

**ROLE OF ACIDITY IN MOBILIZING COLLOIDAL PARTICULATE  
MATTER FROM NATURAL SAND GRAIN SURFACE**

A Thesis

by

JESSICA LYNN HAMMONS

Submitted to the Office of Graduate Studies of  
Texas A&M University  
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

December 2011

Major Subject: Biological and Agricultural Engineering

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Approved by:

Co-Chairs of Committee,	Yongheng Huang Patricia Smith
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## ABSTRACT

The Role of Acidity in Mobilizing Colloidal Particulate  
Matter from Natural Sand Grain Surface. (December 2011)

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Co-Chairs of Advisory Committee: Dr. Yongheng Huang  
Dr. Patricia Smith

Mobilization of colloidal particulate matter (most important, clay particles) from a soil matrix in the subsurface environment is an important environmental process. As many contaminants tend to adsorb onto various colloidal mineral particles, co-transport of contaminants in association with mobilized particles could contribute significantly to the migration of these contaminants in the environment. Numerous studies have observed the effects of pH on colloid mobilization but have overlooked the possible direct role of acidity. This study looked at the role of acidity with  $H^+$  as a chemical agent. Through cyclic elution of a natural sand column with a weak acid and base solution, there was an increase in mobilized clay colloids. It was found that low concentrations of organic acids could assist in detaching surface clays through lysing of labile  $Ca^{2+}$  and  $Mg^{2+}$  ions. The  $H^+$  ions sever the chemical bonds between the grain surface and the colloidal surface by being substituted for the interstitial Ca and Mg ions. This substitution has been found to release over 1 kg of surface clay per 1 mole of  $H^+$  consumed. It was postulated that pH oscillation addition to proton dynamics could play a major role in subsurface colloid transport. The results from this study could help

improve predicting of subsurface contaminant fronts and aid in managing contaminant transport in the soil water environments.

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begin to explain how I feel. Thank you for all of your support, guidance, and love. You made all of this possible for me.

## NOMENCLATURE

A	absorbance
C	Coulombs
cm <sup>3</sup>	cubic centimeters
DI	distilled
pv	pore volume
mL	milliliter, 10 <sup>-3</sup>
Ca <sup>2+</sup>	Calcium ion
g	grams
HCl	Hydrochloric acid
H <sup>+</sup>	Hydrogen ion
J	joules
Mg <sup>2+</sup>	Magnesium ion
μm	micrometer, 10 <sup>-6</sup>
mL	milliliters, 10 <sup>-3</sup>
nm	nanometer, 10 <sup>-9</sup>
N	Newtons
N <sub>2</sub>	Nitrogen gas
<i>N</i>	Normality
Na <sup>+</sup>	Sodium ion
NaCl	Sodium chloride
NaOH	Sodium hydroxide

SEM	Scanning Electron Microscopy
UV/Vis	ultraviolet visible



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## 1. INTRODUCTION

### 1.1 Mobilization of Mineral Colloids

#### 1.1.1 Environmental Implications

Colloids have been recognized as an important factor in predicting mobility and fate of subsurface pollutants. As many contaminants tend to adsorb onto various colloidal mineral particles, co-transport of contaminants in association with mobilized particles could contribute significantly to the migration of these contaminants in the environment [Lenhart and Saiers, 2003; Puls and Powell, 1992].

Colloid facilitated contaminant transport has the ability to move contaminants in the subsurface farther and faster than in the absence of migrating colloids [Kersting *et al.*, 1999]. This increase in velocity can make the colloids bypass the soils natural capabilities to filter and buffer out the contaminants [Flury and Qui, 2008]. When modeling contaminant transport, if colloid mobilization is not taken into consideration it can lead to a major underprediction of the contaminant front [Corapcioglu and Choi, 1996]. Field studies have shown that particles can be mobilized both vertically and laterally, making modeling difficult [Nightingale and Bianchi, 1977].

#### 1.1.2 Theories

A colloid is any particle ranging in linear dimensions between  $10^{-9}$  (1 nm) and  $10^{-6}$  (1  $\mu\text{m}$ ) [Hiemenz and Rajagopalan, 1997]. Colloids can be formed by erosion of secondary minerals, changes in solution pH and ionic strengths, dissolution of cementing minerals, or precipitation of supersaturated phases [Ryan and Gschwend, 1994]. Colloids

can bond and adhere to particles when they collide with enough energy to overcome the electrical double layer repulsive forces that normally act as a barrier. The electrical double layer repulsive force, which is an electrostatic force, can be described by Coulomb's Law [*Luty and van Gunsteren, 1996*].

Coulomb's Law states that the electrical force between two charged objects is directly proportional to the product of the quantity of charge on the objects and inversely proportional to the square of the separation distance between the two objects. The equation for Coulomb's Law is:

$$F = \frac{k \cdot Q_1 \cdot Q_2}{d^2} \quad (1)$$

where  $F$  is the force (N),  $k$  is a proportionality constant known as the Coulomb's constant ( $\text{Nm}^2/\text{C}^2$ ),  $Q_1$  and  $Q_2$  represent the quantity of charge on object 1 and 2, respectively, (C), and  $d$  is the distance of separation between the two objects (m) [*Thamburaj, 2007*]. Since both of the charges are the same the colloid is repulsed from other particles by Coulomb's Law.

The Derjaguin-Landau-Verwey-Overbeek theory (DLVO theory) states colloids or particles stability is dependent on the particles total potential energy. The total potential energy is a combination of van der Waals attractive forces, the electrical double layer repulsive forces, and the potential energy due to the solvent [*Derjaguin and Landau, 1941; Verwey and Overbeek, 1948*]. The DLVO theory has been the backbone of colloidal science since the 1940's. There are extended DLVO or XDLVO models that

take into consideration non-DLVO interactions. These newer models have arisen because frequently the original DLVO theory cannot fully describe certain colloidal interface behaviors [Hoek and Agarwal, 2006; Bhattacharjee et al., 1998; Yotsumoto and Yoon, 1993]. Equation 2 shows the formula for the XDLVO interactions.

$$E_{pp}^{XDLVO}(h) = E_{pp}^{LW}(h) + E_{pp}^{AB}(h) + E_{pp}^{EL}(h) \quad (2)$$

where  $E_{pp}^{XDLVO}(h)$  (J) is the total XDLVO interaction energy per unit area between infinite flat planar surfaces separated by a distance of  $h$  (m), and is a function of the interaction energies per unit area between infinite flat surfaces attributed to Lifshitz-van der Waals (LW), Lewis acid-base (AB), and the constant potential electrostatic double layer (EL), respectively [Hoek and Agarwal, 2006]. The van der Waals attractive interactions and repulsive electrostatic double layer interactions are those stated in the DLVO theory of colloidal stability. It is the non-DLVO, the acid-base interaction that is being added to the extended equation in efforts to overcome reported discrepancies between experimental observation and theory. Other non-DLVO interactions that have begun to be researched are steric and hydrodynamic interfacial forces [Hoek and Agarwal, 2006].

