FIELD PUSH-PULL TEST INVESTIGATION OF IN SITU NEUTRALIZATION OF ACIDIC SEDIMENT

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Introduction

Past mining activities have the potential to result in releases of acidity and heavy metals into natural systems (acid mine drainage – AMD). When AMD enters an alluvial aquifer, the aqueous acidity can consume the acid-neutralizing potential of the sediment. The metals, such as aluminium and iron, form oxyhydroxysulfate precipitates [$AlSO_4OH$ and $KFe_3(OH)_6(SO_4)_2$]. Metals such as copper, manganese, and zinc can sorb onto cation-exchange sites of clays and minerals such as ferrihydrite and gibbsite.

The above processes result in the sediment acting as a store of acidity and metals that can come in contact with groundwater as it migrates through the aquifer after the source(s) of metals and acidity have been controlled. The oxyhydroxysulfate minerals transform into hydroxides and release hydrogen ions as the pH of the aqueous phase increases. For example:

$$Al(SO_4)(OH) + 2H_2O = Al(OH)_3 + SO_4^{2-} + 2 H^+ \qquad (1)$$

Higher pH values induce hydrolysis, which releases additional hydrogen ions:

$$Fe^{2+} + H_2O = Fe(OH)^+ + H^+ \qquad (2)$$

Pump-and-treat is one method that can used to remediate an aquifer impacted by AMD. Groundwater is typically pumped to the surface and treated with an alkaline reagent (such as lime) to increase the pH and force the metals from solution via precipitation. This approach to remediation relies on the migration of affected groundwater to a wellfield, which can take a long time because solid phase reactions (dissolution and precipitation) pose kinetic limitations on the release of stored acidity and metals to the aqueous phase.

In situ application of alkali to the aquifer is a potential alternative method that neutralizes sediment acidity and sequesters metals. Previous work indicated that sodium bicarbonate ($NaHCO_3$), sodium sesquicarbonate ($NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$) and Lime (CaO) are promising alkali reagents for in situ remediation (confidential reports). Column testing results showed if the treated system pH increased above 8.5, metals were remobilized, resulting in exceedances of remedial action objectives.

NaHCO$_3$ was chosen as the alkali reagent for this push-pull test (PPT) as it is easily handled, has a high solubility, and has the lowest treatment solution pH.

PPTs have been used at many sites to determine in situ reaction rates in subsurface environments (Istok et al., 1997). The test consists of adding a reactive solute and conservative tracer to the aquifer during the injection (push) phase, and then monitoring the reactive solute and other constituent concentrations during the extraction (pull) phase. Numerical solutions have been developed to estimate zero- and first-order reaction rates by comparing the reactive solute concentrations to the conservative tracer concentrations (Snodgrass and Kitanidis, 1998; Scroth and Istok, 2005; and Scroth and Istok, 2006).

This paper describes a field-scale PPT performed to evaluate the effectiveness and implementability of the in situ neutralization of an aquifer impacted by AMD. An idealized representation of the alluvial aquifer during the injection phase of a PPT is presented in Figure 1. The injection volume is represented by a cylinder where the radius is a function of the injection volume, the saturated thickness or well screen length, and the porosity of the alluvium. The exact shape of the injection volume will be affected by the presence of aquifer heterogeneities and groundwater mounding. The reaction volume may be a portion of the injection volume, depending on the reaction rate of the alkaline reagent and the relative equivalents of the system acidity and injection alkalinity.

One potential issue with introducing an alkali reagent into the acidic alluvial aquifer is the fouling of the system due to the mineral precipitation. To evaluate the potential effects of mineral precipitation on aquifer formation damage, aquifer step tests were performed before and after the PPT.

Methodology

Test Preparation

The acidity of nearby sediment was estimated to be 675 milligrams per kilogram as calcium carbonate (mg/kg as CaCO$_3$) using a method developed for sediment based on standard methods for measuring aqueous acidity. Assuming a sediment density of 2.68 grams per centimeter cubed (g/cm^3) and a porosity of 25%, the aqueous alkalinity needed to neutralize the sediment acidity at the site was estimated to be 5,427 milligrams per liter as calcium carbonate (mg/L as CaCO$_3$). NaHCO$_3$ was added to approximately 20,000 gallons of unimpacted groundwater to result in an alkalinity of approximately 5,000 mg/L as CaCO$_3$ (injectate). Sodium bromide (NaBr) was added as a tracer (103 milligrams per liter [mg/l]).
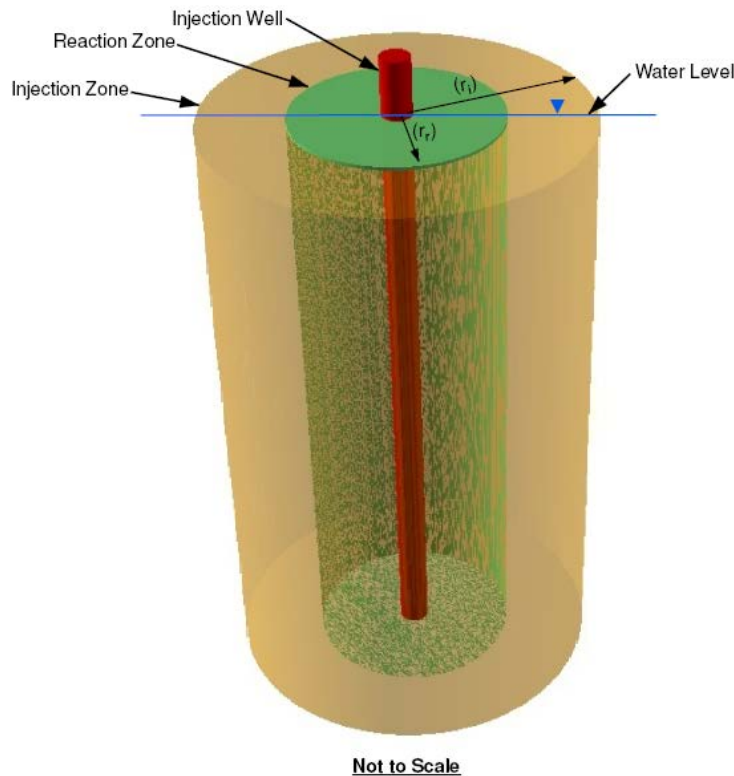
Not to Scale

Figure 1. Schematic of the Hypothetical Injection and Reaction Zones

This schematic is of the alluvial aquifer affected by the PPT. The injection zone represents the total volume of the aquifer expected to be contacted by the injectate. The reaction zone is the hypothetical volume of aquifer that will be contacted by the reactant (NaHCO$_3$), which is determined by the reaction rate kinetics.

