UNIVERSITY OF WASHINGTON

Examination of Silica Precipitation, Gelation and Hydraulic Fouling in Occidental Chemical Corporation (OCC) Soils

Report to Project Sponsors

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Contents

Executive Summary

This study quantified physico-chemical interactions pertinent to hydraulic fouling (associated with the formation of voluminous precipitates, or gelation) in high-pH, high-silica groundwater/soil systems at the former Occidental Chemical Corporation (OCC) facility in Tacoma, Washington (Site).

The initial experimental plan was divided into several tasks and sub-tasks, as presented in an abridged form below. That plan was amended as the project progressed, as activities in some of the tasks (e.g., evaluation of the performance of Si precipitation inhibitors, comparison of the behavior of reactive vs. non-reactive fractions of Si solutes) were scaled down while those in selected others (e.g., examination of the dissolution of OCC soils, tracer experiments, removal of Si in *ex situ* operations) were scaled up. The sequence of tasks in the original experimental plan and corresponding sections of this report that outline relevant results are listed below.

Task B-1 Procurement of Soil Samples

- *Section 1 of the report.*

Task B-2 - Batch experiments to determine properties of soil and soil/ground water systems relevant to gelation

Subtask B-2A - Characterization of solids formed in extracted ground water and soil/ground water systems.

- *(Section 2)* Determine rates of formation of gels and solids in batch systems containing unaltered high-pH/ high-Si ground water when mixed and exposed to the normal atmosphere;
- Examine possible presence of reactive vs. non-reactive fractions of silica in the OCC site groundwater;
    a. *This task was not pursued because further experiments did not support the notion of possible presence of reactive vs. non-reactive Si fraction.*
- *(Section 2)* Determine effects of ground water dilution and pH on the formation of gels and solids in batch systems;
- *(Sections 2, 4, 9 and 10)* Determine differences in the properties of solids formed in high-pH/high-Si ground water vs. those formed in ground water/soil systems, in batch conditions.

Subtask B-2B - Conditions conducive to stabilization or dissolution of solids formed in ground water/soil systems.

- Determine general aspects of structural stability and compaction of gels formed in batch conditions.
    a. *This task was not pursued as such due to difficulties of mechanical measurements for amorphous precipitates and more emphasis on the other tasks.*
- *(Section 2)* Determine the susceptibility of such solids to destabilization and dissolution (e.g., in the case of pH increase).

Subtask B-2C - Reactivity of soils towards dissolution in high pH water

- *(Section 4)* Determine the acid/base properties of soils from the site that have not been exposed to high-pH ground water, and determine their capacity to neutralize the basicity of contaminated ground water.
- *(Section 4)* Determine the acid-neutralizing capacity of soils affected by contact with high pH/high-Si water.
- *(Section 5)* Determine acid/based capacity and concentrations of representative elements in pore water present in the extracted soils and in groundwater collected from existing monitoring wells collocated with the sites of soil extraction;
    a. *Selected data relevant to this task (e.g., release of pH and salts from OCC soils) are presented in Section 5. Otherwise, activities in this task were scaled down due to more emphasis on other tasks.*
- *(Section 4)* Determine properties of solids formed on surfaces of exposed soils and in the ambient water at varying degrees of neutralization of the contaminated soils' basicity.
- *(Section 4)* Determine rates of release of silica from uncontaminated soils when exposed to water at varying pHs and ionic compositions.

Task B-3. - Design and Commission of Columns Packed with Representative Soil.

- *Sections 1 and 7*

Task B-4. Exposures of Soil Columns to High Si, High pH Water and Its Blends

- *Sections 7 and 8.*

Task B-5 - Options to Reverse Gelation in Affected Soil

- (*Section 7*) Establish relationships between decreases of the hydraulic conductivty and properties of gels and solids formed in impacted soils. Determine parameters that are indicative of incipient failure of the hydraulic conductivity of impacted soils.
- *(Sections 7 and 8)* Determine effects of flushing with selected chemical agents (e.g., solution of bases) on the hydraulic conductivity of soils that have been partially or completely plugged by precipitation reactions.

- Ascertain effects of selected gelation inhibitors on the behavior of soils that appear to be in a state of incipient failure of hydraulic conductivity.
    - *As mentioned above, experiments with precipitation inhibitors were scaled down after relevant measurements had shown that such inhibitors exert practically no effects on the precipitation.*

Task B-6 - In situ Barriers to Control Groundwater Movement

- *(Section 8)* Determine options for *in situ* dissolution of gels and associated solids that have formed as a result of contamination or remedial activities
- *(Section 9)* Attempt to identify approaches that are conducive to formation of gels that, in conjunction with the ambient soils, generate continuous layers of very low hydraulic conductivity (e.g., injection of concentrated mineral acids or CO_2 gas in soils affected by high-pH/high-Si ground water).
- *(Sections 2 and 8)* Ascertain short- to long-term stability of solid formed in the pores of soils in contact with high-pH/high-Si ground water.

As a result of the reorganization of the project activities outlined above, their data are presented in a sequence that is somewhat different from that outlined in the original plan. Main results of these activities, as presented in Chapters 1 to 10 are outlined below.

1. Experimental Methods and Approaches

Chapter 1 describes main features of the experimental methods used in the study, location of sampling points and related information.

2. Chemical Properties of OCC Groundwater and Effects of pH on Solute Concentrations

Analytical measurements of concentrations of major components of OCC groundwater ((e.g., silicon, hydroxyl-ion, carbonate, other anions, Al, Ca, Mg and other elements) showed that the chemistry of Well 7 and other related groundwater from the examined site is dominated by extremely high Si concentrations. These concentrations tend to be many times higher than those predicted based on thermodynamic calculations performed using Visual MINTEQ software. The exceedingly high Si concentrations result from the high reactivity of OCC soils, long soil/high pH solution contact times and the presence of polynuclear and colloidal, possibly micellar Si species unaccounted for in databases describing nominal equilibria of aquatic Si species. In contrast, effects of pH on the concentrations of other important solution components, for instance Ca and Mg, were well modeled by existing geochemical models.

Batch experiments led to practically complete removal of Al and Si at pH <11.5. The data indicate that soluble Si compounds in OCC groundwater are metastable and their precipitation may be triggered by decreases of pH, dilution (in which case polynuclear and colloidal Si species are destabilized), and addition of Al or hardness cations (which can initiate or play a synergistic role in the formation of Si solids).

3. Acid-Neutralizing Capacity of OCC Site Soils

Acid-neutralizing capacity (ANC) of OCC soils was measured in batch experiments to assess the ability of the soils to neutralize acids that might enter the ground either naturally or as part of a remediation activity, for instance in the case of in situ formation of hydraulic barriers controlling the flow of OCC groundwater.

Batch titrations to determine ANC values were performed for soils from a relatively unaffected area (e.g., Well 46), a moderately to strongly affected area (Well 83) and a strongly affected area (Well 82) of the site. The range of ANC values for Well 46 soils was 0.6 to 22 μeq acid/g soil, confirming the low content of base in the unaltered soils. ANC values for Well 83 soils collected at up to 122 ft BGS were from 0.7 to 22.2 μeq acid/g soil. Well 83 soils from deeper strata had ANC values 176 to 199 μeq acid/g, which indicate a moderate level of the alteration of soil properties by high pH effluents. Well 82 soils from 54 to 79 ft BGS had extremely high ANC values (ca. 1200 to 2600 μeq acid/g) , and lower but still elevated ANC values (ca. 60 to 220 μeq acid/g) at shallower and deeper locations. When represented in a log scale, the ANC values were well correlated with pH values measured in suspensions of these soils.

These results indicate that the generation of *in situ barriers* at the OCC site is likely to require large amounts of strong acids that must be used to decrease the pH of groundwater/soil system to an a priori determined threshold value, for instance <10.5. In this case the required amount of a strong acid such as HCl would be as high as 1 mol per kg of an affected soil. The neutralization of base for soils located in the vicinity of wells other than Well 82 is likely to require amounts of HCl that are several times lower than that estimated for the most affected Well 82 soils.

4. Release of Silica and Aluminum from OCC Soils

When exposed to strong base (1 M NaOH), OCC soils readily released silica at concentrations that were many times higher than those for comparable experiments with model Si-containing phases exemplified by sand and clays. For instance, after exposure of OCC soils to 1 M NaOH for several weeks, the solutions contained up to 10,000 mg/L Si, while <500 mg/L Si dissolved during exposure of sand under similar conditions.

Release of Si from OCC soils when they were exposed to strong base increased monotonically with time, and the release proceeded at comparable rates regardless of whether or not the soils had previously been affected by contact with high pH groundwater. In contrast, the concentration of Al mobilized increased immediately, after which the Al concentration decreased to practically non-detectable levels. This result is likely to indicate changes in the identity of the solid phases controlling Al solubility in exposed soils, for instance via the formation of aluminosilicates. The presence of these solids may be important for the development of hydraulic fouling in pump-and-treat operations, as discussed elsewhere in the report.

Exposures of model clay minerals (montmorillonite, kaoline, bentonite) selected to mimic the clay phases on OCC soils showed that concentrations of Si released from these minerals behaved non-monotonically vs. time and tended to be much lower than those for exposures of OCC soils. Al concentrations also behaved non-monotonically vs. time in these experiments. These results further support the possibility that formation of new solids when OCC soils interact with high pH water may have important implications for the development of hydraulic fouling in these soils.

5. Release of Salt and Base (High pH) from OCC Soils

Release of retained salts and base (quantified as conductivity and high pH, respectively) from OCC soils was examined by comparing changes of the conductivity and pH of water that was passed through columns packed with the soils. The measurements showed that salts were readily mobilized from exposed soils but base (OH^-) release was more persistent. When the influent had a circumneutral or slightly acidic pH, the pH of the effluent tended to be close to that of suspensions of affected OCC soils. Only when column influents were strongly acidic (e.g., containing 0.005 to 0.02 M HCl, pH from 1.7 to 2.3) was the injected acid capable of neutralizing the ANC capacity of the Oxy soils within a short period of observation. The amount of acid consumed to neutralize the base retained by both affected and unaffected Oxy site soils in the column experiments was correlated with, yet appreciably lower than, that measured for the same soils in the batch experiments whose results are outlined in the preceding section of this summary. This demonstrates that, in realistic field conditions when incoming water is likely to have a circumneutral pH, release of retained base from affected soils will continue for a long time. The amount of acid required to neutralize and counteract such base release will ultimately be comparable with, albeit potentially somewhat lower than that calculated based on ANC values determined in relevant batch experiments.

While the pH of water exiting highly affected areas of the site may be high, the ability of that water to mobilize massive amounts of silica from OCC soils is likely to be notably lower than that of the high strength chlor-alkali effluents released into the subsurface during the period of industrial activity. That is, the removal of high-pH, high-Si groundwater by pump-and-treat operations and its replacement by the ingress of water that initially has a circumneutral pH and low to medium alkalinity will result in a notable increase in the pH of the replacement water, but also a drastic reduction in its tendency to mobilize silica from the exposed soils.

6. Effects of Precipitation Inhibitors on Gelation and Precipitation in OCC Groundwater

The potential of the commercial product Carbosperse K-XP229 (Lubrizol Corporation) to prevent the acid-induced precipitation of Si-based solids from OCC groundwater was examined. This product is marketed as an inhibitor of silica scaling and fouling in cooling, reverse osmosis, geothermal and related applications and is typically used in solutions with Si concentrations that are orders of magnitude lower than those in the OCC groundwater. In batch experiments, this inhibitor had no meaningful effect on the precipitation/gelation phenomena, even at the highest concentration tested (ca. 1 g/L).

Humic acid has significant effects on precipitation of environmentally relevant solids due to its ability to complex metals. Therefore, its effects on the behavior of Al were examined in experiments using soil packed columns. When 500 mg/L Aldrich humic acid (AHA) was added to synthetic Al-containing solutions that were applied to the soil columns, it delayed but did not prevent hydraulic soil fouling, and a dose of 100 mg/L AHA had no significant effect at all. Given that compounds similar to AHA occur naturally in OCC groundwater due to the mobilization of humic species from soil at high pHs, dosing of commercial humic acid products is unlikely to appreciably augment any beneficial effects of those species. Overall, given the extremely high levels of Si in OCC groundwater, there is little likelihood of effective prevention of gelation/precipitation of Si-based solids by commercially available or naturally occurring compounds.

7. Experiments to Determine Hydraulic Fouling in Soil-Packed Columns

The occurrence of hydraulic fouling in OCC soils was examined in soil column experiments in which trans-column pressure and, in some cases, concentrations of indicator elements (Al, Si) in the effluent solutions were analyzed. These measurements were carried out for high pH high Si Well 7 groundwater, its blends containing variable fractions of surface water, and in the presence of variable levels of aluminum or AHA added to Well 7 groundwater or synthetic solutions.

The development of hydraulic fouling in these experiments depended on the nature of the exposed soils and even more prominently on the velocity of movement of groundwater through the column (Darcy velocity). Hydraulic fouling tended to develop slower in soils that had been affected by high pH, high Si groundwater; conversely, soils originating from largely unaffected areas of the site developed such fouling more readily. This behavior is consistent with the observation that affected OCC soils cause little change of the pH of high-pH, high-Si groundwater in contact with them, while unaffected soils, even though their base-neutralizing capacity is generally low, may cause some decrease of the pH in the front of the plume of high pH, high Si groundwater moving through pores of exposed unaffected soils.

Al and Si were neither retained by nor released from the soil to a significant extent as water passed through the columns. This result was unexpected. However, given the extremely high concentration of Si in Well 7 water, the precision of the analyses may not have been adequate to discern minor changes in the analyte concentrations.

Another unexpected finding was that the incidence of hydraulic fouling depended on the Darcy velocity of groundwater moving through exposed soil. In general, Darcy velocities less than ca. 20 ft/day and ca. 60 ft/day for unaffected and affected soils, respectively, resulted in the absence or slow development of hydraulic fouling, whereas higher Darcy velocities caused hydraulic fouling to develop rapidly.

Experiments with synthetic solutions showed that higher levels of aluminum in column influents tended to promote hydraulic fouling, while increases in the concentration of organic carbon tended to suppress it. This pattern might be related to the formation of insoluble mixed aluminosilicates in the pores of exposed soils and the acceleration of that process by precipitation nuclei, for instance polynuclear Si colloidal species present in Well 7 groundwater. Formation of insoluble aluminosilicates may be also accelerated by local decreases of pH caused by the neutralization of highly basic Well 7 groundwater by soil minerals that have higher ANC values than those for the average soil matrix.

8. Tracer Measurements of Incipient Changes of Hydraulic Conductivity and Its Reversibility

Incipient gelation/hydraulic fouling and its reversal were examined based on tracer injections into soil-packed columns. In the context of this study, the term “incipient hydraulic fouling” refers to the phase of groundwater movement through exposed soils accompanied by a marginal (e.g., several psi) increase of the trans-column pressure.

Incipient hydraulic fouling that was assumed to be associated with the deposition of small amounts of solids in soil pores could be reversed by high pH (caustic) treatment solutions, or regenerants. Tracer data indicated a decrease in the apparent pore volume in soils exposed to high Si high pH groundwater under incipient (e.g., those not exceeding a few psi) hydraulic fouling conditions. Flushing the exposed soils with 0.01 M or 0.1 M NaOH caused this phenomenon to reverse. There was relatively little difference in the performance of 0.01 and 0.1 M NaOH regenerants in the reversal of incipient fouling, although use of high concentrations of caustic may be beneficial in field conditions.

These results show that as long as the amount of solid deposited in soil pores does not block the ingress of a regenerant solution into the pores, application of an appropriate caustic solution is likely to result in partial or complete mobilization of the deposited phases and unclogging of affected soils. Tracer data also indicate that repeated exposures of OCC soils to high Si groundwater followed by their treatment with a caustic regenerant may stabilize the soil/groundwater system, and less hydraulic fouling may occur in repeated cycles of groundwater loading/caustic regeneration. That is, if a well is in a state of incipient hydraulic fouling, it may be beneficial to flood that well with caustic to flush the soil and to improve the well's operability in long-term operations. An alternative option is to modulate pump rates starting with a relatively low pump rate, then allow the soil to stabilize, possibly in the presence of caustic regenerants, after which pumping may resume at a higher rate.

The development and reversal of incipient hydraulic fouling may be quantified via conventional means (e.g., measuring changes of the water level in the well) and/or via injections of a tracer through a supplemental monitoring well located in the vicinity of an extraction well. The modeling of the tracer breakthrough in such a case will be more complex than for the simple case of cylindrical soil-packed columns employed in this study, but analytical or numerical solutions for such configurations are likely to exist or can be developed. Given that the groundwater typical for the OCC has relatively high concentrations of bromide, this ion is not as attractive as it might otherwise be for use as the tracer, and an alternative (e.g., iodide, lithium) might be used instead.

9. *In Situ* Formation of Hydraulic Barriers in OCC Soils

In situ formation of impermeable barriers was examined in column experiments in which the flow of high-pH, high-Si groundwater was combined with the flow of base-neutralizing agents. The introduction of the latter component was done through the permeable wall of a ceramic tube whose inner volume was packed with an OCC soil specimen.

Injections carried out in this mode led to formation of voluminous Si-based solids dispersed though the column. The precipitation of these solids tended to occur readily upon the introduction of mineral acids such HCl, or upon contact with alternative less acidic agents such as $NaHCO_3$. The latter salt can be used in its nominal form (solutions of sodium bicarbonate) or it will be formed in the subsurface zone upon the dissolution of CO_2 that can be injected to treat high pH high Si groundwater. It is our current view that the use of $NaHCO_3$ or CO_2 may be preferable for practical applications due to the inability of these agents to create extremely high local acidity which may destabilize soil minerals.

The solids formed upon injections of base-neutralizing agents appear to be predominated by hydrated silica. As such, these solids may undergo slow structural changes via the loss of water, formation of more crystalline phases, compaction and possibly development of fissures. Aging-related changes of the morphology and structure of the solids forming impermeable barriers in OCC soil/groundwater were not examined in this study. Related batch experiments reported in more detail in the section dealing with ex situ destabilization and removal of excess Si showed that the formation of solid phases in the subsurface zone can be caused by injections of solutions of Ca or Mg salts, in which case the formed solids are likely to be dominated by Ca or Mg hydroxides, carbonates, silicates and their mixed phases. Such solids may be structurally somewhat more stable that those dominated by hydrated silica.

Column measurements showed that there is a threshold concentration of base neutralizing agents below which little or no formation of blocking solids takes place. In the experimental conditions used in this study, the concentration of HCl or $NaHCO_3$ that caused the formation of solids was ca. 1 M. This indicates that high concentrations and/or masses of base-neutralizing agents need to be injected in the subsurface zone to form stable impermeable barriers that have the stability and spatial extent sufficient to block the movement of contaminated groundwater. Another observation pertinent to *in situ* solids formation in the column experiments is that due to local variations of hydraulic permeability and the presence of localized channels of movement of injected agents, the precipitated solids tend to be distributed non-uniformly through the soil column.

To circumvent the formation of spatially limited and/or non-uniform areas of solids formation, it may be preferable to ramp up the concentration of base-neutralizing agents slowly so as to ensure a uniform pattern of the permeation of such agents throughout the targeted area. Other sequences of injection of base-neutralizing and/or Si-destabilizing agents to create impermeable barriers should be considered as well. It is our opinion that the formation of in situ generated hydraulic barriers can be optimally achieved via controlled injections of $NaHCO_3$ or CO_2 gas through a system of wells designed to cause slow and uniform permeation of CO_2 (or $NaHCO_3$) to induce the deposition of stable Si-based solids in the control zone.

10. Treatment and Processing of Solids generated in *Ex-Situ* Treatment of OCC Groundwater

Although the research did not identify practical options for inhibiting Si precipitation *in situ* in the OCC soils, it did establish that practically all the dissolved silica can be removed from OCC groundwater in ex situ operations, either by adjusting the pH to an appropriate level (<10.5) or adding salts of calcium or magnesium to form insoluble silicates. These experiments showed that rapid addition of acids such as HCl or carbon dioxide cause massive gelation of treated water, but a controlled slow addition of these reagents results in formation of more compact solids that allow better solid/liquid separation.

Nevertheless, even with an optimal rate of addition of acid, the volume of the formed solids is substantial due to the occlusion of water in the solid phase. A large part of the occluded water can be eliminated by press-filtration and/or mild heating (to ca. 30 °C). The solids formed via such a process are almost pure SiO_2, with low levels of residual hydration water and an insignificant admixture of other elements.

While the preceding approach for *ex situ* removal of dissolved silica from groundwater is reasonably easily implementable technically, its practicality depends on other considerations, notably costs of base-neutralizing agents, transportation, and landfill fees etc. An important challenge associated with the ex situ treatment is the amount of solids produced by such process. Calculations indicate that for a 150 gpm pumping rate, the volume of produced solids would be ca. 13 m^3/day. However, it is likely that the amount of extremely high Si groundwater that needs to be treated may be limited, and once it has been removed and treated, the need to implement full scale ex situ Si removal operations will subside and perhaps ultimately disappear.

11. Conclusions

Key observations and conclusions of the study can be summarized as follows:

- When exposed to highly caustic solutions, OCC soils readily release high amounts of silica;
- OCC soils that have been affected by high pH solutions tend to release the retained caustic species (high pH) for a long time, but the amount of base released from such soils is probably insufficient to mobilize large amounts of silica from unaffected soils;
- Practically all the silica present in high pH high Si groundwater can be removed by *ex situ* water treatment; several options (e.g., decrease of pH by slow addition of HCl, addition of solutions of calcium or magnesium salts) exist for such treatment and post-treatment solids’ handling. The volume of solids produced in such operations may be a significant challenge;
- Realistic levels of silica precipitation inhibitors do not affect gelation phenomena in these systems;

- OCC soils unaffected by long-term contact with high-Si, high-pH groundwater are more prone to develop hydraulic fouling that those that have been affected by the contaminated groundwater;

- Slow pumping of high Si, high pH groundwater does not appear to cause rapid hydraulic fouling;

- Development of hydraulic fouling is likely to be associated with local decreases of pH in the soil, natural occurrence or enhanced formation of aluminosilicates and the presence of precipitation nuclei in the groundwater;

- Incipient hydraulic fouling can be reversed via injection of caustic regenerants;

- Injection of acidic agents into OCC Site soils affected by high pH will likely result in the formation of hydrated silica precipitates near the injection point. The formation of the precipitates will reduce the hydraulic conductivity of the aquifer in which the precipitates form. However, the extent of the reduction and the radius of the area of reduced hydraulic conductivity cannot be determined from the results of the current testing. Current data are also insufficient to ascertain whether hydrated silica precipitates formed in such conditions have adequate long-term stability.

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Abbreviations

AHA	Aldrich Humic Acid
ANC	Acid Neutralizing Capacity
BGS	Below Ground Surface
DI	Deionized (water)
DIC	Dissolved Inorganic Carbon
DOC	Dissolved Organic Carbon
HRT	Hydraulic Residence Time
ICP/MS	Inductively Couple Plasma/Mass Spectrometer
ISE	Ion Selective Electrode
NMR	Nuclear Magnetic Resonance
OCC	Occidental Chemical Corporation
ORP	Oxidation Reduction Potential
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
TOC	Total Organic Carbon
VM	Visual MINTEQ
VOC	Volatile Organic Compounds
XAFS	X-Ray Absorption Spectroscopy
XRD	X-Ray Diffraction

1. Experimental Methods and Approaches

This section describes main aspects of experiments carried out in this study. Due to the diversity of these experiments, additional details of their conditions and other important features are described in relevant sections (e.g., those concerned with results of column experiments, examination of release of high pH and conductivity etc.).

1.1. Chemicals and consumables

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.

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% HNO_3 for one to three hours prior to rinsing at least three times with DI water.

1.2. 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, Al, Ca and Mg.

An Agilent Data Acquisition/Switch Unit (Model 34970A, Agilent Technologies) was used for continuous data monitoring of various parameters during column tests. An electrochemical multimeter (Orion^{TM} Versa Star) was used with a high-pH electrode (Model 5994-23, Cole

Parmer) to record the pH of solutions in tests other than the column tests. The electrode was periodically calibrated using buffers at pH 4, 7, 10, and 12.45 prior to use with this instrument.

1.3. Instrumental analytical methods

ICP-MS measurements of concentrations of elements of concern

Due to the high concentration of matrix elements present in groundwater samples, a method that accounted for matrix effects was developed. This method reported in more detail in *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. Initial 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.

Concentrations of analytes 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.

Measurements of concentrations of total organic carbon (TOC)

A Sievers 900 Portable Total Organic Carbon TOC Analyzer (General Electric) was used to determine TOC concentrations. The analyzer in nominally calibrated for TOC concentrations up to 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.

1.4. Provenance and soil and groundwater samples

Groundwater and soil core samples used in the experiments were collected at the OCC site by Conestoga-Rovers & Associates (now GHD). 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 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 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'.

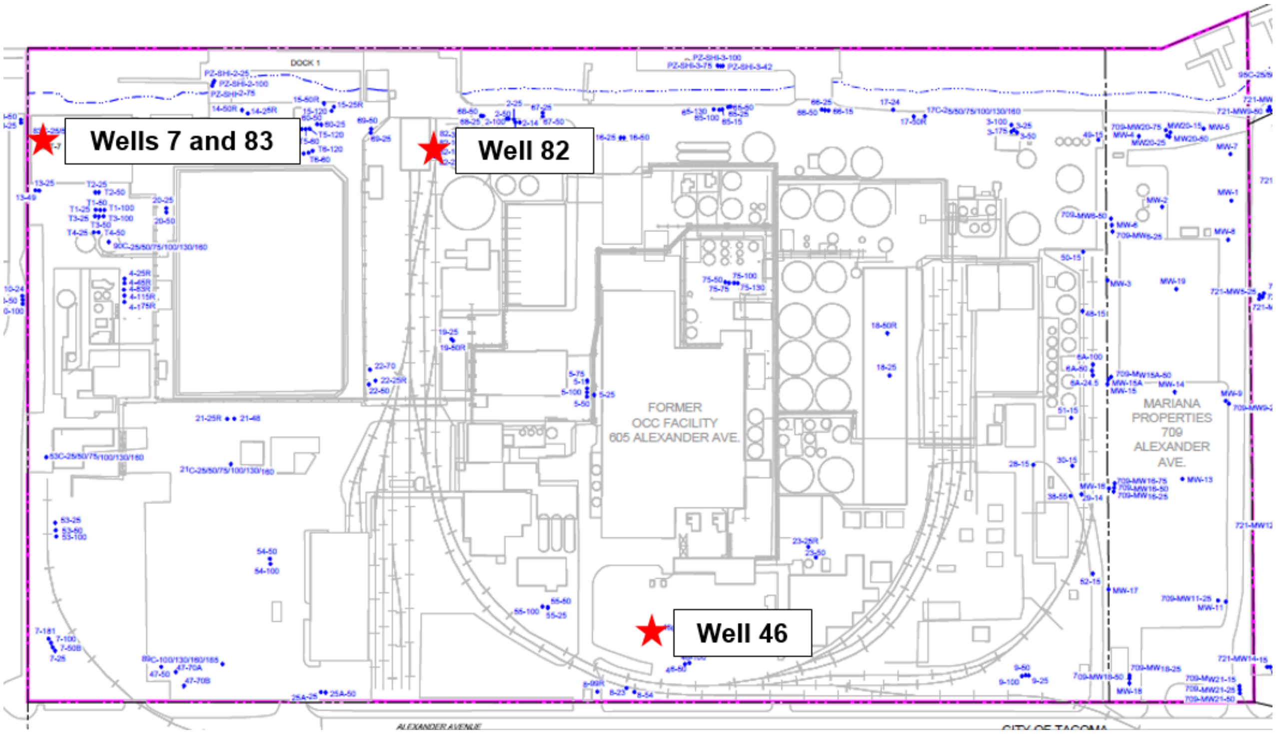


Figure 1 *General map of the OCC site with location of wells used to provide soil cores and groundwater samples for this study.*

Table 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 its soils are considered to be affected by the high pH, VOC, Si plume (Table 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 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 GHD 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.

1.5. Column test setup

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. In general, the design of column experiments reported in the reported followed recommendations presented in prior studies (e.g., *von Gunten and Zobrist* 1993; *Lewis and Sjöstrom* 2010).

Hardware of column tests

Column tests were conducted using one experimental setup for the duration of the study (Figure 2). Feed was injected into columns via a Cole-Parmer peristaltic pump. When needed, two such pumps were connected in parallel to achieve higher flows. When one or both pumps were operated near their maximum speeds, a Cole Parmer pulsation dampener was connected between the pumps and column to decrease hydraulic pulsation and vibration and enhance reliability of test results.

The pump(s) was connected using a polytetrafluoroethylene (PTFE) tubing to a Kontes Chromaflex column. The tubing was secured to the end of the column with a flangeless fitting. The Kontes Chromaflex glass column 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. The pressure transducers were connected to the flow system with polyvinylidene fluoride (PVDF) compression tees (McMaster-Carr). The transducers allowed measuring 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 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.

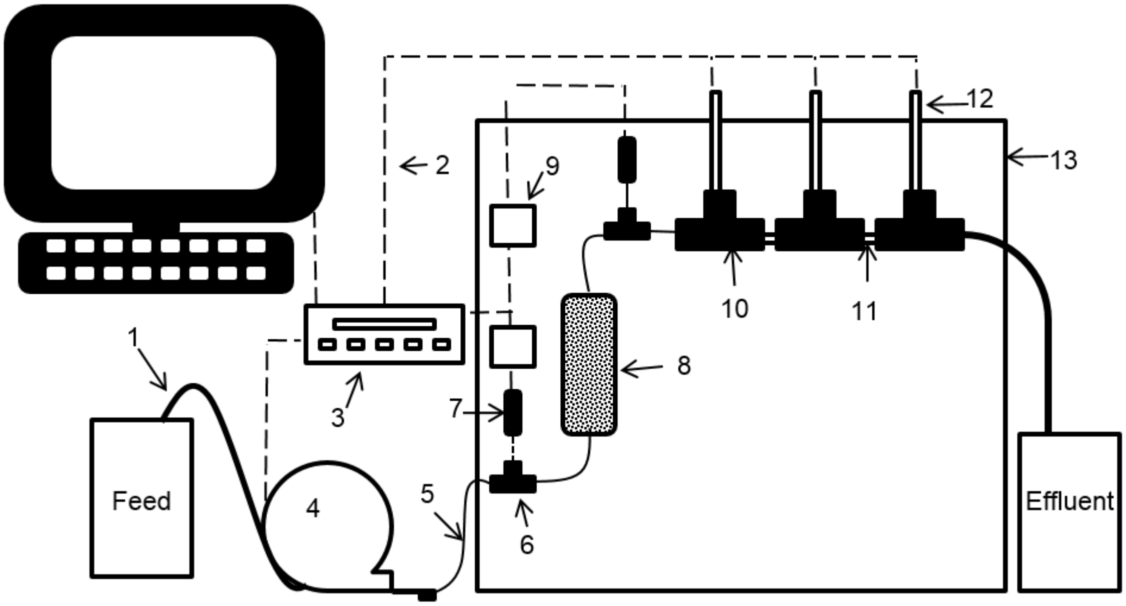


Figure 2 Schematic of column test setup. Labels are for the following equipment: 1. Masterflex Tygon pump tubing (Cole Parmer); 2. Electrical inputs/output Agilent Unit; 3. 20-channel Agilent Data Acquisition/Switch Unit (Model 34970A, Agilent Technologies); 4. Masterflex L/S Series Precision pump, peristaltic (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

Data acquisition in column tests

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.

1.6. Preparation for column tests

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 (in selected cases noted in the sections that follow, the use of glass wool was avoided). 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.

As already mentioned, the pH electrode was routinely 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.

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.

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. These results are presented in the *Results and Discussion* section of this paper.

Soil porosity measurements

Porosity of soils used in the column tests was measured using two methods, which yielded similar results. These porosity measurements were used to estimate the nominal 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= $V_{\text{water used in wet packing}} / V_{\text{column}}$

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

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

5. Dry samples in oven at 110°C for at least three hours
6. Allow samples to cool and weight contents

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

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

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

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

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

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

14. Compute porosity

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

Experiments on the dissolution of soils and model solid phases

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)

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 (containing a requisite amount of NaOH to increase its pH) 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 re-dissolve the solids, and samples were 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.

2. Chemical Properties of OCC Groundwater and Effects of pH on Solute Concentrations

Activities in these section were carried out to generate information relevant to these aspects of the exploration of OCC groundwater/soil systems:

- *To establish extent of variations of concentration of major components of examined groundwater;*
- *To determine their changes as a function of pH and other parameters such as blending;*
- *To examine whether observed concentrations of relevant elements are in agreement with predictions made based on general aspects of relevant geochemical equilibria examined using Visual MINTEQ.*

2.1. Concentrations of major components in OCC groundwater

Results of pH measurements for the groundwater samples representing the ambient water in contact with the examined OCC soils are presented in *Table 3*. As shown in the table, the pH of the groundwater varied from circumneutral which indicates a low or non-existent level of contamination with highly basic effluents released in the subsurface zone, to ca. 11.6 indicative of considerable contamination.

Table 3 Measured pH of OCC groundwater samples

Groundwater from Well # - depth (in ft bgs)	pH s.u.	Groundwater from Well # - depth (in ft bgs)	pH s.u.
7-130	11.6	82-100	11.6
46C-25	9.3	83C-25	7.00
46C-50	8.2	83C-50	7.00
46C-75	7.9	83C-75	7.8
46C-100	8.1	83C-100	9.8
46C-130	7.6	83C-130	11.4
82-30	11.3		

Table 4 presents concentrations of each ICP/MS-determined analyte in the groundwater samples. In these measurements, groundwater from Well 7 was analyzed separately because that water had a significantly higher concentration of Si than the rest of the groundwater samples. This made it necessary to use in that case additional calibration standards and a different dilution (x8000 times) that was needed to avoid over-saturation of the ICP-MS detector with Si ions. The last two columns of Table 4 present percent spike recovery and percent instrument drift during Groundwater 7 analyses. The percent spike recovery ranged from 96% - 122% and percent drift ranged from -3.7 % to 22%.

The concentration of each analyte vs. pH followed a consistent trend (increasing or decreasing, depending on the analyte) with pH. Visual Minteq (http://vminteq.lwr.kth.se/) modeling was used to predict the equilibrium concentration of the analytes and interpret the observed trends for the most geochemically important and in some cases abundant elements such as Si, Al, Ca, and Mg.

An input file that reflected the concentrations of all analyzed species at their maximum concentrations in the groundwater (selected from the data for all the groundwater samples, Table 4) was created in Visual Minteq (VM). The model input included the average concentration of total inorganic carbon (TIC), F^-, Cl^-, Br^-, NO_3^-, SO_4^{-2}, and PO_4^{-3}. These anions were analyzed separately and results of these analysis are presented in Table 5. As evident from the data in Table 5, some of the OCC groundwaters (82-100 and 83C-130) contain a significant amount of Total Organic Carbon (TOC). TOC concentrations show an increasing trend with increasing pH. However, because the characteristics of the DOC molecules were not known, the DOC was excluded from VM data input.

In the VM simulations, pH was varied from 7 to 14. Precipitation of thermodynamically possible solid phases that had lowest threshold of exceeding relevant solubility products was allowed. Variations in total dissolved concentration of the relevant analytes (e.g., H_4SiO_4, Al^{+3}, Ca^{+2}, Mg^{+2}) in the solution were examined at varying pHs. If the predicted concentration vs pH trend for the analyte was not as prominent or if the direction of the trend was contrary to experimental observations, an alternative solid phase was included as a precipitate. Figure 3 to Figure 6 compare VM model predictions of Si, Al, Ca and Mg levels with the observed concentration trends in the groundwater samples.

The trends predicted for selected elements (Si, Al, Ca, Mg) deemed to be important for gaining insight into the nature of processes in OCC groundwater are comparable with those observed in the experiments in which the pH of the groundwater was varied. Characteristically, the model predictions for the thresholds of dissolution for Si and Al (pH 11 onwards) and precipitation for Ca and Mg (pH 8 onwards) coincide with the observations made based on the groundwater analyses.

Model-predicted solution phase concentrations of Si and Al at pH>11 are lower than those actually measured in the groundwater when its pH was varied in our experiments (Figure 3 to Figure 6). One plausible explanation for this difference could be the formation of soluble complexes of Si and Al with organic compounds present in the groundwater and the colloidal mobilization of particles containing Si, Al and possibly other constituents (Abe et al. 2011, Taheri et al. 2013). Since the VM model input did not include organic carbon nor can it be used to model formation of colloidal species, the geochemical modeling approach did not account for possible impacts of complexes of silica as well as its binary and ternary complexes with metal cations with DOC thus resulting in lower predicted Si concentrations at high pHs.

Based on these observations, we conclude that Si concentration trends determined in the groundwater cannot be explained by the presence of only monomeric Si species as our data and those of prior research show that it is practically certain that multiple polynuclear and possibly micellar Si species are present in solution (*Lippmaa et al*. 1980; *Kinrade and Swaddle*, 1988; *Chan* 1989; *Kinrade et al.* 1998A; *Kinrade et al.* 1998B; *Bremere et* al. 2000; *Simonsen et al.* 2009). A simplified generic formula for the formation of dimeric Si complexes at a high pH (when $H_3SiO_4^-$ or $H_2SiO_4^{2-}$ anionic forms of silicic acid is expected to predominate) is presented below, similar formulas can be developed for other dimeric and polymeric complexes:

$$2 \cdot H_2SiO_4^{2-} + 2H^+ \leftrightarrow SiO(OH_2)OSi(OH_2)^{2-} + H_2O$$

$$K_{\mathrm{dimer}} = \frac{\left\{SiO(OH_2)OSi(OH_2)^{2-}\right\}}{\left\{H_2SiO_4^{2-}\right\}^2\left\{H^+\right\}^2}$$

Thermodynamic data concening the formation of dimeric, oligomeric and polynuclear Si species are not included in Visual Minteq database. If further modeling of equilibria relevant to Si speciation and solubility is warranted, relevant equilibria constants need to be determined and incorporated in the VM database.

VM calculations for Ca and Mg resulted in reasonably close predictions of the concentrations of these elements albeit those for Ca resulted in higher concentrations of the latter element compared with those determined for the examined groundwaters, especially at lower pHs (Figure 5). A possible explanation for the observed difference could be that VM-predicted Ca concentrations are based on the precipitation of a specific solid phase (calcite) while for actual aquifer conditions, other Ca solids may exist as well, or the solubility product for calcite formed in extreme conditions (high pH, very high ionic strenght) can differ from that in the VM database.