### 1.1.3 Factors

Colloid mobilization arises from both chemical and physical mechanisms. These mechanisms include, but are not limited to: pH, ion strength, ion exchanges, and particle size and flow rate.

### 1.1.3.1 pH

The DLVO theory includes pH as a key factor in colloidal science which has resulted in multiple studies. These studies have discovered that increasing pH may increase the rate of colloids released [Kolakowski and Matijevic, 1979; Bunn *et al.*, 2002; Ryan and Elimelech, 1996]. pH may change a positively charged surface to a negatively charged surface by increasing the pH from below to above the point of zero net charge. This increase in pH produces an increase in the electrostatic repulsion between the colloids and the grain surface. When the repulsion forces overcome the attractive forces the colloids can then disperse.

*Kolakowski and Matijevic* (1979) found that a pH of 11.5 paired with a low ionic strength can yield optimal particle removal rates. Increasing the pH beyond this optimal combination will result in decreasing release of colloid particles. The upper limit for pH colloid release is dependent on numerous variables. *Bunn et al.* (2002) created two column experiments: one used sequential exposure of the same sediment to solutions of increasing pH and the second had separate exposure to fresh sediments both with a different pH. This experiment found that the ionic strength began to limit the release of sediment at a pH of 12.5 in the sequential columns and at 13.1 in the separate columns.

### 1.1.3.2 Ionic Strength

Changing the ionic strength of the solution that the sand is in can create changes in the electrostatic interactions between the colloid and grain surface. When ionic strength is reduced it increases the repulsive electrostatic double-layer forces between the like charged colloids and soil surfaces which in turn release the attached colloids



[*Saiers and Lenhart*, 2003]. In research it was found that increasing ionic strength while concurrently increasing pH can limit the release of colloid released [*Bunn et al.*, 2002]. This occurs because raising the ionic strength decreases the electrostatic forces between the colloid and the soil surface.

#### **1.1.3.3 Ion Exchanges**

Wan et al. (2004) observed ion exchange occurred in a column experiment investigating colloid formation in waste solution plumes from a U.S. Department of Energy site. It was observed that a highly concentrated  $\text{Na}^+$  waste solution removed both  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from the cation exchange sites. The  $\text{Na}^+$  replaced the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the soil and mobilized the surface colloids. This is pertinent as one possible role of  $\text{H}^+$  is the exchange between  $\text{H}^+$  and  $\text{Ca}^{2+}$ . While exchange between  $\text{Na}^+$  and divalent ions have often been studied and cited [*Wan et al.*, 2004], the similar possible role of naturally occurring  $\text{H}^+$  in colloid release has largely been neglected.

#### **1.1.3.4 Other Factors**

Colloids can be mobilized not only by chemical perturbation but also by physical perturbation [*Ryan and Gschwend*, 1994]. When flow rate increases, the detachment rate of colloids increases. An increase in velocity can mobilize these colloids from additional hydrodynamic shear. Though the detachment rate may increase, this does not mean that there will ultimately be more colloids released during this time [*Ryan and Gschwend*, 1994]. The detachment rate will increase and will remove the weakly bonded colloids at an increased rate but the velocity increase will only be able to remove the

weakly bonded colloids. Ultimately, the equivalent amount of colloids will be released independent of the rate.

#### 1.1.4 Current Knowledge and Gaps

Despite the recognition of the importance of pH, few studies have paid attention to the possible quantitative relationship between acidity and the amount of colloids released. Acidity, which denotes the amount of  $H^+$  available for reaction, is often overlooked when discussing pH which denotes the concentration of  $H^+$ .

Acid strength is denoted by the acid dissociation constant, or the tendency of a compound to donate a proton ( $H^+$ ), known as  $K_a$ .

$$K_a = \frac{[A^-][H^+]}{[HA]} \quad (3)$$

$A^-$  is the conjugate base,  $H^+$  is the hydrogen ion or proton, and  $HA$  is a generic acid.  $K_a$  values span many orders of magnitude; therefore scientists use the logarithmic measure shown in Equation 4.

$$pK_a = -\log K_a \quad (4)$$

where  $pK_a$  is the logarithmic constant and  $K_a$  is the acid dissociation constant.

Generally, more negative  $pK_a$  values correspond to stronger acids and more positive  $pK_a$

values correspond to weaker acids. Strong acids are unstable in water, have a small attraction to their protons and therefore want to dissociate from them.

The Brønsten-Lowry definition of an acid is a substance that can donate a proton [Bender, 2003]. Using this definition and what is known about the affect of pH on colloid mobilization, further investigation into the effect that acidity, amount of  $H^+$ , can have on subsurface science is needed. One role of  $H^+$  in colloidal mobilization could be its presence as surface acidity through protonation/deprotonation.

Discrepancies between results and theories, as well as recent studies have raised questions regarding acidities potential role in subsurface transport. Humic acid and oxalic acid, both found in the natural environment, were found to facilitate colloid mobilization [Swartz and Gschwend, 1998]. For all that is known about acidity, there is a lack of knowledge and recognition about natural acidity and its potential role in colloid mobilization.

## **1.2 Scope of Thesis**

### **1.2.1 Objective**

Dr. Yongheng Huang, of Texas A&M University, during a brief preliminary study found that alternating exposure to an acid and then base could efficiently remove clay particles from a sand grain surface and that there is a strong correlation between water pH change during the acid rinsing stage and the amount of clay particles released during the base rinsing stage. For this research, it is hypothesized that:

1. The acid is consumed to sever or weaken the inner-sphere bond that may be responsible for the strong attachment of the clay particles to the sand surface.
2. The base wash releases the clay particles from the sand surface following the acid wash. A higher pH may reduce the electrostatic forces that bind mineral particles to the surface thus mobilize the particles, but not those that are bound by the inner-sphere bonds.
3. The amount of clay released is proportional to amount of acid consumed.

The prime objective of this research was to demonstrate the importance of acidity in mobilizing colloidal particulate matter from a natural sand media under a controlled supply of protons. The intention was to find a direct quantitative correlation between the acidity consumed in the sand column and the amount of colloid released.

### **1.2.2 General Approach**

To test the hypotheses, a sand-packed column was used to investigate the relationship between acidity consumption and clay particle released. A laboratory setting was chosen to create an experiment that was reproducible and to give the ability to control the acidity of the solution entering the sand. The sand media was rinsed alternatively with acidic, basic, and NaCl solutions with controlled ionic strengths. The effluent was collected and the parameters (acidity, turbidity, and cation concentration) were measured. Hydrochloric Acid (inorganic acid) and citric acid ( $C_6H_8O_7$ , organic acid) were used in this study. Surface characteristics of sand media and the

compositions of the surface attached colloidal particles were analyzed by other laboratories on the Texas A&M University campus.