To perform the PPT, an existing extraction well was equipped with an injection line screened in the saturated zone only. The well was also equipped with a pressure transducer to record water levels, a gate valve to control the flow rate, a totalizing flow meter to measure flow rates, and a sample port.

Aquifer Step Tests

The pre-PPT and post-PPT aquifer step tests consisted of three successive 1-hour pumping periods of approximately 40, 100, and 190 gallons per minute (gpm) and were conducted before and after the PPT to evaluate if the injection of an NaHCO$_3$ solution into the acidic saturated zone resulted in adverse changes to the well screen, filter pack, and/or aquifer formation. The flow rate was controlled by adjusting the in-line gate valve. Flow rates were measured using a totalizing flow meter and the instantaneous flow rates and volume of water pumped were recorded at regular intervals. Water levels were measured at regular intervals with a manual sounder to confirm transducer measurements. Water quality samples were collected during the pre-PPT aquifer step test to establish baseline water quality conditions.

Push-Pull Test

The injection phase consisted of injecting NaHCO$_3$-amended groundwater at 100 gpm for 3.25 hours. During the injection phase, the flow rate was monitored at least every 10 to 15 minutes and adjusted to maintain a flow rate of 100 gpm. The average flow rate was calculated using the totalizer volumes. The water level was monitored with a manual sounder during the injection phase to assess mounding conditions and to confirm transducer measurements

Samples of the alkali-amended water were collected periodically during the injection phase of the test, and were analyzed for alkali and trace metals, and wet chemistry. Field parameters (pH, temperature [T], electrical conductivity [EC], and bromide [Br]) were collected for each of the samples and periodically throughout the injection phase.

The extraction phase was initiated immediately following the injection phase. During the extraction phase the flow rate was monitored periodically to maintain a flow rate of 100 gpm. Manual water levels were collected at the same time intervals as sample collection activities to monitor drawdown and to confirm transducer measurements during extraction.

Groundwater samples were collected throughout the extraction phase to assess water quality changes in the vicinity of the well after treatment with NaHCO$_3$. Field parameters pH, EC, T, and Br of the samples were measured to assess if the parameters achieved baseline conditions established during the Pre-PPT aquifer step test. The extraction phase lasted for 2,524 minutes (1.75 days).

The system was allowed to recover and a final set of samples was collected during the post-PPT aquifer step test (referred to as Day 6 samples).

Hydraulic Analytical Methodology

The hydraulics of the Pre-PPT and Post-PPT aquifer step tests were evaluated by the following methods:

- A regression analysis of the groundwater pumping rate versus the specific drawdown was used to obtain well-specific coefficients and to estimate the amount of drawdown due to well losses as described in The Analysis and Planning of Step Drawdown Tests (Clark, 1977)
- Transmissivity values were estimated from the aquifer step test drawdown plots calculated from the transducer data using the Theis Step Test solution HydroSOLVE Inc.'s AQTESOLV software
- Transmissivity values were estimated graphically from the aquifer step tests and the PPT recovery data using the Theis Recovery solution

Chemistry Analytical Methodology

Normalized analyte concentrations (C_N) were used to evaluate the water chemistry results by:

- Visual inspection of analyte and conservative tracer C_N plots versus time to provide qualitative information of relative amounts of removal of the analytes
- Calculation of retention factors (RFs) to provide quantitative information on the relative amounts of analyte removal

<u>Normalized Concentrations</u>

The normalized concentration of Br, $C_{N,Br}$, was calculated by:

$$C_{N,Br} = (C_{t,Br} - C_{bkg,Br})/(C_{inj,Br} - C_{bkg,Br}) \tag{1}$$

where $C_{t,Br}$ is the concentration of the Br at time t, and $C_{inj,Br}$ and $C_{bkg,Br}$ are the injectate and baseline Br concentrations, respectively.

If the analyte, or reactant, baseline groundwater is greater than the injectate concentration, C_N was calculated by:

$$C_{N,r} = (C_{t,r} - C_{inj,r})/(C_{bkg,r} - C_{inj,r}) \tag{2}$$

where $C_{N,r}$ is the normalized reactant concentration, $C_{t,r}$ is the concentration of the reactant at time t, and $C_{inj,r}$ and $C_{bkg,r}$ are the injectate and baseline reactant concentrations, respectively.

If the injectate concentration of the reactant is greater than the baseline concentration (the case for the alkali anion, total inorganic carbon, and some trace elements), C_N was calculated in the same way as for Br:

$$C_{N,r} = (C_{t,r} - C_{bkg,r})/(C_{inj,r} - C_{bkg,r}) \tag{3}$$

The various values of C_N represent the following:

- If C_N is equal to 1, then the concentration of the constituent is equal to the larger of the injectate and baseline concentrations.
- If C_N is equal to 0, then the constituent concentration is equal to the smaller of the injectate and background concentrations.
- If C_N is between 0 and 1, then the concentration of the constituent is between the concentrations of the injectate and the baseline.
- If C_N is greater than 1, then the constituent was released by the sediment.
- If C_N is less than 0, then the constituent was retained by the sediment.