Notwithstanding the observed differences, we conclude that VM calculations result in an acceptable level of representativeness of the behavior of some components of OCC groundwater (Ca, Mg). These calculations allow estabishing the general location of the threshold of precipitation/mobilization of other system components, for instance Al and Si.

Table 4 Results of ICP/MS groundwater with data demonstrating spike recovery and relative instrument drift

Analyte	**UOM**	**Recovery**	**Drift**	**82-100**	**82-30**	**46C-25**	**46C-50**	**46C-75**	**46C-100**	**46C-130**	**83C-25**	**83C-50**	**83C-75**	**83C-100**	**83C-130**	**GW #7**	**Recovery**	**drift**
																	GW # 7 analysis	
pH				11.636	11.3	9.342	8.173	7.848	8.101	7.551	6.975	6.964	7.814	9.801	11.407	11.6		
Al	ppb	108.4%	8.4%	77621	7032	172	13	46	BD	BD	BD	BD	BD	BD	344663	539823	120.0%	19.6%
As	ppb	99.4%	-0.5%	94	0	BD	BD	BD	0	BD	BD	0	19	94	206	378	99.4%	-0.7%
Ba	ppb	111.0%	11.0%	510	BD	BD	325	565	243	464	500	613	367	10	BD	42	98.1%	-1.9%
Ca (48)	ppm	99.8%	-0.2%	BD	BD	BD	142	169	125	315	385	526	240	4	BD	BD	104.7%	4.7%
Ca(44)	ppm	98.6%	-1.4%	353	47	BD	139	169	129	325	350	489	214	16	558	405	102.3%	2.3%
Ca (42)	ppm	97.3%	-2.7%	1	BD	BD	131	166	140	342	364	525	252	42	15	BD	103.3%	3.3%
Cd	ppb	106.2%	6.2%	BD	6	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	97.9%	-2.1%
Cr	ppb	103.3%	3.3%	10	90	53	73	43	60	113	123	123	86	123	146	31	102.4%	2.4%
Cu	ppb	102.4%	2.4%	533	43	18	141	110	368	147	61	196	208	760	355	211	99.6%	-0.4%
Fe (54)	ppb	99.1%	-1.2%	515	1216	561	3836	2620	94	1871	421	BD	1591	140	5333	6130	99.2%	-0.5%
Fe (57)	ppb	103.6%	3.3%	331	1058	331	2446	1851	132	1521	1058	992	1521	397	2711	2977	97.2%	-3.1%
Mg	ppb	96.3%	-3.7%	189	76	132	180173	186225	146005	722143	757762	823968	280391	504	BD	134	104.4%	4.3%
Mn	ppb	101.3%	1.4%	2	12	4	366	314	150	540	44	2377	243	BD	BD	56	103.1%	3.1%
Ni	ppb	102.6%	2.6%	BD	BD	BD	0	5	44	146	BD	131	34	BD	44	245	100.5%	0.5%
Pb	ppb	121.5%	21.5%	57	BD	BD	BD	BD	BD	BD	BD	57	BD	BD	BD	71	95.9%	-4.1%
Si	ppm	105.3%	5.3%	22524	3592	BD	BD	BD	BD	BD	BD	BD	BD	107	35749	48109	114.0%	14.0%
Sr	ppb	103.3%	3.3%	220	76	8	2997	3650	2938	6826	6154	9285	5199	919	205	214	102.4%	2.4%
Tl	ppb	122.0%	22.0%	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	96.0%	-4.1%
V	ppb	104.0%	4.0%	1861	156	BD	261	96	107	89	78	99	198	482	1634	1057	102.8%	2.8%
Zn (64)	ppb	100.5%	0.5%	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	1727	106.0%	6.0%
Zn (66)	ppb	99.1%	-0.9%	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	1765	104.5%	4.5%
Zn (68)	ppb	98.7%	-1.2%	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	1862	103.2%	3.2%

BD Below detection

Table 5 Concentrations of total organic carbon (TOC) and important anions found in the OCC groundwater

Groundwater	pH	TIC	TOC	F	Cl	Br	NO3-N	PO4-P	SO4-S
		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
46C-25	9.34	847.4	6.8	6.3	12.3	ND	16.0	0.7	2.8
46C-50	8.17		29.7	9.5	12411.0	ND	21.6	4.1	0.7
46C-75	7.85	123.6	24.5	64.1	19303.0	ND	49.2	ND	0.8
46C-100	8.10	91.2	20.0	75.3	24396.0	ND	90.4	7.1	60.4
46C-130	7.55	237.6	12.5	55.2	20834.0	77.8	37.3	6.0	1.0
82-30	11.30	1673.1	56.2	25.5	2239.0	ND	0.9	1.7	353.0
82-100	11.64	5297.8	225.6	89.1	34326.0	ND	35.6	50.4	974.0
83C-25	6.98	17.8	1.9	52.2	17658.0	89.2	27.6	6.6	690.0
83C-50	6.96	41.8	6.4	54.9	20633.0	104.0	27.9	5.8	764.0
83C-75	7.81	78.7	20.8	71.5	36871.0	ND	33.9	10.6	772.0
83C-100	9.80	101.8	83.4	38.6	36953.0	ND	27.7	9.3	223.0
83C-130	11.41	2146.3	548.8	143.0	55167.0	ND	42.4	70.8	1392.0

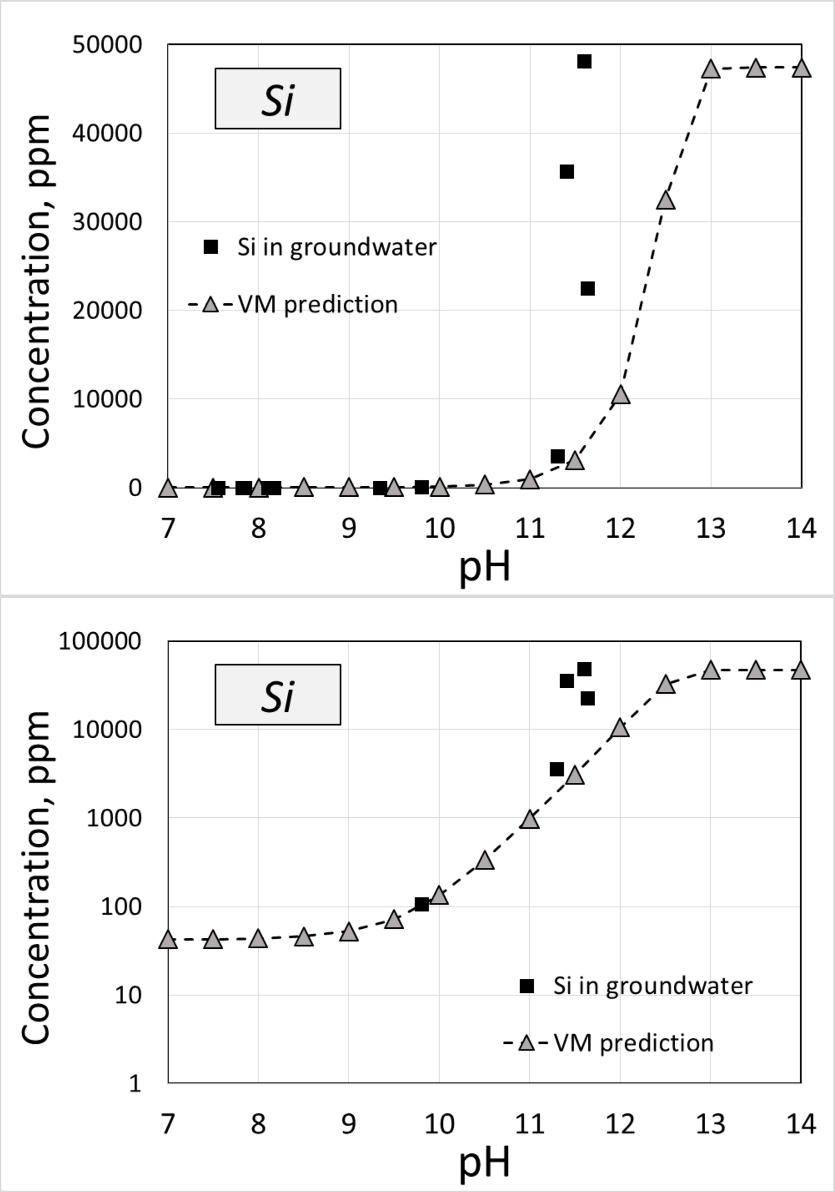


Figure 3 Comparison of effects of pH on Si concentrations measured experimentally in the OCC groundwater and predicted using VM modeling. Linear and log-scale representation of Si concentrations.

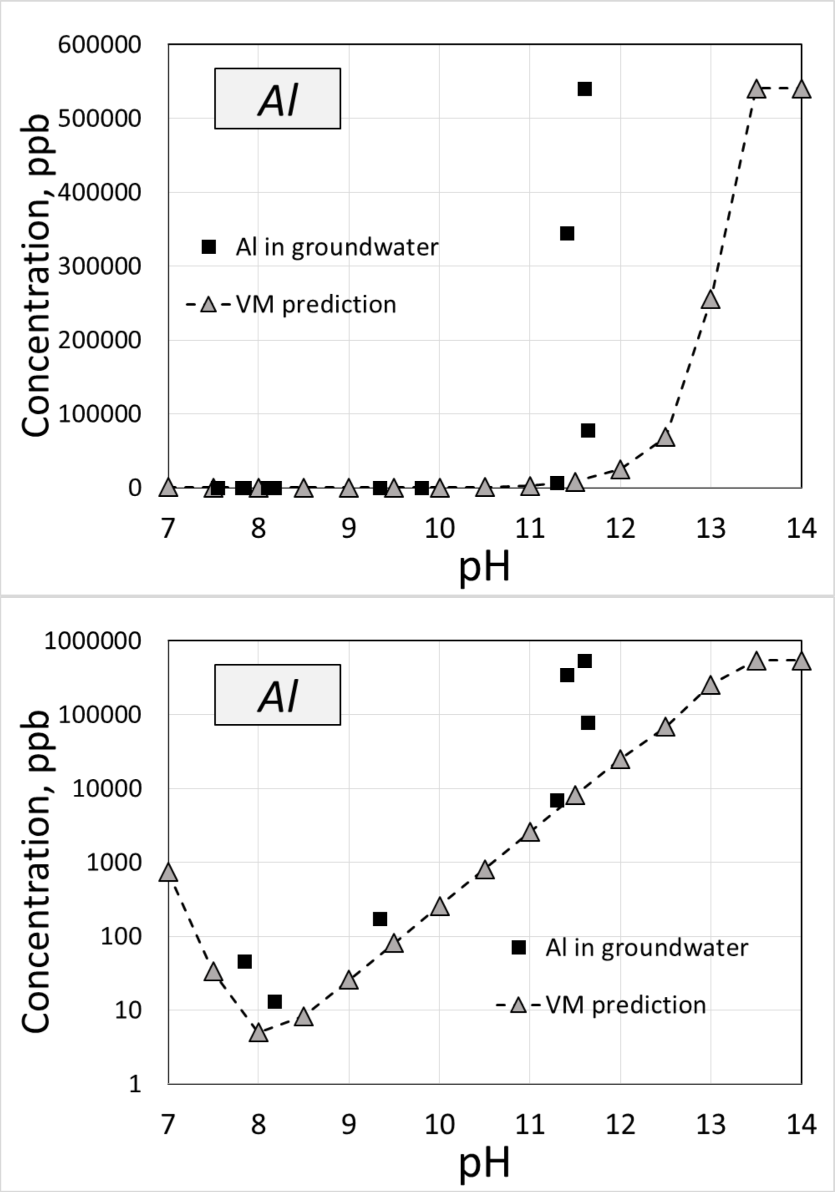


Figure 4 Comparison of effects of pH on Al concentrations measured experimentally in the OCC groundwater and predicted using VM modeling. Linear and log-scale representation of Al concentrations.

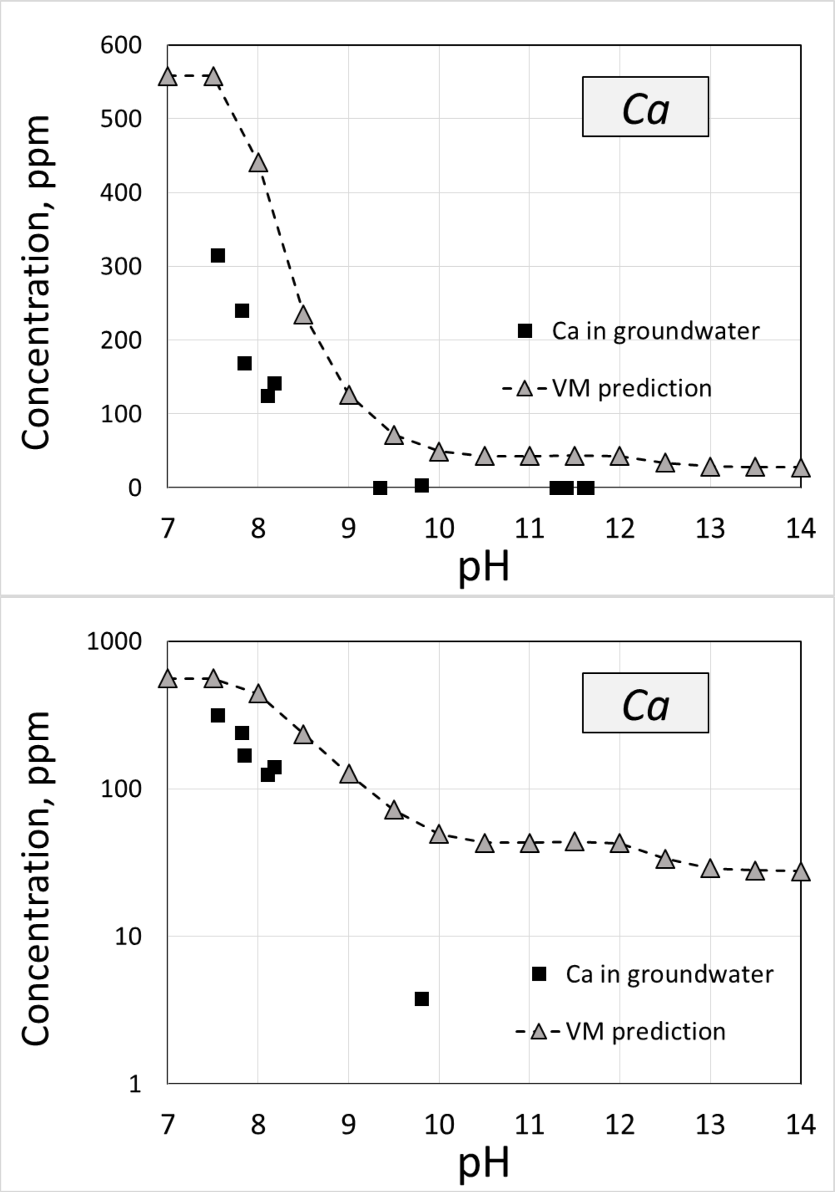


Figure 5 Comparison of effects of pH on Ca concentrations measured experimentally in the OCC groundwater and predicted using VM modeling. Linear and log-scale representation of Ca concentrations.

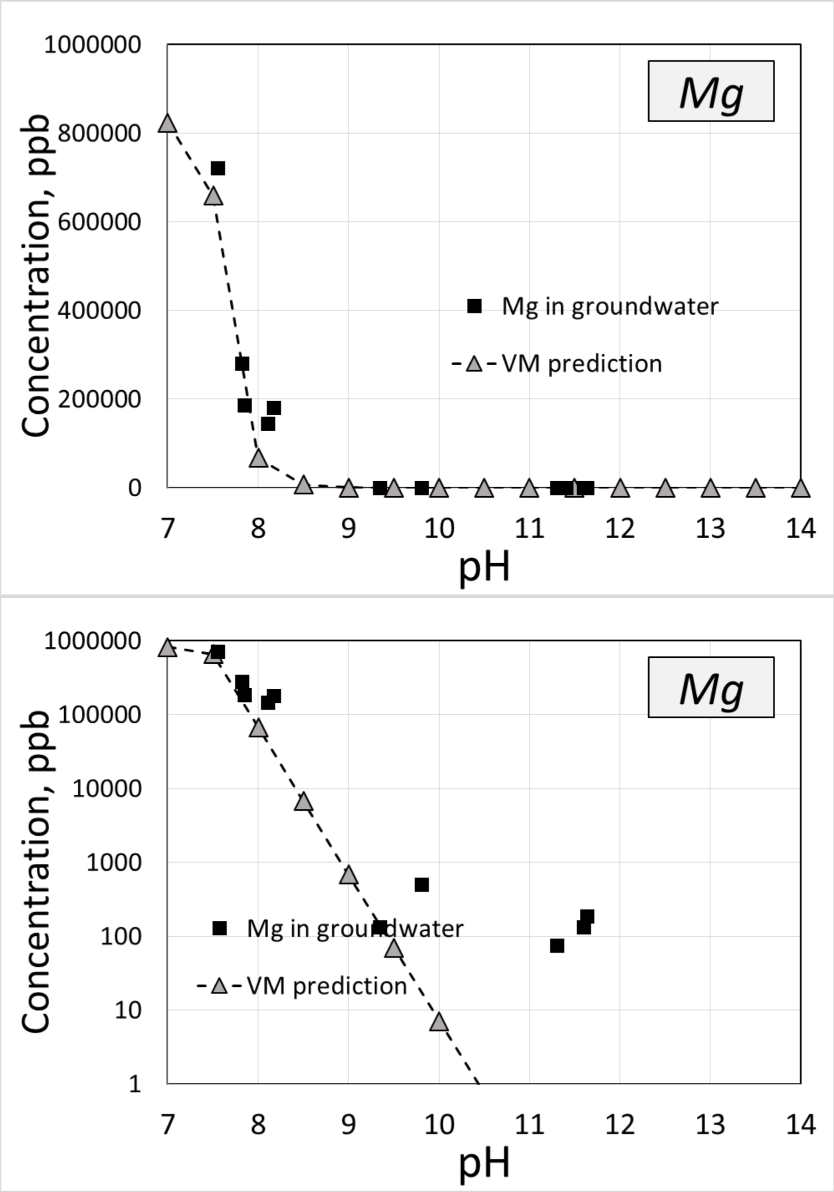


Figure 6 Comparison of effects of pH on Mg concentrations measured experimentally in the OCC groundwater and predicted using VM modeling. Linear and log-scale representation of Mg concentrations.

2.2. Aging of precipitates formed in OCC Groundwater.

Additional experiments were performed to determine how aging affects the stability of precipitated formed in pH-adjusted OCC groundwater. Experimental procedures used in these experiments were identical to those described in the sections above, with the pH being adjusted to 9.5 and concentrations of Si in the supernatant measured using the ICP/MS technique. Following the initial pH adjustment, containers with the recipitates and the supernatant were held for one hour, 10 days and 5.5 months. After that the pH was gradually increased and concentrations of Si solutes as a function of pH were measured. Results of these measurements together with those of modeling which is explained below are shown in Figure 7.

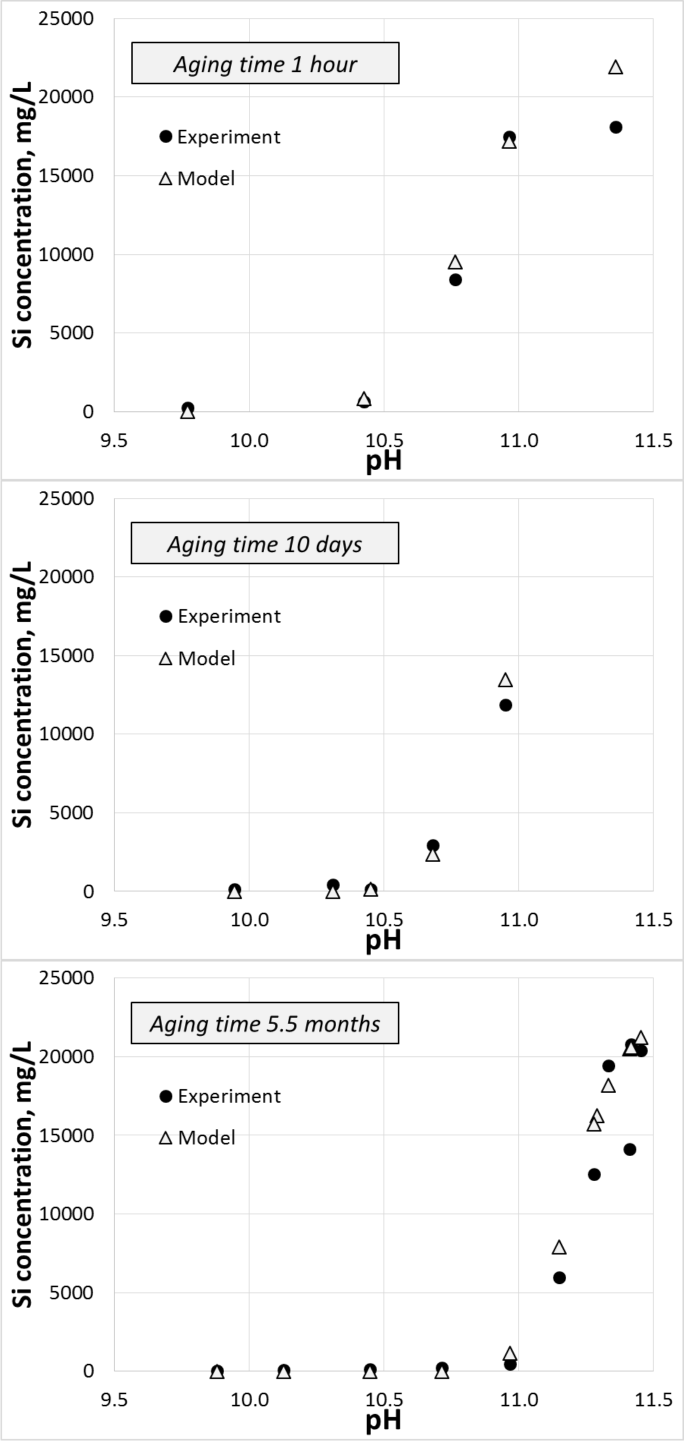


Figure 7 Effects of pH on the concentration of soluble Si species precipitated from OCC ground water and aged for 1 hours, 10 days and 5.5 months.

The data presented in Figure 7 showed that aging caused relatively small but consistent changes of the pH stability of the precipitates, with the edge of the initiation of precipitation moving to higher pHs as the aging time increased. To quantify this observation in more detail, the experimental pH data were fitted with a phenomenological fitting function shown below:

$$TOTSi = TOTSi_{\max}\left[1 - 0.5erfc\left(\frac{pH - pH_0}{\Delta}\right)\right]$$

In the above equation, pH_0 corresponds to the pH at which 50% of the total Si in the system is dissolved, Δ is the width of the edge of Si dissolution on the pH scale, $TOTSi_{max}$ is the maximum Si concentration, and *erfc* is the complementary error function (it is a standard function in Excel or Matlab). Results shown in Figure 7 demonstrate a close correspondence between the experimental and modeling data. The modeling also showed that the pH_0 values were 10.8, 10.9 and 11.3 for aging times 1 hour, 10 days and 5.5 months, respectively, while the Δ values for these conditions were 0.30, 0.25 and 0.20. These observations demonstrate that the aging of the precipitates is accompanied by some increase of their stability at pHs below ca. 11. However, the pH becomes closer to the pH_0 value determined for each aging time, the mobilization of Si from the precipitates increases more rapidly as these precipitates undergo aging. The fitting equation explained above was also used to estimate pH values corresponding to the mobilization of an *a priori* determined fraction (e.g., 5% or 10%) of total Si in the system. These calculations demonstrated that pH values that correspond to the mobilization of a 5% or 10% of the total Si in the precipitates increased nearly linearly with the logarithm of time, as shown in Figure 8. There results also show that changes of the pH stability of the precipitated solids will be relatively less noticeable with increases of aging time above ca. six month. Similar observations have been made in prior research concerned with the stability of Si solutes and precipitates (Alexander et al. 1954; Wiley 1980; Steffens et al. 2003).

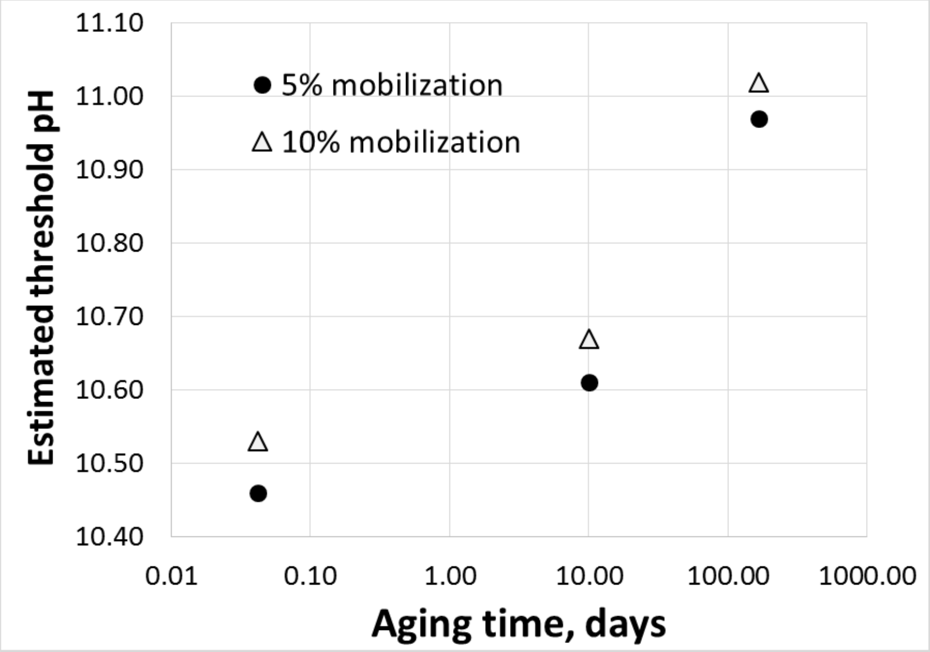


Figure 8 Effects of aging on the pH values associated with the dissolution of 5% and 10% of solids precipitated from OCC groundwater.

2.3. Precipitation in blended OCC Groundwater. Results of batch experiments

Batch experiments with OCC groundwater examined factors that may induce the precipitation of Si-based solids affecting the hydraulic conductivity of OCC soils. Groundwater from Extraction Well 7 was used in the majority of these experiments while in some of these experiments, groundwater of alternative provenance was used for blending. The occurrence of precipitation in groundwater blends was detected visually after a day-long period following which supernatant aliquots were taken for elemental analyses.

2.3.1. Blending of Well 7 groundwater and pH-adjusted deionized water

Effects of interactions of Well 7 groundwater with DI water are deemed to mimic those induced by the percolation of precipitation into the aquifer, and resultant dilution of Well 7 groundwater. Given that as precipitation moves across the aquifer, its pH will increase to, approximately, that of the ambient groundwater, the pH of DI water was increased by adding a requisite amount of NaOH to 12.5 prior to blending of this water with Well 7 groundwater. Well 7 groundwater was blended with this high pH-adjusted DI water at 10% increments.

No precipitation was observed within two hours after mixing yet within a day, precipitation was visually detectable for blends containing 50% to 70% of Well 7 groundwater. In contrast, visually detectable precipitation did not occur in the blends that had 80% and 90% Well 7 groundwater.

The occurrence of precipitation of Si based solids in Well 7 groundwater blended with pH-adjusted DI suggests that Si species in Well 7 groundwater contain polymeric Si species in addition to monomers of H_4SiO_4 and its deprotonated forms. This conclusion was made based on the results of VM modeling of the solubility of Si controlled by amorphous SiO_2 at varying concentrations of NaCl, as explained below.

Because NaCl is the major contributor to the ionic strength of Well 7 water and its blends, VM calculations were carried out for a pH range from 8 and 13 and varying ionic strengths. The ionic strength was controlled in these calculations by variations of NaCl concentrations. The VM calculations showed that decreases of the ionic strength similar to those that take place in the case of blending of Well 7 groundwater and pH-adjusted DI water are likely to cause an increase rather than a decrease of Si solubility (Figure 9) if the Si speciation is predominated by monomeric Si species. However, the opposite trend, that is to say the precipitation of Si solids was observed experimentally in these conditions. The difference between these observations and the opposite trend predicted by VM modeling indicates that the Si species other than the monomeric forms of silicic acid may control Si solubility and stability in Well 7 groundwater.

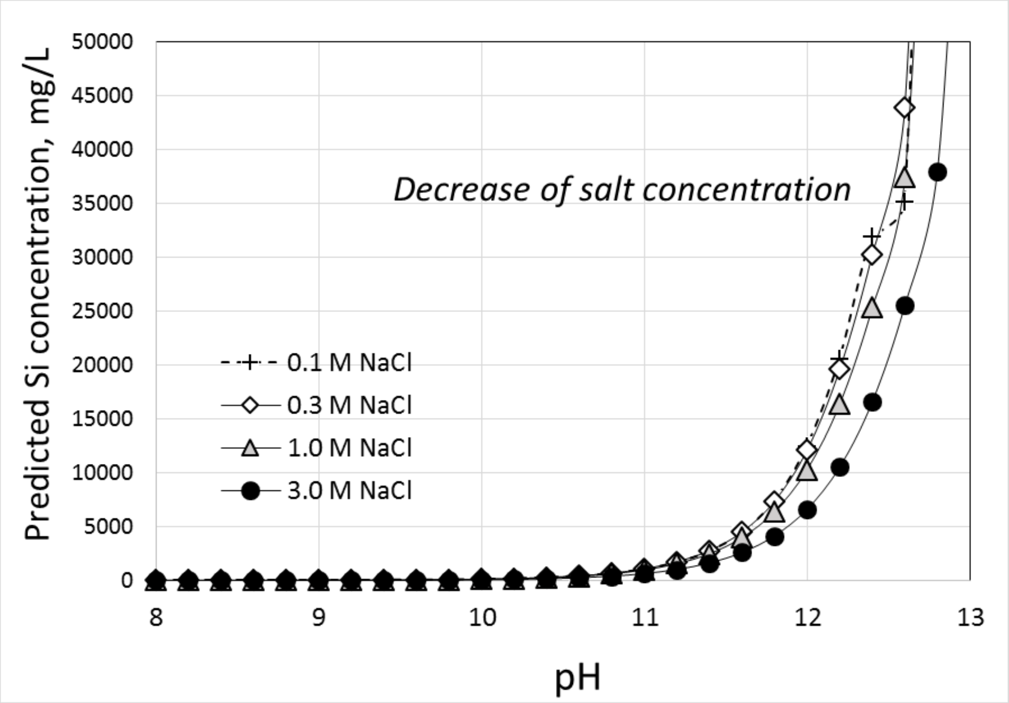


Figure 9 Effects of varying concentrations of background salt (NaCl) on total Si concentration in equilibrium with amorphous SiO_2. Results of Visual MINTEQ calculations.

The precipitates formed in Well 7 water blended with pH-adjusted DI water were small flocs that were morphologically different from the voluminous precipitate formed upon direct injection of acid and lowering the pH of Well 7 groundwater. ICP/MS analyses showed that the precipitates formed in the DI/Well 7 groundwater blends were largely based on Si with trace amounts of Al and Ca (Table 6). The similarity of the compositions of solids formed in the case of blended OCC groundwater and those precipitated when the pH of that groundwater was decreased may indicate that the initiation of the precipitation of Si-based solids is associated with the breakdown of colloidal Si-containing particles possibly stabilized by humic species that are abundant in OCC groundwater.

Table 6 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 Fraction in Precipitated Solids		
	Si	Al	Ca
70% Well 7/30% DI	97.4%	1.2%	1.4%
60% Well 7/40% DI	96.5%	2.1%	1.4%
50% Well 7/50% DI	95.2%	3.4%	1.4%

2.3.2. Blending with Si-free Well 7 groundwater

Further experiments examined effects of blending of Well 7 groundwater with the same groundwater from which a major part of Si had been eliminated. The elimination of Si was done by slowly lowering, using HCl, the pH of the water to 9.7, removing the precipitates by filtration and then increasing the pH of the filtered supernatant to the initial pH of 11.7.

Blending these two components using fractions of Si-free Well 7 water that were varied from 0 to 100% did not result in any precipitation for contact times up to a day. Thus it can be concluded that Well 7 water has components that, when present at relevant levels, inhibit Si precipitation. We posit that organic species extracted from OCC soils during their historically long-term interactions with high pH chlor-alkali effluents act as precipitation inhibitors, as was also observed in the column experiments described in the section that follows and elsewhere in the report.

2.3.3. Effects of incremental increases of concentrations of aluminum, calcium, organic carbon and sodium chloride

Further experiments were conducted to examine effects of varying concentrations of Al, organic carbon (quantified as TOC), and salts on the precipitation in Well 7 groundwater. Because earlier experiments showed that dilution of Well 7 groundwater to blends containing more than 20% of DI results in precipitation, these experiments were performed for blends containing 80% or more of Well 7 groundwater. All synthetic solutions blended with Well 7 groundwater had a pH at or slightly above 11.7 to ensure that changes in pH were not responsible for inducing precipitation.

In experiments to determine effects of aluminum, stock solution contained 2.5 g/l Al added as $AlCl_3*H_2O$ to DI water. The pH of this solution was adjusted to 12.6 with 1 *M* NaOH. Total concentrations of Al in Well 7 groundwater with additional Al levels were of 695 mg/l, 790 mg/l, and 980 mg/l.

Additions of Al resulted in a more prominent trend to form precipitates, as visibly detectable solids formed in the blends within 10 minutes in the sample with 980 mg/l Al. Similarly, precipitation was observed for 695 mg/l and 790 mg/l Al concentrations within a day of Al injection. Given that the concentration of Al naturally present in Well 7 groundwater was ca. 540 mg/L, the selected increment of Al concentrations allowed increasing its levels by ca. three times. Morphologically, the precipitates in the presence of increased Al concentrations were voluminous 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 7).

To examine effects of organic carbon, the TOC concentration in Well 7 groundwater was increased by blending a TOC solution with Well 7 groundwater. The TOC solution had a 2.5 g/L concentration of organic carbon and its pH was adjusted to pH 12.1. TOC was added as commercial Aldrich humic acid (its carbon content was assumed to be ca. 50% C) to DI water whose pH was increased with 1 *M* NaOH. The TOC solution and Well 7 groundwater were blended to yield samples with the following increments of TOC concentrations over that initially present in Well 7 water: 0.87 g/l, 0.95 g/l, and 1.12 g/l. These TOC levels allowed increasing the overall DOC concentrations in Well 7 groundwater from its initial level of ca. 0.55 mg/L (in the absence of additions of Aldrich humic acid) to ca. 1.67 g/L at its highest concentration.

No precipitation was observed in the 0.87 g/l TOC increment sample but 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 7).

The effect of increasing the salt concentrations of Well 7 groundwater was investigated by adding additional NaCl to the groundwater. The levels of NaCl chosen for these experiments allowed increasing the concentration of NaCl by up to three times over its initial level. Blends with an incremental NaCl concentration below 509 g/l (ca. 8.7 mol/L NaCl) did not result in precipitation, though there was visible precipitation within one day in the sample for a sample containing a 636 g/l NaCl (10.9 mol/L) concentration. The mass fractions of the major metals in the solids formed in these experimental were similar to those in the TOC blends and from acid addition (Table 7).

Table 7 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%

Formation of flake-like solids was also observed in the groundwater once calcium chloride was added to it. Similar observation for relevant albeit chemical distinct systems were reported in prior studies, for instance *Lakshtanov and Stipp* 2010. The flakes were harder to break than those formed in the acid addition experiment; a higher mixing speed was therefore used to break them into smaller particles. Solids comprised a large portion of the suspension at the end of the experiment, occupying about 50% of the suspension after a day of settling (Figure 10). Dissolved Si concentration decreased and the corresponding percent Si precipitated increased after each $CaCl_2$ addition. The $CaCl_2$ addition did not dilute the groundwater noticeably, so the percent groundwater was assumed to remain at 100% throughout the experiment. The pH of the suspension was ~11 at the end of the experiment.

Figure 11 shows increasing Si precipitation with $CaCl_2$ addition. The percent Si precipitated is linear with $CaCl_2$ addition. About 80% Si was precipitated with 2 g of $CaCl_2$ addition to 100-ml groundwater. If these results are extrapolated, about 2.6 g $CaCl_2$ per 100-ml of groundwater would be required for 100% Si removal.

The visual observations and analytical data presented above indicated that rapid addition of either $CaCl_2$ or acid to groundwater generates a large volume of solids that require further processing and disposal, whereas slow addition of acid or salt generates a much lower amount of solids (about 40-50%) of total batch volume. Thus, rapid addition of reagents should not be used for Si removal from the groundwater. It appeared that slow addition of $CaCl_2$ resulted in a marginally larger volume of solids than slower acid addition.

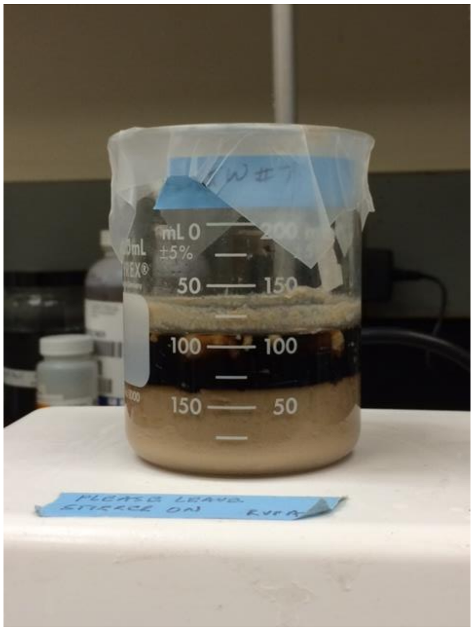


Figure 10 Visual appearance of solids precipitated as a result of slow $CaCl_2$ addition to groundwater from Well 7 at 130-ft depth (initial pH: 11.6, Final pH: 11.09)

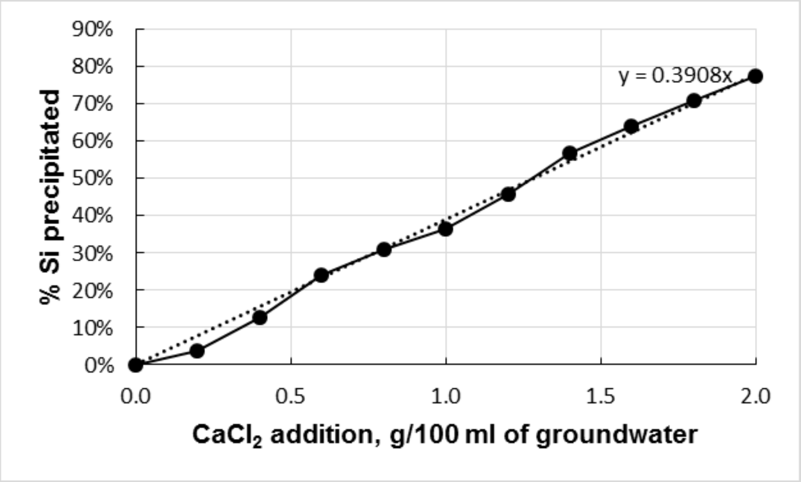


Figure 11 Percent Si precipitated as a result of slow $CaCl_2$ addition (Groundwater from Well 7 at depth 130-ft)

2.4. Blending different OCC groundwaters

The heterogeneity of the OCC site results in the occurrence of groundwaters with very different chemistries. As results, *in situ* blending of these groundwaters may cause precipitation of solids. An extreme case of such blending was simulated by mixing Well 7 groundwater with largely 'unaffected' Well 46C-130 groundwater.