## **2. MATERIALS AND METHODS**

### **2.1 Experimental Set-up and Procedures**

#### **2.1.1 Schematic of Experimental Set-up**

The experiment was performed in the Water Quality Lab for the Biological and Agricultural Engineering Department. This laboratory is housed inside the Hobgood Building on the West Campus of Texas A&M University. The experimental system set-up began with DI water in a 4 liter plastic capped carboy being pumped through Masterflex chemical Tygon tubing with an inner diameter of 0.152 cm, through a peristaltic Cole-Palmer Instrument Company brand Masterflex Console Drive pump, and into the top of the wet-packed sand, vertical column. There was an inlet in the center of the lid of the sand column where the tubing was connected to inject the chemical solutions. There was also an outlet on the bottom of the sand column where tubing was connected to remove the effluent. The chemical solution traveled down through the sand column and the effluent moved out through Tygon lab tubing before being captured in a Spectra Chromotography CF-Fraction Collector. The remainder of the effluent that was not used for testing was released into an 18.9 liter bucket which was disposed of at the end of every cycle. The schematic for the experimental setup is shown in Figure 1.

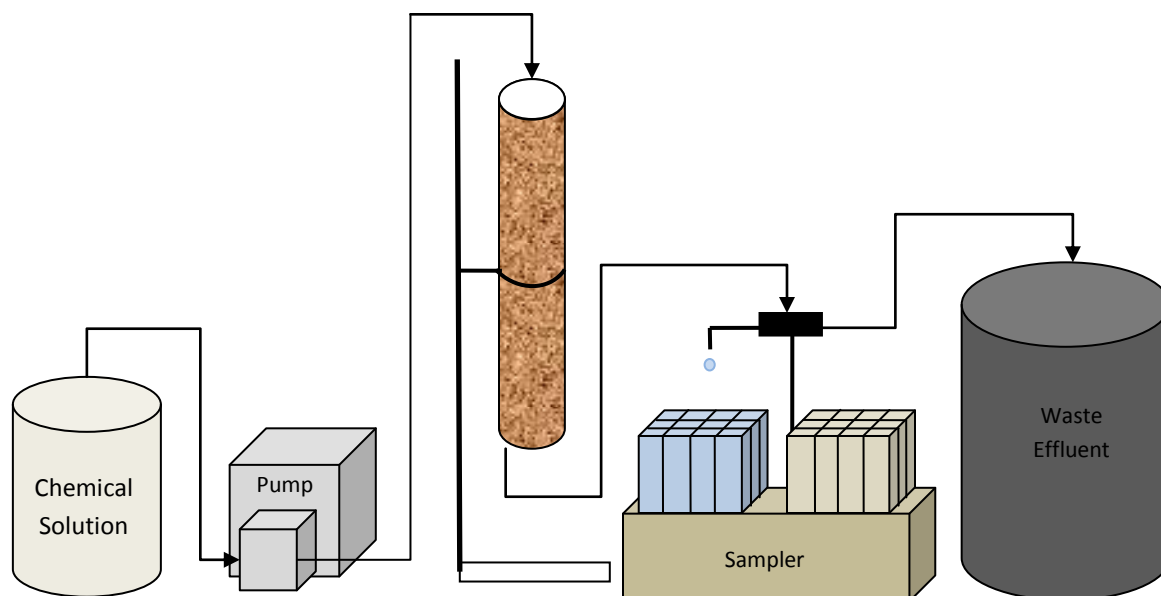


Figure 1: Schematic of experimental setup.

### 2.1.2 Sand Column Wet Packing Procedure

The sand column is a wet packed column; this method was used to reduce the chances of air pockets in the column. A wet packed column was created by securely sealing the bottom end of a column. Once there was a tight seal, distilled water was added to the column followed by sand. It was imperative that as the column was being filled the sand continuously stayed beneath the water line, or that there was always a layer of ponding on top of the sand. When new sand was added, the column was shaken to settle the sand and release air pockets. These steps were repeated until the sand reached the top of the column and there were no bubbles trapped in the column. The top

was then securely added to the column. The wet packed column procedure is shown below in Figure 2.

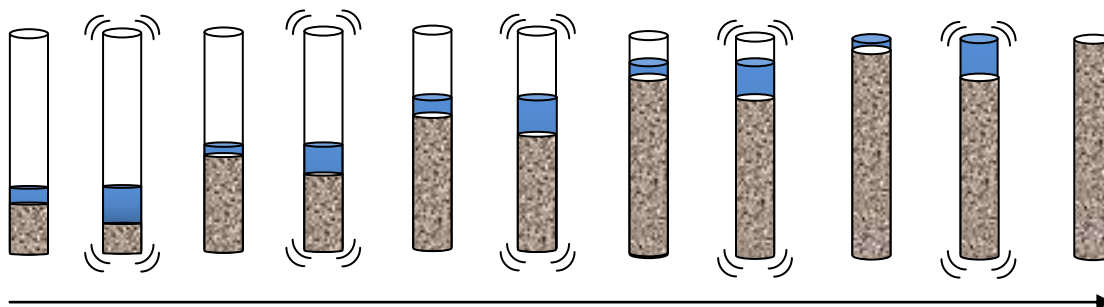


Figure 2: Column wet packing process.

### 2.1.3 Experimental Procedure

The flow-through test required cyclical elution of the sand column with acid, NaCl, and base solutions. Each flow-through test was conducted in two phases and with similar procedures. The first flow-through test used HCl and NaOH solutions. Each chemical solution was introduced into the sand column at a rate of 1.72 mL/min throughout the duration of the tests, making the hydraulic retention time 2 hours. The flow rate was calculated by dividing the pore volume of the column by the desired hydraulic retention time of 120 minutes.



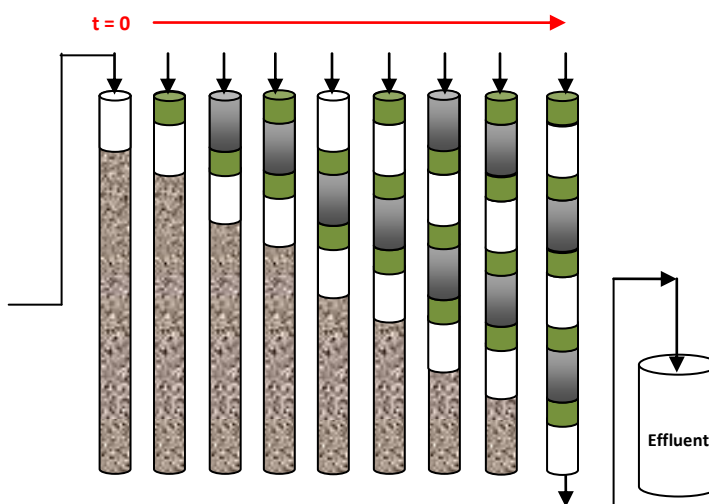


Figure 3: Experiment injection process.