Retention Factors

The RF is the ratio of the transport time of the reactant to transport time of the conservative tracer (Br). The RF quantifies the relative removal or release of the reactant compared to the conservative tracer, and allows for comparisons between reactants of differing baseline and/or injectate concentrations. The RF of Br, by definition, is equal to 1. The RF is calculated using the plots of C_N versus time:

- The area under the curve of $C_{N,Br}$ versus time (A_{Br}) is calculated by integration and set equal to 1.
- If the baseline concentration is greater than the injectate concentration, then the area above the curve of $C_{N,r}$ up to a C_N value of one versus time is calculated ($A_{bkg-inj}$). If $C_{N,r}$ is greater than 1 at any time, the area between the curve and a value of one is subtracted (i.e. the sediment is releasing the constituent). If $C_{N,r}$ increases less rapidly than the inverse of $C_{N,Br}$, then the area between the two curves is the relative amount of reactant retained, and the RF is determined by dividing $A_{bkg-inj}$ by A_{Br} (Figure 2).
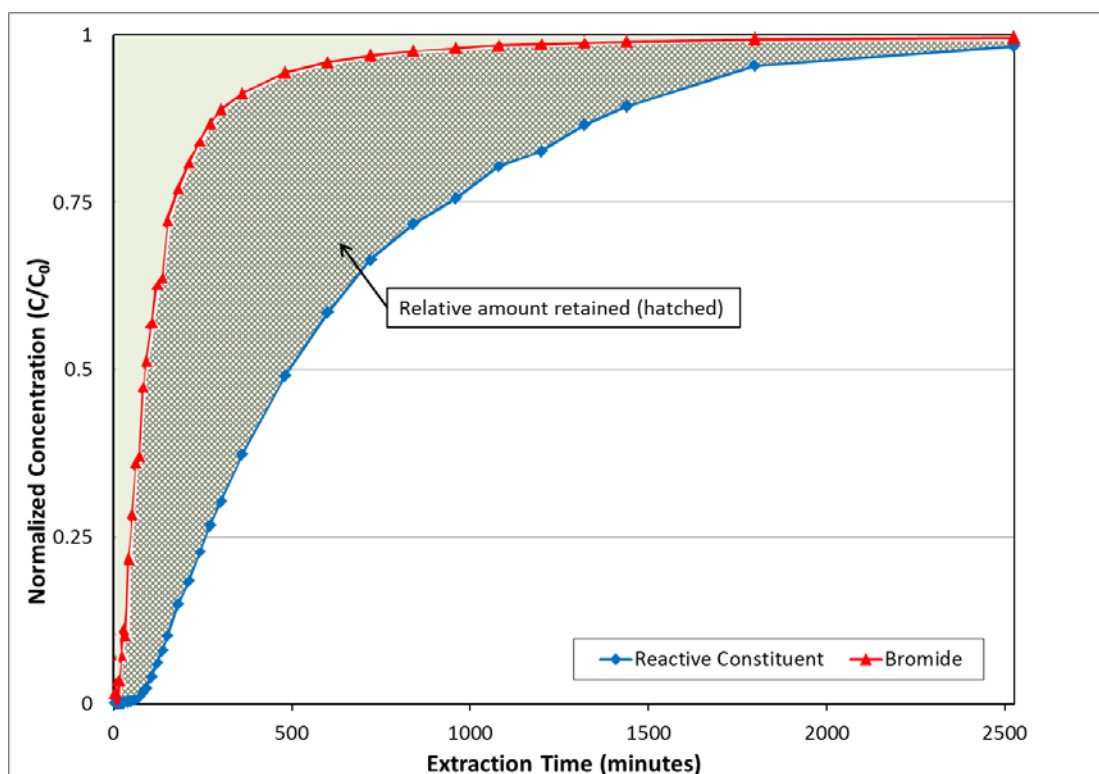

Figure 2. Integration of Normalized Concentration Area when the Baseline is Greater than the Injectate

Integration of normalized concentration profiles is used to determine the relative amount of a reactant retained during the extraction phase of the PPT, which is then used to determine the retention factor.

If the injectate concentration is greater than the baseline concentration, the area under the curve of CN,r versus time is calculated (Ainj-bkg). If CN,r decreases

more rapidly than CN,Br, then the area between the two curves is the relative amount of reactant retained, and the RF is determined by dividing ABr by Ainj-bkg.

Results

Hydraulic Results

During the pre-PPT aquifer step test, the well was pumped for three 1-hour intervals at average discharge rates of 41.6, 99.6 and 194.2 gpm, and drawdowns of 0.60, 1.65 and 4.92 feet were measured at the end of each step, respectively (Figure 3). During the post-PPT aquifer step test, the well was pumped for three 1-hour intervals at average discharge rates of 41.1, 99.8 and 192.0 gpm, and drawdowns of 0.76, 2.13 and 6.48 feet were measured at the end of each step, respectively.
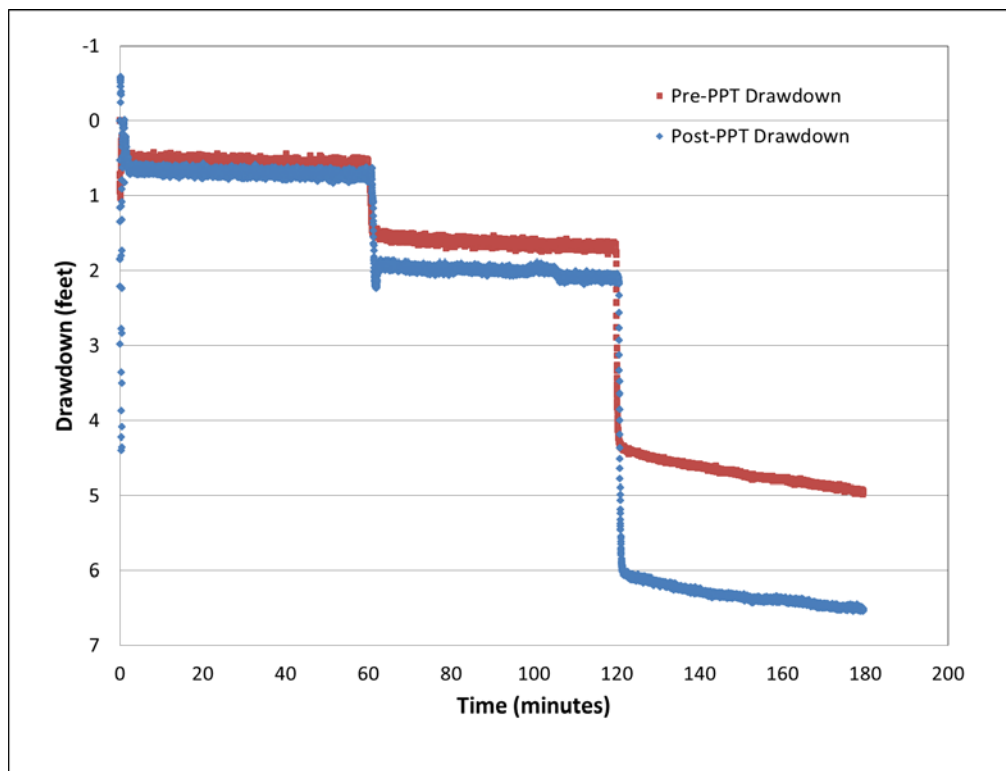