These experiments showed that blends that contained > 5% of Well 46C-130 groundwater exhibited relatively rapid precipitation. This was despite the fact that blends whose compositions ranged from 90% Well 7/10% 46C-130 to 50% Well 7/50% 46C-130 all had pH close to 11.7. We posit that precipitation may have occurred due to highly localized pH decreases that may have taken place during the addition of Well 46C-130 groundwater that has a circumneutral pH. It was notable that 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 8).

Another plausible blending scenario associated with the pump and treat operations at the OCC site is that of mixing of Well 7 and Well 83C-100 groundwaters, and also Well 83C-100 and Well 82-100 groundwaters. Specifically, we posit the extraction of Well 7 groundwater could cause vertical mixing with groundwater from above-position strata of the aquifer, for example Well 83C-100 groundwater. Similarly, Well 83C-100 groundwater may also need to be extracted because it is highly contaminated with VOCs, and extraction of this groundwater may likely cause horizontal mixing with groundwater from Well 82-100.

Measurements showed that a blend with 75% Well 7/25% 83C-100 did not result in precipitation within one day but precipitation did occur 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%. This was similar to the behavior of Well 7 groundwater with pH-adjusted DI water, as described in the preceding section of the report. The composition of the solids formed was similar to those for the Well 7/46C-130 blends (Table 8).

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 8).

Table 8 Mass fractions of Si, Al, and Ca 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%

2.5. Summary of results from batch experiments concerning with effects of blending on the precipitation of Si-based solids

The data discussed above show that the precipitation of Si-based solids from blends predominated by Well 7 groundwater was affected by pH, rate of mixing/addition, dilution of Well 7 groundwater, and concentrations of constituents in the groundwater. Effects of these factors are summarized in Figure 12.

This figure shows that increasing Al, salt and TOC concentrations in Well 7 groundwater results in precipitation. Precipitation induced by increasing NaCl concentrations with Na levels above 200 g/l may be due to increasing ionic strength. However, it is unlikely that the Na concentration in Well 7 groundwater will naturally exceed this concentration.

Increasing the Al concentration also results in precipitation, most likely due to the formation of mixed Al-Si solid phases which have a wide range of compositions and, in some cases, low solubility. Somewhat more prominent precipitation observed for increased TOC levels may indicate that effects of humic acid are more complex than predicted based on the assumption that humic acid increases Al complexation and thus should lower rather than increase the susceptibility to precipitation.. In all observed cases, Si made up by far the largest mass fraction of metals in the precipitates

Blending OCC site groundwaters may induce precipitation in some important cases. For instance the formation of Well 7/Well 46C-130 blends was observed to cause precipitation although the pH of the blends was stable. Mechanisms associated with this phenomenon are unclear albeit we posit that this precipitation might have been induced by temporary localized lowering of pH and resultant formation of reactive micronuclei that catalyze further growth of solid phases. The actual occurrence of this or similar effects in field conditions is unclear since much more gradual blending than that tested in our experiments will likely occur in the field.

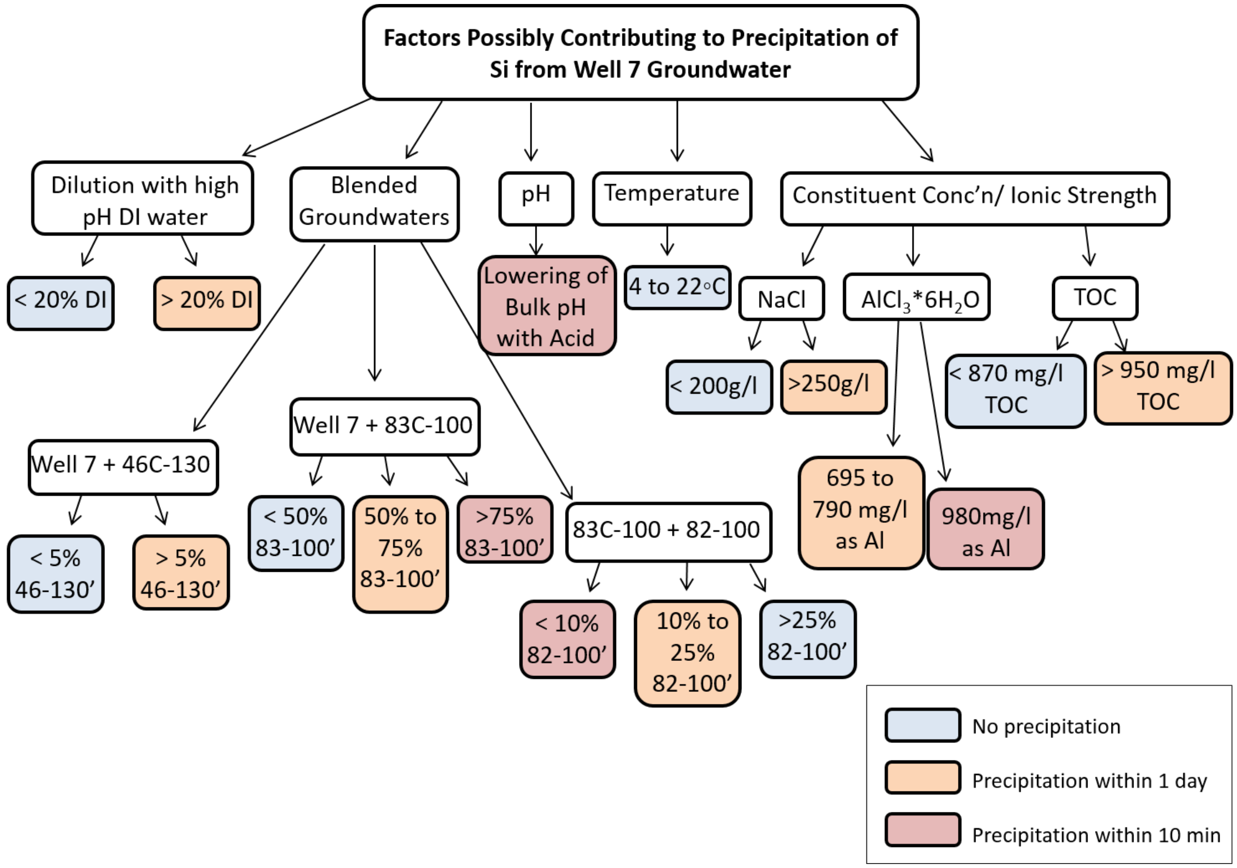


Figure 12 Flow chart describing trends associated with effects of different factors on the occurrence and rate of precipitation of Si-based solids in blended Well 7 groundwater.

3. Acid-Neutralizing Capacity of OCC Soils (Task B-2C)

Experiments described in this section were conducted to quantitate the capacity of OCC soils, both affected and unaffected, to interact with and consume acidic species that are present in ambient water as H^+ or, as discussed in other sections of the report, other components that can release protons, for instance bicarbonate ions. Values of the acid neutralizing capacity (ANC) of OCC soils are expected to be useful in two remediation-relevant contexts. First, the ANC is a measure of how much base may be released from a known amount of soil interacting with uncontaminated groundwater that enters the site. Second, ANC values can be used to estimate the extent of the decrease of pH caused by the Specifically, the experiments sought to answer these questions:

- *What is the range of acid neutralizing capacity (ANC) values of OCC soils?*
- *How different are the ANC values of affected and unaffected soils?*
- *Can the pH of soil suspensions be used as a measure of ANC values of the suspended soil?*

ANC values of OCC soils were examined based on potentiometric titrations of soil suspensions (typically, 10 g dry soil per 50 mL of solution). These titrations used standardized 0.01 mol/L, 0.1mol/L, and 1mol/L HCl titrants for well 46, well 83 and well 82 respectively. The titrations were carried out using an automatic Mettler - Toledo G20 titrator and a high-precision pH probe. The procedure included an initial equilibration period with gentle mixing (around two minutes) during which the pH of soils suspensions stabilized to reach an initial pH value characteristic of each soil. The initial pH value determined for each stabilized soil suspension was correlated with the extent of acid neutralization degree of that soil.

As outlined in prior sections of the report, the titrations were carried for soils extracted from a largely unaffected site area (Well 46), a partially affected area (Well 83) and a strongly affected area (Well 82). The latter well is largely collocated with the origin of the high pH plume characteristic of the OCC.

The titrations yielded dependences of pH of soil suspensions vs. volume of titrant added. These data were converted to amounts of acid added per unit of dry soil weight. These calculations gave estimates of acid-neutralizing capacity of OCC soils expressed in μeq acid/g dry soil units.

The data showed that the ANC values of the examined soils varied by several orders of magnitude depending on soil provenance and its contact with high pH effluents. Typical titration profiles for selected soils from Well 46 and Well 82 are compared in Figure 13. It demonstrates that for soils whose suspensions had high initial pH values (e.g., pH >9), titration profiles tended to have inflections that are potentially indicative of specific types of groups consuming the added acid. These groups are likely to be associated with carbonate and hydroxyl species in the soils but their nature needs to be examined in more detail. On the other hand, potentiometric curves for soils whose suspension had initial pH values <9 tended to lack pronounced features.

The ANC values of soils from unaffected and affected areas of the site were compared based on the amount of acid needed to decrease the pH of soils suspension from its initial value to a pre-determined point (e.g., pH 5.5). The ANC values defined in this way were correlated with the initial pH of the soils suspensions. Figure 14 demonstrates this relationship for soils from

Wells 46, 82 and 83 separately, and the relatively strong linear correlation determined for the entire set of the examined OCC soils (R^2 0.80). Given that in practically all cases the ANC values were highest (up to > 1000 μg acid/g soil) for samples originating from Well 82, there is little doubt that contact with high pH groundwater increases the ANC values by orders of magnitude compared with largely unaffected soils whose ANC values tended to be < 25 μg acid/g soil.

To provide more specific observations, the measurements showed that the range of ANC values for Well 46 soils was 0.6 to 22 μeq acid/g soil, confirming the low content of base in the unaltered soils. ANC values for Well 83 soils collected at up to 122 ft BGS were from 0.7 to 22.2 μeq acid/g soil. Well 83 soils from deeper strata had ANC values of 176 to 199 μeq acid/g, which indicate a moderate level of the alteration of soil properties by high pH effluents. Well 82 soils from 54 to 79 ft BGS had extremely high ANC values (ca. 1200 to 2600 μeq acid/g), and lower but still elevated ANC values (ca. 60 to 220 μeq acid/g) at shallower and deeper locations.

These results indicate that the generation of *in situ barriers* are likely require large amounts of strong acids that must be used to decrease the pH of groundwater/soil system to an a priori determined threshold value, for instance <10.5. In this case the required amount of a strong acid such as HCl would be as high as 1 mol per kg of an affected soil with a 1000 μeq acid/g ANC value (Figure 13). However, the neutralization of base in the vicinity of wells other than Well 82, for instance Well 83 are likely to require amounts of HCl that are several times lower than that estimated for Well 82 soils.

The observed correlation between ANC values of OCC soils and pH of ambient water in equilibrium with these soils may allow estimating ANC values for any area of the site in some situations, for instance when the groundwater moves through ambient soils slowly enough to equilibrate with its dominant solid phases. Such data in combination with other parameters may be of considerable help for practical treatment operations as well as for fate and transport modeling for the OCC.

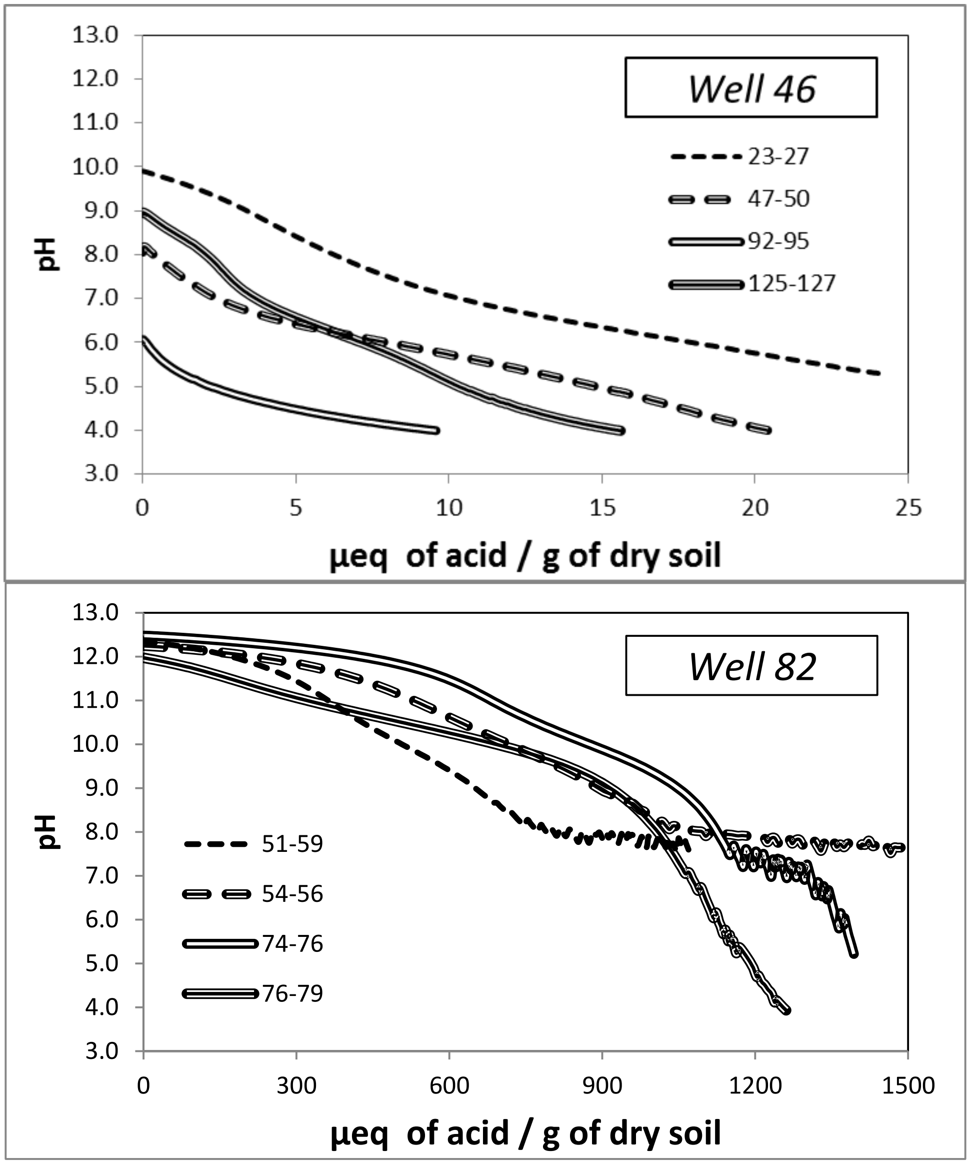


Figure 13 Comparison of titration data for suspensions of soils originating from Well 46 (largely unaffected area of the site) and Well 82 (highly impacted area of the site).

Table 9 pH of water/soils suspensions and acid neutralizing capacity of soils from Well 46 (samples are unaffected by high pH, high Si groundwater)

	Soil samples from Well 46		
Depth, feet bgs	pH of water/soil suspension	Q, μeq acid/g soil	logQ, μeq acid/g soil
23-27	9.9	22.2	1.35
47-50	8.1	11.6	1.06
50-52	9.0	4.3	0.64
70-72	7.0	0.6	-0.24
72-75	7.8	4.2	0.62
92-95	6.1	0.8	-0.10
95-97	6.9	4.3	0.63
97-100	8.7	6.6	0.82
100-102	9.1	4.3	0.63
112-115	8.7	15.7	1.20
125-127	9.0	8.9	0.95

Table 10 pH of water/soils suspensions and acid neutralizing capacity of soils from Well 83 (samples are unaffected or moderately affected by high pH, high Si groundwater)

Soil samples from Well 83			
Depth, feet bgs	pH of water/soil suspension	Q, µeq acid/g soil	logQ, µeq acid/g soil
20-22	7.1	5.4	0.73
47-50	6.4	1.0	-0.01
50-52	6.1	0.7	-0.15
52-55	6.7	2.6	0.42
70-72	8.5	15.9	1.20
72-75	8.9	22.2	1.35
75-77	8.8	1.3	0.11
79-80	10.2	4.5	0.65
80-82	10.4	16.0	1.20
90-92	8.4	7.3	0.86
102-105	9.0	1.2	0.08
109-112	11.2	186.0	2.27
115-117	11.2	185.0	2.27
125-127	11.0	199.0	2.30
127-130	11.2	176.0	2.25

Table 11 pH of water/soil suspensions and acid neutralizing capacity of soils from Well 82 (most samples are highly affected by high pH, high Si groundwater)

Soil samples from Well 82			
Depth, feet bgs	pH of water/soil suspension	Q, µeq acid/g soil	logQ, µeq acid/g soil
16-19	10.5	162.0	2.21
29-31	10.8	153.0	2.18
31-34	10.3	57.0	1.76
54-56	12.2	2588.0	3.41
74-76	12.5	1400.0	3.15
76-79	12.0	1192.0	3.08
91-94	10.9	219.0	2.34

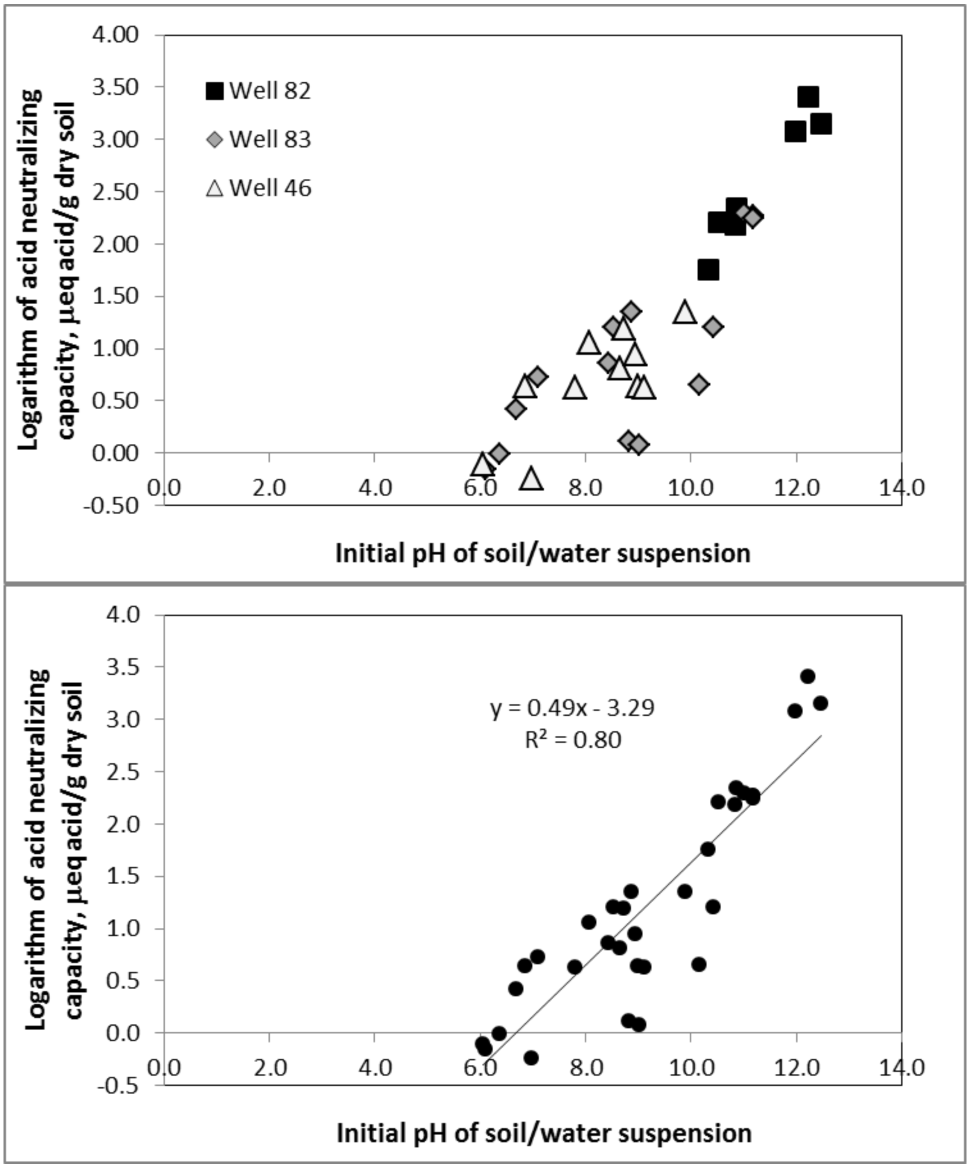


Figure 14 (A) Comparison of acid-neutralizing capacities of soils originating from unaffected and affected areas of the OCC. Shown data correspond to the specific amount of acid needed to decrease the pH from its initial value in each soil/water suspension to pH 5.5; (B) Correlations between the initial of pH of soil/water suspensions and corresponding acid neutralizing capacities for all OCC soils.

4. Release of Silica and Aluminum from OCC Soils

Goals of the experiments described in this section were to quantify release of Si and Al from OCC soils, as a function of time, ambient temperature and soil provenance. Model solid phases whose behavior in relevant conditions was explored in prior studies (e.g., *Fleming and Crerar* 1982; *House and Hickinbotham* 1992; *Niibori et al.* 2000) were also used in these activities which sought to answer several questions:

- *How rapidly are Si and Al released from OCC soils and model compounds exposed to high pH solutions?*
- *Are there differences between the behavior of OCC soils and model compounds?*
- *Can interactions observed for high pH solution/soil or model solid systems lead to structural changes potentially relevant to the development of incipient or full scale fouling in OCC soils?*

These activities utilized exposures of representative OCC soils, and model compounds (sand and three types of clay minerals) to 1 M NaOH at temperatures varying from 4C to 55C. For comparison, OCC soils and sand were also exposed at 55C to Well 86-30 groundwater that had a 3.6 g/L Si concentration and pH 11.3 which is much lower than that of 1 M NaOH (pH 13.8).

The rationale for experiments carried out at varying temperatures was two-fold. First, measurements of temperatures of groundwater in the OCC zone indicated that in some cases the temperature is elevated by several degrees C compared with the ambient temperature of the subsurface zone. The nature of the observed increases of the temperature in the subsurface zone is unclear but it is likely to be related to the occurrence of exothermic reactions between hydroxide ions and silica-based solids. Further quantitation of the thermochemistry of such interactions may be extremely valuable for the remedial activities and modeling of the processes at the OCC but in the context of this study this warranted having a comparison of results of NaOH/solids interactions at normal and increased temperatures. A second rationale for carrying out experiments at increased temperatures is to accelerate the reactions and obtain needed data within a feasible time period (e.g., several weeks) compared with the many decades-long interactions in the actual locus of these reactions.

Two soil samples including an unaffected soil from Well 46, depth 47 feet and an affected soil from Well 83, depth 128 feet were selected for batch dissolution experiments. Selected model compounds included standard Ottawa sand deemed to represent the behavior of SiO_2 solids in their crystalline form, and clay minerals bentonite, kaolinite and montmorillonite. The latter solids were deemed to mimic relevant properties of clays found at the OCC; these clays are also readily available commercially.

In the first batch experiment, soils from the OCC site and sand were exposed to 1 *M* NaOH at 55°C. The same solids were also exposed to Well 82-30 groundwater, which has a lower pH and notable albeit relatively lower, compared with those for Well 7 groundwater, concentration of Si, Al and TOC. The exposures in the latter case were at 25°C, 35°C, and 55°C. Supernatant samples were taken as needed, typically weekly from all samples for ICP/MS analyses.

Visually, interactions of the examined solids with 1 M NaOH commenced almost immediately after the initiation of the exposure. Within a week of exposure, the color of the supernatant formed in the presence of OCC soils was well developed while the solid phase was less dark visually compared with its color prior to the exposures (Figure 15). ICP/MS analyses of supernatant samples showed that there was a rapid release of Si from the OCC site soils, with somewhat more dissolution occurring from the 'affected' Well 83C-128 soil than 'unaffected' Well 46C-47 soil (Figure 16).

It is noteworthy that the concentration of Si in the supernatant in batch experiments with soils from Well 46C-47 and Well 83C-128 was only slightly below 10 g/L. This level is comparable albeit ca. four times lower than the concentrations of Si in Well 7 groundwater. Given that the exposure time in the subsurface zone was many decades, the comparable concentrations of Si found in the short-term batch experiments and those in extremely long-term exposures point to a very high reactivity of OCC soils towards caustic effluents with sufficiently high OH^- concentrations. This is all the more notable that, in contrast, release of Si from the sand model phase was relatively insignificant.

Aluminum was initially rapidly released from OCC soils but its concentrations detected in the beginning of the batch exposures were two orders of magnitude lower than those of Si (Figure 17). Following the initial spike of Al levels, its concentrations decreased in all samples. After ca. two weeks of exposure, the Al concentrations were comparable to those found for the batch exposures of sand. This indicates that Al is a labile component of OCC groundwater, and its non-monotonic behavior and a rapid removal in the presence of OCC soils is indicative of secondary reactions, most likely formation of alumosilicates that do not exert a strongly limiting influence on the solubility of Si species yet they control the behavior of Al (*Ohman et al.* 1991). This finding may be important due to its implications in the interpretations of the data of soil column experiments in which Al was observed to promote hydraulic fouling, as discussed in the sections that follow.

The second experiment was conducted by exposing the same solids to Well 82-30 groundwater at various temperatures. As was observed in experiments with 1 M NaOH, one week of incubation caused considerable changes of the color of the supernatant (Figure 18) which is clearly associated with the dissolution of organic matter from the soil. TOC analyses showed that increases of the ambient temperature were associated with a somewhat more rapid TOC release, and that the mobilization of organic species was slightly more prominent from the affected Well 83C-128 soil compared with the data for unaffected Well 46C-47 soil but these changes were of secondary importance (Figure 19).

Variations of temperature did not cause significant changes of the levels of Al released from either of the exposed soils (Figure 20 and Figure 21). We also observed that Si levels in the supernatant formed for OCC soils in contact with Well 83-20 groundwater practically did not increase (data not shown) albeit ca. 1.5 g/l Si was released almost immediately from Well 83C-128 soil following which Si concentrations were stable at all temperatures. This result is clearly indicative of the effects of hydroxide ion concentrations, which are several order of magnitude lower in Well 83C-40 groundwater (pH 11.3) compared with 1 M NaOH (pH=13.7).

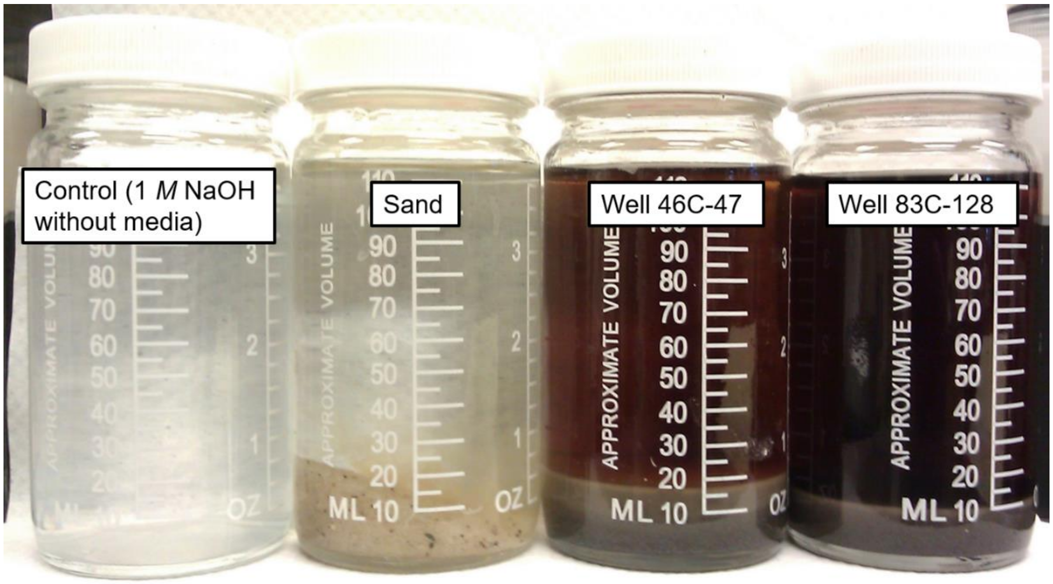


Figure 15 Visual appearance of supernatants in contact with sand and OCC soils exposed to 1 M NaOH at 55°C after one week of incubation

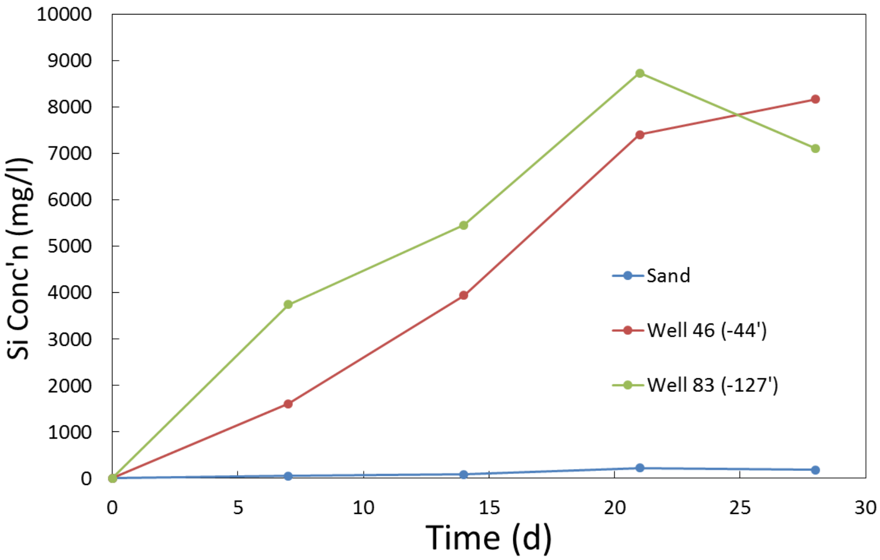


Figure 16 Silica release from sand and OCC soils Well 46C-47, and Well 83C-123 in contact with 1 M NaOH, 55°C.

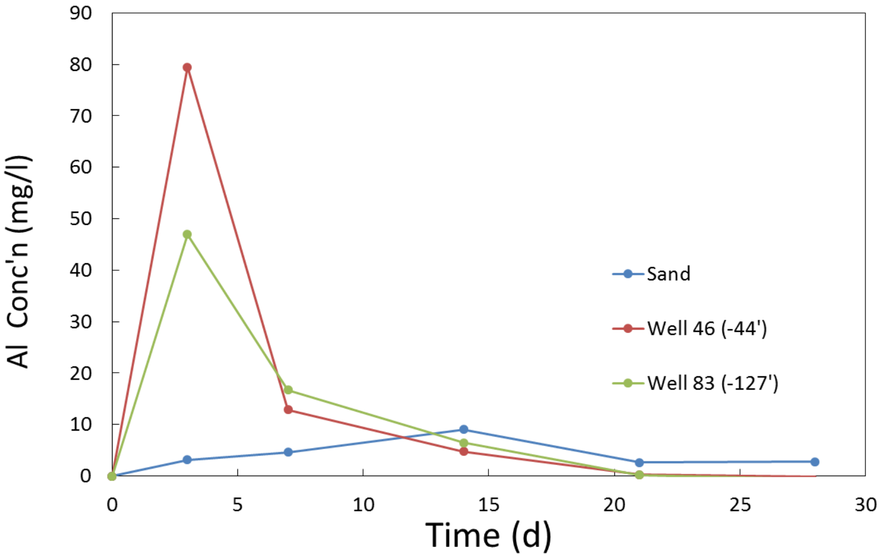


Figure 17 Aluminum release from sand, OCC soils Well 46C-47, Well 83C-127 in contact with 1 M NaOH, 55°C.

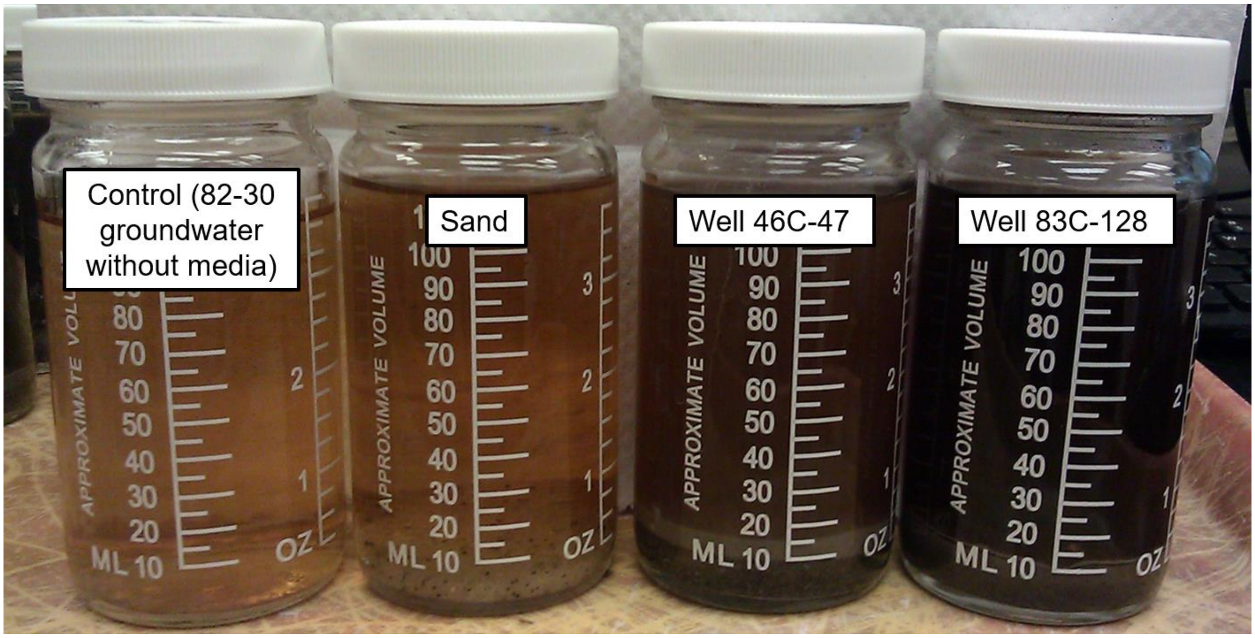


Figure 18 Visual appearances of supernatants in contact with Well 82-30 groundwater. Ambient temperature 55°C, one week of exposure.

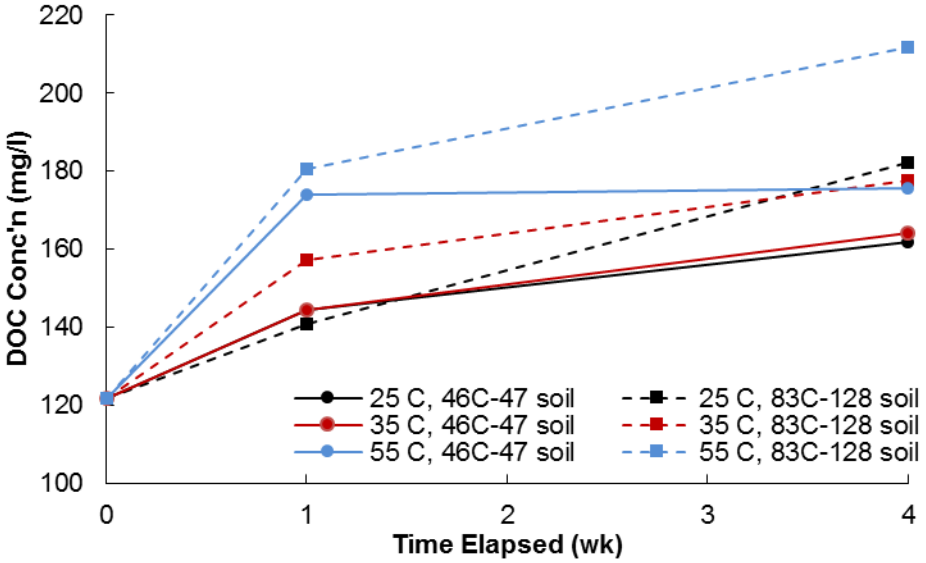


Figure 19 Organic carbon release from OCC soils Well 46C-47 and Well 83C-128 in contact with Well 82-30 groundwater. Varying ambient temperatures.

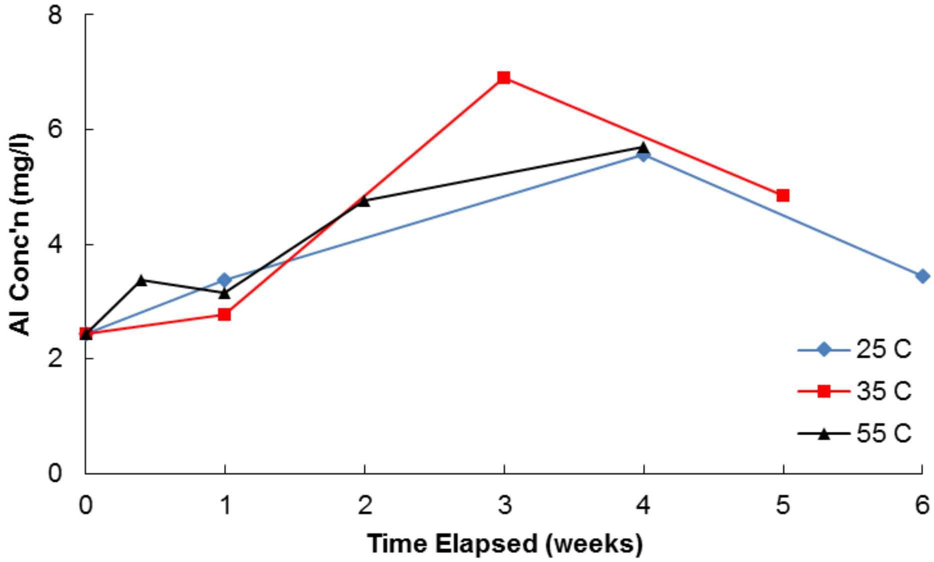


Figure 20 Aluminum release from OCC soil Well 46C-47 in contact with Well 82-30 groundwater. Varying ambient temperatures.