The first phase had a sequential injection sequence of: NaCl, NaOH, NaCl, NaOH and went from pore volumes 0 to 24. This injection sequence is shown in Figure 3. This phase was used to release any colloid particles that were not strongly bound to the sand surface. Phase two consisted of four consecutive cycles of NaCl, HCl, NaCl, NaOH; each cycle lasted for 48 hours or 24 pv. Each chemical solution injection lasted for 12 hours or 6 pv.

#### 2.1.4 Sampling

Samples were collected in 25 mL test tubes with a Spectra Chromatography CF-Fraction Collector automatic sampling machine. Samples were collected at 30 minute intervals for a total sampling time of 10 minutes at the beginning of each 30 minute interval. For example, in one hour a sample was collected during the first 10 minutes, and then 20 minutes later another sample run would begin. The remainder of the effluent not used for testing was released into an 18.9 liter bucket and dumped at the end of every cycle.

## **2.2 Materials**

### **2.2.1 Sand**

A sand column was constructed in the Hobgood laboratory to study the effects of the chemical conditions on colloid mobilization. The colloids that were removed naturally existed in the sand when it was received. The sand in the test column was natural silica sand classified between US sieve sizes No. 40-60 (0.25-0.42 mm pore size) from the Accusand, Unimin Corp. No chemical treatment was used during sand preparation with the exception of rinsing the column three times with distilled water before the beginning of each cycle. Rinsing the sand yielded no significant amount of colloids. The glass column had an inner diameter of 48 mm and a length of 300 mm. The packed sand had a volume of 543 cm<sup>3</sup> with 916±5 g dry sand and a porosity of 38±0.2%. The volume of the water in the column was determined to be 206 mL, which was calculated by multiplying the volume of the column by the porosity. The volume of water in the column coincides with the pore volume recorded.

### **2.2.2 Chemicals**

A NaCl solution was used as a neutral buffer for all experiments. The buffer was used to separate acid and base solutions in order to avoid chemical reactions between the acid and base. There were two phases used in the experiment cycle. Phase I had a sequential injection sequence of: NaCl, NaOH, NaCl, NaOH. The injection sequence was repeated twice and went from 0 to 24 pore volumes. The purpose of Phase I was used to remove any loosely bonded colloids from the sand column. The Phase 2

injection sequence was: NaCl, Acid, NaCl, NaOH and was repeated four times. This elution cycle was used to remove the strongly bound colloids layer by layer.

All chemical solutions were prepared using E-pure DI water. The inorganic acid used was hydrochloric acid with an acid solution of 0.5 mM HCl + 0.5 mM NaCl. This acid solution was paired with a base solution of 1.0 mM NaOH for the experimental cycle. The ionic strength of all the solutions was 2.0 mM.

The organic acid used was citric acid with an acid solution of 0.3 mM citric acid + 0.7 mM sodium citric, which was also paired with 1.0 mM NaOH. The citric acid solution did not have the same 2.0 mM ionic strength as the NaOH and NaCl solutions. The ionic strength of citric acid solution depends on the dissociation/ionization of citric acid to citrate and  $\text{H}^+$ , which is dictated by its  $\text{pK}_a$  constants. The ionization of citric acid depends greatly on the pH. For 0.3 mM citric acid + 0.7 mM NaCl, the pH was 5.1, which means that the  $\text{H}^+$  concentration was pretty low ( $<0.01$  mM), therefore the dissociation/ionization of citric acid was pretty low ( $<0.01$  mM). The initial ionic strength was mostly from the 0.7 mM NaCl while the 0.3 mM citric acid contribution to the overall ionic strength was negligible. As the citric acid solution passed through the column,  $\text{H}^+$  was consumed and pH increased resulting in the release of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  and thereby the overall ionic strength was increased. Therefore, the ionic strength was not a constant in the sand column during the acid/base elution process.

The citric solution had an acidic pH of 5.1, while the HCl had a lower pH of 3.3. However, HCl has a lower acidity because it can only provide one  $\text{H}^+$  compared to citric acid that can provide 3  $\text{H}^+$ . This means that the citric acid solution has two more  $\text{H}^+$  to

be consumed in a reaction. HCl has a  $pK_{a1}$ , or acid dissociation constant, of -6.2 and citric acid has a  $pK_{a1}$  of 3.09, a  $pK_{a2}$  of 4.75, and a  $pK_{a3}$  of 6.4. An acid with a  $pK_a$  value less than approximately a -2 can be classified as a strong acid, while those in the approximate range of -2 to 12 are said to be weak acids.

HCl was the only inorganic acid that was tested during this study; however, other organic acids were investigated but not used. For example, it was decided that acetic acid would be too complex of an acid at this level of analysis. When deciding on the citric acid solution, different concentrations were tested and 0.3 mM citric acid + 0.7 mM sodium citric was chosen because it gave a steady flow of colloid release without clogging the tubing leading to the automatic sampler.

## **2.3 Analytical Methods**

### **2.3.1 pH Measurement**

The pH of the effluent from the sand column was analyzed with a Thermo Scientific brand Orion 5-Star Plus Benchtop Multimeter. Immediate measurement of pH after sampling can reduce the magnitude of the pH change caused by the reaction of effluent acidity with the  $CO_2$  in the atmosphere. If the pH of the effluent could not be tested immediately after collection, the sample was placed in an anaerobic chamber so no reaction would occur. The pH meter was calibrated approximately twice a week to make sure that the data collected from the samples was accurate. It was calibrated by testing chemical solutions of a known pH.