Figure 3. Aquifer Step Tests Drawdown Results

Drawdown for the pre- and post-PPT aquifer step tests. Data are from the calibrated pressure transducer (confirmed by manual measurements with an electronic sounder).

Chemistry Results

The field pH, EC, and Br all decreased from near the injectate values towards the baseline values during the extraction phase (Figure 4). While the EC returned to the baseline value, the pH and Br remained elevated with respect to baseline values at the end of extraction. The average Day 6 pH and Br values were also elevated with respect to the baseline values.
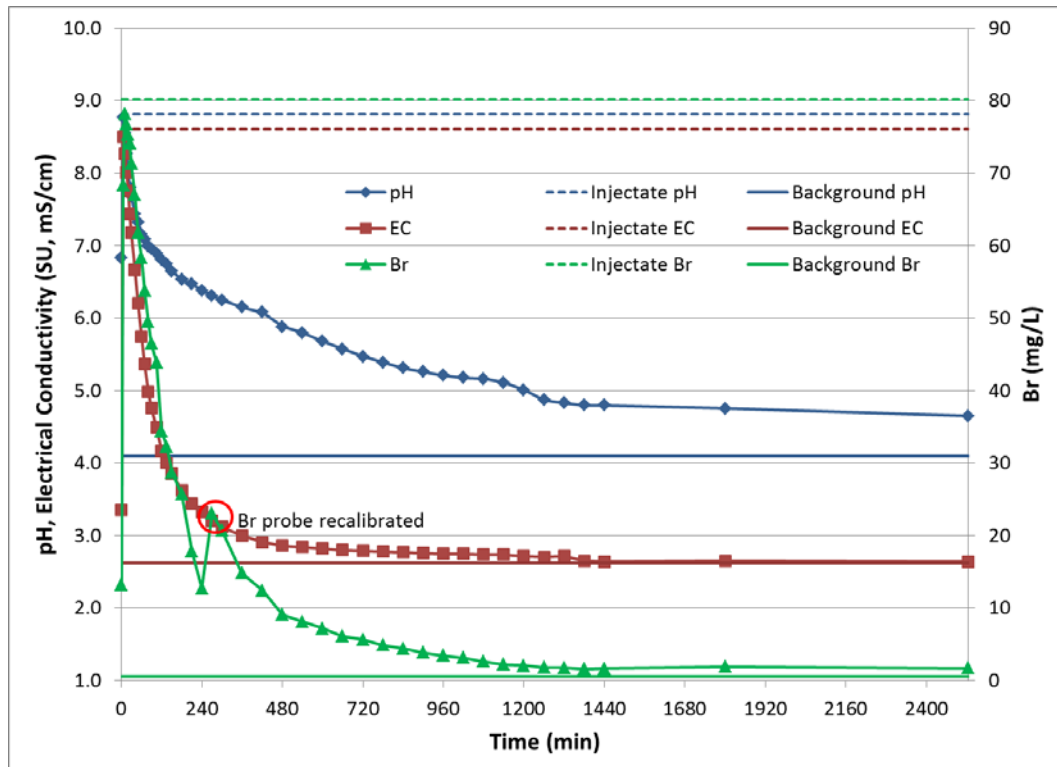

Figure 4. Field Water Quality Parameters during the Extraction Phase

pH, electrical conductivity, and bromide tracer field measurements collected during the PPT extraction phase. The baseline and injectate values are included for comparison purposes.

The average baseline and injectate, the initial and final extraction, and average day 6 pH and acidity, alkalinity, and total inorganic carbon (TIC) concentrations are presented in Table 1. Figure 5 presents the results of the acidity, alkalinity, TIC, and pH versus time.