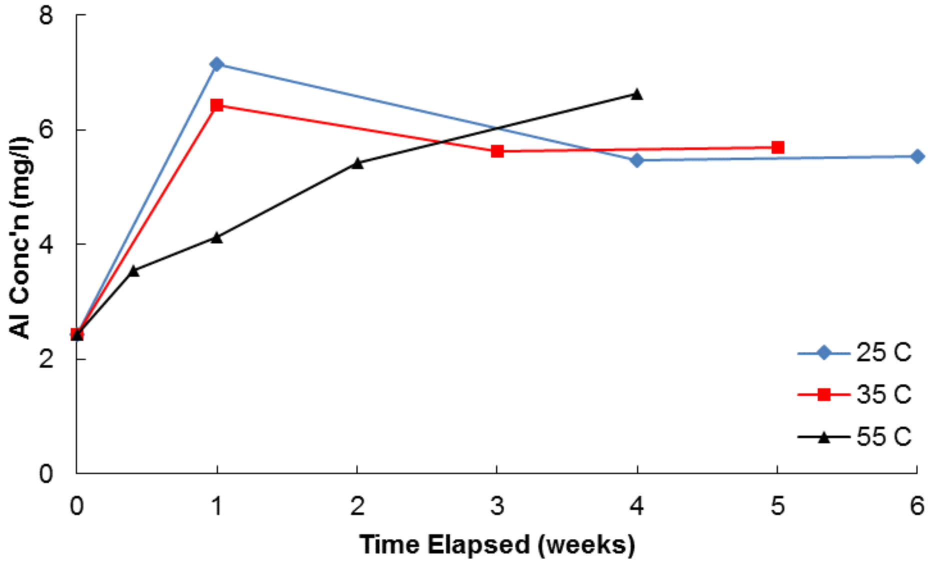


Figure 21 Aluminum release from soil Well 83C-soil in contact with Well 82-30 groundwater. Varying ambient temperatures.

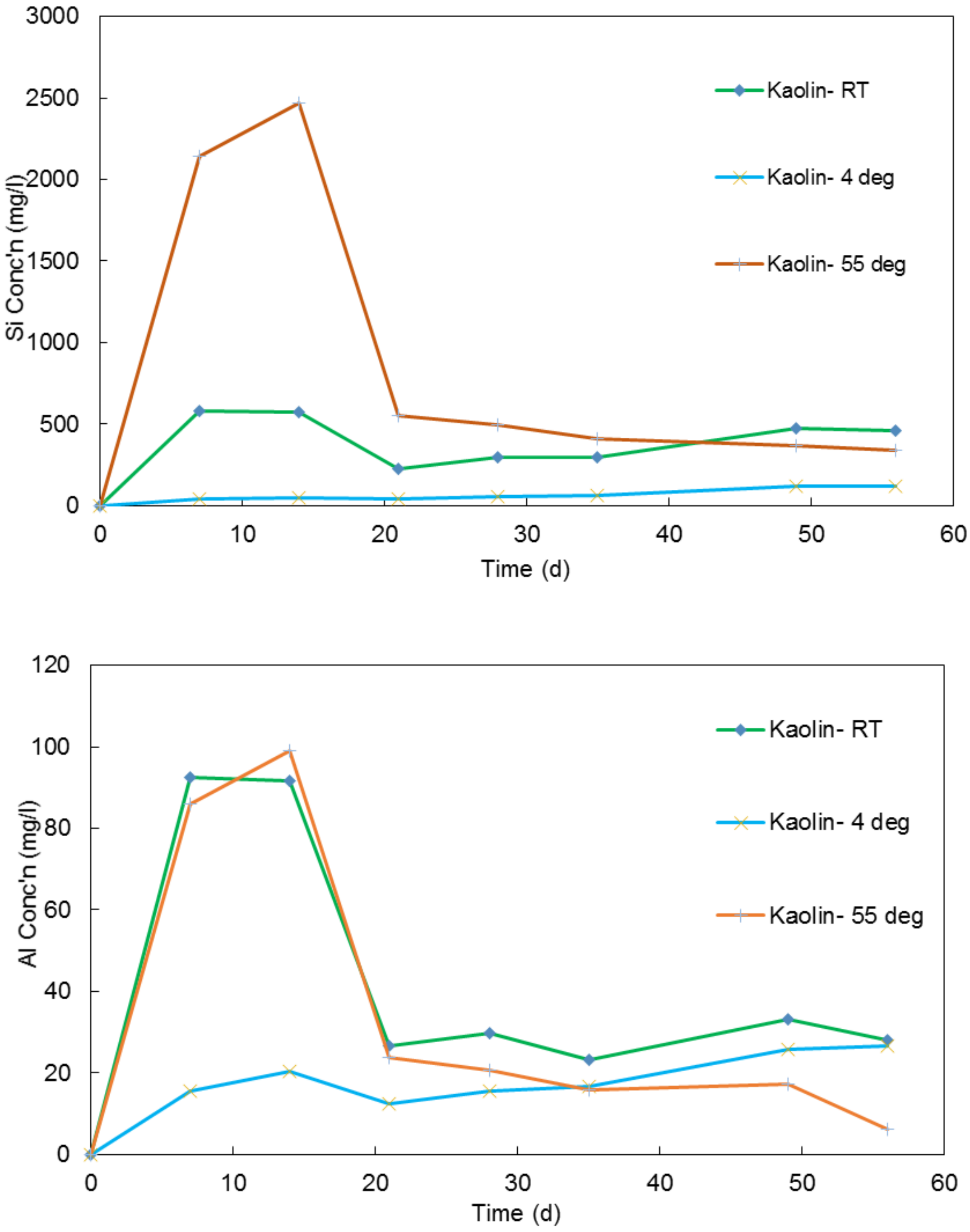


Figure 22 Time profiles of Si and Al concentrations released from kaolin exposed to 1 M NaOH at varying temperatures.

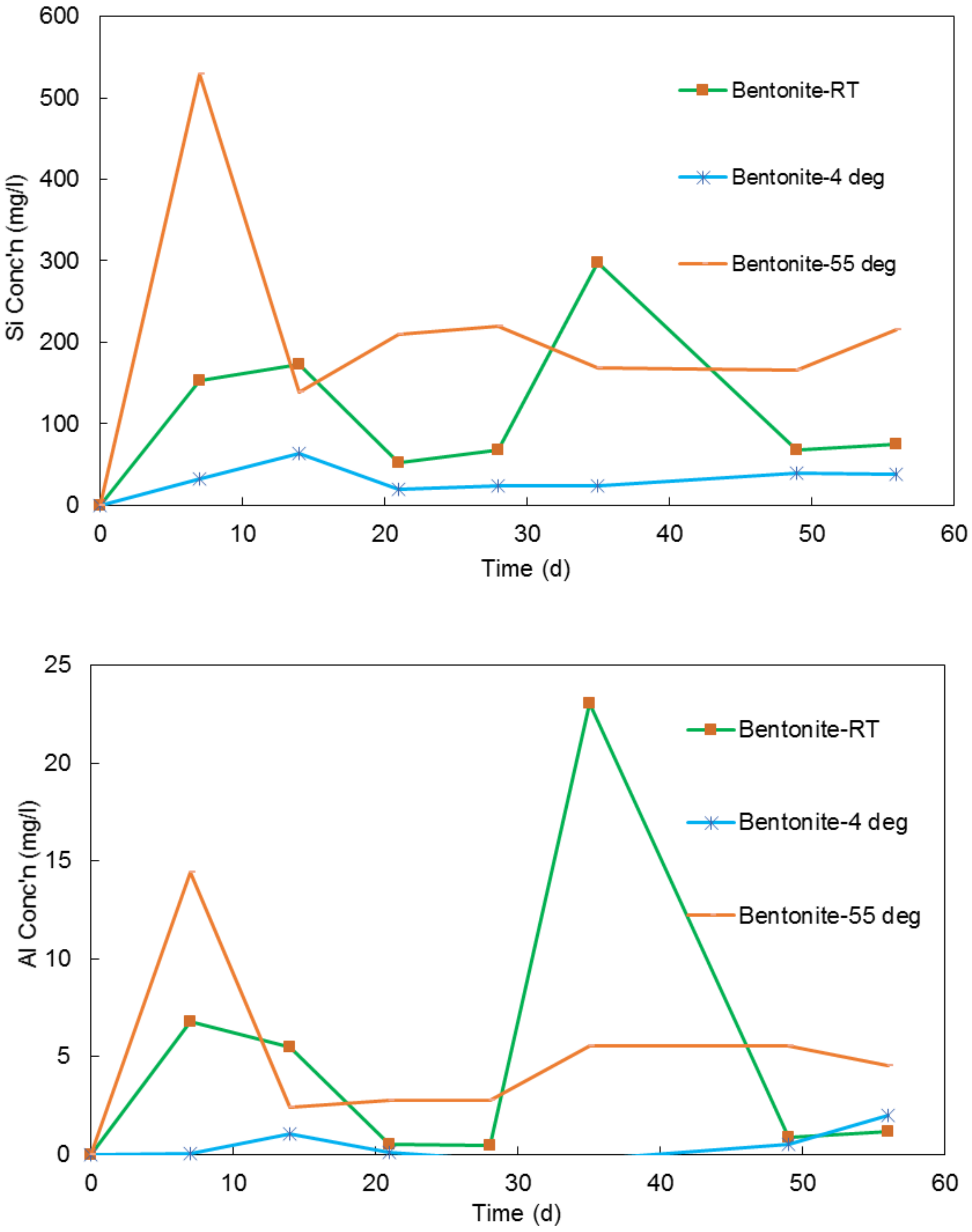
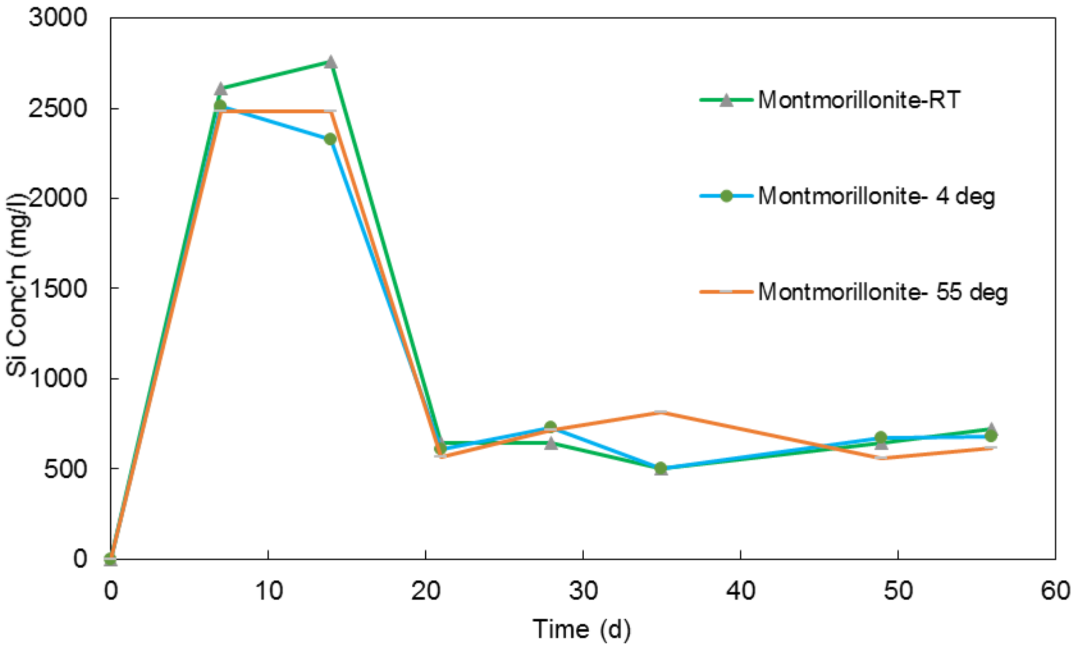


Figure 23: Time profiles of Si and Al concentrations released from bentonite exposed to 1 M NaOH at varying temperatures.



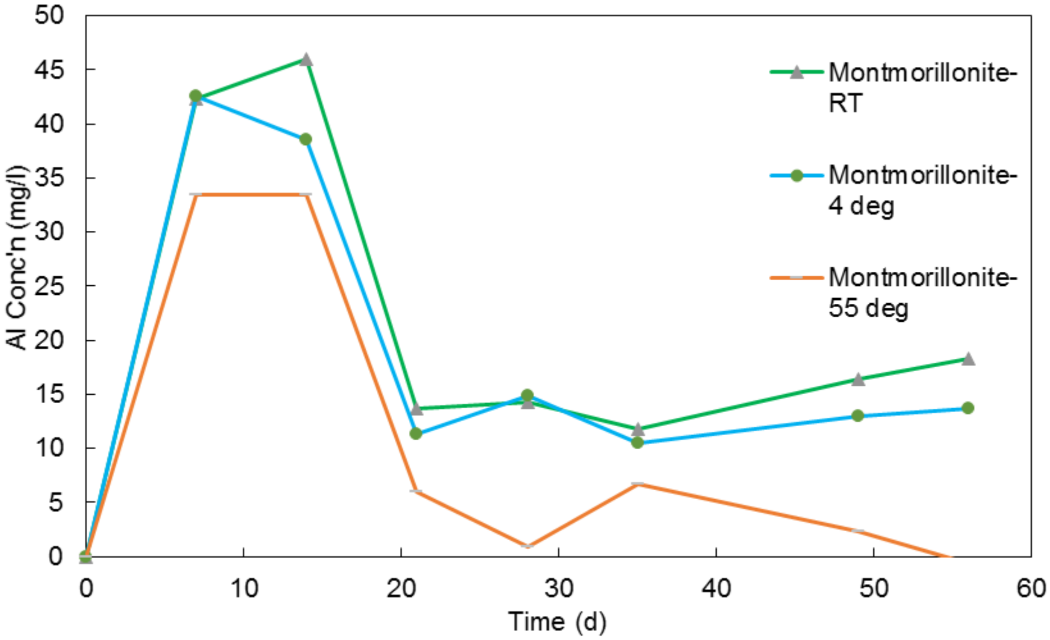


Figure 24: Time profiles of Si and Al concentrations released from montmorillonite exposed to 1 M NaOH at varying temperatures.

In the case of Al release, batch exposures of selected clay minerals (montmorillonite, kaolin, and bentonite) confirmed major trends in the effects of temperature and exposure time seen in the experiments with actual OCC soils. Release of Si from the exposed clays exhibited a non-monotonic behavior similar to that of Al but it was different from that from the exposed OCC soils. (Relevant data are compiled in Figure 22 to Figure 24 for kaolin, bentonite and montmorillonite, respectively). These observations may indicate that Al release from OCC soils may be controlled by clays present in these solids while Si release is controlled by a different class of minerals, most likely dispersed silica oxides.

These data show the presence of a transient period of metal release from the exposed clays. During the phase, metal release is non-monotonic, and the concentrations of Si released from kaolin and montmorillonite rapidly reach a high level (almost 3 g/L) although Si concentrations mobilized from bentonite are several times lower. Al release follows largely the same pattern but Al concentrations in the supernatants are always at least an order of magnitude lower than those of Si.

Within three weeks of exposure, concentrations of Al and Si released from the model phases stabilized and exhibited little change as the exposure time increased. At this quasi-steady phase of exposures, the concentrations of Si and Al did not appreciably depend on the temperature of ambient water. The concentrations of these elements observed during the initial non-monotonic phase of metal release tended to be much higher for 55C for bentonite and kaoline but changes of temperature had little effect on the mobilization of Si and Al from montmorillonite.

4.1. Structural data for exposed model phases

Measurements of Al and Si concentrations for OCC soils and model clays exposed in highly basic solutions indicate the occurrence of relatively rapid reactions that may affect their morphology and structural identity. This aspect of interactions in the system was examined using structure-sensitive methods of X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). XRD measurements carried out with clay samples taken from the jars containing suspended model solids showed that in the case of bentonite and montmorillonite, exposures to 1 M NaOH at all examined temperatures did not appreciably change their XRD spectra (Figure 25 and Figure 26) that had relatively high background scatter contributions due to the largely amorphous nature of these solids. SEM examination of bentonite and montmorillonite particles sampled prior to and after their exposures to 1 M NaOH confirmed the absence of distinct morphological features in all examined samples.

Similar results were seen for kaolin exposed at 4C and 20C but exposures of this model phase to 1 M NaOH at 55C resulted in a prominent change of its XRD spectrum (Figure 27). The sharp intense peaks present in the XRD spectra of kaolin exposed at 55C reveal a dramatic increase of its crystallinity and the formation of a new crystallographically distinct phase. This was confirmed by the SEM data (Figure 28 and Figure 29) demonstrating that prior to exposure kaolin particles did not exhibit any reasonably distinct morphological pattern albeit the presence of thin irregularly shaped platelets could be discerned. The exposure to 1 M NaOH at 55 C caused multiple well-defined tetragonally or pyramidally shaped features to appear. Relatively small crystals (size ca. 1 μm or less) that have this morphological habit form multiple fused clusters that seem to occupy most of the volume of the sample used for SEM examination.

These data demonstrate that exposures of clay materials and, by inference, OCC soils to high pH effluents may cause pronounced changes in the structure and solubility of alumosilicates.

Although such changes were unambiguously confirmed by XRD and SEM data only for kaolin exposed at 55C, the commonalities in the behavior of Si and Al vs. time for all three model phases and a wide range of temperature indicate that similar processes may take place in all cases, with the likely difference that in the case of kaolin at 55C, the structural transformation involved a large fraction of the volume of the solid while in others such change may have extended only to the surface layers. We posit that long-term exposures are likely to cause clay phases present in OCC soils to undergo transformations similar to those seen for kaolin.

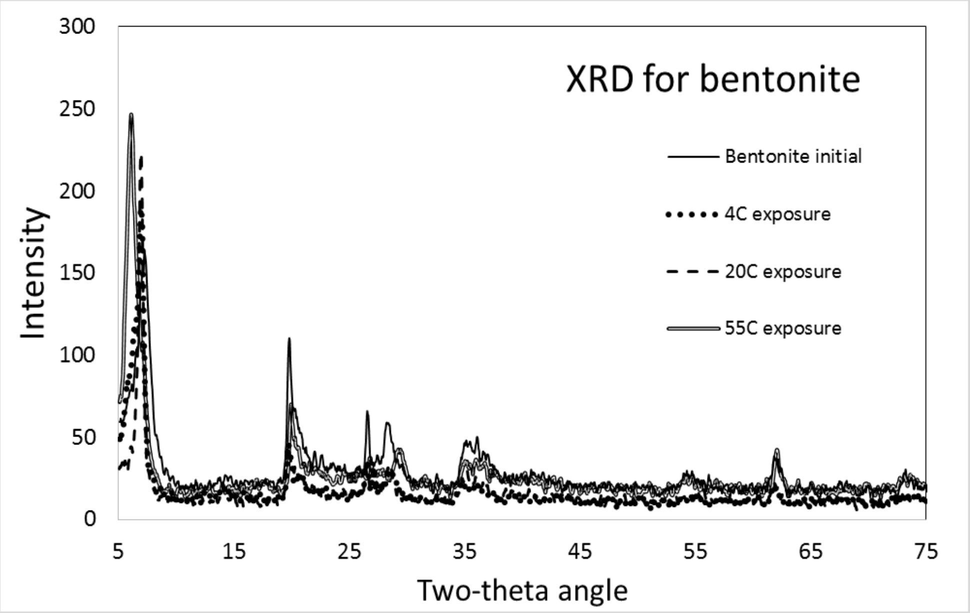


Figure 25 Comparison of XRD data for bentonite before and after 7 week-long exposure in 1 M NaOH.

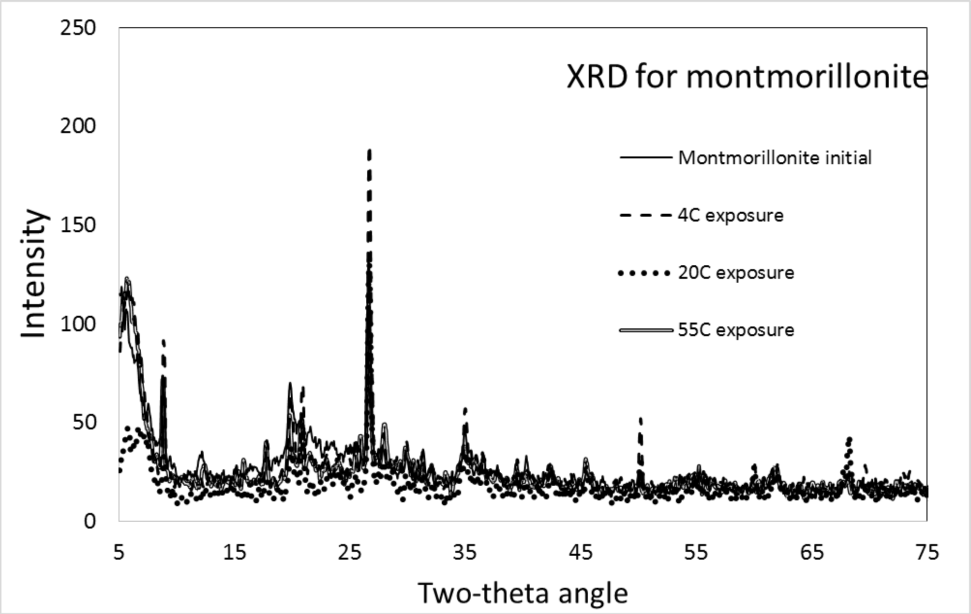


Figure 26 Comparison of XRD data for montmorillonite before and after 7 week-long exposure in 1 M NaOH.

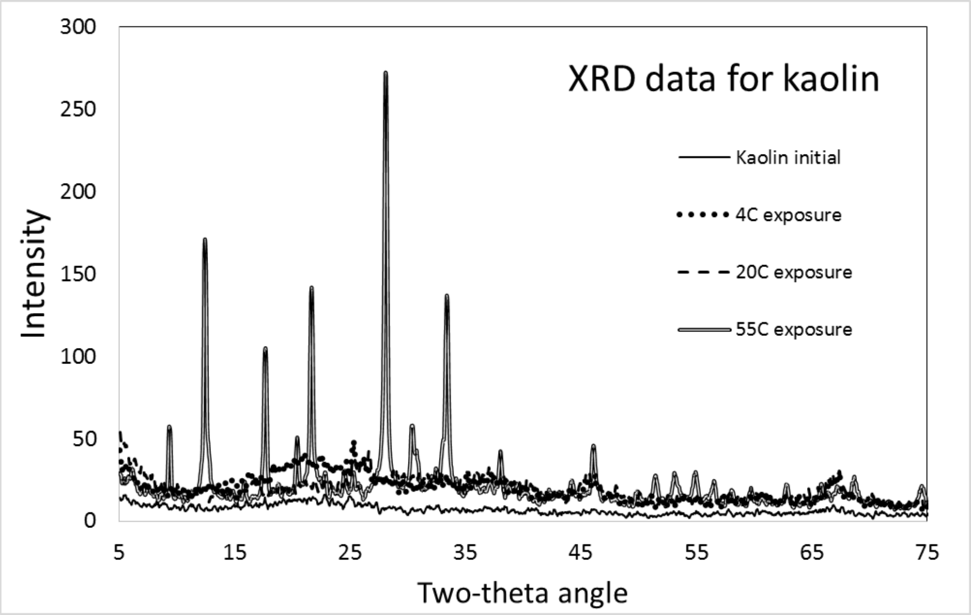


Figure 27 Comparison of XRD data for kaolin before and after 7 week-long exposure in 1 M NaOH.

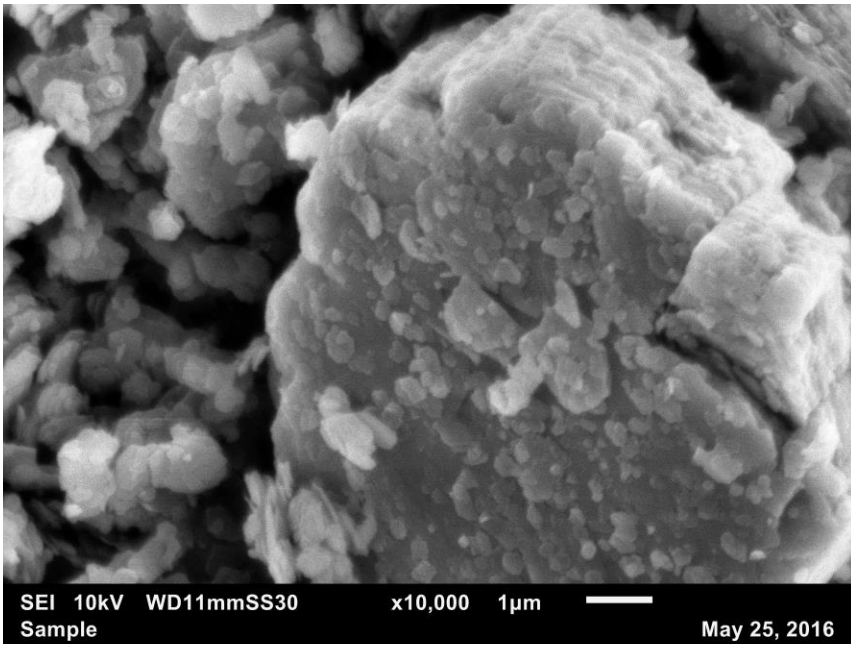


Figure 28 Morphology of kaolin particles prior to exposures.

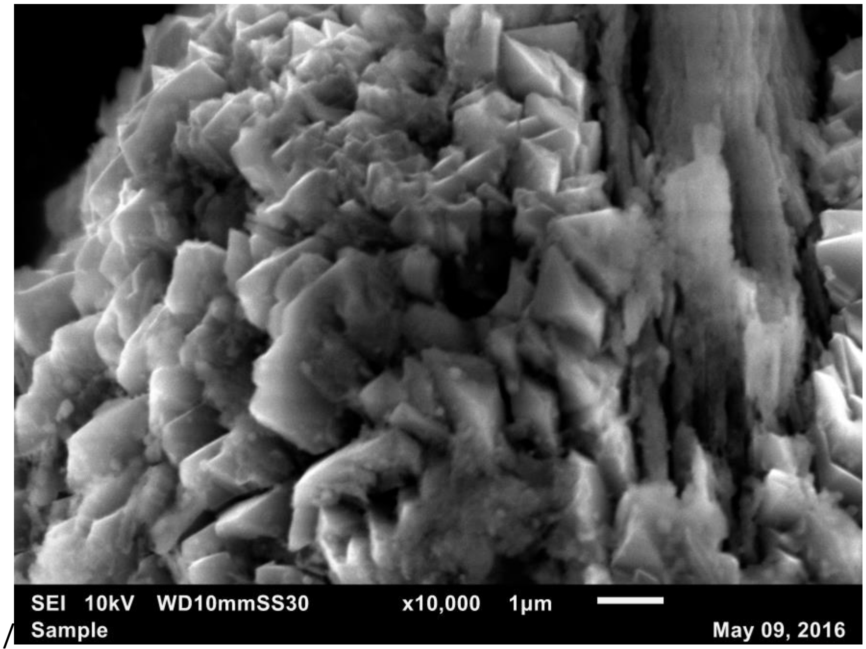


Figure 29 Morphology of kaolin particles after 7 week-long exposure in 1 M 7 NaOH.

4.2. Summary of observations concerning the reactivity of OCC soils and model solids with high pH solutions

The data discussed above show that OCC soils react readily with caustic effluents. When exposed to such solutions, they release within a short period of time high concentrations of Si solutes. This process strongly depends on the concentration of hydroxyl ions, being very prominent for exposures in 1 M NaOH and less notable at lower pHs, for instance pH 11.3.

Interactions between OCC soils and caustic effluents cannot be reduced to solely dissolutive reactions that result in the mobilization of high levels of silica. The consistent occurrence of non-monotonic behavior of aluminum released from OCC soils and model clays, as well as the structural transformations that are prominent in some limited but potentially important cases show that clay fractions of OCC soils exposed to high pH effluents are likely to be sensitive to that environment undergoing changes that affect Si solubility and hydraulic fouling.

Aluminum solutes and resultant solids may have a specific role in such transformations, for instance by promoting the formation of micronuclei that initiate and catalyze the precipitation of solid phases that eventually caused extensive hydraulic fouling observed for OCC soils (see below in the section discussing our experiments with soil-packed columns). The experimentally observed promoting effect of aluminum added to Well 7 groundwater on the onset of hydraulic fouling is consistent with this point of view.

It is recognized that even if the critical role of aluminum in the initiation of hydraulic fouling is confirmed, the removal of this component from OCC groundwater is not a practically actionable option for remedial activities..

5. Release of Retained Base (pH) and Salt from OCC Soils

Experiments described in this section were conducted to ascertain the persistence of the release of retained base and salts from affected OCC soils. These experiments were to provide answers to the following questions:

- *How persistent will be the release of retained base (measured as high pH) and salts from contaminated OCC soils?*
- *Will the resulting pH of the solution be high enough to induce further dissolution of OCC soils?*

These experiments were carried out using columns packed with soils from Well 46, 82 and 83. The measurements were done with uniformly blended sand/soil mixtures (ratios of 1:1 to 3:1, length 6 cm). The mixture was positioned in the middle of a column equipped with sand buffers of ca. 3 cm length positioned on either side of the column. The need to use sand/soil mixtures rather than soil only was caused by the development of hydraulic fouling and soil destabilization when the acid neutralizing capacity of exposed soils was exhausted and the pH of column effluents changed rapidly, as described below. We also found that in these experiments it was necessary to replace the bottom column filters with some extra glass wool.

In all cases, the column was preconditioned using 0.01 M NaCl that was passed through the column for 45 -50 minutes. Darcy velocities used in the experiments varied due to the need to maintain a reasonable level of trans-column pressures. Accordingly, the range of Darcy velocities was ca. 7 to 19 ft/day.

Initial experiments showed that when the pH of column influents was in the circumneutral range, the pH of column effluents was very close to that of suspensions of relevant soils, as described in Section 4, for a very long time, possibly exceeding many months or years. To accelerate laboratory measurements of the mobilization of pH and salts from representative OCC soils, the majority of experiments concerned with these phenomena utilized highly acidic influents containing from 0.005 to 0.02 M HCl. The use of such influent induced sufficiently prominent changes of pH and conductivity values of column effluents within a few hours.

Selected results of the measurements of pH and conductivity are shown in Figure 30 through Figure 37. For instance, measurements for soils from Well 46 located in a relatively unaffected area of the site (Figure 30 and Figure 31) showed that when relatively weak acidic influents were used (HCl concentration 0.005 M), the pH of the effluents changed relatively rapidly while the trans-column pressure was low (ca. 2 psi).

Changes of pH and conductivity data for soils from Wells 82 and 83 are shown in Figure 32 to Figure 36. As mentioned above, some of these experiments required that sand/soil ratios 3:1 be used due to the challenging texture of these soils.

To summarize, the data are indicative that in practically all cases, the conductivity of column effluents started decreasing immediately after the introduction of acidic influents. In contrast, the pH of column effluents tended to be stable for a considerable duration of time after the initiation of HCl injection but after reaching a distinct threshold, it decreased rapidly. The conductivity of effluents measured in the second phase of the column experiments during which pH underwent a rapid change tended to be nearly constant and appreciably lower than that observed after the initiation of each experiments. It is to be noted that the initial conductivities of column effluents were considerably higher than that of the 0.01 M NaCl solution that was used to condition the column packing.

The data indicate that salts occluded in the examined soils tended to be mobilized from the solid matrix and eluted prior to the exhaustion of the acid neutralizing capacity (ANC) of the exposed soils. In contrast, the release of retained base persisted for a long time. To examine whether the persistence of high pH is a function of the ANC value of OCC soils, the amount of acid needed to decrease the pH of column effluents from their respective initial values to ca. 5 was calculated via by calculating the product of the bed volume of influent multiplied the molar concentration of HCl in the influent. That value was then normalized by the mass of soil present ion the column.

These calculations show that the amount of acid consumed in the column experiments was correlated with the ANC values of OCC soils (Figure 37, one outlier was excluded from this figure). The correlation also shows that the amount of acid consumed in the column experiments was lower (about three times) than that consumed in batch experiments with soil suspensions. This shows that the column experiments are likely to underestimate the persistence of release of retained based from affected OCC soils.

The data demonstrates that in realistic field conditions, base release from affected soils will continue for a long time, and the amount of acid required to neutralize it will be ultimately comparable albeit potentially lower than that calculated based on ANC values determined in batch experiments.

While the pH of water exiting highly affected areas of the site may be high, the ability of that water to mobilize massive amounts of silica from OCC soils is likely to be notably lower than that of the high strength chlor-alkali effluents released into the subsurface during the period of industrial activity. That is, the removal of high-pH, high-Si groundwater by pump-and-treat operations and its replacement by the ingress of water that initially has a circumneutral pH and low to medium alkalinity will result in a notable increase in the pH of the replacement water, but also a drastic reduction in its tendency to mobilize silica from the exposed soils.

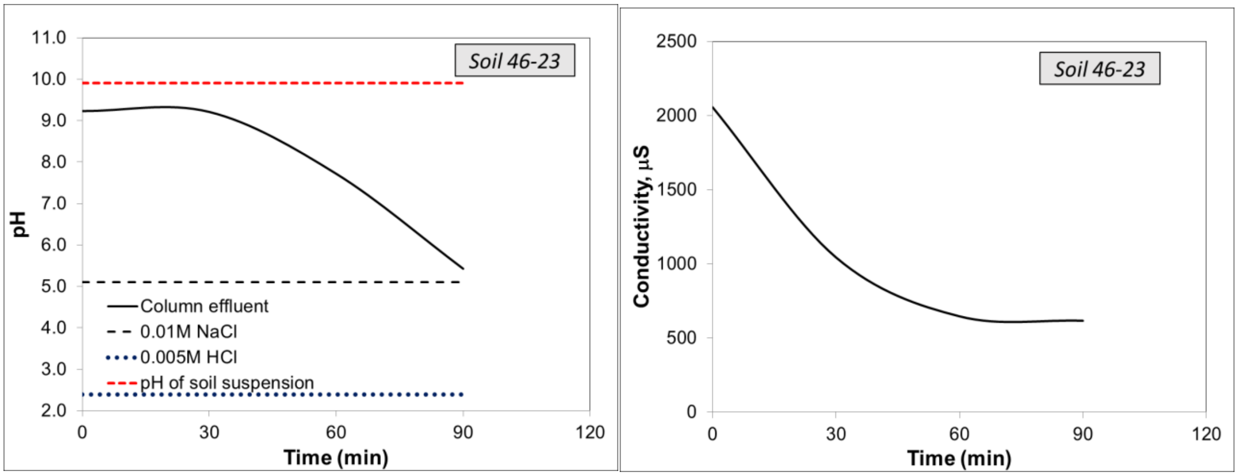


Figure 30 Time profile of pH and conductivity of the effluent from a column packed with soil from Well 46 (depth 23-26 feet). 0.005 M HCl influent, Darcy velocity 17.2 ft/day.

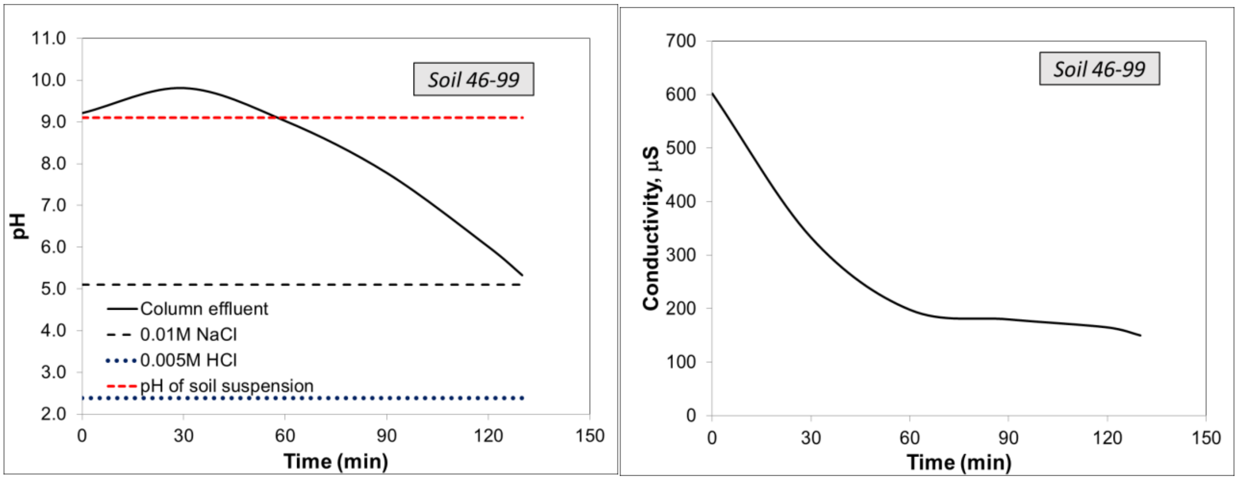


Figure 31 Time profile of pH and conductivity of the effluent from a column packed with 1:1 mixture of sand/soil from Well 46 (depth 99-102 feet). 0.005 M HCl influent. Darcy velocity 17.8 ft/day.

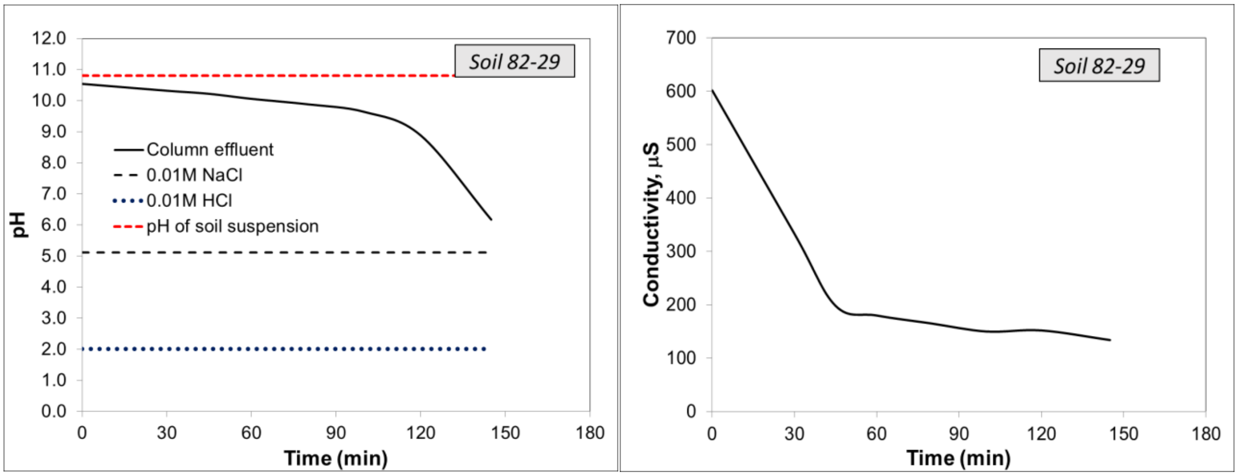


Figure 32 Time profile of pH and conductivity of the effluent from a column packed with 1:1 mixture of sand/soil from Well 82 (depth 29-32 feet). 0.005 M HCl influent. Darcy velocity 10.3 ft/day.