### 2.3.2 Turbidity Measurement

The samples were tested for turbidity using the PG Instrument Brand T80+ Double Beamed Ultraviolet Visible (UV/Vis) Spectrometer. A glass cuvette was filled with 3.5mL of well mixed sample and placed in the spectrometer. The tungsten lamp was disabled because the wavelength chosen was beneath the lamps 360-2000 nm spectral range. The only lamp used was an UV lamp, with a wavelength to measure turbidity set at 250 nm. Standard samples and a blank sample of DI water were placed in the spectrometer to calibrate the machine. Since there should be no impurities in the DI water, the spectrometer readout should measure 0.000 for the absorbency. After calibration, the samples were analyzed. Each sample was tested once and then turned 180° and tested again; the samples were replicated to reduce error. If the difference in the readings was within 0.002 absorbance (A), the lower turbidity was recorded. If the readings were not within 0.002 A the sample was tested a third time. At this point, if the reading was not within 0.002 A of a previous reading, the machine was recalibrated and the samples were retested. If the reading was within 0.002 A of a previous reading, the turbidity was measured one more time to see if it was still within 0.002 A and if it was the lower reading was recorded. If it was not, the spectrometer was recalibrated and the samples were retested. The samples were then reported as the equivalent turbidity when compared to a kaolinite suspension standard. The 100 mg/L kaolinite standard was prepared in the lab using a previously reported method [*Saiers and Hornberger, 1996*]. The characteristics of the effluent colloids collected in our experiment did not have the exact characteristics of the kaolinite particles used for the standard. It should thus be

noted that a turbidity of 100 mg/L would not be exactly equivalent to 100 mg of colloid/L.

### 2.3.3 Acidity Measurement

Acidity of water samples was measured using a titration method following the Standard Methods for the Examination of Water and Wastewater [APHA *et al.*, 1998]. The process to measure the acidity consumed began by boiling three liters of water, with a pH above 6.0, over a laboratory hot plate set to a temperature of 450-500°C. After 2-3 hours the temperature of the hot plate was lowered to 105-110°C for 10-15 minutes. The water was boiled to release any CO<sub>2</sub> trapped in the water that could react with the NaOH normality solution. The boiled water was used in three steps of the acidity measurement process. The titration solution was a mixture of 100 mL of boiled water, 0.5 g of dried potassium hydrogen phthalate (KHC<sub>8</sub>H<sub>4</sub>O<sub>4</sub>), the acid used in the titration reaction, and four drops of phenolphthalein indicator. The phenolphthalein indicator was chosen because its pH is close to 8.3 which corresponds to the stoichiometric neutralization point of most weak acids.

In order to get the 0.5 grams of dried KHC<sub>8</sub>H<sub>4</sub>O<sub>4</sub>, 10-20 grams of KHC<sub>8</sub>H<sub>4</sub>O<sub>4</sub> were measured out and dried at a temperature of 105-110°. When measuring out the 0.5 g of dried KHC<sub>8</sub>H<sub>4</sub>O<sub>4</sub> care was taken to measure to four significant figures to ensure an accurate NaOH solution. The portion of the compound that was not used was stored for future titrations.

A 0.1 M/L NaOH normality solution was created to find an accurate standard solution. This solution was made using the boiled water. The normality of a solution is

simply a multiple of the molarity of the solution, which is used to compare solutions on the basis of concentration of ions. The NaOH normality solution ( $N$ ) was found by using Equation 5:

$$\text{NaOH normality solution} = \frac{A \times B}{(C) \times 204.23} \quad (5)$$

where A is the mass of  $\text{KHC}_8\text{H}_4\text{O}_4$  weighed into a 1-L flask (g), B is the volume of  $\text{KHC}_8\text{H}_4\text{O}_4$  solution taken for titration (mL), C is the volume of NaOH solution consumed (mL), and 204.23 is the molecular weight of  $\text{KHC}_8\text{H}_4\text{O}_4$  (g/mol) [APHA et al., 1998].

The boiled water was additionally used in the blank solution that contains boiled water and 4 drops of the phenolphthalein indicator. The NaOH solution was diluted to a normality of 0.020N because the effluent samples that were being tested were less than 1000 mg ( $\text{CaCO}_3$ )/L. The indicator solution was then released a drop at a time into an Erlenmeyer flask and titrated until there was a persistent color change. The color at the equivalence point can be checked by adding the same concentration of indicator to the blank solution. Equation 6 was used to measure the total acidity in mg/L of  $\text{CaCO}_3$ .

$$\frac{\text{mg}}{\text{L}} \text{CaCO}_3 = \frac{M \times V_2 \times 50.05 \times 1000}{V} \quad (6)$$

where  $M$  is 0.0200 mol/L,  $V_2$  is the volume consumed of NaOH (mL), 50.05 is half of the molecular weight of  $\text{CaCO}_3$  (g/mol), 1000 is a conversion factor, and  $V$  is the volume of the sample (mL).

### 2.3.4 Cation/ Anion

$\text{Cl}^-$  and  $\text{SO}_4^{2-}$  were measured using a Dionex DX 500 model ion chromatograph (IC) with an AS 50 autosampler and a CD 20 conductivity detector. Separation was achieved using a Dionex IonPac AS-22 column (4×250 mm) with an AG-22 guard column (4×50 mm). The eluent was 4.5 mM  $\text{Na}_2\text{CO}_3$  and 1.4 mM  $\text{NaHCO}_3$  at a flow rate of 1.5 mL/min. Though the cations were not used in the results, they were tested.

$\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$  were analyzed using a conductivity detector (CD20) and SRS (CSRS 300 4-mm). An IonPac CS12A (4×50mm) guard column and (4×250 mm) separation column were used with 11mM  $\text{H}_2\text{SO}_4$  as the eluent at a flow rate of 1.0 mL/min. This method had a detection limit of 0.05 mg/L for these ions.

The results of analyzing the ions were recorded in mg/L and were then converted into mM/L with the conversion shown in Equation 7.

$$\frac{\text{mM}}{\text{L}} = \frac{\frac{\text{mg}}{\text{L}}}{\text{atomic weight}} \quad (7)$$

where atomic weight can be found on the periodic table of elements for that specific element. Equation 8 was used to get the results into milliequivalents, which is used to show chemical equivalence.



$$\text{meq} = K \left( \frac{\text{mM}}{\text{L}} \right) + \left[ \text{Ca} \left( \frac{\text{mM}}{\text{L}} \right) * 2 \right] + \left[ \text{Mg} \left( \frac{\text{mM}}{\text{L}} \right) * 2 \right] \quad (8)$$

where K is potassium, Ca is calcium, and Mg is magnesium.

### 2.3.5 Surface Characterization of Sand

The surface of the sand was characterized using a Scanning Electron Microscopy (SEM). A dried sample of sand was sent to the Texas A&M University Microscopic Imaging Center.

### 2.3.6 Characterization of Mineral Colloids

The mineralogy of the eluted colloids was analyzed with a Bruker D8 Advance X-ray diffractometer. 10 to 20 mL of effluent suspension was filtered through a 0.1  $\mu\text{m}$  membrane with a diameter of 25 mm. The filtrate was discarded and the filter membrane with the captured colloids was placed in a desiccator for 72 hours to dry the colloids. The membrane was then transferred onto a 25.4-mm microprobe glass disc (Hugh Courtright & Co.). Before the transfer, a drop of distilled water was smeared on the disc to ensure good contact between the membrane and the disc and thus a flat surface for the x-ray diffraction analysis. A Cu k radiation operated at 35 kV and 40 mA was used in the XRD analysis. The XRD pattern was recorded with a 1-dimensional 192-strip detector at a step size of 0.01716 degrees 2-theta and a 0.1 second/step scan speed. It is important to note that the XRD can only identify crystalline substances that exist in a sample.