Table 1. Acidity, Alkalinity, Total Inorganic Carbon, and pH Summary

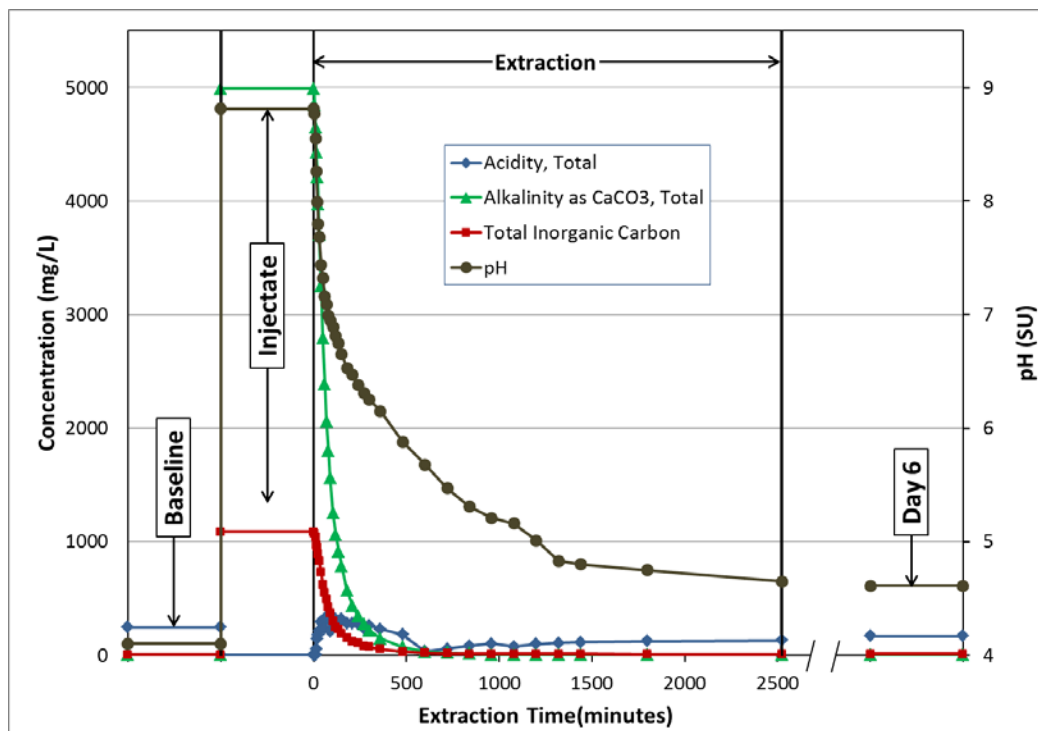| Sample	Acidity	Alkalinity	TIC	pH
	(mg/L)	(mg/L as CaCO$_3$)	(mg/L)	(SU)
Average Baseline	246	<1.0	5.5	4.10
Average Injectate	<2.0	4,993	1,088	8.82
Initial Extraction	<2.0	4,850	1,070	8.77
Final Extraction	132	3.1	9.3	4.65
Average Day 6	169	<3.0	10.1	4.61

Figure 5. Acidity, Alkalinity, pH, and Total Inorganic Carbon versus Time

Acidity, alkalinity, TIC, and pH temporal profiles during the PPT extraction phase, and including the baseline, injectate, and Day 6 values. Results show that the pH and TIC are still greater at Day 6 than baseline, while the acidity is lower at Day 6 than baseline.

The alkalinity, pH, and TIC decreased from the initial injectate values towards baseline conditions for the duration of the extraction and through the end of the test (Day 6). While the alkalinity returned to baseline values at the end of the test (within the limits of the minimum detection limits), both the TIC and pH were elevated at the end of the test above baseline levels.

The acidity increased from non-detect at the initiation of the extraction step to a maximum of 336 mg/L at 70 minutes (pH 7.09), decreased to 35 mg/L at 600 minutes (pH 5.68), and then increased towards baseline conditions, reaching 132 mg/L at the end of extraction (pH 4.65) and 169 mg/L at Day 6 (pH 4.61). The

measured acidity values through the first 480 minutes of extraction (from pH 8.77 to pH 5.88) are mainly due to buffering by the carbonate system and not to mineral acidity from metals such as Al, Cu, Fe, and Mn. The lower acidity at the end of the test than the baseline condition is consistent with the higher final pH.

The concentrations of Br and the major anions and cations versus time are presented in Figure 6. The results are summarized as follows:

- The concentrations of Br and Na trended from the elevated injectate concentrations towards baseline conditions by the end of the test. Br and Na at the end of extraction and at Day 6 were slightly greater than the average baseline concentrations (0.10 mg/l for Br and 5% for Na).
- The concentrations of Ca and Cl increased from the lower injectate concentrations towards the higher average baseline conditions during the extraction step, with no significant difference between average Day 6 and baseline concentrations.
- K and Mg increased from the average lower injectate concentrations to above the higher average baseline concentrations during the extraction step (plus 4% and 9%, respectively), and remained elevated at Day 6 (plus 5% and 6%, respectively).
- The average SO4 concentration increased toward the higher average baseline concentration (1,600 mg/L) during the extraction step (1,540 mg/L at the end of extraction), to 15% above the average baseline concentration at Day 6 (1,850 mg/L).
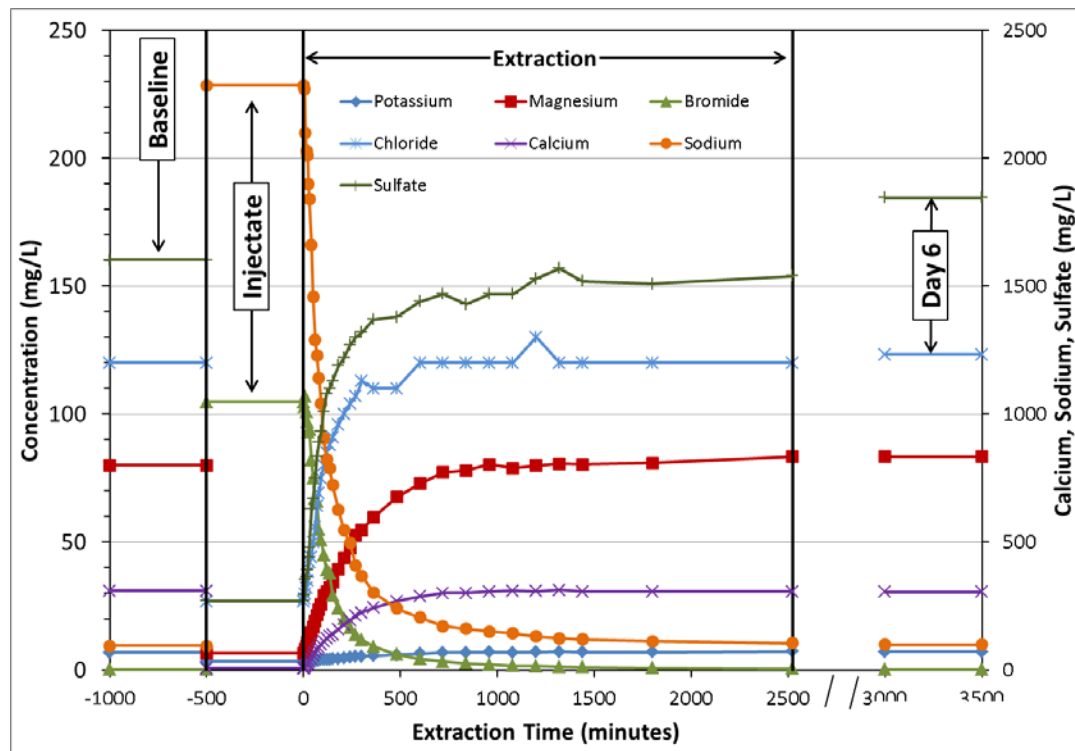