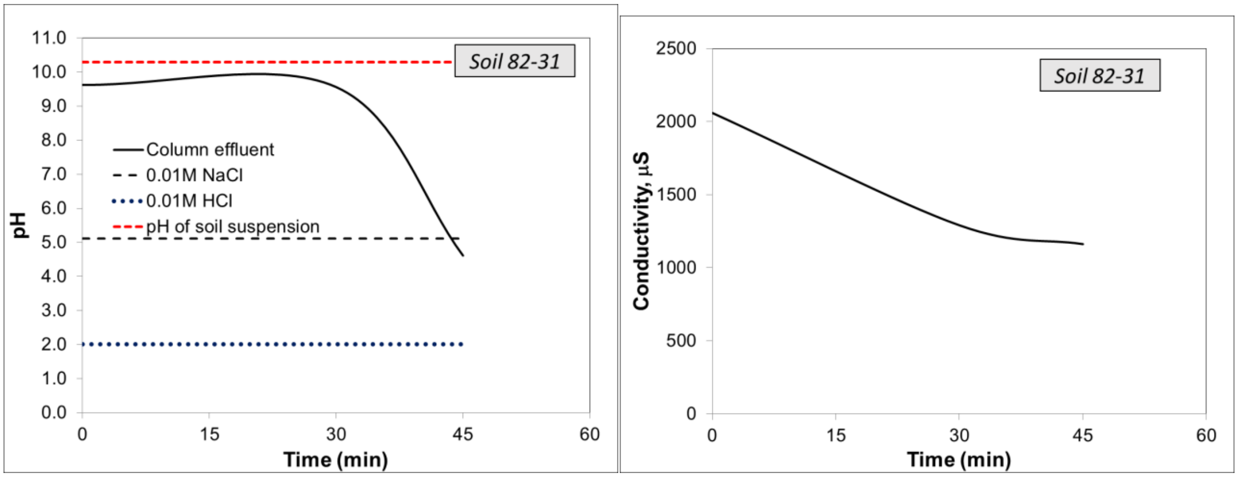


Figure 33 Time profile of pH and conductivity of the effluent from a column packed with 1:1 mixture of sand/soil from Well 82 (depth 31-34 feet). 0.01 M HCl influent. Darcy velocity 17.4 ft/day.

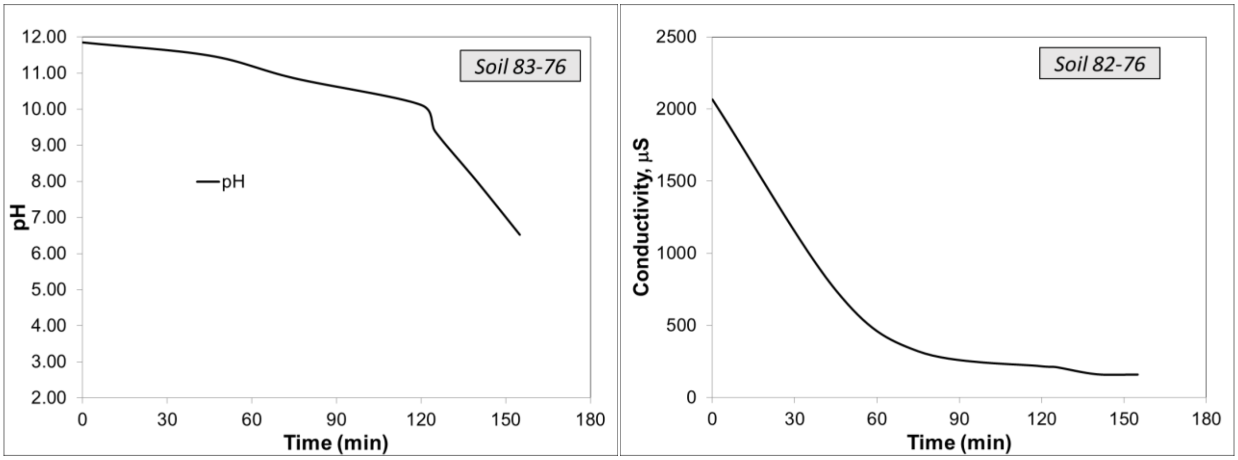


Figure 34 Time profile of pH and conductivity of the effluent from a column packed with 3:1 mixture of sand/soil from Well 82 (depth 76-83 feet). 0.01 M HCl influent. Darcy velocity 7.1 ft/day.

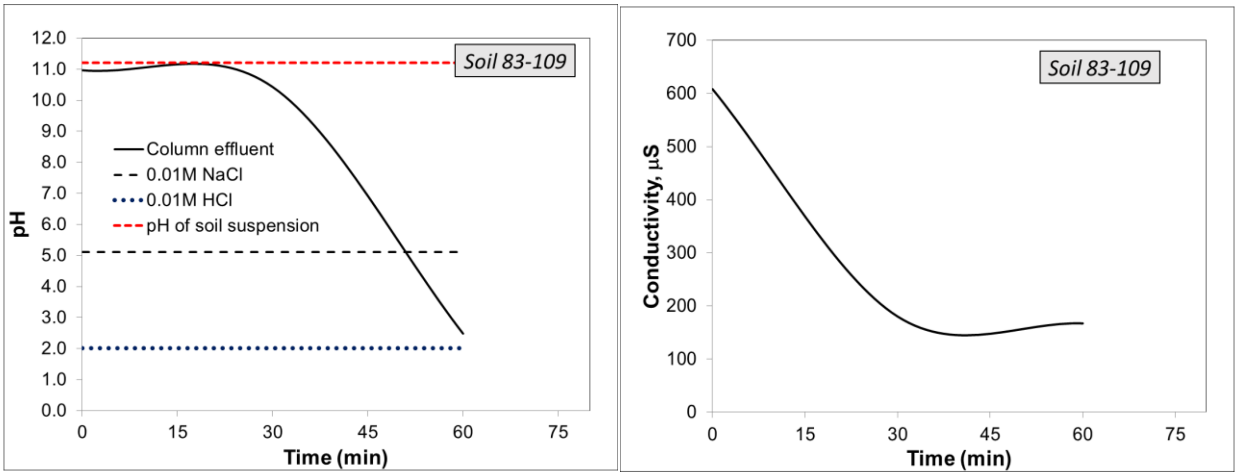


Figure 35 Time profile of pH and conductivity of the effluent from a column packed with 3:1 mixture of sand/soil from Well 83 (depth 109-112 feet). 0.01 M HCl influent. Darcy velocity 12.9 ft/day.

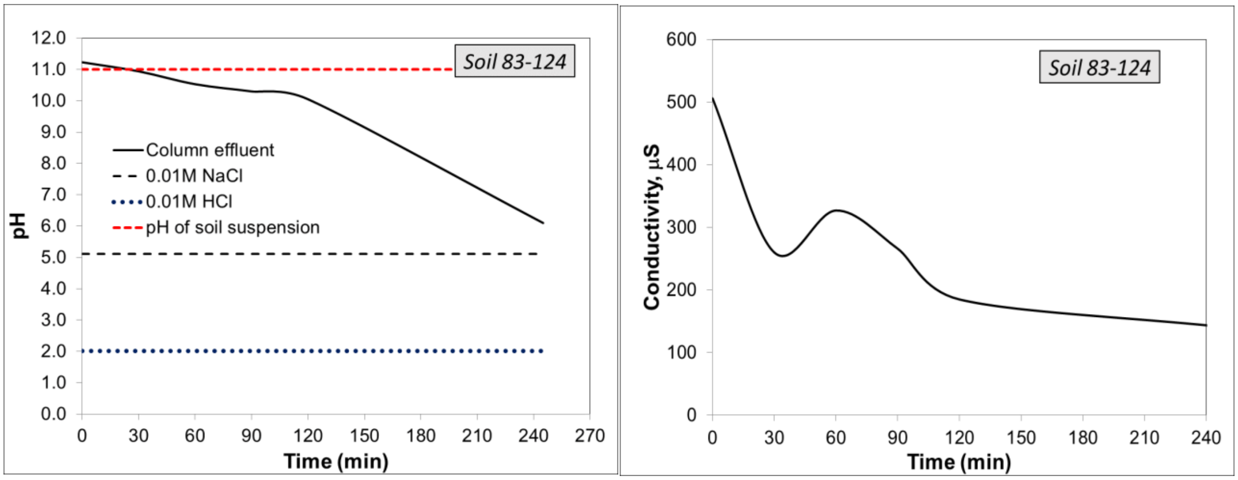


Figure 36 Time profile of pH and conductivity of the effluent from a column packed with 1:1 mixture of sand/soil from Well 83 (depth 124-127 feet). 0.01 M HCl influent. Darcy velocity 19.2 ft/day.

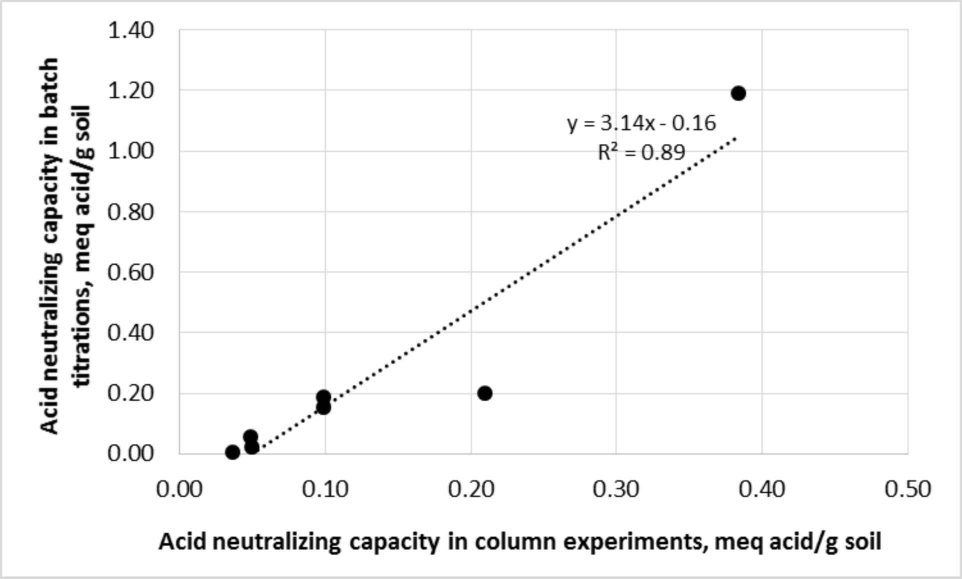


Figure 37 Correlation between acid neutralizing capacities of OCC soils determined in batch and column experiments.

6. Effects of Precipitation Inhibitors on Gelation and Precipitation in OCC Groundwater

This section summarizes results of our attempts to establish whether commercial products or naturally produced substances whose effects on the precipitation of Si-based solids were examined in some detail in prior research (e.g., *Coradin and Livage* 2001; *Gallup* 2002; *Demadis* 2005) have a potential to affect precipitation phenomena in OCC groundwater. As described below, these attempts were unsuccessful.

The potential of the commercial product Carbosperse K-XP229 (Lubrizol Corporation) to prevent the acid-induced precipitation of Si-based solids from OCC groundwater was examined. This product is marketed as an inhibitor of silica scaling and fouling in cooling, reverse osmosis, geothermal and related applications and is typically used in solutions with Si concentrations that are orders of magnitude lower than those in the OCC groundwater. In batch experiments, this inhibitor had no meaningful effect on the precipitation/gelation phenomena, even at the highest concentration tested (ca. 1 g/L).

Humic acid has significant but complex effects on precipitation of environmentally relevant solids due to its ability to bind dissolved metals. Its effects on the behavior of Al were examined in experiments using soil packed columns. When 500 mg/L Aldrich humic acid (AHA) was added to synthetic Al-containing solutions that were applied to the soil columns, it delayed but did not prevent hydraulic soil fouling, and a dose of 100 mg/L AHA had no significant effect at all. Given that compounds similar to AHA occur naturally in OCC groundwater due to the mobilization of humic species from soil at high pHs, dosing of commercial humic acid products is unlikely to significantly augment any beneficial effects of those species. Overall, we conclude that given the extremely high levels of Si in OCC groundwater, there is little likelihood of effective prevention of gelation/precipitation of Si-based solids by commercially available or naturally occurring compounds.

7. Experiments to Determine Hydraulic Fouling in Soil-Packed Columns

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. These tests were aspects of OCC soil/groundwater interactions that potentially affect hydraulic conductivity in the aquifer, for instance:

- *Effects of Darcy velocity,*
- *Effects of feed composition,*
- *Effects of column media (affected or unaffected OCC solis),*
- *Effects of groundwater blending.*

A compilation of results of relevant experiments is presented below. A more detailed description of these activities can be found in *Urbanczyk 2015*.

7.1. Column test reproducibility

Column experiments exhibited variabilities caused by the inherently heterogeneous nature of soils, and possibly the aging of extracted soil and groundwater collected from the OCC site. The need to use modified analytical procedures (e.g., ICP/MS analyses) to overcome severe matrix effects also reduced somewhat the accuracy and precision of such analyses.

Still, reasonably reproducible results of column tests were attained by means of use of a benign solution (that is, containing only inert salts) at the beginning of all tests and the use of a Br^- tracer to assess the potential occurrence of hydraulic short-circuiting and, in other experiments, estimate the reversibility of hydraulic fouling.

Trans-column pressure was the key parameter measured in the 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 data discussed in this report are deemed to be 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.

In the tests, a benign solution, which in the context of this study was defined as a solution with approximately the same pH and, in most cases, 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 moderately strong correlation existed between trans-column pressure and Darcy velocity for injection of a benign solution into OCC site soil (R^2=0.670). This relationship indicates that soil packing was reasonably reproducible across independent column tests but inherent differences existed as well. Specific effects of various system parameters on hydraulic conductivity were ascertained 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 also to assess hydraulic properties of soil-packed columns. 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. In many tests, the apparent hydraulic residence time (HRT) was 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, short circuiting in the column was concluded to be minimal.

7.2. Effects of Darcy velocity on hydraulic fouling

Darcy velocity was found to be a major factor that affects the hydraulic conductivity of OCC site soil. For instance, column tests showed that Well 7 groundwater did not cause decrease of hydraulic conductivity ("plugging") of the OCC site soil at relatively low Darcy velocities, but it demonstrably did so at higher Darcy velocities. The threshold for plugging by Well 7 groundwater was found to depend on whether or not OCC soil was affected by its contact with high-pH groundwater. For 'unaffected' soils, e.g., Well 46C-47 soil specimen from the well location and subsurface stratum known to have been in long-term contact with high pH high Si groundwater, trans-column pressure was low and stable over time when Well 7 water was injected at a Darcy velocity of ≈7 ft/d. However, trans-column pressure for that soil increased notably when Well 7 groundwater was injected into this soil at a Darcy velocity of ≈28 ft/d.

Additional tests were conducted to compare trans-column pressures developed after equal numbers of bed volumes have passed through the column. In these tests, ca. 20 bed volumes of Well 7 groundwater was injected in Well 46C-47 soil for at Darcy velocities of 7 and 28 ft/d. Only the test at a Darcy velocity of 28 ft/d resulted in decreased hydraulic conductivity over time (Figure 38). This supported a conclusion that Darcy velocity rather than the number of bed volumes passed through the soil ultimately affects its hydraulic conductivity.

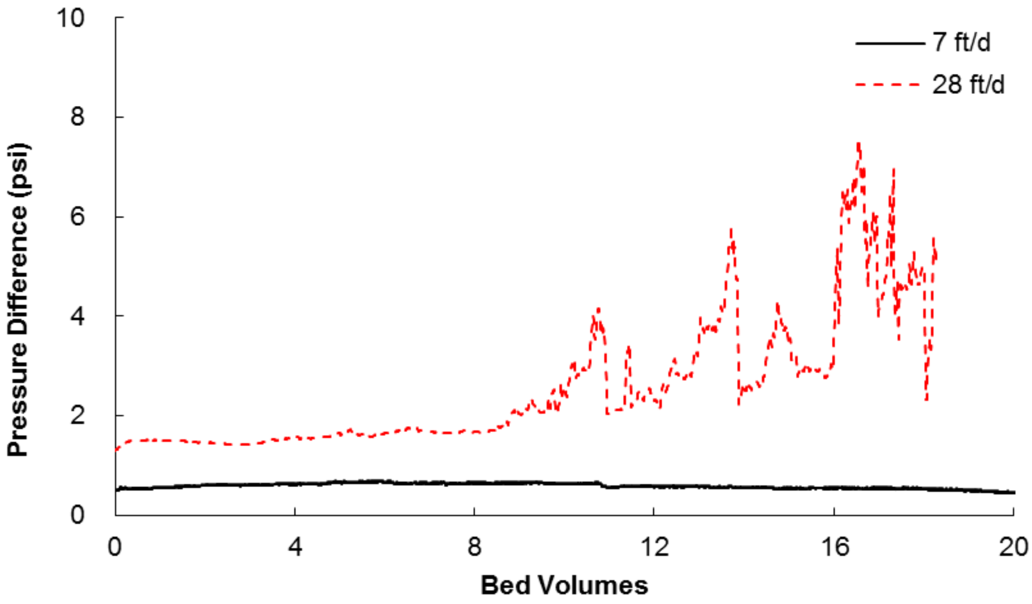


Figure 38 Development of trans-column pressure as a function of bed volumes for tests conducted at a Darcy velocity of 7 ft/d and 28 ft/d. Well 7 groundwater was injected into Well 46C-47 soil-packed column.

To confirm that the hydraulic fouling of the soil was caused by constituents specific to Well 7 groundwater and not solely the Darcy velocity, tests at a similar Darcy velocity were conducted with a benign solution used as feed. In these tests, a solution deemed to be largely unreactive toward soils in conditions used for the column tests (its composition was 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 one. The pressure across the column increased significantly when the feed was Well 7 groundwater (Figure 39). In contrast, the pressure remained low and stable when the benign solution was injected. 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 the 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 40). 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.

The observed dependence of hydraulic conductivity on Darcy velocity was unexpected and this result does not appear to have been discussed in preceding technical literature. Because this finding may have important practical implications for the extraction of high pH, high Si groundwater at the OCC site, additional column tests were performed to better understand why Well 7 water causes hydraulic fouling at relatively high Darcy velocities.

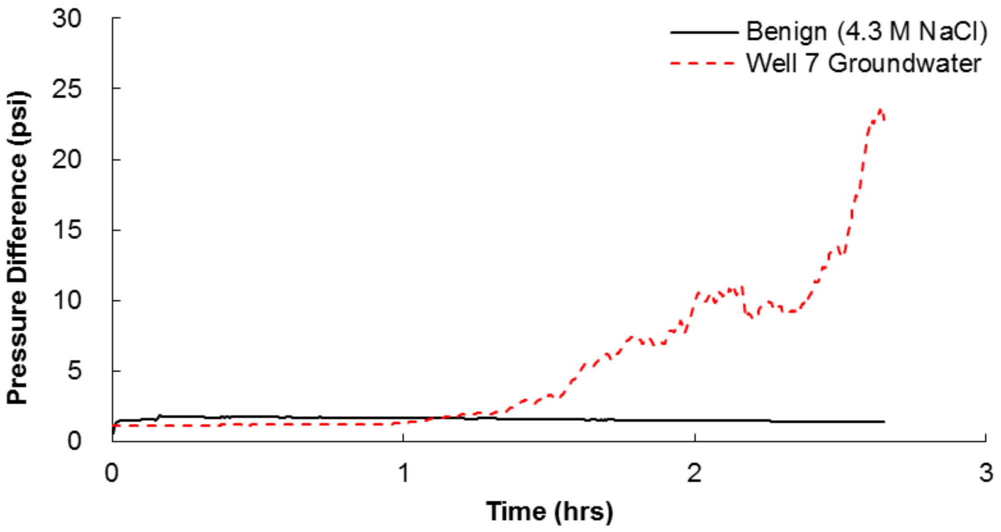


Figure 39 Comparison of the development of trans-column pressure for injections of Well 7 groundwater and benign solution. Well 46C-47 soil-packed column. Darcy velocity 28 ft/d.

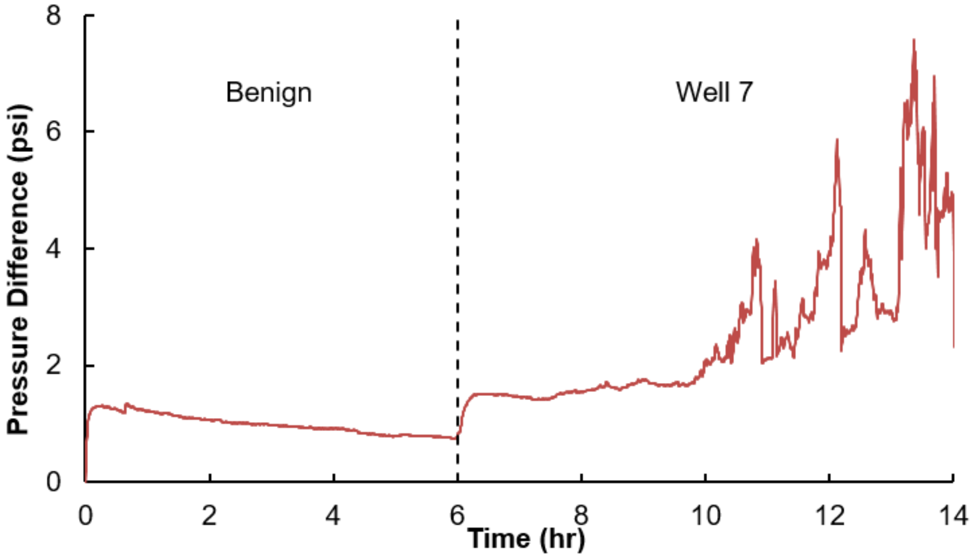


Figure 40 Development of trans-column pressure for benign solution followed by the injection of Well 7 groundwater. Well 46C-47 soil-packed column. Darcy velocity 28 ft/d.

7.3. Effects of constituents of Well 7 groundwater

7.3.1. Effects of silica and aluminum

Because Si is a major constituent of Well 7 groundwater, formation of silicate-based precipitates was considered to be a potentially major mechanism that causes soil plugging. As the concentration of aluminum in Well 7 groundwater is also relatively high and Al is known to form complexes and a wide range of solid phases with Si, Al was also considered to be a potential factor in the development of hydraulic fouling.

To test this hypothesis, a column test was 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 in it 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. 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 throughout the remainder of the test (Figure 41).

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 its pH to <10, filtering out precipitated solids, and raising the pH back to ≈11.7. Thus, 'Si-free' groundwater had approximately the same composition as unaltered Well 7 groundwater, except that Al and Si in it were mostly 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 42). This test further indicates that the major constituents in Well 7 groundwater, such as Si and Al, are primarily responsible for the decline in hydraulic conductivity at the examined relatively high Darcy velocity.

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.

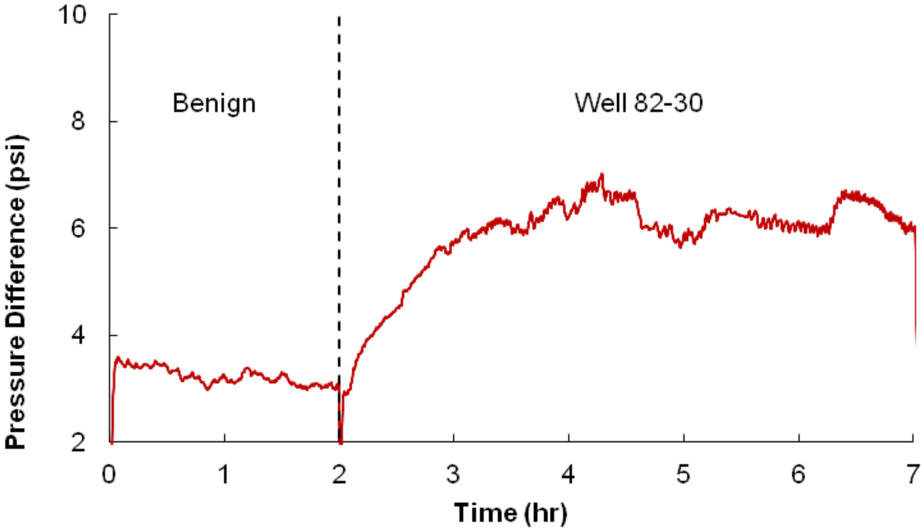


Figure 41 Development of trans-column pressure in the case of injection of Well 82-30 groundwater. Well 46C-47 soil packed column, Darcy velocity 27 ft/d.

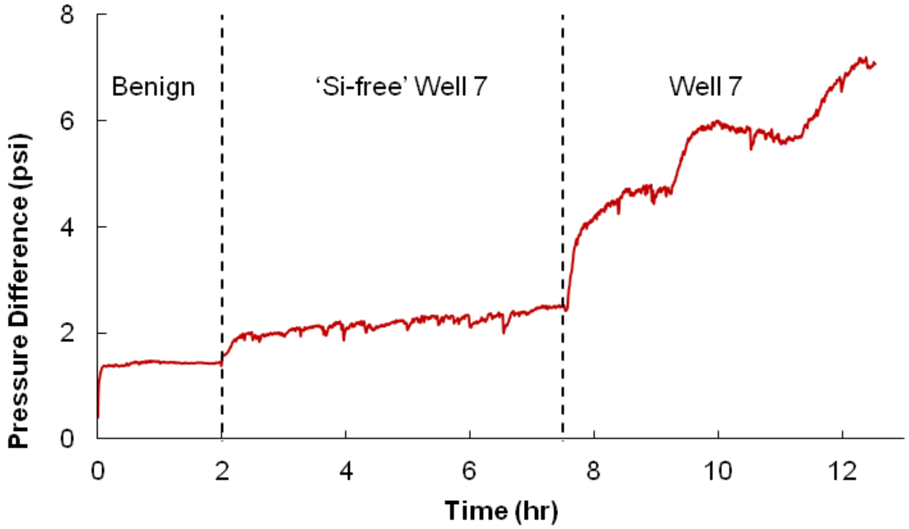


Figure 42 Development of trans-column pressure for injection of pre-treated Si-free Well 7 groundwater followed by untreated Well 7 groundwater. Well 46C-47 soil packed column, Darcy velocity 27 ft/d.

An unexpected observation from these tests was that, even when hydraulic conductivity declined dramatically as a result of Well 7 groundwater injection, no unambiguously determinable declines in the concentrations of Al and Si which are the major constituent likely to be associated with hydraulic fouling, were detected. The differences between influent and effluent concentrations of major constituents measured in tests in which plugging occurred ranged between -6 to 15% of the influent value.

These differences may still indicate the occurrence of some small retention of Al and Si yet they can be attributed to statistical uncertainty of the determinations that required dilutions of at least 800x. Thus, the closeness of Al and Si concentrations in column feed and effluents does not completely eliminate the notion of effects of deposition of Si and Al in the column because precipitation of even an undetectably small (in the context of the precision of ICP/MS analyses) amount of Si could generate enough solids to affect hydraulic conductivity.

As no significant decline in Si and Al concentrations in column effluent were detected, further tests with synthetic solutions were performed to separate the effects of Al and Si on hydraulic conductivity. Synthetic solutions prepared for these experiments had the same pH as Well 7 groundwater (11.7) contained 44 g/l Si and 600 mg/l Al either alone or in combination. Si and Al were added as sodium silicate and aluminum chloride, respectively.

When the solution containing Si but no Al was injected into Well 46C-47 soil at a 27 ft/day Darcy velocity, trans-column pressure increased slightly but it remained relatively stable throughout the test’s duration. In contrast, when the solution with Al but no Si was injected, trans-column pressure increased rapidly.

Injection of the synthetic solution containing both Al and Si caused the trans-column pressure to increase rapidly but over a longer duration (Figure 43). 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 increased dramatically only when column feed had Al in its composition (Figure 44*).* These column tests indicated that though Si may contribute to some soil plugging, Al is likely to play a more critical role, possibly triggering the process.

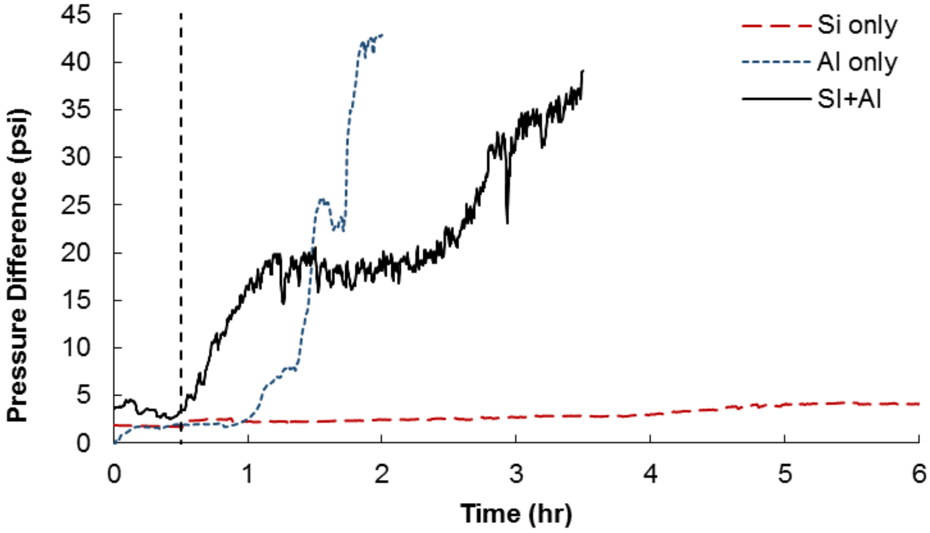


Figure 43 Trans-column pressure for synthetic solutions containing Si only, Al only and Si+Al injected into a column packed with Well 46C-47 soil at an average Darcy velocity of 27 ft/d. The switch from a benign solution to a synthetic solution is shown with the vertical dashed line.

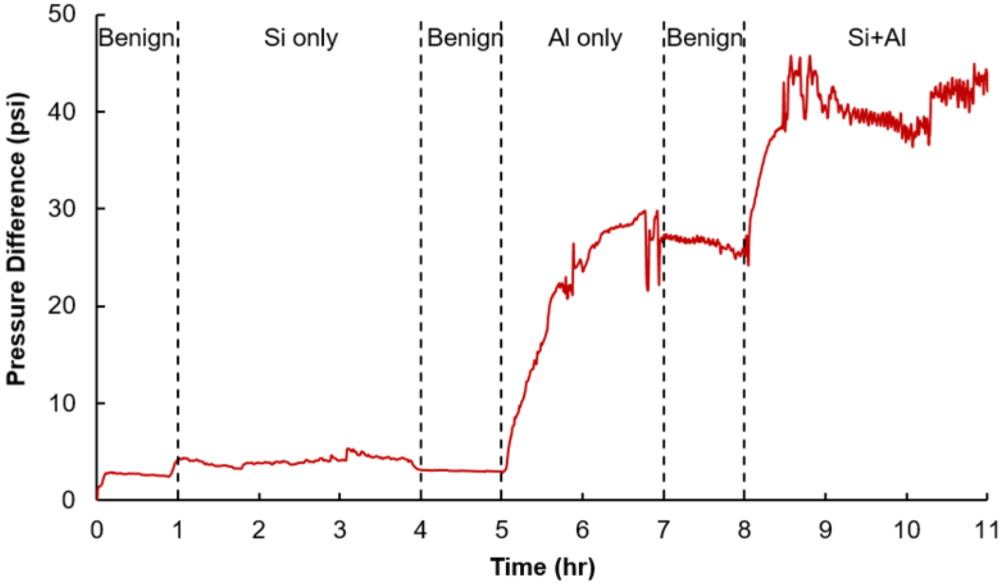


Figure 44 Trans-column pressure as a function of various synthetic solutions sequentially injected into Well 46C-47 soil at a Darcy velocity of 27 ft/d.

7.3.2. Effects of organic carbon

Well 7 groundwater has a high TOC concentration. Given the complexation and surface activity of humic species that are main contributors to TOC are well attested, its effects were examined by means of adding 100 to 500 mg/L commercially available soil-derived Aldrich humic acid to feed synthetic solutions whose composition was the same as hat described in the preceding section.

Initial results of these tests indicated that humic acid reduces soil plugging. To explore this phenomenon, an assumption was made that major effects of humic acid are likely to be associated with its complexation with Al. Correspondingly, column tests were conducted to focus on the effect of humic acid on hydraulic fouling associated with the presence of Al in the synthetic solution. Two experiments 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 column packed with unaffected soil from Well 46C-47. The average Darcy velocity for the test with 100 mg/l and 500 mg/l humic acid was 27 ft/d, respectively. The test with the Al solution with 100 mg/l humic acid was repeated with the order of the synthetic solutions reversed to ensure that injection order was not responsible for the outcome. 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 45).

The observed effect appears to be relevant to Well 7 chemistry and the partial suppression of hydraulic fouling by TOC is likely to be due to complexation between TOC and Al which results in increased Al solubility. Yet increasing the concentration of humic acid in the Al synthetic solution to a high level was not accompanied by a complete mitigate of soil plugging, thus adding or otherwise controlling TOC in OCC groundwater does not represent a viable option in the context of mitigation of hydraulic fouling.

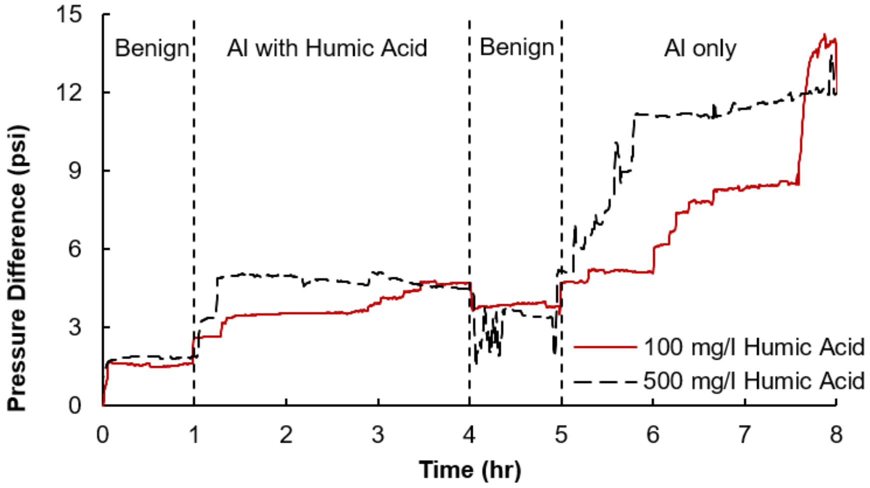


Figure 45 Development of trans-column pressure in response to the injection of Al-continaing synthetic groundwater solutions, with and without humic acid. Well 46C-47 soil-packed column, average Darcy velocity of 27 ft/d.

7.4. Effects of soil properties on hydraulic fouling

Column tests described in the preceding sections were conducted with Well 46C-47 soil, which, as mentioned elsewhere in the report, is considered to be unaffected by the high pH high Si 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 (≈27 ft/d) while at a relatively low Darcy velocity (≈7 ft/d) it does not occur. Therefore, the next series of tests explored the effect of both column media and Darcy velocity on hydraulic conductivity when Well 7 groundwater is injected.

These tests were largely similar to those conducted with ‘unaffected’ Well 46C-47 soil. They employed affected’ soil Well 83C-128. When Well 7 groundwater was injected into Well 83C-128 soil at a Darcy velocity of 80 ft/d for ca. 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 (Figure 46). These tests indicate that ‘affected’ soil is less prone to plugging than ‘unaffected’ soil when Well 7 groundwater is injected.

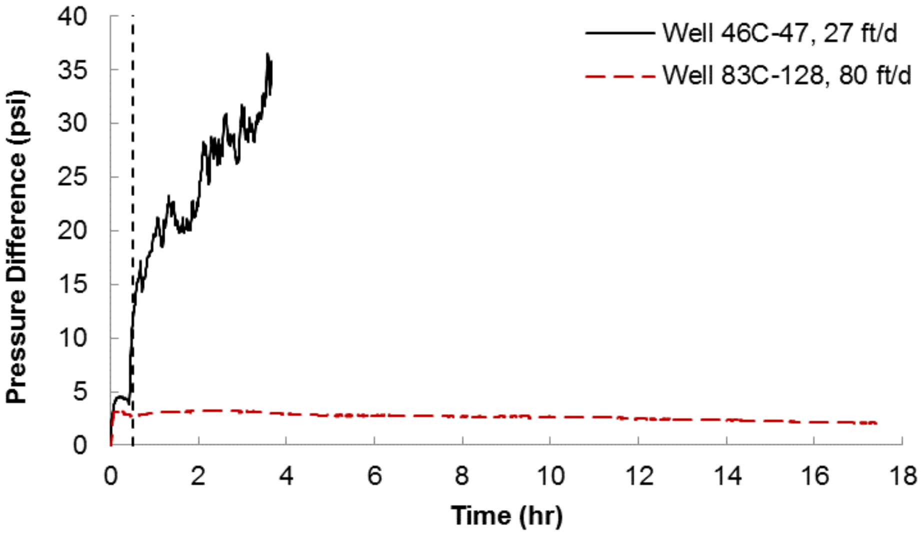


Figure 46 Comparison of the development of trans-column pressure for affected (Well 83C-128) and unaffected (Well 46-47) OCC soils. The vertical dashed line represents the switch from the benign solution to Well 7 groundwater.

Additional column tests were conducted to determine the threshold of Darcy velocities associated with the initiation of plugging of Well 83C-128 soil by Well 7 groundwater. 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 increased in response to the injection of Well 7 groundwater in both tests although more significant plugging occurred over time at the higher Darcy velocity.