### **3. RESULTS AND DISCUSSION**

#### **3.1 HCl Test Results**

The results described in this section are only from a single test but are generally representative of similar tests that we conducted during a series of trial and replicate tests that lead to the refinement of test conditions and sampling schemes. If an aspect of the experiment was changed in a test scenario, the changes as well as what occurred as a result of the changes was documented. This is also true for the results of testing the citric acid. Furthermore, because of the differences stated in 2.3.2 on the turbidity measurements, the effluent colloidal solution that has a turbidity of 100 mg/L with the kaolinite standard was measured to have an actual suspended solid concentration of  $96 \pm 6$  mg/L.

##### **3.1.1 Turbidity Release**

The purpose of Phase one I, from 0-24 PV, was to release and mobilize colloids by NaOH alone. During the first injection of NaCl, from 0 to 6 PV, the colloids released in the effluent were trivial with turbidities ranging from 2 to 4 mg/L. When the first injection of NaOH was introduced into the system from 6 to 12 PV, there was an immediate increase in release of colloids. This demonstrated that the weak alkaline condition was sufficient to break the Van der Waals or other electrostatic forces to begin the release of colloids. The release had an initial steep spike in turbidity, climbing to 180 mg/L and quickly subsiding; by the end of the injection the turbidity had fallen below 20 mg/L. The first injection of NaOH released 61 mg of clay colloid. When the

next injection of NaCl came, from 12 to 18 PV, the turbidity returned to below 3 mg/L. The second dose of NaOH, from 18-24 PV, released a more moderate quantity of colloids. The peak for this injection only reached 24 mg/L and a total of 23 mg clay colloid. Figures 4 and 5 show the changes in turbidity and pH, respectively, compared to time shown in pore volume. The vertical lines indicate the beginning of an injection with NaCl in grey, NaOH in blue, and HCl in red.

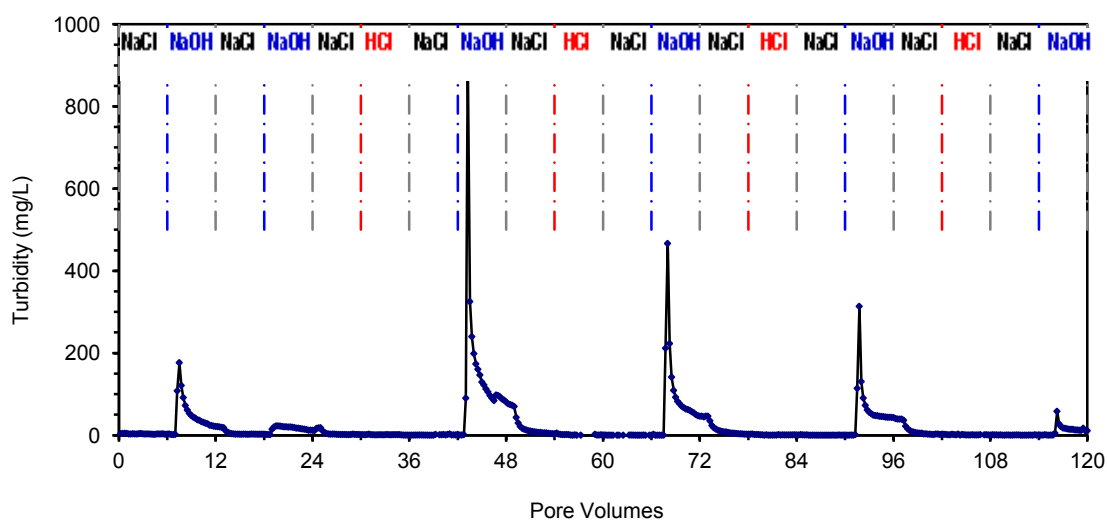


Figure 4. Turbidity (mg/L) over time, expressed in PV during the HCl/NaOH test. The vertical lines indicate the beginning of an injection with NaCl in grey, NaOH in blue, and HCl in red.

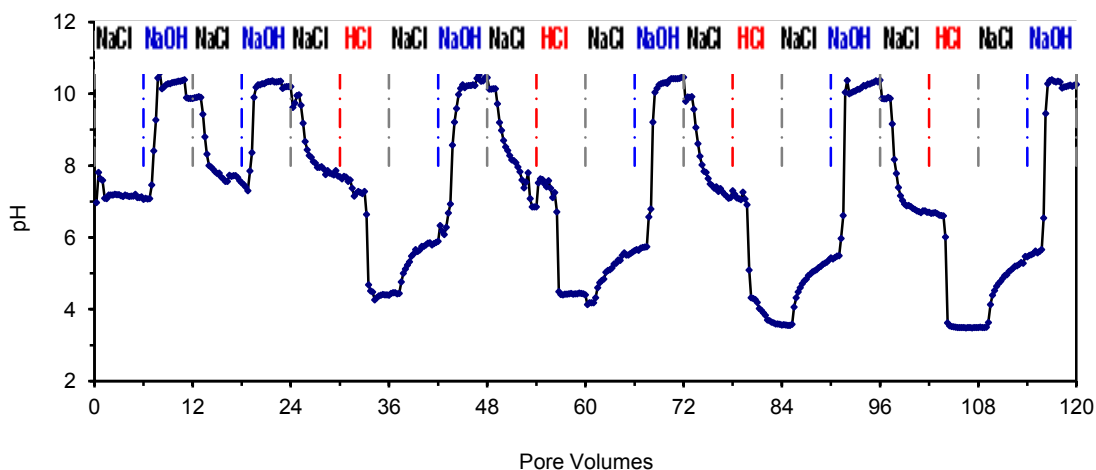


Figure 5. The fluctuations in pH over time, expressed in PV, during the HCl/NaOH test. The vertical lines indicate the beginning of an injection with NaCl in grey, NaOH in blue, and HCl in red.

Phase II, started with the NaCl buffer, from 24-30 PV, releasing the baseline of less than 3 mg/L. The baseline refers to the 3 mg/L turbidity line that was released when NaCl was added to the column, to which the results were compared. At 30 PV, the first cycle with HCl was introduced into the sand column. There was no noticeable release of colloids with a measured turbidity of less than 2 mg/L. This is not surprising because if the hypothesis is correct the acid will just break the inner bonds of the particle and the grain, not remove the surface colloids from the system. This turbidity continued on through the injections of NaCl, from 36-42 PV. When the first dose of NaOH came in phase II there was an instantaneous release of a high quantity of clay colloids. The peak of this dose reached 925 mg/L; this peak was over four times higher than that of the first dose before HCl was added to the system. The NaOH released a total of 206 mg of colloids.