Figure 6. Bromide and Major Anions and Cations versus Time

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Br and major anion and cation temporal profiles during the PPT extraction phase, and including the baseline, injectate, and Day 6 values. Results show that sulfate was being released at Day 6 with the Day 6 average concentration 15% greater than baseline.

The concentrations of the metals Al, Cu, Mn, and pH are presented in Figure 7. The results are summarized as follows:

- The Al concentration increased toward the average baseline concentration during the extraction phase. The Al concentration at the end of extraction (13.7 mg/L) and at the end of the test (16.5 mg/L) was 16% lower than the average baseline concentration (19.7 mg/L).
- The Cu and Mn concentrations increased during the extraction step and the final extraction sample and average Day 6 concentrations were similar to the average baseline groundwater concentrations.
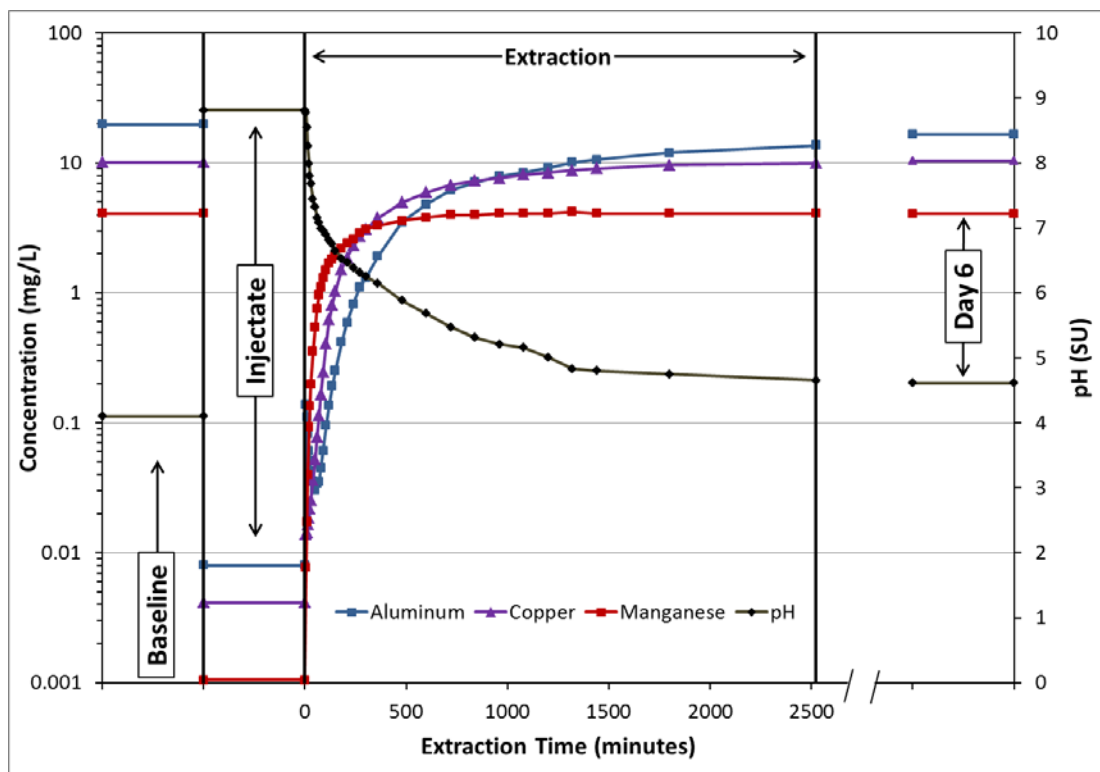

Figure 7. Al, Cu, Mn, and pH Versus Time

Al, Cu, Mn, and pH temporal profiles during the PPT extraction phase, and including the baseline, injectate, and Day 6 values. Results show that Al was being retained at the end of extraction and at Day 6 with the Day average concentration 16% lower than baseline.

Discussion

Hydraulic Discussion

Hydraulic impacts to the aquifer were evaluated through comparison of the data collected during the pre-PPT aquifer step test, the PPT, and the post-PPT aquifer step test to determine if hydraulic conductivity was impacted by precipitate formation during the PPT.

Specific Capacity and Well Efficiency Analysis

The specific capacity decreased in a linear manner through the successively higher pumping rates for both the pre-PPT and post-PPT aquifer step tests. A regression analysis of the specific drawdown versus pumping rate was used to determine coefficients to estimate the amount of the observed drawdown that was due to well inefficiency.

Table 2. Specific Capacity Analysis Summary

Stage	Measured Values			Model Results				
	Average Discharge Rate (gpm)	Drawdown (feet)	Specific Capacity (gpm/ft)	Drawdown (feet)	Well Loss (feet)	Total Drawdown (feet)	Well Efficiency	Specific Capacity (gpm/ft)
Pre-PPT Aquifer Step Test								
1	41.6	0.60	69.3	0.44	0.13	0.57	77%	72.4
2	99.6	1.65	60.3	1.05	0.72	1.77	59%	56.2
3	194.2	4.92	39.5	2.05	2.65	4.70	44%	41.3
Post-PPT Aquifer Step Test								
1	41.1	0.76	54.1	0.53	0.12	0.65	82%	63.5
2	99.8	2.13	46.9	1.30	0.91	2.21	59%	45.1
3	192.0	6.48	29.6	2.49	4.10	6.59	38%	29.1
Percent Change from Pre-PPT Aquifer Step Test to Post-PPT Aquifer Step Test								
1	NA	27%	-22%	19%	-10%	13%	6%	-12%
2	NA	29%	-22%	24%	27%	25%	-1%	-20%
3	NA	32%	-25%	21%	55%	40%	-13%	-29%

Comparison of the specific capacity values calculated from the pre- and post-PPT aquifer step test data indicated a decline in specific capacity. The drawdown increased between 27% and 32% from the pre-PPT to the post-PPT step test, depending on the pumping rate, resulting in the specific capacity decreasing by 22% to 25% (Table 2).