In the next experiment, the Darcy velocity was increased step-wise to determine the threshold at which Well 7 groundwater begins to alter the hydraulic conductivity of Well 83C-128 soil. In that test, trans-column pressure increased somewhat in response to increasing the Darcy velocity, and started increasing rapidly when the Darcy velocity was 104 ft/d (Figure 47). The pressure increased even more dramatically when the Darcy velocity was increased to 118 ft/d. These results indicate that the threshold for plugging of Well 83C-128 soil by Well 7 groundwater is between 85 ft/d and 104 ft/d.

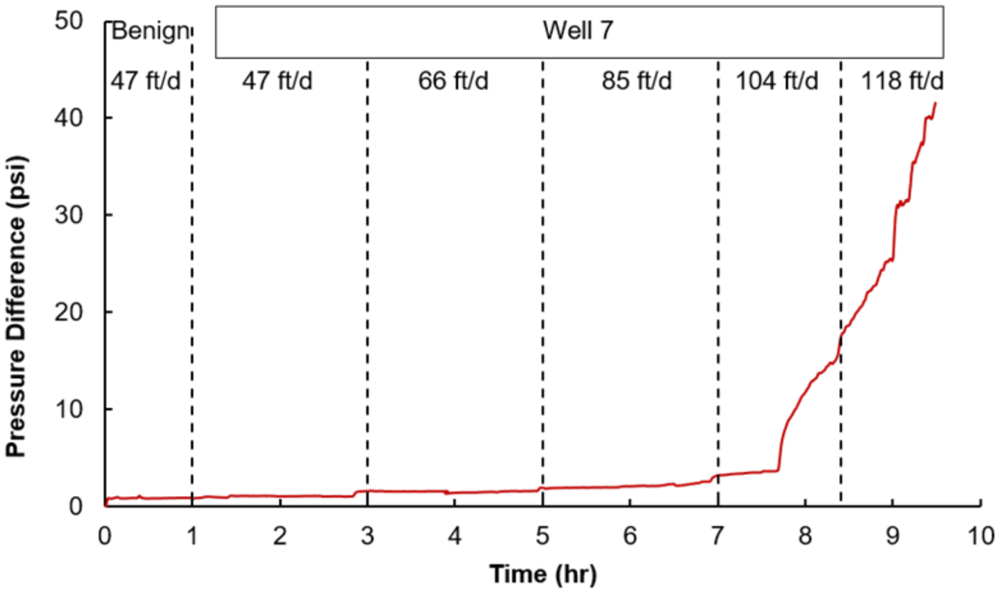


Figure 47 Development of trans-column pressure for Well 7 groundwater injected into Well 83C-128 soil at various Darcy velocities.

To determine whether the observed effects were associated with soil properties rather than possible effects of Darcy velocity of the properties of Well 7 water per se, additional tests were carried out with sand that was used as a model inert solid phase. Two tests conducted at Darcy velocities of 52 and 104 ft/d, and Well 7 groundwater injected in the sand-packed columns. Trans-column pressure remained low and stable throughout both these tests that lasted for up to eight hours. These results indicate that the occurrence of hydraulic fouling is mediated by specific interactions between Well 7 groundwater and OCC site soil, rather than solely based on constituents in the groundwater characteristic for the OCC site.

7.5. Summary of observations of relevant to hydraulic fouling in Well 7 groundwater/Oxy soil interactions

The data shown above demonstrate that injection of Well 7 groundwater causes gradually developing hydraulic fouling. This effect is more prominent when this water interacts with soil deemed to be unaffected by contact with the high pH plume. While exact mechanisms of such plugging are still unclear, we posit that Well 7 groundwater reduces the hydraulic conductivity of previously unaffected soil due to localized pH changes that cause nuclei of solid phases impeding the movement of groundwater to be formed.

We posit that this process is more likely to occur for unaffected soils due their base-neutralizing capacity which, in contrast, is zero or negative for affected soils (that is, such soils release compounds that increase of pH of ambient water). Thus, the presence of measurable base-neutralizing capacity in OCC soils is an important possible cause of hydraulic fouling. It can be furthermore suggested that the higher the base-neutralizing capacity of OCC soil, the more readily its hydraulic conductivity may decrease when Well 7 or similar water flows through its pores.

Given that extraction of groundwater at the OCC site will be from a point source (e.g., Well 7) or an array of similarly positioned wells, the presented data on the effects of Darcy velocity on the threshold of plugging provide an actionable guideline for selecting extraction rates. The available data indicate that as long as groundwater extraction takes place in the zone of affected OCC soils, exceedances of Darcy velocities from the threshold located between ca. 84 and 104 ft/d may ultimately cause the hydraulic conductivity of ‘affected’ soil to decrease, while at lower Darcy velocities the probability and extent of such phenomenon are much less prominent.

The above-mentioned threshold of Darcy velocities is equivalent to an extraction rate of 3100 to 3800 gpd from the assumed geometry of Well 7. While this range of pumping rates does not necessarily exactly correspond to the threshold of soil plugging for actual field operations of Well 7 or a similar extraction well, this result emphasizes the point that that groundwater extraction efforts should begin at a low pumping rate which can be slowly increased to reach a sufficiently high pumping rate that still must be below the expected threshold of the initiation of hydraulic fouling. Further field tests are necessary to explore this point and determine the actual pump rate threshold associated with the triggering of hydraulic fouling in OCC soils.

7.6. Occurrence of hydraulic fouling in soils interacting with groundwater blends

Extraction of groundwater at the OCC site will likely result in blending of groundwater from nearby wells, as well as with groundwater that moves in the extraction zone from other areas of the site. The impact of such blending on hydraulic conductivity of OCC soils was investigated using column tests similar to those described above. To examine possible blending scenarios, several groundwater blends were injected as feed into columns with OCC soils. These included Wells 7/46C-130 groundwater blend, Wells 7/83C-100 groundwater blend, and Wells 83C-100/82-100 groundwater blend which were injected into a column packed with ‘unaffected’ or with ‘affected’ soils. For each soil type, two tests were performed at 47 or 52 ft/d and 95 ft/d Darcy velocities.

7.6.1. Hydraulic fouling in blends of groundwater from Well 7 and Well 46C-130

Blends of groundwater from Wells 7 and 46C-130 represent an extreme scenario that would not necessarily occur readily *per se* due to the large distance between the two wells. However, these blends may represent changes of groundwater associated with long-term pumping operations at the site.

Groundwaters from these wells have very different properties. Well 7 groundwater has a high pH, VOC, Si and Al concentrations, while Well 46C-130 groundwater has a much lower pH, low VOC concentrations, and Si and Al concentrations that are several orders of magnitude lower than those in Well 7 groundwater. As described in the report section concerned with precipitation phenomena in batch experiments with OCC groundwater, Well 7/46C-130 blends containing >5% Well 46C-130 groundwater exhibit some precipitation of solid phases. 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.

The experiments carried out using groundwater blends with gradually increasing fractions of Well 46C-130 groundwater showed that Well 46C-47 soil injected at the Darcy velocities of 52 and 95 ft/d exhibited pronounced hydraulic plugging within a few hours, with more rapid plugging occurring during the test with the higher Darcy velocity (Figure 48). 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 49).

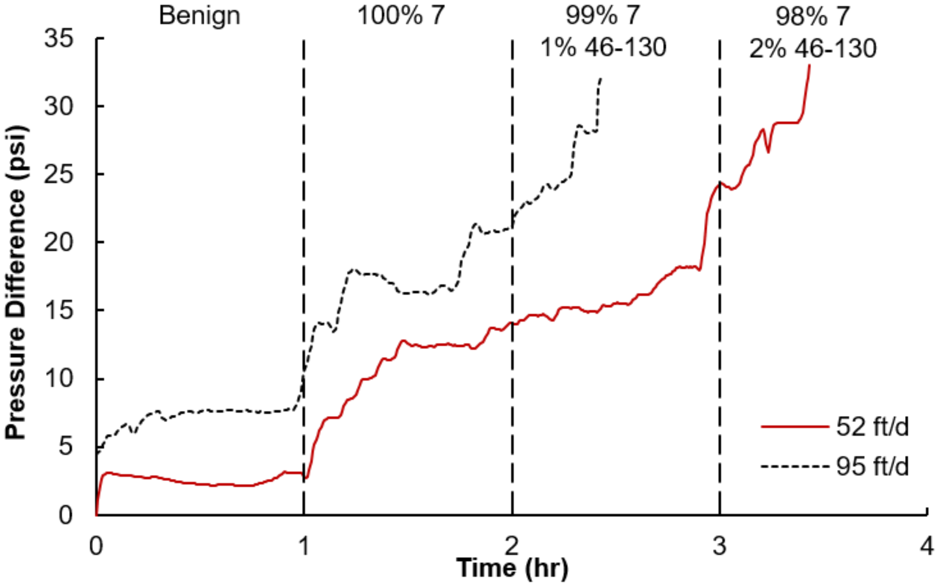


Figure 48 Development of trans-column pressure for blends of Well 7 and Well 46C-130 injected into 'unaffected' Well 46C-47 soil at Darcy velocities of 52 and 95 ft/d.

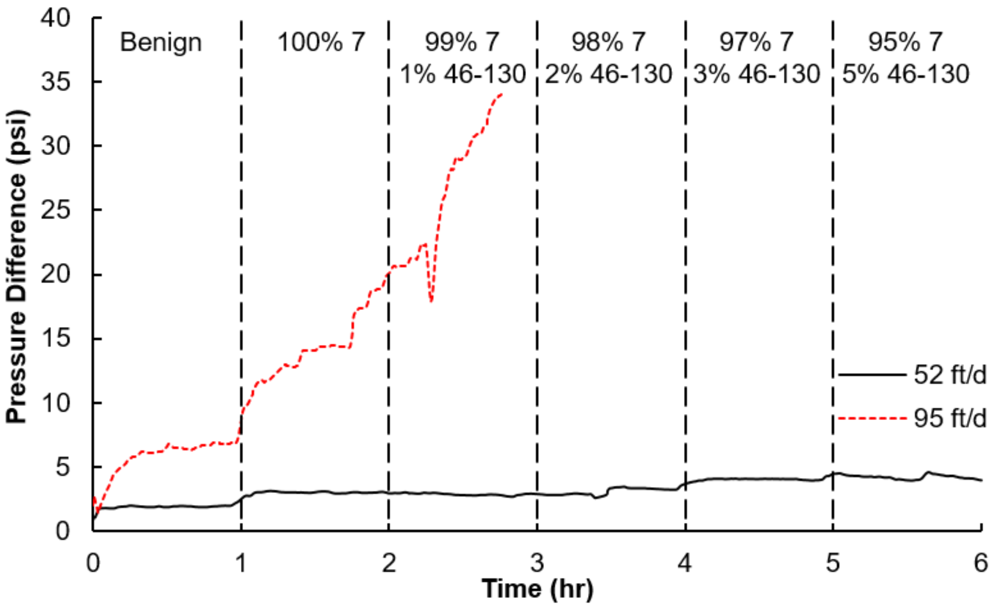


Figure 49 Development of trans-column pressure for blends of Well 7 and Well 46C-130 injected into 'affected' Well 83C-128 soil at Darcy velocities of 52 and 95 ft/d.

7.6.2. Hydraulic fouling in blends of groundwater from Well 7 and Well 83C-100

Blends of groundwater from Wells 7 and 83C-100 may occur due to vertical mixing, which may intensify due to 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. Prior experiments showed that blends with ≥75% Well 7 did not exhibit precipitation within a few hours, so the following blends were sequentially 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 50). 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 51). 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.

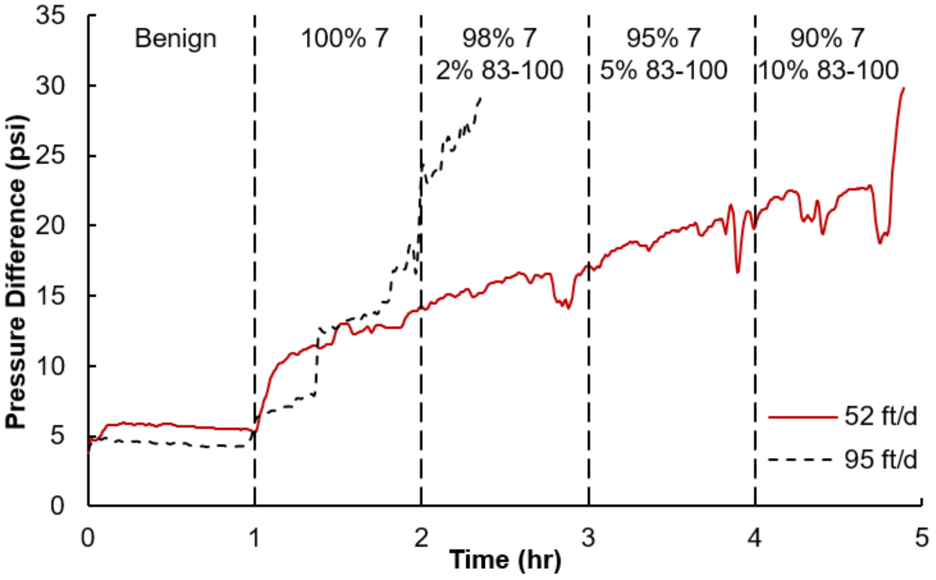


Figure 50 Development of trans-column pressure for blends of Well 7 and Well 83C-100 injected into 'unaffected' Well 46C-47 soil at Darcy velocities of 52 and 95 ft/d.

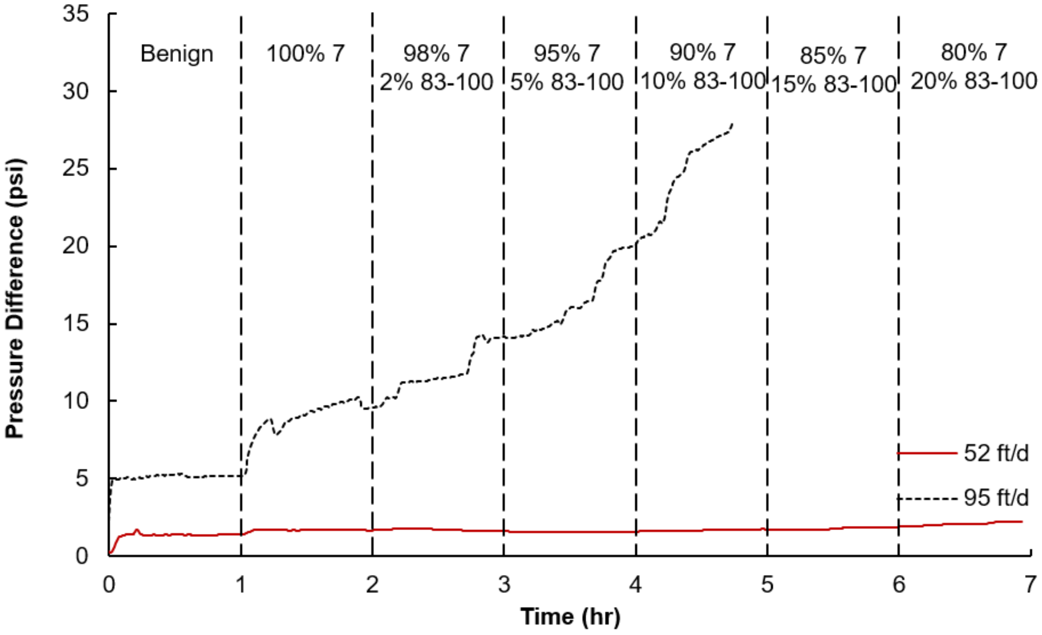


Figure 51 Development of trans-column pressure for Well 7 and Well 83C-100 injected into 'affected' Well 83C-128 soil at Darcy velocities of 52 and 95 ft/d.

7.6.3. Hydraulic fouling in blends of groundwater from Well 83C-100 and Well 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 sequentially injected for one hour each after the 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 52). The gradual increase in trans-column pressure over time likely occurred because blends had more Well 82-100 groundwater by volume, which is more ‘affected’ by the high pH plume than Well 83C-100 groundwater.

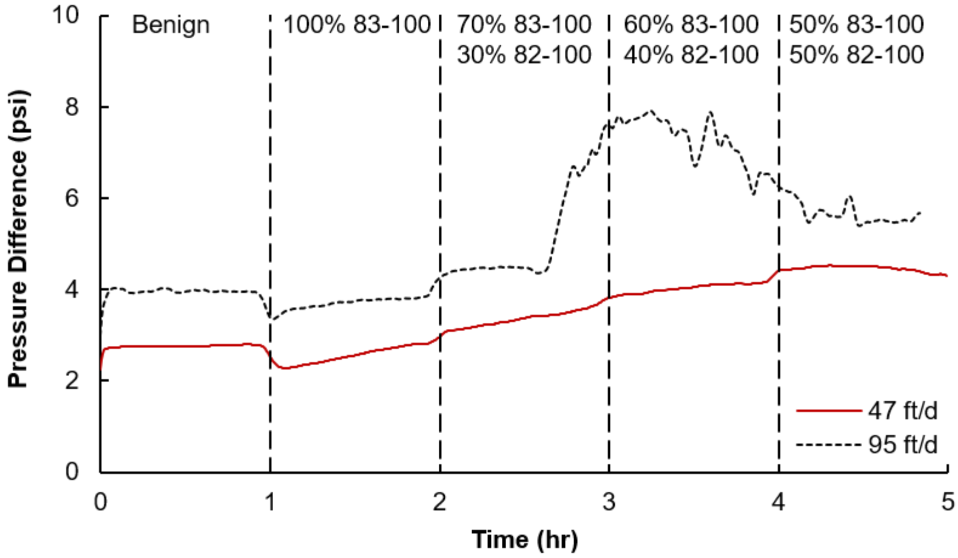


Figure 52 Development of trans-column pressure for blends of Well 83C-100 and Well 82-100 injected into ‘affected’ Well 83C-103 soil at Darcy velocities of 47 and 95 ft/d.

7.6.4. Summary of observations related to effects of groundwater blending on hydraulic fouling

Blends of groundwater from different OCC site wells were injected into columns packed with ‘affected’ and ‘unaffected’ soils at two different Darcy velocities. 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 unblended 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 unblended 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 investigated only 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.

7.7. Conclusions and recommendations derived from the column tests data

The data presented in this section show that hydraulic fouling in Oxy soil packed columns is affected by a variety of factors, notably:

- *Relatively high Darcy velocities,*
- *Elevated Al concentrations,*
- *Specific soil interactions,*
- *Groundwater blending.*

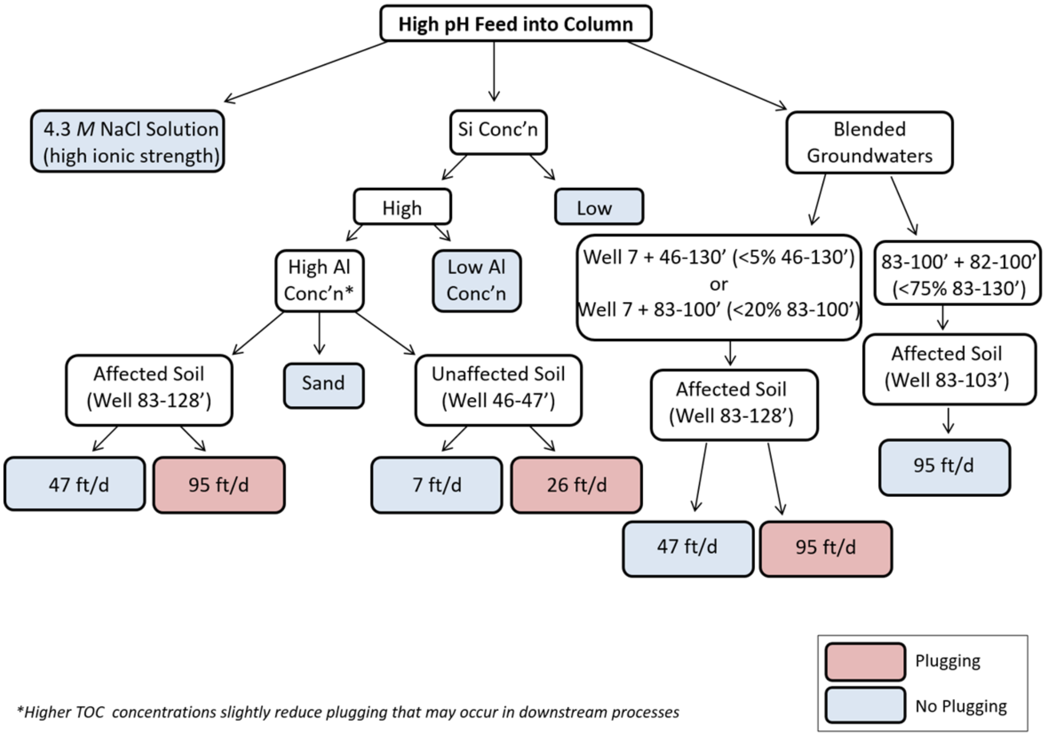
These observations are summarized in Figure 53; that figure can be used as a visual tool that helps identify the combinations of factors that contribute to soil plugging.

To summarize these observations, the development of hydraulic fouling depends on the nature of the exposed soils and even more prominently on the velocity of movement of groundwater through the column (Darcy velocity). Hydraulic fouling tended to develop slower in soils that had been affected by high pH, high Si groundwater. Conversely, soils originating from largely unaffected areas of the site developed such fouling more readily. This behavior is consistent with the observation that affected OCC soils cause little change of the pH of high-pH, high-Si groundwater in contact with them, while unaffected soils, even though their base-neutralizing capacity is generally low, may cause some decrease of the pH in the front of the plume of high pH, high Si groundwater moving through pores of exposed unaffected soils.

Al and Si were neither retained by nor released from the soil to a significant extent as water passed through the columns. This result was unexpected. However, given the extremely high concentration of Si in Well 7 water, the precision of the analyses may not have been adequate to discern minor changes in the analyte concentrations. Another unexpected yet important finding was that the incidence of hydraulic fouling depended on the Darcy velocity of groundwater moving through exposed soil. In general, Darcy velocities less than ca. 20 ft/day and ca. 60 ft/day for unaffected and affected soils, respectively, resulted in the absence or slow development of hydraulic fouling, whereas higher Darcy velocities caused hydraulic fouling to develop rapidly. The mechanism(s) underlying these effects remain to be ascertained.

Experiments with synthetic solutions showed that higher levels of aluminum in column influents tended to promote hydraulic fouling, while increases in the concentration of organic carbon tended to suppress it. This pattern might be related to the formation of insoluble mixed aluminosilicates in the pores of exposed soils and the acceleration of that process by precipitation nuclei, for instance polynuclear and/or colloidal Si species present in Well 7 groundwater. Formation of insoluble aluminosilicates may be also accelerated by local decreases of pH caused by the neutralization of highly basic Well 7 groundwater by soil minerals that have higher ANC values than those for the average soil matrix.

In the context of practicable controls of some of the factors that may cause hydraulic fouling during pumping activities, Darcy velocity appears to be the most significant factor, and it is essential that the Darcy velocity threshold for soil plugging be identified and not exceeded. Darcy velocity thresholds associated with the initiation of hydraulic fouling in field conditions are likely to be different from those identified in our column tests yet all evidence points to the notion that groundwater 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.



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

Figure 53 Schematic comparison of factors affecting hydraulic fouling plugging in OCC site soils. Interpretation of data of column tests.

8. Tracer Measurements of Incipient Changes of Hydraulic Conductivity and Its Reversibility

The intent of the tracer tests was to generate data with which to quantify incipient rather than fully developed hydraulic fouling. In the context of our benchtop measurements, the incipient phase of hydraulic fouling refers to conditions in which the trans-column pressure does not increase appreciably.

The goals of this task can be defined as follows:

- *Can incipient changes of hydraulic conductivity of OCC soils caused by their contact with Well 7 groundwater, its blends and synthetic solutions be discerned experimentally?*

- *Can these changes be reversed by means of injections of caustic regenerants (e.g., 0.01 and 0.1 M NaOH)?*

Experiments to obtain information relevant to the above questions employed tracer injections in columns packed with OCC soils. These measurements used pulse injections of a small amount of a highly concentrated NaBr solution and measurements of Br^- tracer concentrations in the effluent from columns packed with representative OCC soils. Bromide ion was selected as a tracer due to its chemical inertness in conditions of interest for this study, its typically low retardation in soils or sediments, and the relative ease of measurements of its concentrations using a Br- ion selective electrode (ISE). Injections of the Br^- tracer had a 1 minute duration and thus were quasi-instantaneous in the time scale of the reported experiments. The concentration of NaBr in the injected tracer solution was 7 mol/L. The length, cross section and empty bed volume of the column were 12 cm, 18.1 cm^2 and 217.2 cm^3, respectively. Concentrations of bromide in column effluents were determined using a Cole-Parmer Br-sensitive ISE. The electrode was calibrated using NaBr solutions with concentrations ranging from 10^{-6} to 0.1 mol/L. Flow rates in the tracer experiments were varied as needed and were in some cases equivalent to Darcy velocities as high as 36 ft/day.

As before, OCC soils used in the tracer experiments were from Well 46, Well 82 and Well 83. Well 46 is located an unaffected area of the OCC. The soils from this locus used in the tracer experiments were from depths ca. 47 and 75 feet bgs. pH values of the pore water in contact with soils 46-47 and 46-74 were 8.1 to 8.5 and 7.9, respectively. The circumneutral pH values and low acid neutralizing capacity (ANC) of these soils (11.6 and 4.2 μeq/g soil, respectively) determined in the titration experiments confirmed that these soils had not been affected by high pH effluents. Soils from Wells 82 and 83 used in the tracer experiments were taken at depths of 91 and 124 feet bgs, respectively. pH values of groundwater in contact with these soils were 10.9 and 11, respectively. These high pHs together with high ANC values determined for these soils (219 and 199 μeq/g soil) are indicative of significant changes of these soils' chemistry induced by their exposures to the high pH effluent.

Initial tracer measurements were carried out for soils 46-75 and 46-47 injected with Well 7 water. These measurements also utilized model solutions containing varying levels of Al^{3+}. The latter type of synthetic solutions was used to examine in more detail effects of Al^{3+} whose presence, in accord with our results presented in the preceding sections of the report and data of prior research (e.g., *May et al. 1986; Bauer and Berger 1998; Qafoku et al. 2003; Mashal et* *al. 2004; Amram and Ganor 2005; Bickmore et al. 2006; Golubev et al. 2006; Wang and Um 2012*) was expected to contribute to the initiation of hydraulic fouling in OCC soils.

The soil columns were injected with influents whose typical sequence is shown in Figure 54. (Other sequences were used in the tracer experiments as needed). The sequence was always initiated by passing 0.01 M NaCl, pH 11.7 benign solution whose purpose was to equilibrate the soil and establish a trans-column pressure baseline. The equilibration step was followed by a tracer pulse and continuing injection of the benign solution to generate a tracer breakthrough profile that was used a reference with which subsequent tracer breakthrough profiles were compared.

After the initial tracer injection was completed, Well 7 groundwater, or its blends or a synthetic solution was injected. The duration of this phase varied depending on the specific goal of any particular experiment. Once the injection of Well 7 water or similar solution was stopped, one pulse of NaBr tracer was introduced and bromide concentrations in the column effluent were measured again to determine whether discernible changes of the hydraulic properties of the column have taken place. In many cases additional tracer injections were performed after the soil column was flushed with 0.01 or 0.1 M NaOH. These solutions were used to dissolve solids that may have been formed as a result of interactions of Well 7 groundwater or other solutions with the soils.

Tracer experiments for soil 46-75 showed that the injection of Well 7 groundwater did not cause significant changes of the trans-column pressure which increased only by ca. 1 psi (Figure 54). Flushing the column with 0.1 M NaOH caused the pressure to decrease. This may indicate that incipient solid phases deposited in the pores as a result of interactions of soil 46-75 with Well 7 groundwater were partially or completely removed and/or that Well 7 groundwater that is likely to have a higher viscosity than 0.1 M NaOH solution was flushed from the pores.

Tracer data generated for this experiment (Figure 55) show that the bromide breakthrough profiles generated prior to the exposure of soil 46-75 to Well 7 groundwater/0.1 M NaOH sequence and after it do not exhibit considerable changes, and in both cases the maximum of bromide concentrations in the breakthrough profile is located near the nominal hydraulic residence time (HRT) of the soil column calculated using the known flow rate, total volume of the column and the effective soil porosity (ca. 38%) that was adjusted from its nominal value (32%) for the tracer data to be reasonably readily interpretable. The breakthrough profile was broad and considerable bromide concentrations were seen for HRT-normalized elution times from ca. 0.4 to 2.4. This indicates that, as expected for complex materials such as Oxy soils, the movement of the tracers through the column was affected by the presence of different diameters and tortuosity of soil pores, dispersion and possibly some tracer retardation.

The data for injections of Well 7 groundwater were compared with those generated for synthetic solutions containing varying levels of Al^{3+} (Figure 56 to Figure 58). These results showed some variability of the tracer profiles obtained prior to the introduction of Al^{3+}-containing solutions. In some cases the location of the maximum of tracer concentrations in the breakthrough profiles differed from the HRT value calculated assuming a constant soil porosity. Because, as mentioned above, physical properties of Oxy soils packed in the column (e.g., their effective porosity, presence of voids and channeling) can vary from one experiment to another due to difficult to control variations of soil packing, such deviations are largely expected. Still, the data presented in Figure 56 demonstrate the occurrence of some irreversible changes of the tracer profile in the case of injection of the synthetic solution containing 0.5 g/L Al. In contrast, little changes were observed for soil 46-75 injected with 1.0 and 2 mg/L Al and then flushed with 0.01 M NaOH (Figure 57 and Figure 58).

Similar data were obtained for injections of Al-containing synthetic solutions in soil 46-47. In that case, the trans-column pressure increased upon the injection of the solution containing 1 g/L Al (Figure 59). It decreased somewhat upon the introduction of 0.1 M NaOH solution, similarly to the observations shown in Figure 54. Yet the treatment with 0.1 M NaOH did not eliminate completely changes of the soil properties associated with relatively minor development of hydraulic fouling seen in this experiment, as indicated by the elevated trans-column pressure observed in the end of experiments shown in Figure 59 and changes of the tracer profiles that indicated the occurrence of a faster breakthrough of bromide through the pores of soil 46-47 after it was exposed to elevated levels of aluminum (Figure 60).

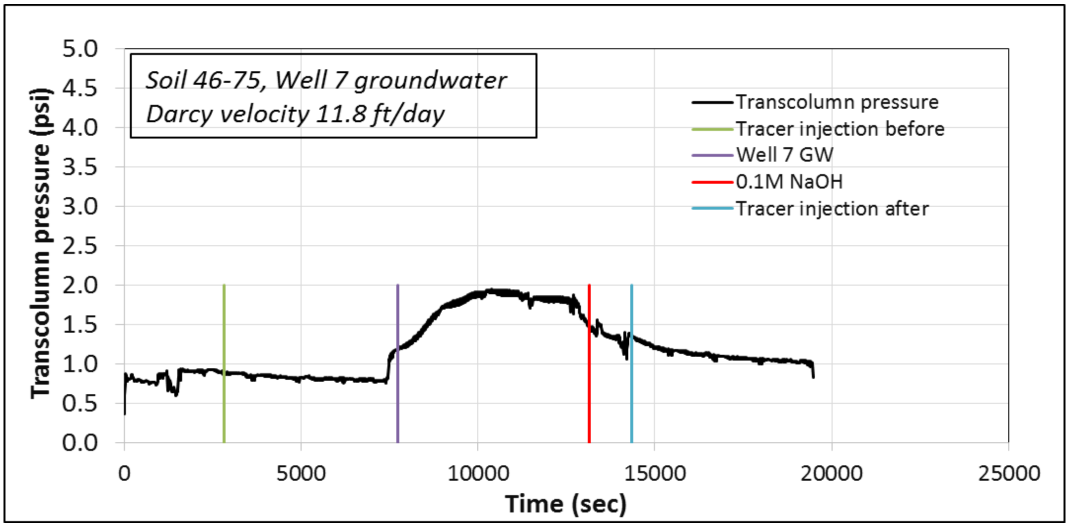


Figure 54 Changes of trans-column pressure in a column packed with soil 46-75 for injections of Well 7 groundwater followed by 0.1 M NaOH. Darcy velocity 11.8 ft/day.

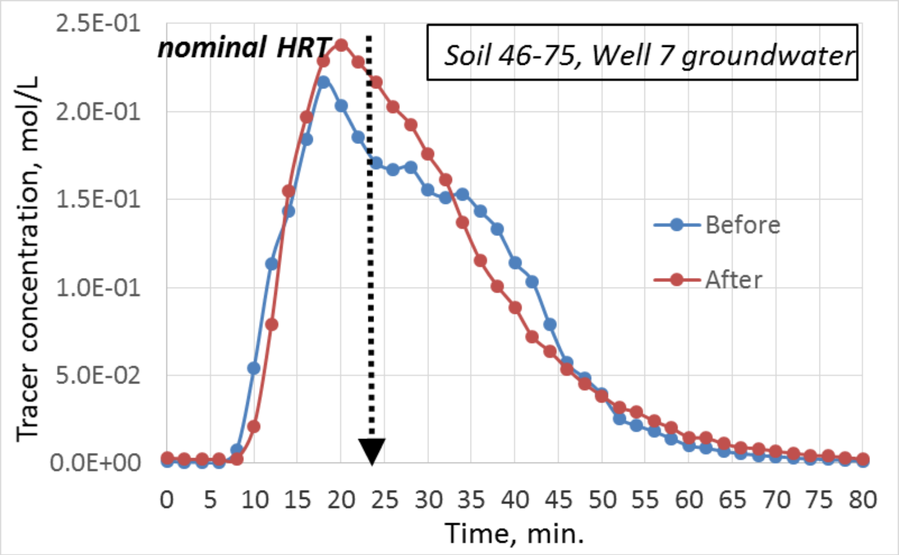


Figure 55 Tracer breakthrough profiles for a column packed with soil 46-75 before and after injections of Well 7 groundwater followed by 0.1 M NaOH. Darcy velocity 11.8 ft/day.

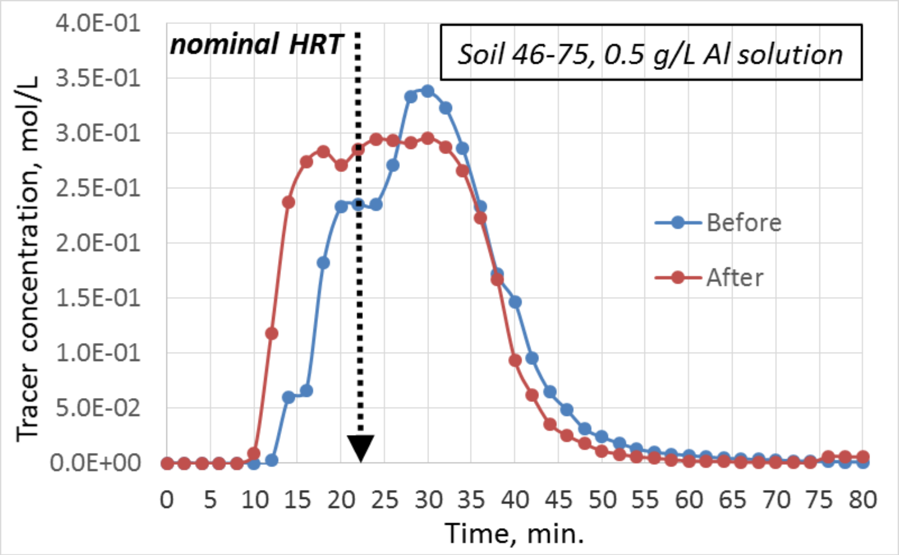


Figure 56 Tracer breakthrough profiles for a column packed with soil 46-75 before and after injections of synthetic solutions containing 0.5 g/L Al followed by 0.1 M NaOH. Darcy velocity 10.3 ft/day.

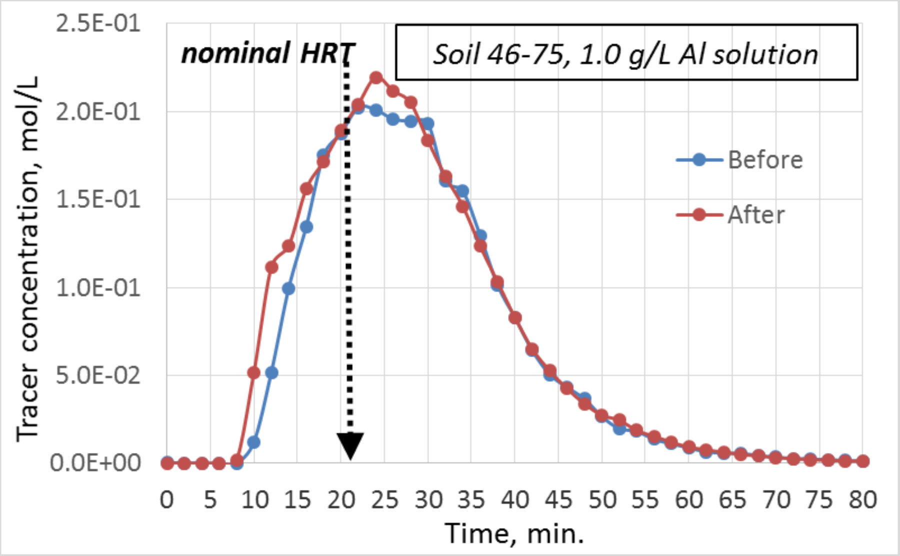


Figure 57 Tracer breakthrough profiles for a column packed with soil 46-75 before and after injections of synthetic solutions containing 1.0 g/L Al followed by 0.1 M NaOH. Darcy velocity 11.0 ft/day.

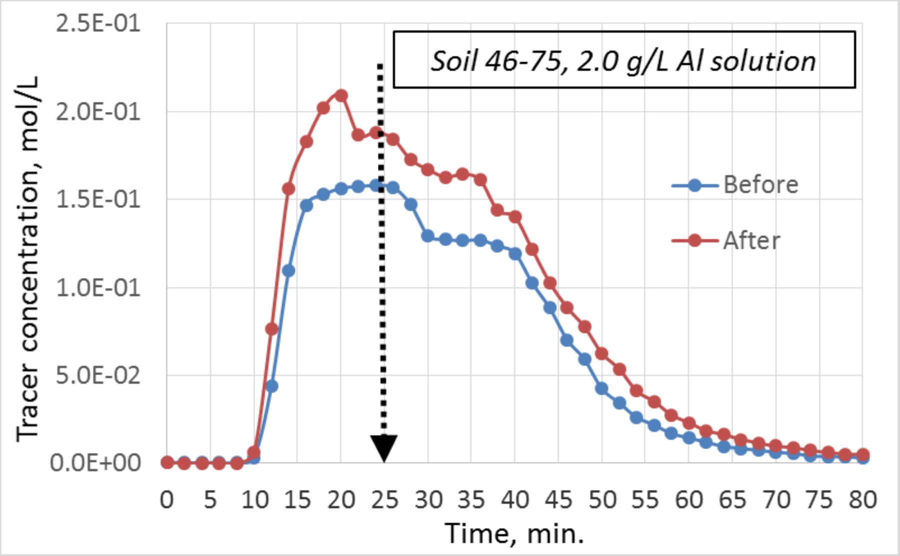


Figure 58 Tracer breakthrough profiles for a column packed with soil 46-75 before and after injections of synthetic solutions containing 2.0 g/L Al followed by 0.1 M NaOH. Darcy velocity 9.1 ft/day.