The first NaCl injection of the second cycle continued releasing colloids from the previous cycle. The first turbidities in this injection were over 76 mg/L and never dropped below 2 mg/L. The second cycle of NaOH added after the HCl treatment released a total mass of 118 mg of colloids, significantly smaller than that of the first round but still an adequate amount. The third cycle resulted in a discharge of 85 mg of colloid, while the fourth cycle only produced 15 mg of colloids. For the last three cycles, the NaCl and HCl turbidities were not expressed separately because the readings stayed close to the baseline rates.

The turbidity results from phase I showed that treating a sand medium with 1.0 mM NaOH at a pH of 11 could release a significant amount of surface colloids. The original dose of NaOH was able to remove the weakly bonded colloids with electrostatic conditions produced by its higher pH. The turbidity in the second round of phase I was approximately half of the first round because it was removing a portion of the remaining weakly bonded colloids. It is believed to be the remaining portion of colloids in the first layer of surface particles, compared to a layer closer to the grain surface, because when looking at the first injection of NaOH the turbidity has a tailing trend. This suggests that if the NaOH injection continued more colloids would have been released because there were still weakly bonded colloids on the outer surface.

Once phase II began and HCl was introduced to the system, the HCl was able to reduce the bonding strength of the originally strongly bound colloids. The NaOH was then able to mobilize the remaining colloids and flush them out of the sand column. The results suggest that each cycle of HCl loosened the bonds of the outermost layer of

colloids. The NaOH was then able to remove this layer until multiple layers of surface colloids were removed and the distinct feature of silicon dioxide,  $\text{SiO}_2$ , quartz could be seen (Figure 6). The XRD analysis identified kaolinite, muscovite, and quartz at the three major minerals in the samples. These three colloidal minerals are among the most common found in soils.

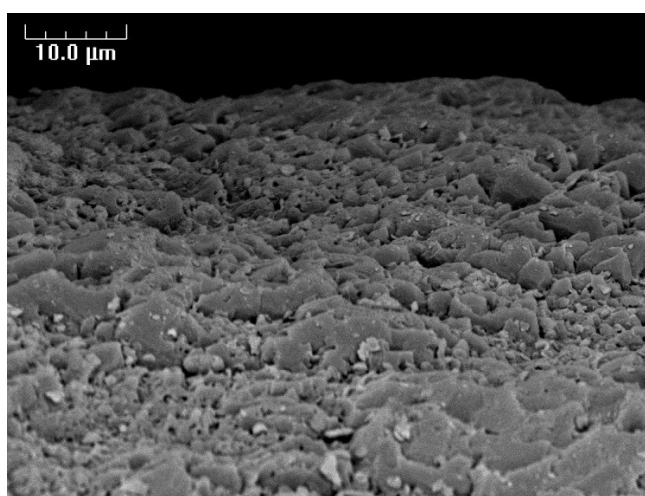


Figure 6. A SEM micrograph of the sand after the HCl/NaOH treatment.

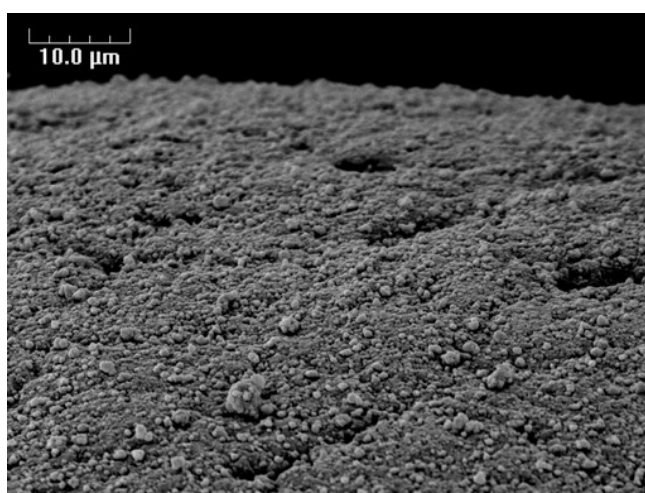


Figure 7. A SEM micrograph of the untreated sand.

Figure 7 is the SEM image of the untreated sand grains and shows how their surface was thoroughly covered in layers of clay colloids. The colloids are layered on the surface of the grain, which explains why all the colloids were not able to be removed at once. The acid could only affect the outermost layer of colloids and therefore exterior colloids seem to be the only particles that were available for the  $H^+$  to interact with. That was why multiple cycles of an acid and base treatment seemed imperative to thoroughly release all the surface colloids. A control test was run to see if using a stronger acid, 1 N HCl for a longer duration would affect the bonds of the underlayer colloids. The test confirmed that both the extended time and stronger acid did little to break the bonds in the lower level surface particles.

The HCl/NaOH treatment cycles also confirmed that raising the pH of eluent to approximately 8.0 could break the electrical double layer repulsive force and let the surface colloid be released more effectively; though colloids were released at a pH as low as 6.7. Figures 4 and 5 show the trend that turbidity begins to rise when the pH gets above 8. This is a positive result because it means only a weak base is needed to release surface colloids and weak bases are more easily found in nature.

### **3.1.2 Acidity Consumption**

The acidity of phase I was not recorded because there was no acidity added to the system until phase II. The increase in acidity became apparent after the first dose of HCl. The initial increase in acidity did not occur until sometime after 3 PV or 6 hours (Figure 8) when HCl was introduced to the sand column. This is 12 PV longer than the

hydraulic retention time, which means that during the first two PV or 4 hours of the cycle the acidity was almost completely consumed. The acidity then jumps up to approximately 26-27 mg/L where it remains until about 0.5 pore volumes into the NaCl injection. It is important to discuss the pH jump in the first cycle of HCl. When the HCl was initially injected into the sand column it had a pH of 3.3 however the effluent collected while the test was running showed approximately 4.4. The consumption of  $H^+$  could be the factor behind both the increase in pH and the lag in acidity breakthrough. The total acidity consumed in the first dose of HCl was 0.174 m mole.

The second injection of HCl also experienced a lag in acidity breakthrough. This lag, however, was only about half as long as in the first HCl injection. The second round of HCl only consumed 0.108 m mole of acidity. The third and fourth injections did not show any significant lag behind the hydraulic front. Though the first two injections reached their acidity breakthrough peaks at different times, each of the four injections did show a peak around 27 mg/L. It is natural to see a decrease in the acidity consumed in each of the cycles because there should be fewer bonds to break and replace as the outer particles are removed.