The specific capacity modelling indicates that the well loss increased by 27% and 55% at ~100 and ~190 gpm, respectively, with well efficiency decreasing by 1% at ~100 gpm and 13% at ~190 gpm.

These drawdown data and the specific capacity modelling results suggest that both the well efficiency and the aquifer were affected by the injection of the NaHCO3. However, the effect on the well efficiency was greatest at the highest pumping rate of ~190 gpm, accounting for 77% of the increased observed drawdown, suggesting that most of the increase in drawdown was due to well and near-bore fouling rather than effects in the aquifer formation.

The estimated transmissivity value using the AQTESOLV software (Theis step test solution) for the pre-PPT and post-PPT aquifer step test drawdown were 113,800 gpd/ft and 89,810 gpd/ft, respectively (Table 3). Estimated transmissivity values for the Pre-PPT aquifer step test, the PPT and the Post-PPT aquifer step test recovery data using the Theis Recovery solution were 123,968, 158,800 and 127,151 gpd/ft, respectively (Table 3).

Table 3. Hydraulic Modeling Summary

Drawdown		Recovery		
AQTESOLV Theis Solution		**Graphical Theis Solution**		
Pre-PPT	**Post-PPT**	**Pre-PPT**	**PPT**	**Post-PPT**
Transmissivity (gpd/ft)				
113,800	89,810	123,968	158,800	127,151
Hydraulic Conductivity (ft/day)				
761	600	829	1,061	850

Notes:

Modeling Aquifer thickness (b) value - 20 feet

Modeling Storativity (S) value - 0.0045 based on average S values calculated from previous aquifer tests (confidential report)

Comparison of the drawdown results suggest that the injection of the $NaHCO_3$ solution decreased the transmissivity by about 21%. However, the recovery transmissivity values are statistically equal, suggesting that the alkali treatment did not affect the aquifer formation. Based on the results of the specific capacity and recovery modeling, it would appear that the majority of the impacts of the alkali injection occurred at or near the well screen and filter pack, but the affects were not great enough to impede the alkali injection,

Chemistry Discussion

The injection of $NaHCO_3$ into the acidic sediment for 3.25 hours resulted in elevated pH and decreased metal concentrations. The pH remained elevated for more than 6 days (1.75 days of extraction plus 4.25 days of normal groundwater flow), with a final pH of 4.61 compared to the baseline pH 4.10 (Table 1).

The effectiveness of the alkali treatment was evaluated by comparing the normalized concentrations of alkalinity and Br (Figure 8). The results indicate that approximately 56% of the injected $NaHCO_3$ was utilized (i.e. not recovered during extraction). However, all of the utilized alkalinity was not expected to neutralize sediment acidity. The utilized alkalinity can also impart residual alkalinity to the sediment via precipitation as carbonates (mainly with calcium) and sorption to sediment surfaces. Additionally, some of the alkalinity may have escaped the capture zone.

Analysis of the TIC recovered during extraction suggests that approximately 16% of the utilized alkalinity was used to neutralize sediment acidity (i.e. relatively more TIC was recovered than alkalinity. The excess TIC recovered at pH less than 6.3 will be in the neutralized inorganic carbon form H_2CO_3).
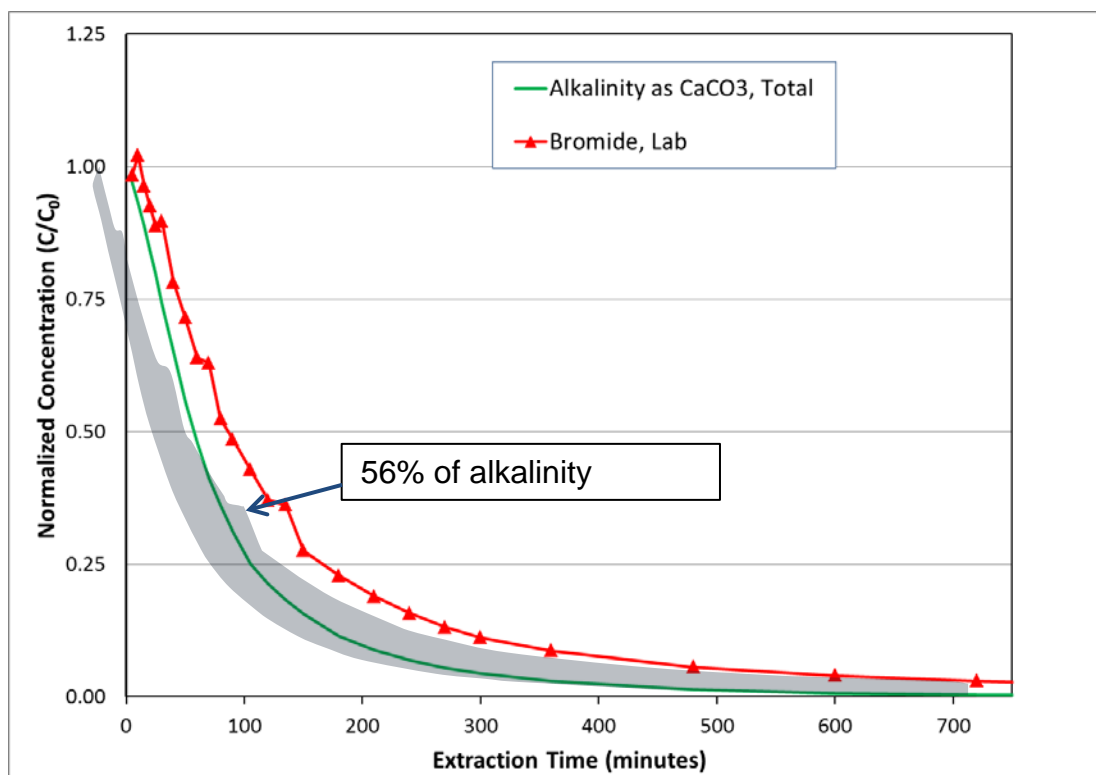

Figure 8. Normalized Concentrations of Alkalinity and Bromide

Normalized concentrations of alkalinity and bromide during the first 750 minutes of extraction indicate that the alkalinity is being utilized within the aquifer.