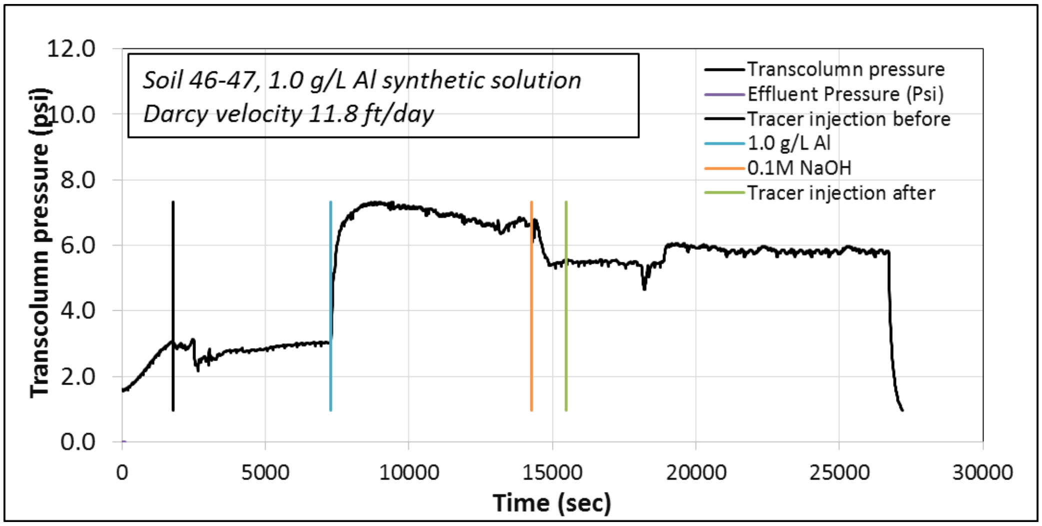


Figure 59 Changes of trans-column pressure in a column packed with soil 46-47 for injections of injections of synthetic solutions containing 1.0 g/L Al followed by 0.1 M NaOH. Darcy velocity 11.8 ft/day.

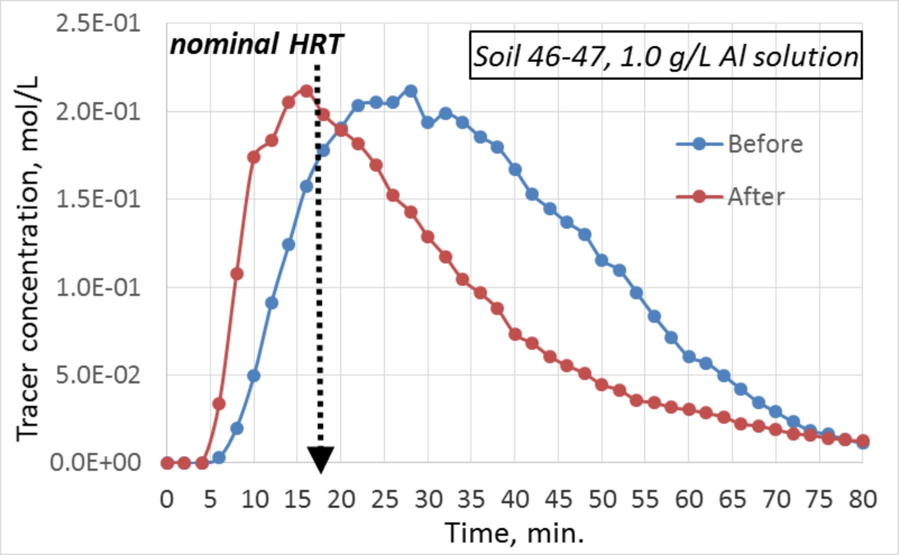


Figure 60 Tracer breakthrough profiles for a column packed with soil 46-47 before and after injections of synthetic solutions containing 1.0 g/L Al followed by 0.1 M NaOH. Darcy velocity 11.8 ft/day.

Tracer data generated for soil 83-124 demonstrate some difficulties in carrying out experiments with OCC soils affected by high pH high Si groundwater. For instance, most of the eluted tracer mass was observed for elution times that were longer than the nominal HRT calculated for this soil assuming its porosity being equal to ca. 32%, as was measured in the preceding experiments. The observed difference may be related to difficult to control changes in the morphology of soil whose clumps had to be dispersed before their use for column packing and possibly some retardation of the tracer which, however, was not appreciable in many other experiments.

Still, measurements for this soil show that the injection of Well 7 water caused a transient and generally reversible increase of the trans-column pressure (Figure 61). These changes were similar for Darcy velocities of 23.6 and 36 ft/day both of which are below the threshold of hydraulic fouling discussed in the preceding section. Injection of the bromide tracer in the column before and after its exposure to Well 7 water demonstrate that, as was the case in the experiments with Well 46 soils, there was a change of the tracer breakthrough profile that appears to indicate a decrease of the pore volume in the exposed soils (Figure 62).

Further experiments discussed in this report were carried out with soils from Well 82-91. Measurements of effects of blending of Well 7 groundwater with surface water on hydraulic fouling induced in this soil were inconclusive as in some cases the tracer breakthrough profile exhibited an expected shift to shorter elution times (Figure 63) while in others, for instance in the cases of blends of Well 7 groundwater containing 10% and 30% of surface water (Figure 64 and Figure 65), the shift was either in an opposite direction, or its extent was insufficient to cause an appreciable changes of the soil pores.

Repeated injections of Well 7 groundwater into a column packed with soil 82-91 confirmed the occurrence of a shift of the tracer maximum concentration to shorter elution times (Figure 66). This change potentially associated with the physical changes of the system of soil pores was susceptible to the post-groundwater exposure treatment with 0.01 and 0.1 M NaOH. The data shown in Figure 66 suggest that the flushing of the soil with 0.01 or 0.1 M NaOH solutions resulted in very similar changes of the tracer elution profiles indicating that the solid phases potentially deposited in the soils as a result of its interactions with Well 7 groundwater water were removed by 0.01 M NaOH and further increase of the concentration of NaOH did not lead to appreciably important changes of the soil pore system.

Similar results were obtained in tracer experiments carried out with soil 82-91 injected with Well 7 groundwater containing a 1 g/L increment of Al concentration (Figure 67). The injection of Well 7 water with increased Al concentration resulted in the enhancement of the feature present in the breakthrough profile generated for this experiment but the post-exposure flush of the column with 0.01 M NaOH resulted in a nearly complete reversal of this effect.

To summarize the data of the tracer injection experiments, we can state that incipient hydraulic fouling can be detected and quantified via the analysis of changes of tracer breakthrough profiles measured prior to and after exposures of OCC soils to Well 7 groundwater or its blends, and also after flushing the exposed soils with caustic regenerants. The data show that a nearly complete reversal of incipient hydraulic fouling is possible and that there is little difference in the efficiency of 0.01 M or 0.1 M NaOH solution in their use for this purpose..

Data of repeated tracer injections also indicate that sequential cycles of exposures of OCC soils to high Si groundwater followed by their treatment with a caustic regenerant tend to stabilize the soil/groundwater system, and less hydraulic fouling may occur in repeated cycles of groundwater loading/caustic regeneration. That is, if a well is in a state of incipient hydraulic fouling, it may be beneficial to flood that well with caustic to flush the soil and to improve the well's operability in long-term operations. An alternative option is to modulate pump rates starting with a relatively low pump rate, then allow the soil to stabilize, possibly in the presence of caustic regenerants, after which pumping may resume at a higher rate.

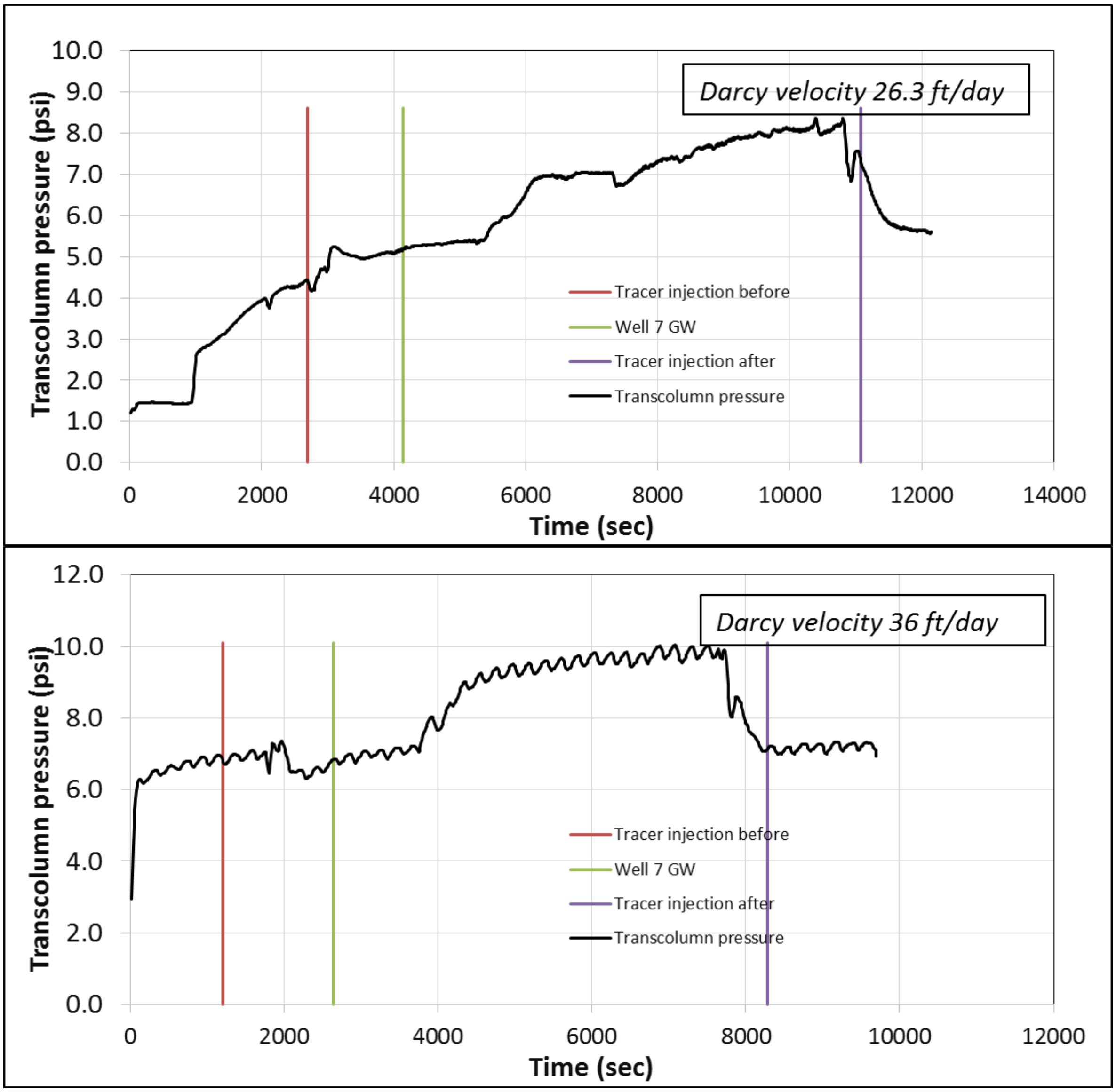


Figure 61 Comparison of changes of trans-column pressure in a column packed with soil 83-124 for injections of Well 7 groundwater, Darcy velocities 26.3 and 36 ft/day.

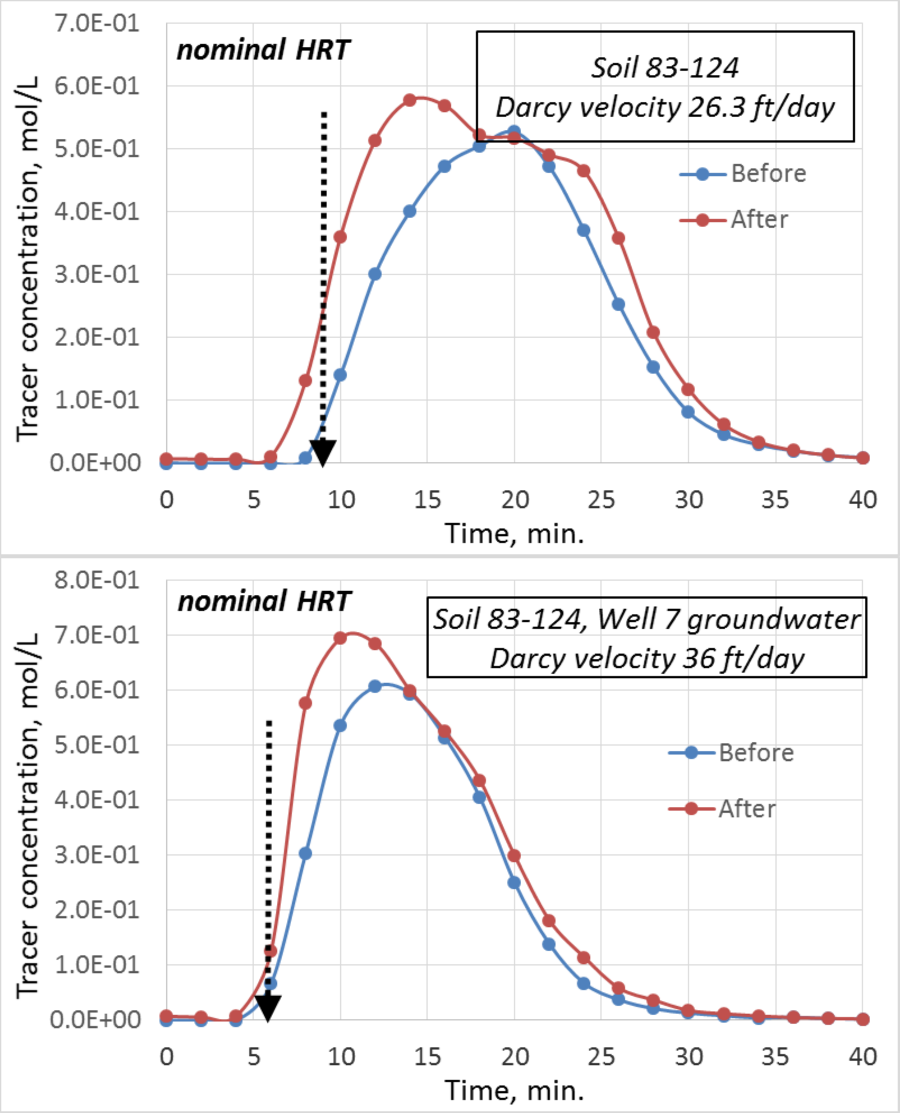


Figure 62 Comparison of tracer breakthrough profiles for a column packed with soil 83-124 before and after injections of Well 7 groundwater. Darcy velocities 26.3 and 36 ft/day.

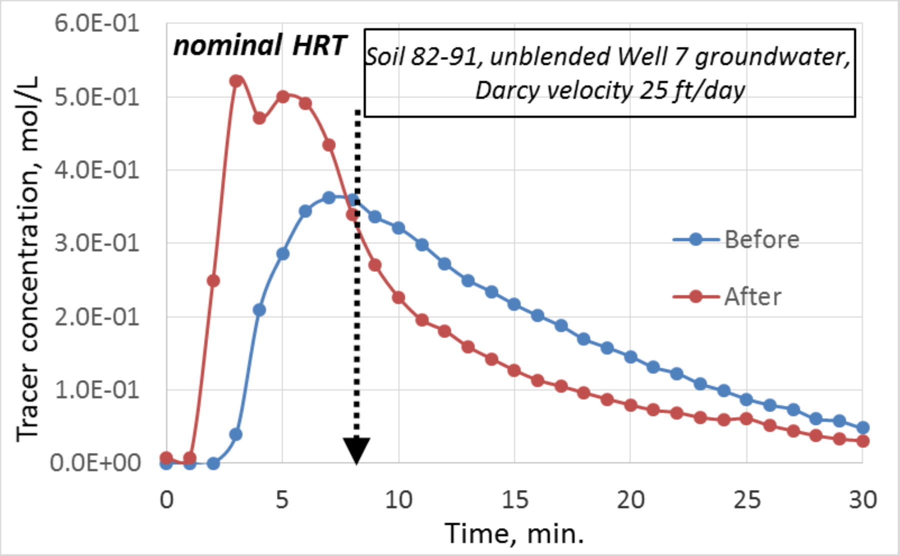


Figure 63 Tracer breakthrough profiles for a column packed with soil 82-91 before and after injections of unblended Well 7 groundwater.

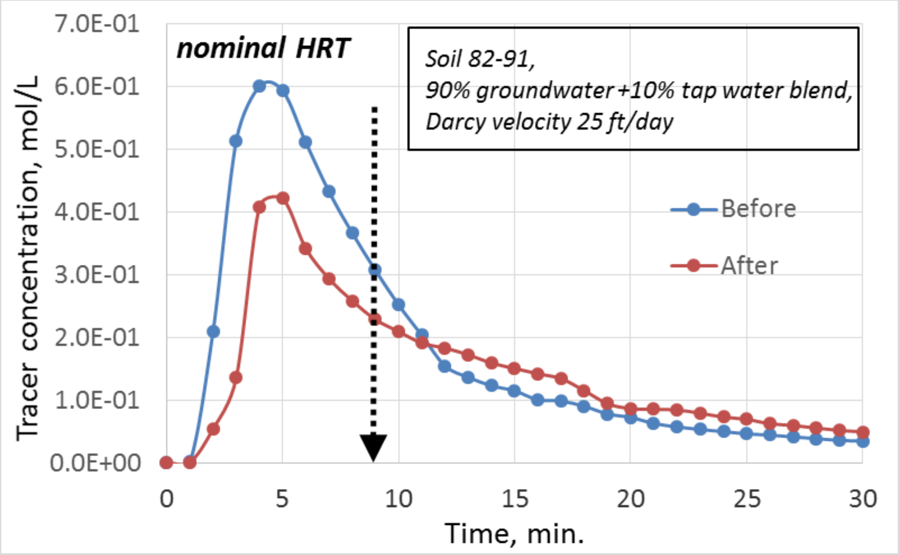


Figure 64 Tracer breakthrough profiles for a column packed with soil 82-91 before and after injection of Well 7 groundwater blended with 10% Seattle tap water.

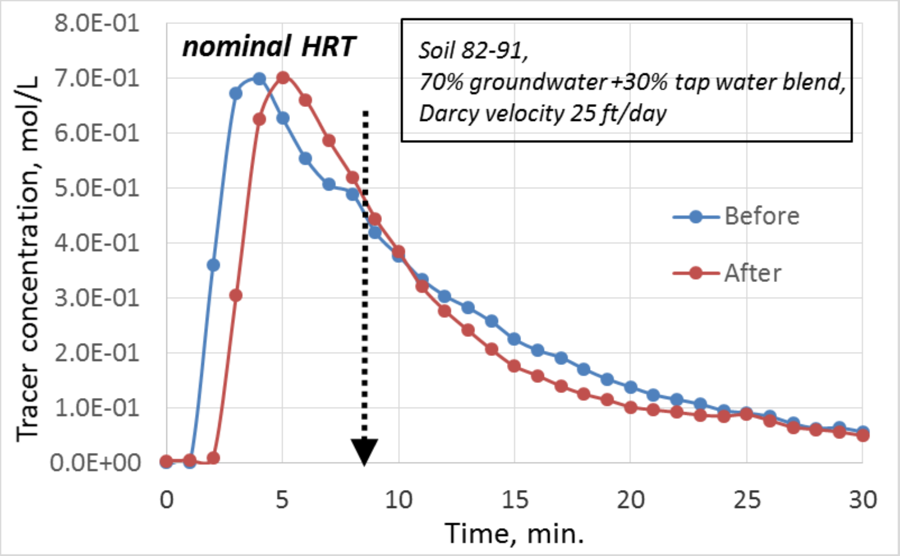


Figure 65 Tracer breakthrough profiles for a column packed with soil 82-91 before and after injection of Well 7 groundwater blended with 30% Seattle tap water.

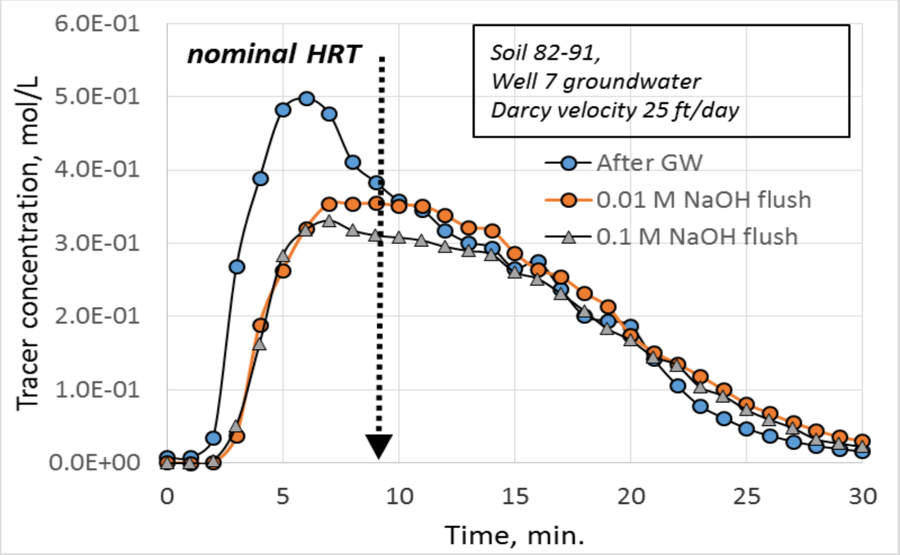


Figure 66 Comparison of tracer breakthrough profiles for a column packed with soil 82-91 before and after injections of Well 7 groundwater and a follow-up injections of 0.01 M and 1 M NaOH. Darcy velocity 25 ft/day.

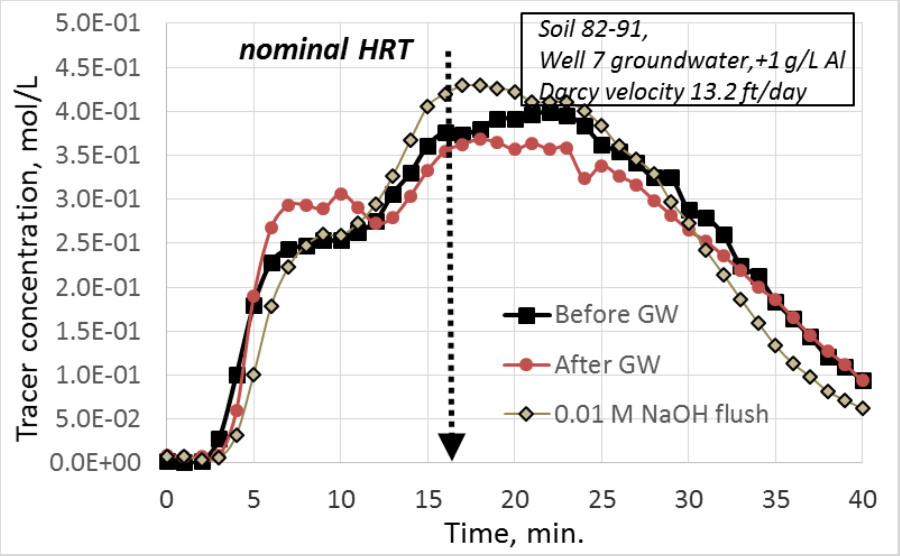


Figure 67 Comparison of tracer breakthrough profiles for a column packed with soil 82-91 before and after injections of Well 7 groundwater with added 1 g/L Al and a follow-up injections of 0.01 M NaOH. Darcy velocity 13.2 ft/day.

9. *In Situ* Formation of Hydraulic Barriers in OCC Soils

Experiments in this task were to test the formation of a hydraulic barrier in the aquifer soil by precipitation of solids accompanying the pH neutralization of high-Si groundwater. Specific aspects examined in this task were:

- *What acidities of solutions injected in the aquifer are needed to initiate the formation of hydraulic barriers?*
- *What chemistries of base-neutralizing solutions are suitable for this purpose?*
- *Are solids formed via the injection of acidic solutions in the aquifer uniformly distributed?*

Experiments to obtained information needed to answer these questions were carried out using a setup described below. More information about these experiments and their results is presented in *Pandya* 2015.

To inject base-neutralizing agent quasi-uniformly along the length of a soil column, a porous ceramic tube (ca. 0.5" ID and 1.0" OD) was installed coaxially inside a 2"-ID Plexiglas tube. The entire apparatus was sealed on both ends, with separate inlets to the interior of the ceramic tube and to the middle of the Plexiglas shell. These inlets were used to inject the groundwater influent and a base-neutralizing agent, respectively. The only outlet was at the downstream end of the ceramic tube (Figure 68).

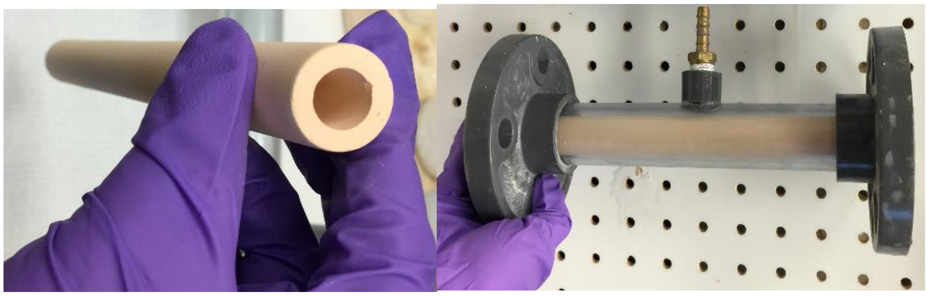


Figure 68 (a) Porous ceramic tube used in tests of the possible in situ formation of a hydraulic barrier. (b) Complete apparatus used in the tests.

In the initial experiments, unaffected soil from Well 46C, a 49' depth was packed into the inner ceramic tube. During the test, groundwater from Extraction Well 7 (pH ~11.5) was injected into the soil in the ceramic tube at a flowrate of 5 mL/min. Hydrochloric acid (HCl) was injected through the inlet port in the Plexiglas shell. The acid then permeated through the ceramic tube and mixed with the groundwater as it passed through the inner ceramic. As mentioned above, the mixture exited at the downstream end of the tube. A transducer was installed upstream of the groundwater inlet to monitor the pressure require to maintain the fixed groundwater flow rate. The pressure at the outlet was atmospheric, that is the reading of the transducer indicated a 0 psi difference vs, the atmospheric pressure.

In the initial phase of the test, the system was set up and groundwater, but no acid, was injected. As shown in Figure 69, the minimal initial inlet pressure increased to approximately 2 psi within 40 min and it was then stable for the remainder of the 3 hour test.

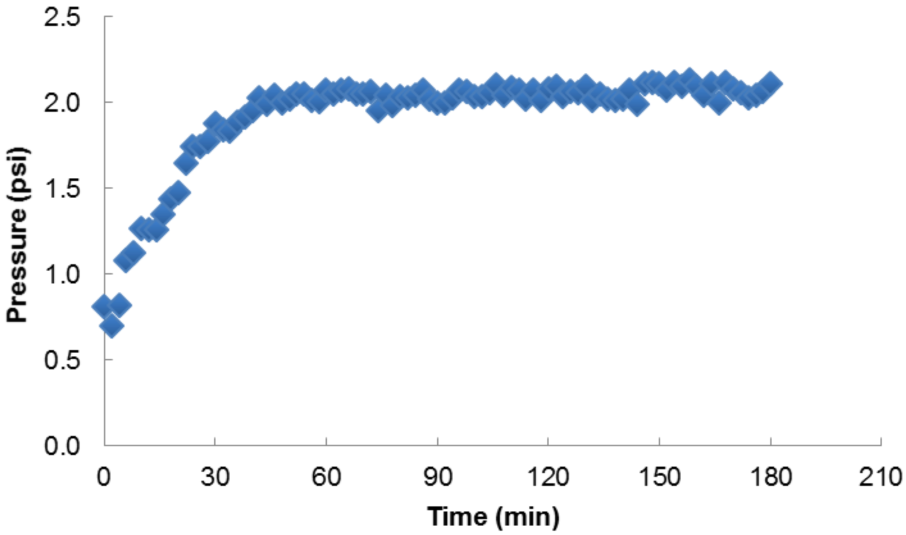


Figure 69 Pressure profile for system with groundwater flow only (without acid injection)

In the next test, the groundwater flow rate was identical to that in the previous test, but an additional flow of a solution containing HCl in deionized water was injected into the Plexiglas shell at a flow rate of 0.82 mL/min. The HCl concentration in this solution was increased step-wise from 0.2 M HCl for the first 110 min, to 0.5 M from 110 to 180 min, and 1 M thereafter.

As shown in Figure 70, the inlet pressure was higher at the beginning of this test than in the prior one, presumably because of the higher net flow rate through the soil. The pressure reached ~6 psi within a few minutes after the 0.2 M HCl acid was injected and then increased gradually to ~7.5 psi over the next ~110 minutes, when the acid concentration was increased to 0.5 M. This concentration of HCl was injected for the next 70 min, during which the pressure continued to increase gradually to a final value of ~10 psi. However, when the acid concentration was increased to 1.0 M, the pressure increased more rapidly, reaching values in excess of 30 psi within 20 min. The pH of the effluent sampled at 110 and 150 min was 11.43 and 11.39, respectively, compared to the influent pH of 11.46. Thus, it appears that severe plugging of the soils can occur even with a minimal acidification of the Extraction Well 7 groundwater.

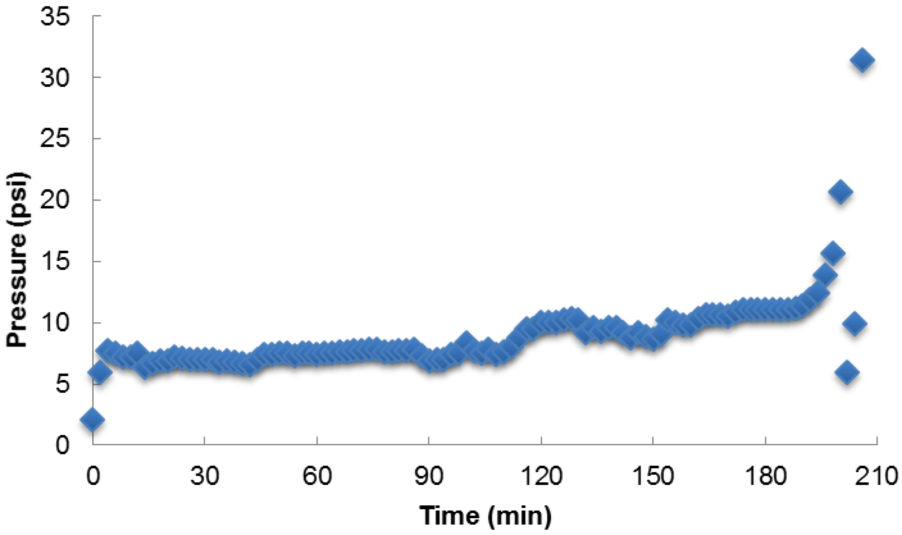


Figure 70 Pressure profile for system with acids (HCl) of increased concentrations injected into the system. 0~110 min: 0.2 M HCl; 110~180 min: 0.5 M HCl; 180~200 min: 1 M HCl.

A follow-up test exploring the same phenomena was conducted using soil collected from Well 46C at a depth of 49 ft. As before, the soil was packed into the center of a porous (0.2-μm) ceramic tube with a 1-in OD and 0.5-in ID. To start the test, groundwater from Extraction Well 7 was applied as feed to the soil column at a flow rate of 5.8 mL/min, and 0.5 M HCl was simultaneously injected at a flow rate of 1.24 mL/min into the Plexiglas shell holding the tube. These injections were continued for 55 min, after which the pressure across the column had reached approximately 27 psi. The inflows were then stopped briefly to drain the acid from the shell side of the porous tube, and flow into the soil column was resumed, but the source was switched from the groundwater to a benign solution of 2.3 M NaCl adjusted to pH 11.5. No fluid was injected into the shell side of the system during this second stage of the test, which lasted ~160 min.

Figure 71 shows that the pressure drop across the column increased from ~2 psi to almost 30 psi during the first stage of the test and then it decreased to ~18 psi during the first ~35 min of the second stage. Following this phase, it was stable for the remainder of the test. The most likely explanation for these observations is that precipitation and/or other changes in the soil column caused the initial increase in hydraulic resistance, and that the precipitates started to dissolve, or the other causative factors were reversed, when the acid injection stopped and the highly alkaline benign solution was passed through the column. However, once a sufficient amount of the increase in hydraulic resistance has been reversed, the benign solution passed primarily through the flow paths where the conductivity was high, so the 'clearing' of the remaining clogged pathways slowed dramatically.

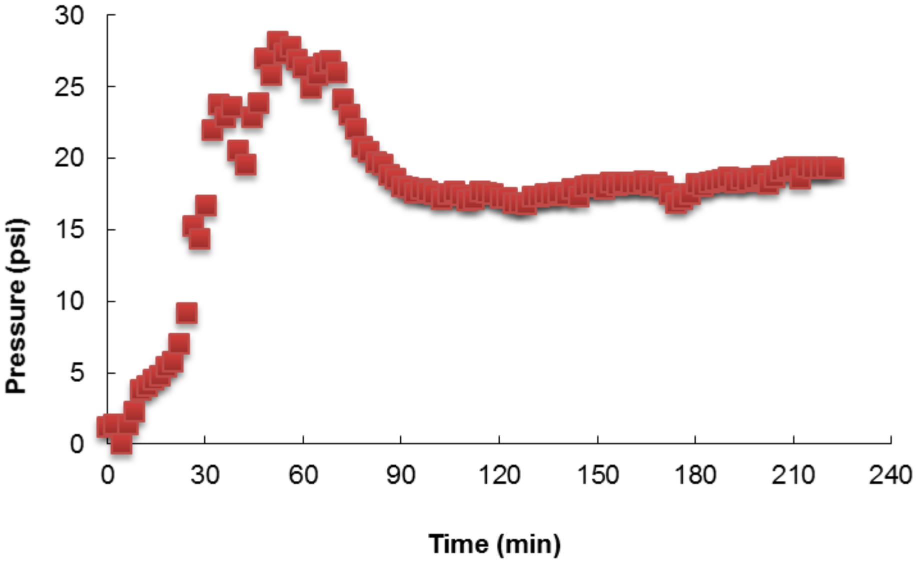


Figure 71 Pressure profile for reversibility test of hydraulic barrier: 0~55 min: acid injection to groundwater flowing through the soil column; 55~222 min: acid injection was stopped and influent was switched from groundwater to benign solution.

These experiments were continued using (a) 0.1 *M* HCl or (b) bicarbonate (HCO_3^-) ions as the neutralizing agent. In these tests, 0.1 *M* HCl was prepared by diluting 1 *M* HCl with deionized water, and the bicarbonate solutions were prepared either by bubbling pure CO_2 into water or by adding $NaHCO_3$ to water. Two more solutions were prepared with gaseous CO_2, one by bubbling the gas in deionized water without other additives (yielding a pH near 3.5), and the other by adding 5 *M* NaOH during the bubbling period to maintain the solution at pH ~8.2. The other HCO_3^--containing solution was prepared as 1 *M* $NaHCO_3$ in deionized water, yielding a solution at pH 8.8. These solutions were used in tests where high-pH groundwater was injected into a soil column packed into a porous ceramic tube.

The base-neutralizing solution was injected under pressure into the annular space between the ceramic tube and the housing, with the intent being to cause the neutralizing solution to enter the soil column along the entire length of the ceramic tube. Based on the results of prior tests and some preliminary batch tests, a ratio in the range of 3.5:1 to 4.0:1 was chosen for the relative flowrates of the groundwater and the neutralizing solution. The absolute flowrates of these solutions are summarized in Table 12. The flowrates were intended to be identical to those in the prior experiments. However, because precise flow control was difficult in these experiments, the shown flowrates are approximate. As explained shortly, the flowrates were decreased in the final experiment in an attempt to reduce migration of precipitated solids out of the column.

Table 12 Flowrates for groundwater and acidic solution in soil column neutralization experiments

Feed solution(s)	Groundwater (mL/min)	Acid (mL/min)
GW7 only	5.0	0
GW7 + 0.1 *M* HCl	5.6	1.6
GW7 + CO_2 + DI water (pH 3.3)	6.0	1.6
GW7 + CO_2 + DI water + NaOH (pH 8.2)	5.8	1.6
GW7 + 1 *M* $NaHCO_3$	1.9	0.47

Figure 72 demonstrates that the injection of 0.1 *M* HCl led to a rapid increase in the pressure across the soil column, followed by a partial reversion to lower values and then stabilization at ~8 psi for approximately one hour. During the final hour of the test, the pressure appeared to be increasing again, though not rapidly. Throughout the test, the pressure buildup was much less than in the prior test using 0.5 *M* HCl (reaching 28 psi after about 50 min). An image of the soil inside the tube at the end of the test is provided in Figure 73. Although some details are difficult to see in this image, small white particles were observed throughout the column indicating that some precipitation had occurred.

Figure 72 also shows that, in contrast to the outcome when either 0.1 *M* or 0.5 *M* HCl was injected into the shell side of the experimental apparatus, injection of neutralizing solutions prepared by bubbling CO_2 into water did not lead to any noticeable increase in hydraulic resistance during the run, regardless of whether the final pH of the water was 3.5 or 8.2; a similar result was obtained in a control experiment in which no neutralizing solution was injected. In the run at pH 8.2, white flocs were visible in the solution exiting the soil column, and white precipitates were more apparent inside the soil column at the end of the test (Figure 74) than they were in the test with 0.1 *M* HCl or the one with CO_2 at pH 3.5.

