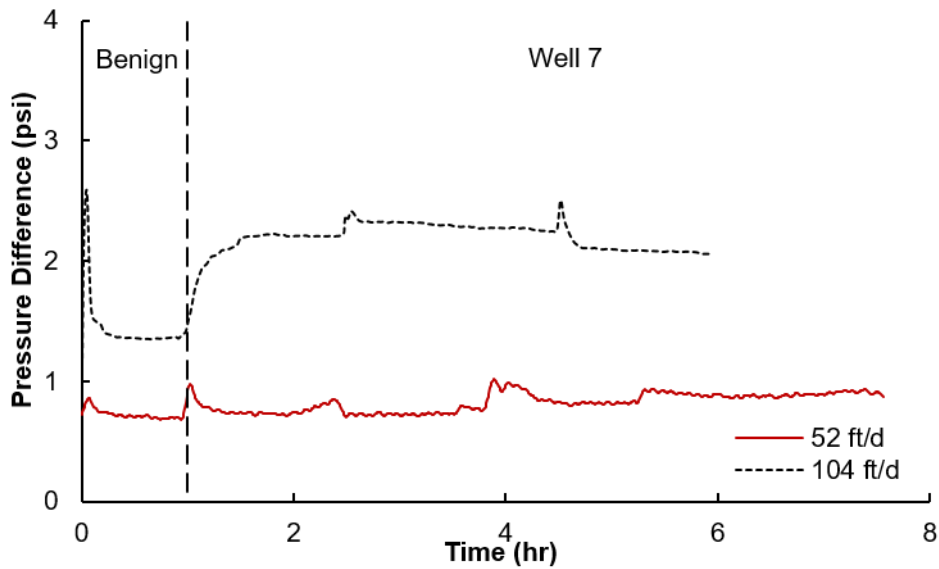

Figure 7-8. Transcolumn pressure when Well 7 groundwater is injected into sand at two relatively high Darcy velocities.