The elevated pH resulted in metals being retained within the aquifer as can been seen in Figure 9. Al was retained at a higher rate and for a longer period of time than Cu; Mn was retained the least. This result is expected based on pH-metal solubility relationships where Al solubility decreases at a much lower pH than Cu or Mn (Stumm and Morgan, 1981).

Retention factors were calculated for alkali and heavy metals (Table 4). While Na is not retained at all as indicated by the RF of 1.0, Ca, K, and Mg were all retained to a small degree with RFs of 1.5, 1.4, and 1.5, respectively. These RFs indicate that the reacted sediment acts as a sink for Ca, K, and Mg. The results may suggest surface sorption and/or cation exchange or, in the case of Ca and Mg, some precipitation due to elevated pHs and inorganic carbon concentration.

The RFs for Al, Cu, and Mn through the end of extraction were 9.0, 4.2, and 1.4, respectively, indicating that Al was more strongly retained than Cu, which was more strongly retained than Mn. This order of relative immobilization is consistent with sorption data where Al sorption to sediment occurs at a lower pH than Cu, and Mn sorption occurs at the highest pH.
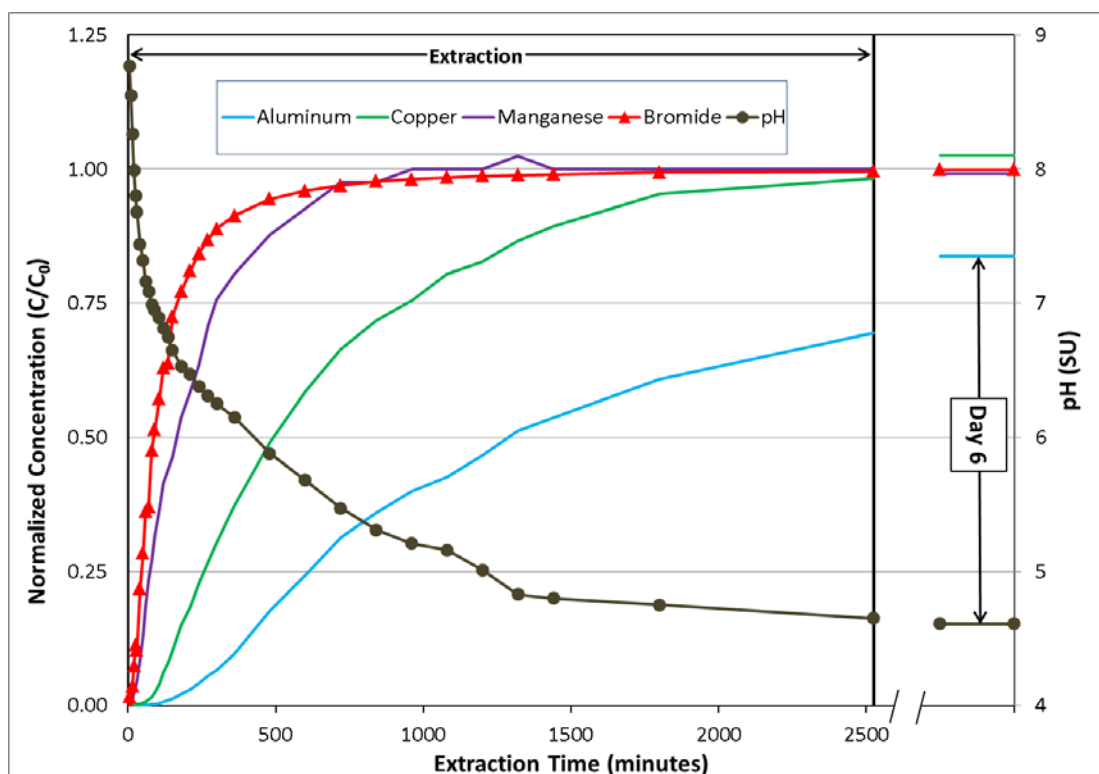

Figure 9. Normalized Concentrations of Aluminum, Copper, and Manganese

Normalized concentrations of aluminium, copper, manganese, and bromide during extraction indicate that the metals are being retained within the aquifer.

Table 4. Retention Factors

Constituent	Retention Factor
Calcium	1.5
Magnesium	1.5
Potassium	1.4
Sodium	1.0
Aluminum	9.0
Cobalt	2.1
Copper	4.2
Manganese	1.4
Nickel	2.2
Zinc	2.0

Conclusions

The results presented indicated that in situ remediation of acidic, metal-laden sediment by $NaHCO_3$ neutralization can be implemented and be effective. While the injection of alkali into the aquifer resulted in increased drawdown during extraction post-PPT compared to pre-PPT, most of the fouling occurred within the vicinity of the well screen and filter pack and not in the aquifer formation. Any fouling that occurred was insufficient to impede the injection of the alkali for the duration of the test.

The 3.25-hour alkali injection into the saturated zone was effective at neutralizing acidity as it resulted in an elevated pH for at least 6 days (pH at the end of the test was 4.6 compared to the baseline pH of 4.1). This elevated pH resulted in lower aqueous metal concentrations, with Al concentrations remaining lower for at least 6 days.

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