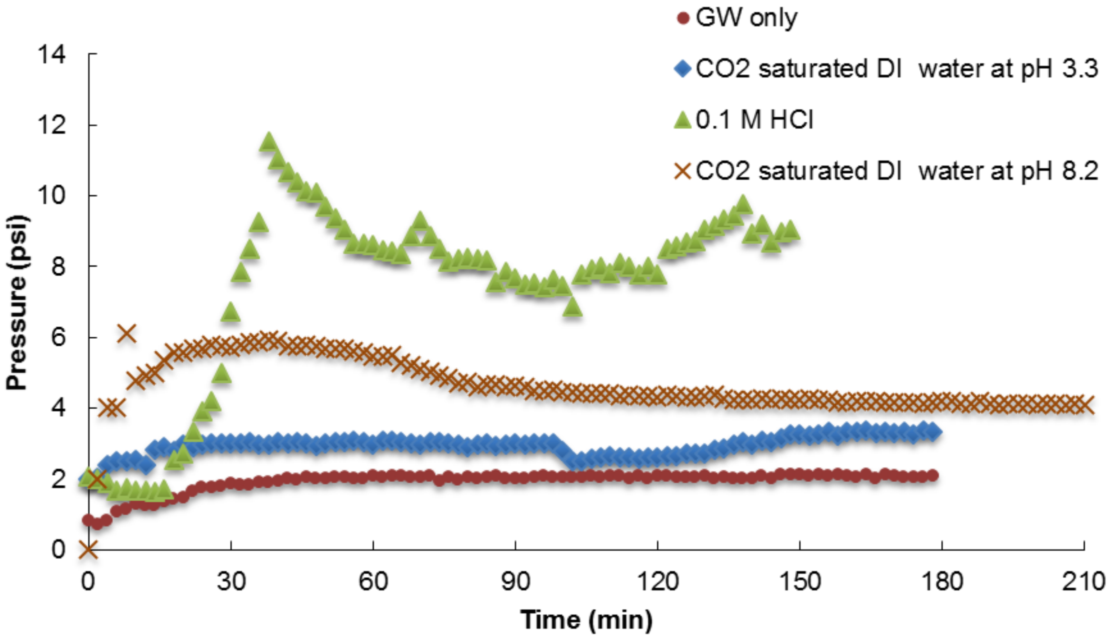


Figure 72 Pressure profiles for soil column injected with alternative base-neutralizing solutions.

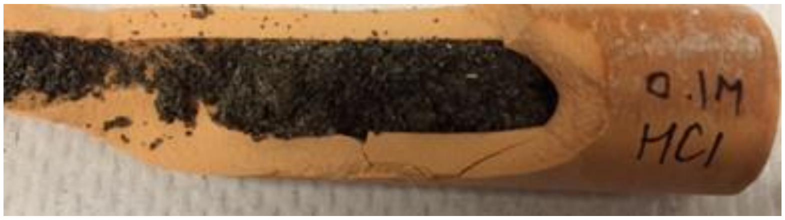


Figure 73 General view of the contents of soil column after injection of 0.1 M HCl.

Figure 74 Two sections of the soil column after injection of pH 8.2 water that had been bubbled with pure CO_2.

Another experiment used 1 *M* $NaHCO_3$ as the neutralizing solution. This solution was used both because it was easier to prepare it than a solution equilibrated with pure CO_2 and because its composition could be more easily controlled. In addition, the injection rates of both the groundwater and neutralizing solutions were reduced by approximately a factor of three to reduce the nominal Darcy velocity at the end of the soil column from 7.6 to 2.4 cm/min, in an attempt to reduce the likelihood that precipitates formed in the soil would be flushed out by the flow.

The pressure profile for this experiment is shown in Figure 75. The pressure increased from an initial value of 1 psi (close to the value for injection of only groundwater, without neutralizing solution, at the same flowrate as in the experiment) to about 2 psi after two hours, and then stabilized at that value. Assuming that the pressure loss is proportional to the flow rate, this stable pressure loss is close to that in the previous experiment using 0.1 *M* HCl as the neutralizing solution.

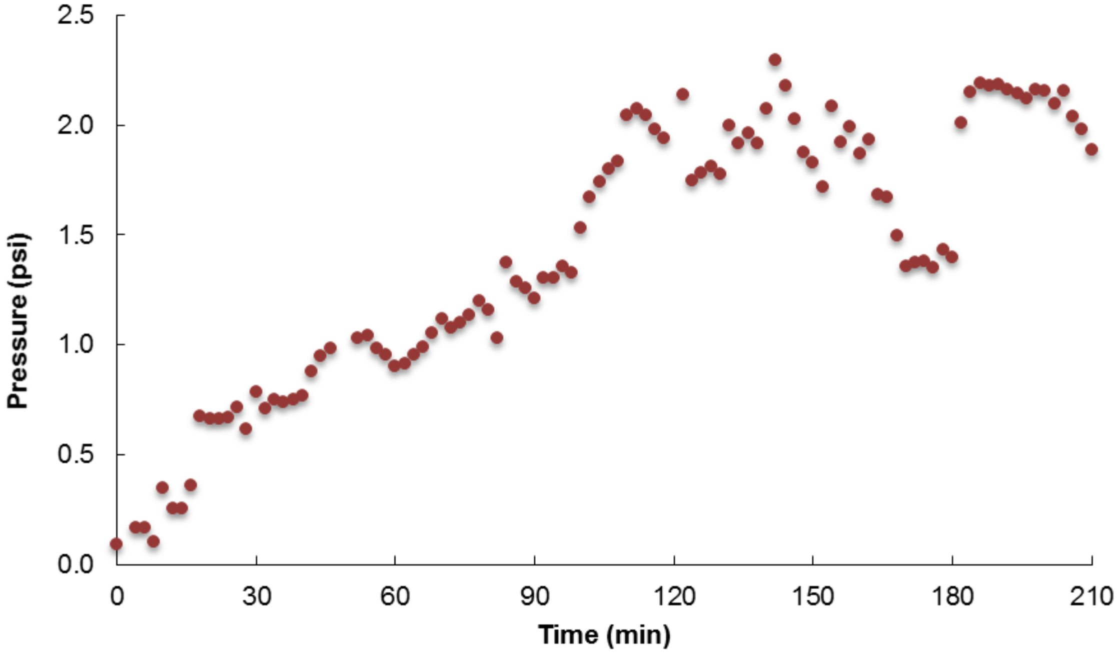


Figure 75 Pressure profiles for soil column with injection of 1 M $NaHCO_3$.

Much more white precipitate was formed in this experiment than in the two prior experiments (using CO_2-saturated water for neutralization). The precipitate that remained in the soil was concentrated at the inside wall and near the outlet of the column (Figure 76). In addition, significant amounts of precipitate were observed in the flow exiting the column.

These observations suggest that the neutralizing fluid was not necessarily migrating into the bulk of the soil, but rather was likely to be passing through the ceramic tube and traveling along the wall to the outlet and/or entering the soil near the downstream end of the column and then exiting with the flow before much could be filtered out by the soil. Such a scenario is consistent with the idea that the liquid on the shell side of the system would take the “path of least resistance” to the outlet. A similar conceptual situation would apply in the field, but without the geometric constraints of the laboratory system.

The solids formed upon injections of base-neutralizing agents appear to be predominated by hydrated silica. As such, these solids may undergo slow structural changes via the loss of water, formation of more crystalline phases, compaction and possibly development of fissures. Aging-related changes of the morphology and structure of the solids forming impermeable barriers in OCC soil/groundwater were not examined in this study. Related batch experiments described elsewhere in this report showed that the formation of solid phases in the subsurface zone can be caused by injections of solutions of Ca or Mg salts, in which case the formed solids are likely to be dominated by Ca or Mg hydroxides, carbonates, silicates and their mixed phases. Such solids may be structurally more stable that those dominated by hydrated silica.

Column measurements showed that there is a threshold concentration of base neutralizing agents below which little or no formation of blocking solids takes place. In the experimental conditions used in this study, the concentration of HCl or $NaHCO_3$ that caused the formation of solids was ca. 1 M. This indicates that high concentrations and/or masses of base-neutralizing agents need to be injected in the subsurface zone to form stable impermeable barriers that have the stability and spatial extent sufficient to block the movement of contaminated groundwater. Another observation pertinent to *in situ* solids formation in the column experiments is that due to local variations of hydraulic permeability and the presence of localized channels of movement of injected agents, the precipitated solids tend to be distributed non-uniformly through the soil column.

To circumvent the formation of spatially limited and/or non-uniform areas of solids formation, it may be preferable to ramp up the concentration of base-neutralizing agents slowly so as to ensure a uniform pattern of the permeation of such agents throughout the targeted area. Other sequences of injection of base-neutralizing and/or Si-destabilizing agents to create impermeable barriers should be considered as well. It is our opinion that the formation of in situ generated hydraulic barriers can be optimally achieved via controlled injections of $NaHCO_3$ or CO_2 gas through a system of wells designed to cause slow and uniform permeation of CO_2 (or $NaHCO_3$) to induce the deposition of stable Si-based solids in the control zone.

Figure 76 View of the cross-section of a split soil column after injection of 1 M $NaHCO_3$.

10. Treatment and Processing of Solids generated in *Ex-Situ* Treatment of OCC Groundwater

This section presents an outline of results of the approach investigated to reduce the volume of the solids after precipitation. More detailed description of these can be found in *Pandya 2015*. In general, these experiments were carried out to examine the following:

Can the volume of Si-based solids precipitated as a result of ex situ treatment of high Si, high pH OCC groundwater be reduced?

What practically actionable options are available for solids' volume reduction?

What is the chemical nature of precipitated solids?

Selected results of relevant experiments are presented below for the case of Well 7 groundwater treatment by addition HCl. Table 13 presents the yields of wet solids and the fractional removal of Si from the groundwater by acidification. Figure 77 shows the visual appearance of precipitated wet solids prior to their post-treatment.

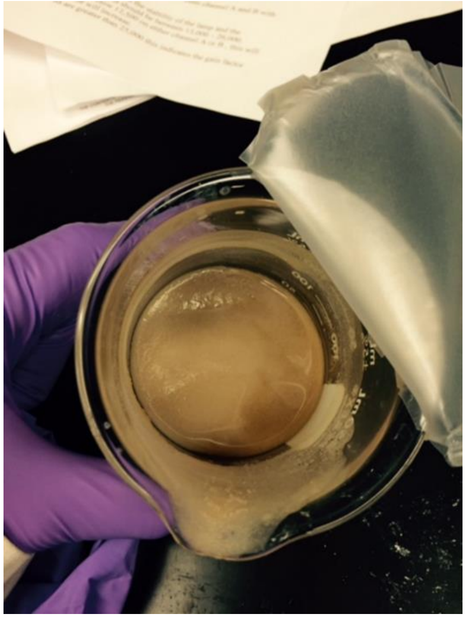


Figure 77 Visual appearance of wet solids collected after decanting the supernatant (Groundwater: Well 82 @ 100-ft depth)

Table 13 Yields of wet solids and Si removal resultant from the acidification of groundwater

	Calculation step	Well 7-130	Well 82-100	Well 82-100 (Repeat)
Volume of groundwater, ml		100	100	100
Weight of groundwater, g	A	113.9	108.6	108.6
Volume of HCl added, ml		39	27	27
Weight of batch after HCl addition, g	B	151.2	133.0	134.2
Volume of solids (Visual observation), % of batch volume		33% (after 6 d of settling)	40% (after 1 d settling)	Data not available
Supernatant decanted, g	C	100.6	86.2	91.5
Weight of wet solids, g	D = B-C	50.7	46.8	42.7
% yield of wet solids based on groundwater weight	E = D/A	44.5%	43.1%	39.3%
% Si precipitation				ND
Dissolved Si in raw groundwater, ppm		40,108	21,691	
Dissolved Si in supernatant, ppm		141	106	
% groundwater in system after acidification (Ref: Appendix 2)		72%	78.7%	
% Si precipitation (Ref: Appendix 3)		99.5%	99.4%	

ND: Not determined

10.1. Mechanical treatment (press-filtering) to dewater produced wet solids

The yield of dewatered solids and associated calculations are shown in Table 14. Figure 78 shows the visual appearance of dewatered solids generated as a result of the sequence of pH adjustments, precipitation and press-filtration of solid phases formed in Well 82 groundwater sampled at a 100-ft depth.

Table 14 Yield of dewatered solids generated from mechanical squeezing of the wet solids

	Calculation step	Well 7-130	Well 82-100	Well 82-100 (Repeat experiment)
Weight of wet solids squeezed, g	F	7.8	12.8	18.2
Weight of dewatered solids, g	G	3.4	4.8	7.1
% weight reduction by dewatering	(F-G) / F	56.3%	62.5%	61.3%
Weight of dewatered solids (if applied to entire batch of wet solids), g	H = (D/F) * G	22.1	17.6	16.6
% yield of dewatered solids based on groundwater weight	H/A	19.4%	16.2%	15.2%

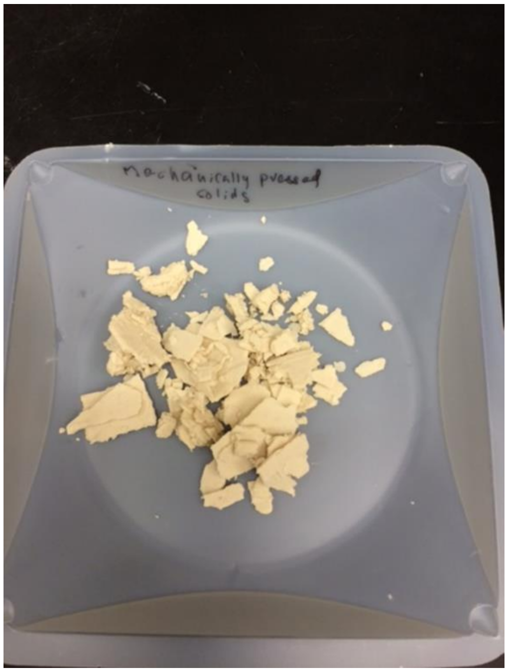


Figure 78 Visual appearance of dewatered solids (Groundwater: Well 82 @ 100-ft depth)

Table 15 Composition of the dewatered solids

	Calculation step	Well 7-130	Well 82-100	Well 82-100 (repeat experiment)
Weight of dewatered solids dissolved, g	I	0.1605	0.0932	0.1706
Volume of solution prepared, ml	J	0.5449	0.2808	0.5491
Dissolved Si analyzed in solution using ICP-MS, ppm	K	52856	53381	44521
Dissolved Ca analyzed in solution using ICP-MS, ppm	L	ND	ND	712.6
Si in solution prepared, g	M = ((K/1000)*J)/1000	0.0288	0.0150	0.0244
Ca in solution prepared, mg	N = ((L/1000)*J)/1000	ND	ND	0.39
% Si in solids	M/I	17.9%	16.1%	14.3%
% Ca in solids	N/I	ND	ND	0.2%

ND: Not determined

10.2. Thermogravimetric analysis (TGA) of dewatered solids and effects of drying

Figure 79 and Figure 80 show TGA results for the dewatered solids. The TGA results for the dewatered solids generated as a result of treatment of Well 7 groundwater (Figure 79) showed that the sample lost about 30% of its weight when it was dried at temperatures <40^{o}C and that the solids lost an additional 10% of their weight when the temperature was increased to 110^{o}C. The rate of decrease of weight was maximal in the temperature range of 20-40^{o}C. These results suggest that most of the benefits of drying can be achieved by heating the solids to between 20-40^{o}C.

Based on these results, in the next run of TGA analyses of dewatered solids, the sample was held at 30^{o}C for about an hour. The sample had lost more than 50% of its weight at the end of the isothermal period at 30^{o}C, and it lost an additional ~5% of its weight upon further increase of temperature (Figure 79). Based on these data, a drying temperature of 30^{o}C was chosen. The composition of solids dried at this temperature is summarized in Table 17. (Figure 81) shows the dried solids. The dried solids were friable and thus were easily ground into a powder. Such a powder was generated (Figure 81) had a 2.17 g/cm^3 density.

These results confirmed that *ex situ* treatment of OCC groundwater can be effectively used to remove practically all Si solutes that this water contains. Such treatment includes four steps: 1) slow addition of a neutralizing agent to achieve the threshold of the precipitation of Si-based solids; 2) solids precipitation and decanting the supernatant; 3) used of press-filtration to remove occluded water and 4) mild heating to 30C for one hour to remove residual occluded water. The solid phase produced in this sequence can be landfilled while the Si-free water can undergo relevant unit operations, notably air stripping and GAC adsorption, to remove VOCs from it.

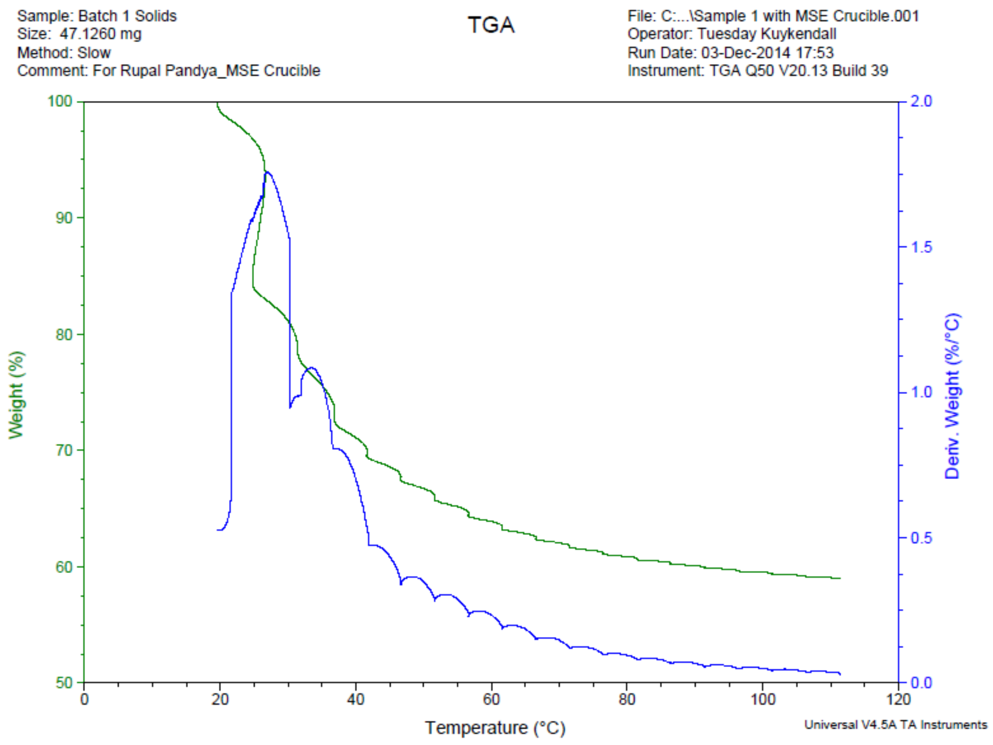


Figure 79 TGA result of dewatered solids generated from Well 7 groundwater at depth 130-ft

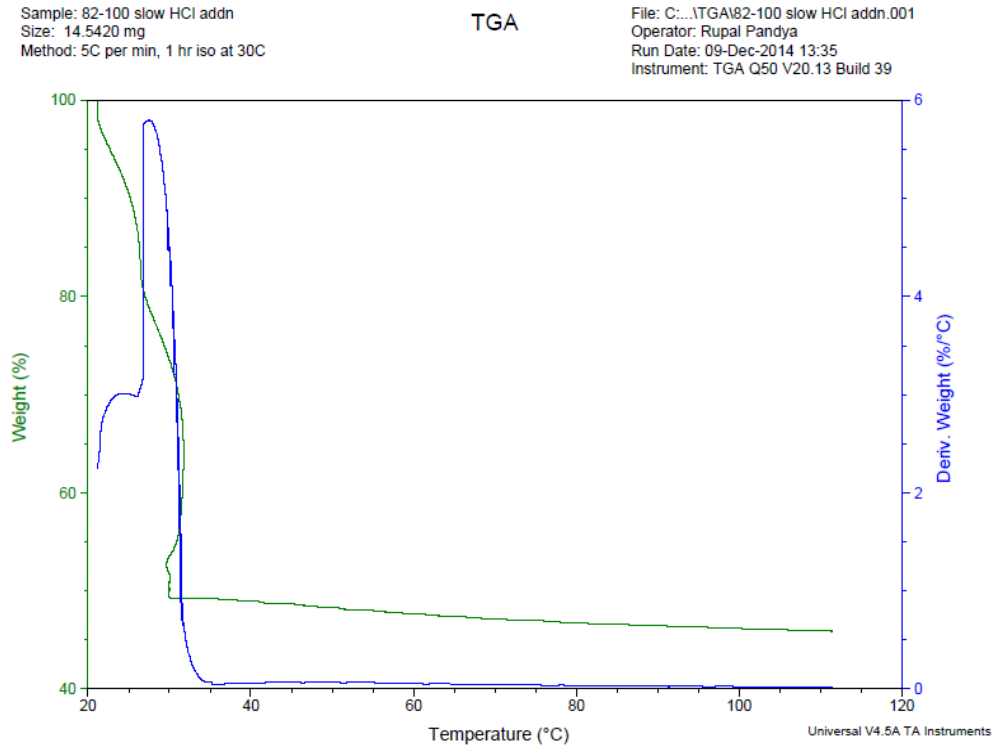


Figure 80 TGA result of dewatered solids generated from Well 82 groundwater at depth 100-ft.

Table 16 Percent yield of dried solids after drying the dewatered solids at T=30°C for ca. 24 hours

	Calculation step	Well 82-100
Weight of dewatered solids, g	O	7.057
Weight of dried solids, g	P	3.093
% Weight reduction by drying	(O-P)/O	56.2%
Weight of dried solids (if applied to entire batch of dewatered solids), g	Q=(H/O)*P	7.3
% yield of dried solids based on groundwater weight	Q/A	6.7%

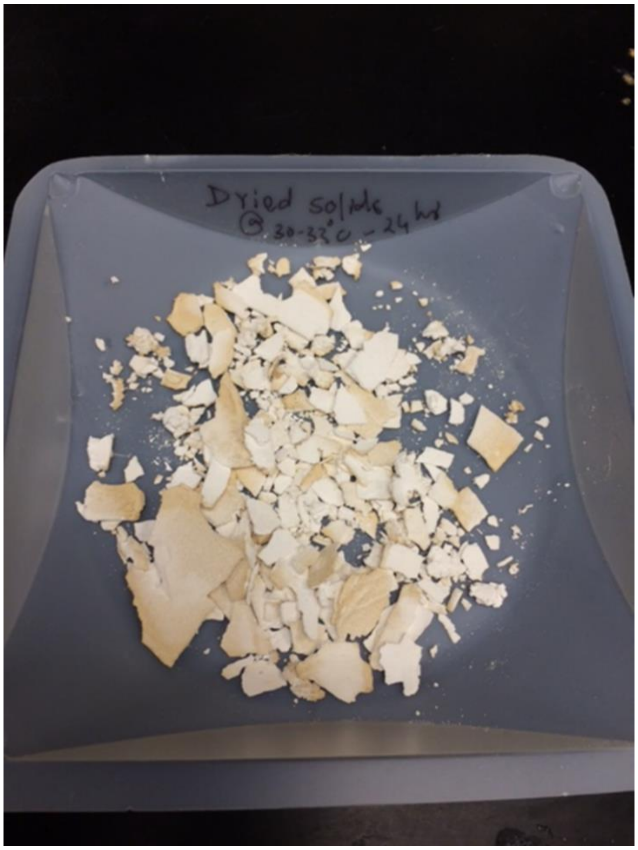


Figure 81 Visual appearance of dried solids (Well 82 groundwater @ 100-ft depth)

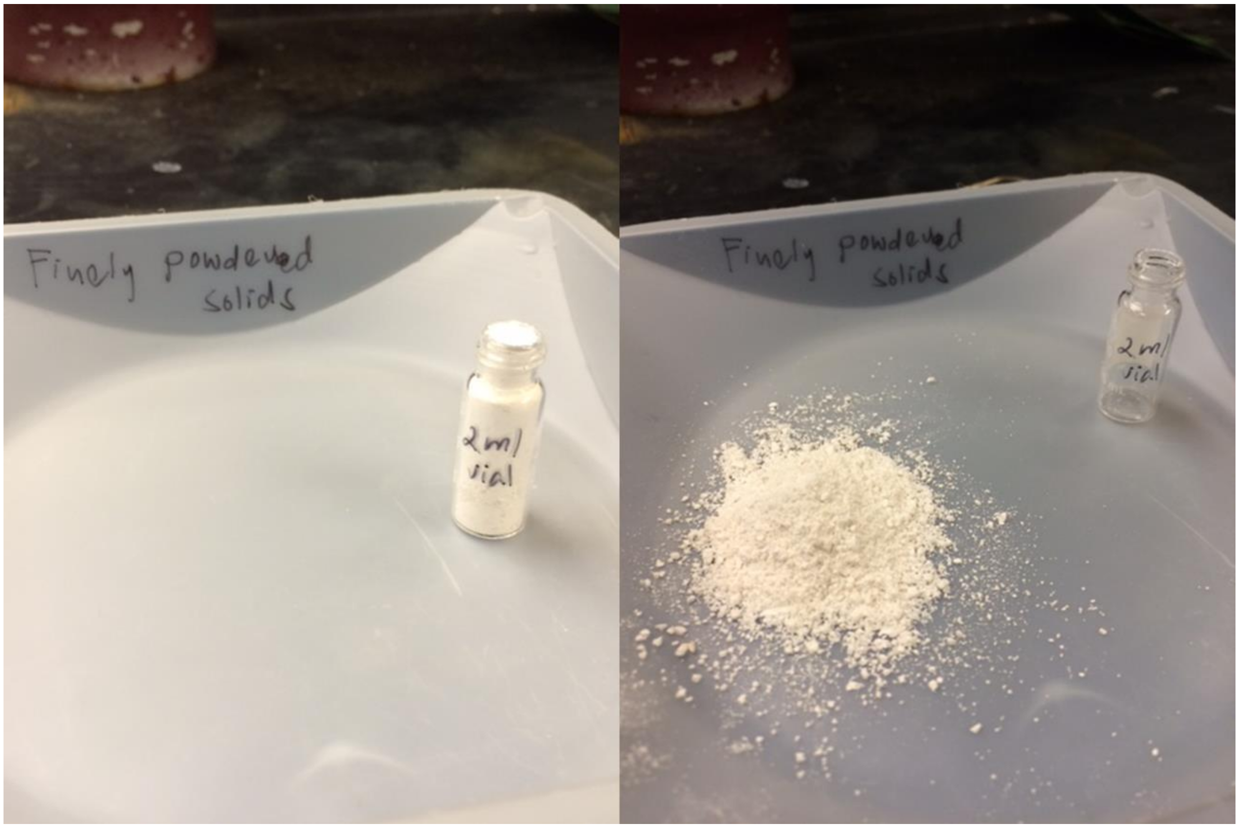


Figure 82 Visual appearance of finely ground powdered dried solids placed in 2-ml vial

Table 17 Major contents analyzed in dried solids generated by 24 hours drying at T = 30°C

	Calculation step	Well 7-130	Well 82-100 (Repeat experiment)
Weight of dried solids dissolved, g	R	0.1199	0.1141
Volume of solution prepared, ml	S	0.695	0.706
Dissolved Si analyzed in solution, ppm	T	64,691.7	63,831
Dissolved Ca analyzed in solution, ppm	U	769	870.5
Dissolved Al analyzed in solution, ppm	V	740.5	163
Si in solution prepared, mg	W = ((T/1000)*S)/1000	44.96	45.1
Ca in solution prepared, mg	X = ((U/1000)*S)/1000	0.53	0.61
Al in solution prepared, mg	Y = ((V/1000)*S)/1000	0.515	0.115
% Si in solids	W/R	37.5%	39.5%
% Ca in solids	X/R	0.4%	0.5%
% Al in solids	Y/R	0.4%	0.1%

These data show that a large part of the occluded water can be eliminated by press-filtration and/or mild heating (to ca. 30C). The solids formed via such a process are mostly SiO_2, with low levels of residual hydration water and an insignificant admixture of other elements. These solids are unlikely to have inherent toxicity and could probably be safely landfilled albeit further analyses are needed to confirm this point.

While the described approach for *ex situ* removal of dissolved silica from groundwater is reasonably easily implementable technically, its practicality depends on costs of base-neutralizing agents, transportation and landfill fees and other factors. A clearly significant complication associated with this approach is the amount of produced solids. Calculations indicate that in the case of a slow pumping (25 gmp) of OCC groundwater containing ca. 35 g/L of Si, the mass of produced solids would be ca. 4.8 tons/day and their volume, given the solids' density of 2.17 g/cm^3, would be 2.2 m^3/day. For higher pumping rates, for instance 150 gpm, the volume of solids would be 13.2 m^3/day. Handling and disposal of this amount of solids may be a significant challenge. It can be posited, however, that the concentration of Si in OCC groundwater is unlikely to persist at a level as high as 35 mg/L. As the groundwater with highest Si levels is withdrawn and treated, the concentration of Si in it will gradually decrease. The actual overall amount of Si-based solids generated in *ex situ* operations can be estimated based on the geometry of the high pH, high Si plumes, distribution of pH values and associated Si concentrations in them, and other relevant information.

11. Conclusions

Key observations and conclusions of the study can be summarized as follows:

- When exposed to highly caustic solutions, OCC soils readily release high amounts of silica;
- OCC soils that have been affected by high pH solutions tend to release the retained caustic species (high pH) for a long time, but the amount of base released from such soils is probably insufficient to mobilize large amounts of silica from unaffected soils;
- Practically all the silica present in high pH high Si groundwater can be removed by ex situ water treatment; several options (e.g., decrease of pH by slow addition of HCl, addition of solutions of $CaCl_2$ or $MgCl_2$) exist for such treatment and post-treatment solids' handling; The volume of solids produced in such operations may be a significant challenge;
- Realistic levels of silica precipitation inhibitors do not affect gelation phenomena in these systems;
- OCC soils unaffected by long-term contact with high-Si, high-pH groundwater are more prone to develop hydraulic fouling that those that have been affected by the contaminated groundwater;
- Slow pumping of high Si, high pH groundwater does not appear to cause rapid hydraulic fouling;
- Development of hydraulic fouling is likely to be associated with local decreases of pH in the soil, natural occurrence or enhanced formation of aluminosilicates and the presence of precipitation nuclei in the groundwater;
- Incipient hydraulic fouling can be reversed via injection of caustic regenerants;
- Injection of acidic agents into OCC Site soils affected by high pH will likely result in the formation of hydrated silica precipitates near the injection point. The formation of the precipitates will reduce the hydraulic conductivity of the aquifer in which the precipitates form. However, the extent of the reduction and the radius of the area of reduced hydraulic conductivity cannot be determined from the results of the current testing. Current data are also insufficient to ascertain whether hydrated silica precipitates formed in such conditions have adequate long-term stability.

12. References

Abe, T., Kobayashi, S., & Kobayashi, M. (2011). Aggregation of colloidal silica particles in the presence of fulvic acid, humic acid, or alginate: Effects of ionic composition. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 379(1), 21-26.

Amram, K., & Ganor, J. (2005). The combined effect of pH and temperature on smectite dissolution rate under acidic conditions. *Geochimica et Cosmochimica Acta*, *69*(10), 2535-2546.

Alexander, G. B., Heston, W. M., & Iler, R. K. (1954). The solubility of amorphous silica in water. *The Journal of Physical Chemistry*, *58*(6), 453-455.

Bałdyga, J., Jasińska, M., Jodko, K., & Petelski, P. (2012). Precipitation of amorphous colloidal silica from aqueous solutions—Aggregation problem. *Chemical Engineering Science*, 77, 207-216.

Bauer, A., & Berger, G. (1998). Kaolinite and smectite dissolution rate in high molar KOH solutions at 35 and 80 C. *Applied Geochemistry*, *13*(7), 905-916.

Bickmore, B. R., Nagy, K. L., Gray, A. K., & Brinkerhoff, A. R. (2006). The effect of Al (OH) 4− on the dissolution rate of quartz. *Geochimica et Cosmochimica Acta*, *70*(2), 290-305.

Bremere, I., Kennedy, M., Mhyio, S., Jaljuli, A., Witkamp, G. J., & Schippers, J. (2000). Prevention of silica scale in membrane systems: removal of monomer and polymer silica. *Desalination*, 132(1), 89-100.

Carbonaro, R. F., Mutch Jr, R. D., Changa-Moon, D. C., Gupta, P. K., Morris, J. J., Nambiar, A., & O'Loughlin, J. M. (2014). In Situ CO_2 Sparging. I: Neutralization of a Caustic Brine Plume and Reduction of Mercury Levels. *Journal of Hazardous, Toxic, and Radioactive Waste*, 19(1), C4014005.

Chan, S. H. (1989). A review on solubility and polymerization of silica. *Geothermics*, 18(1-2), 49-56.

Coradin, T., & Livage, J. (2001). Effect of some amino acids and peptides on silicic acid polymerization*. Colloids and Surfaces B: Biointerfaces*, 21(4), 329-336.

Demadis, K. D. (2005). A structure/function study of polyaminoamide dendrimers as silica scale growth inhibitors. *Journal of Chemical Technology and Biotechnology*, 80(6), 630-640.

Fleming, B. A., & Crerar, D. A. (1982). Silicic acid ionization and calculation of silica solubility at elevated temperature and pH application to geothermal fluid processing and reinjection. *Geothermics*, 11(1), 15-29.

Gallup, D. L. (2002). Investigations of organic inhibitors for silica scale control in geothermal brines. *Geothermics*, 31(4), 415-430.

Golubev, S. V., Bauer, A., & Pokrovsky, O. S. (2006). Effect of pH and organic ligands on the kinetics of smectite dissolution at 25 C. *Geochimica et Cosmochimica Acta*, *70*(17), 4436-4451.

House, W. A., & Hickinbotham, L. A. (1992). Dissolution kinetics of silica between 5 and 35° C. Application of a titrimetric method. *Journal of the Chemical Society, Faraday Transactions,* 88(14), 2021-2026.

Kinrade, S. D., Knight, C. T., Pole, D. L., & Syvitski, R. T. (1998A). Silicon-29 NMR studies of tetraalkylammonium silicate solutions. 1. Equilibria, 29Si chemical shifts, and 29Si relaxation. *Inorganic chemistry*, 37(17), 4272-4277.

Kinrade, S. D., Knight, C. T., Pole, D. L., & Syvitski, R. T. (1998B). Silicon-29 NMR studies of tetraalkylammonium silicate solutions. 2. Polymerization kinetics. *Inorganic chemistry,* 37(17), 4278-4283.

Kinrade, S. D., & Swaddle, T. W. (1988). Silicon-29 NMR studies of aqueous silicate solutions. 1. Chemical shifts and equilibria. *Inorganic Chemistry*, 27(23), 4253-4259.

Lakshtanov, L. Z., & Stipp, S. L. S. (2010). Interaction between dissolved silica and calcium carbonate: 1. Spontaneous precipitation of calcium carbonate in the presence of dissolved silica. *Geochimica et Cosmochimica Acta*, 74(9), 2655-2664.

Lee, E. S., Liu, G., Schwartz, F. W., Kim, Y., & Ibaraki, M. (2008). Model-based evaluation of controlled-release systems in the remediation of dissolved plumes in groundwater. *Chemosphere*, 72(2), 165-173.

Lewis, J., & Sjöstrom, J. (2010). Optimizing the experimental design of soil columns in saturated and unsaturated transport experiments. *Journal of Contaminant Hydrology*, 115(1), 1-13.

Lippmaa, E., Mägi, M., Samoson, A., Engelhardt, G., & Grimmer, A. R. (1980). Structural studies of silicates by solid-state high-resolution silicon-29 NMR. *Journal of the American Chemical Society*, 102(15), 4889-4893.

May, H. M., Klnniburgh, D. G., Helmke, P. A., & Jackson, M. L. (1986). Aqueous dissolution, solubilities and thermodynamic stabilities of common aluminosilicate clay minerals: Kaolinite and smectites. *Geochimica et Cosmochimica Acta*, *50*(8), 1667-1677.

Mashal, K., Harsh, J. B., Flury, M., Felmy, A. R., & Zhao, H. (2004). Colloid formation in Hanford sediments reacted with simulated tank waste. *Environmental science & technology*, *38*(21), 5750-5756.

Mutch Jr, R. D., Carbonaro, R. F., Changa-Moon, D. C., Gupta, P. K., Morris, J. J., Nambiar, A., & O'Loughlin, J. M. (2014). In Situ CO_2 Sparging. II: Groundwater Mounding and Impacts on Aquifer Properties. *Journal of Hazardous, Toxic, and Radioactive Waste*, 19(1), C4014006.

Niibori, Y., Kunita, M., Tochiyama, O., & Chida, T. (2000). Dissolution rates of amorphous silica in highly alkaline solution. *Journal of Nuclear Science and Technology*, 37(4), 349-357.

Pandya, R. (2015). *Precipitation and Processing of Solids from High pH, High Si Groundwater.* Master's Thesis, University of Washington.

Ohman, L. O., Nordin, A., Sedeh, I. F., & Sjoberg, S. (1991). Equilibrium and Structural Studies of Silicon (IV) and Aluminium (III) in Aqueous Solution. 28. Formation of Soluble Silicic Acid-Ligand Complexes as Studied by Potentiometrie and Solubility Measurements. *Acta Chemica Scandinavica*, 45, 335-341.

Qafoku, N. P., Ainsworth, C. C., Szecsody, J. E., & Qafoku, O. S. (2003). Aluminum Effect on Dissolution and Precipitation under Hyperalkaline Conditions. *Journal of environmental quality*, *32*(6), 2354-2363.

Simonsen, M. E., Sønderby, C., & Søgaard, E. G. (2009). Synthesis and characterization of silicate polymers. *Journal of Sol-Gel Science and Technology*, 50(3), 372-382.

Steffens, A., Li, K., & Coussy, O. (2003). Aging approach to water effect on alkali-silica reaction degradation of structures. *Journal of engineering mechanics*, *129*(1), 50-59.

Taheri, A. H., Sim, L. N., Haur, C. T., Akhondi, E., & Fane, A. G. (2013). The fouling potential of colloidal silica and humic acid and their mixtures. *Journal of Membrane Science*, 433, 112-120.

Urbanczyk, C. (2015). *Factors Affecting Hydraulic Conductivity of High pH, High Silica Groundwater at the Former Occidental Chemical Corporation Facility*. Master's Thesis, University of Washington.

Von Gunten, U., & Zobrist, J. (1993). Biogeochemical changes in groundwater-infiltration systems: column studies. *Geochimica et Cosmochimica Acta*, 57(16), 3895-3906.

Wang, G., & Um, W. (2012). Mineral dissolution and secondary precipitation on quartz sand in simulated Hanford tank solutions affecting subsurface porosity. *Journal of Hydrology*, *472*, 159-168.

Willey, J. D. (1980). Effects of aging on silica solubility: a laboratory study. *Geochimica et Cosmochimica Acta*, *44*(4), 573-578.