The next step was to compare the colloids released versus acidity consumed. Only the first three rounds of the HCl treatment were used because the fourth only released a trivial amount of colloid and using the minimal colloid release could distort the findings. To make the comparison, the total mass of particles released was graphed against the corresponding acidity consumed. From this data, a linear correlation was



obtained (Figure 9). Using the graph, a formula was derived that showed that for every one m mole of  $H^+$  consumed up to 1175 mg of colloids could be released.

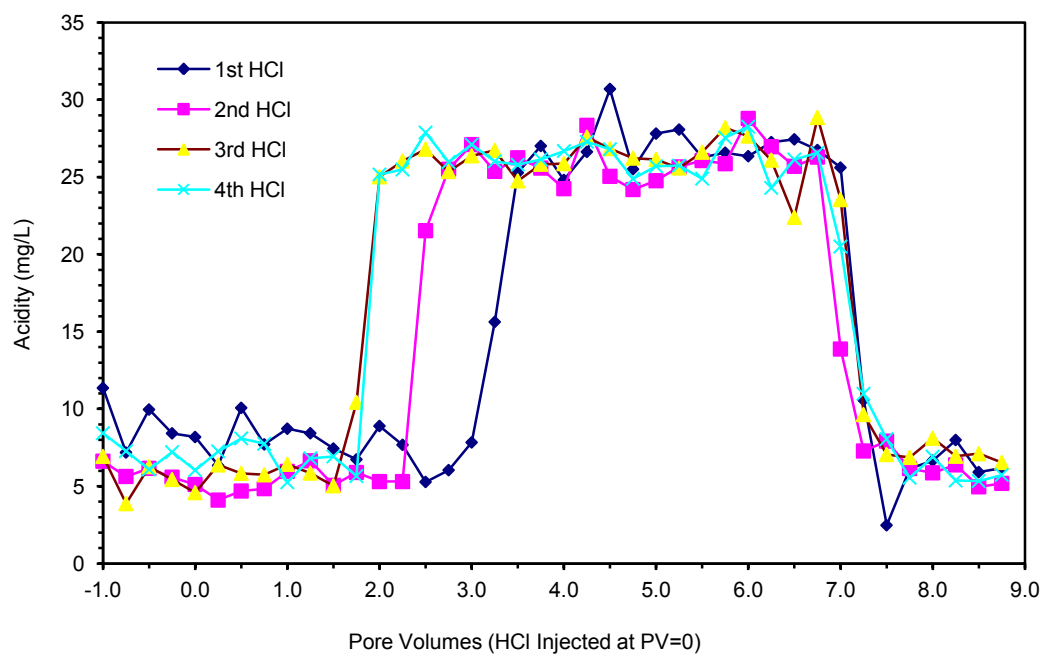


Figure 8. The acidity in the effluent in relation to time expressed in pore volume. The injection time of the HCl is offset to when PV is 0 so that the four cycles of HCl could be compared.

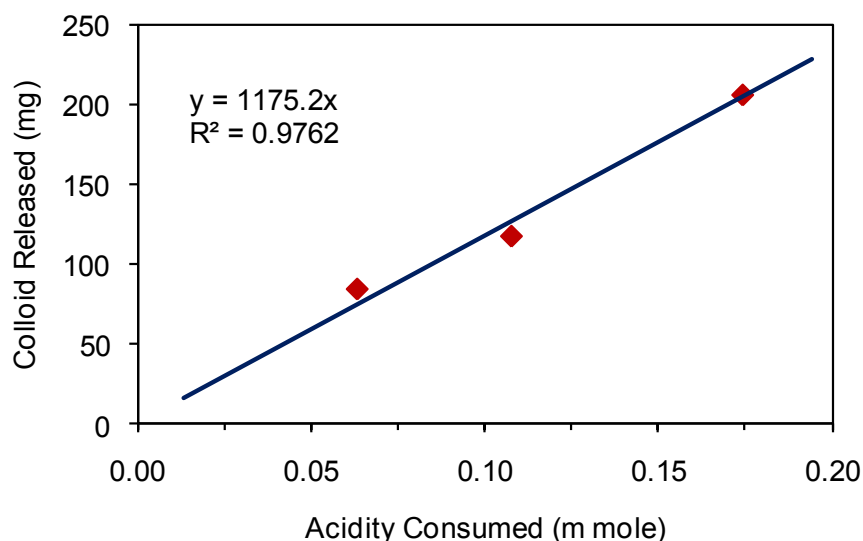


Figure 9. The release of colloids has a linear correlation to the consumption of acidity.

### 3.1.3 Cation and Anion Release

During phase I there were no significant quantities of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  released in the effluent of the column. A small amount of  $\text{K}^{+}$  was released, while  $\text{Na}^{+}$  did not have a change between initial and final concentration. When phase II began, the amounts of cations released began to increase drastically. The results from the first injection of HCl showed a dramatic increase in  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  cation concentrations, around 0.09 mM and 0.15 mM respectively (Figure 10). The increase in these cation releases corresponds to the  $\text{H}^{+}$  consumed in the column. When  $\text{H}^{+}$  was consumed an equivalent amount of cations were released (Figure 11). This is because two  $\text{H}^{+}$  ion were consumed to sever the bonds of the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  to the grain surface. This occurs to maintain an aqueous ionic balance in the sand column. These elevated cation releases lasted for 2 PV or 4 hours. There was no significant amount of  $\text{Na}^{+}$  throughout any of phase II.

During the second injection of HCl both the acidity consumed and the release of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  both decreased slightly. The main difference between the first injection of HCl and the second injection of HCl is that the  $\text{K}^{+}$  cation release increased. The third and fourth injections followed the decreasing trend in both acidity consumed and cations released. Figure 10 displays that  $\text{Ca}^{2+}$  consistently had the highest concentration releases, followed closely by  $\text{Mg}^{2+}$ . These results show that  $\text{H}^{+}$  was primarily consumed to aid in the removal of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  cations.

This study suggests that  $\text{H}^{+}$  could be more effective than  $\text{Na}^{+}$  as an ion to replace  $\text{Ca}^{2+}$  during ion exchanges in the soil. This could be because of the much smaller size of  $\text{H}^{+}$  and its ability to permeate into interstitial spaces between particles.  $\text{Na}^{+}$ , however, is much closer in size to  $\text{Ca}^{2+}$  and two  $\text{Na}^{+}$  ions are needed to replace one  $\text{Ca}^{2+}$ . This could be an obstacle if soil is not being inundated with a solution with a high  $\text{Na}^{+}$  concentration as studied in Wan et al. (2004).

The total concentration of cations released was calculated by summing the  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^{+}$  releases together. It can be seen then that the initial spike in acidity consumed corresponds with the initial spike in cations release, but it is important to note that cation concentration continues to be released for approximately 6 PV after acidity has dropped to its baseline (Figure 11).

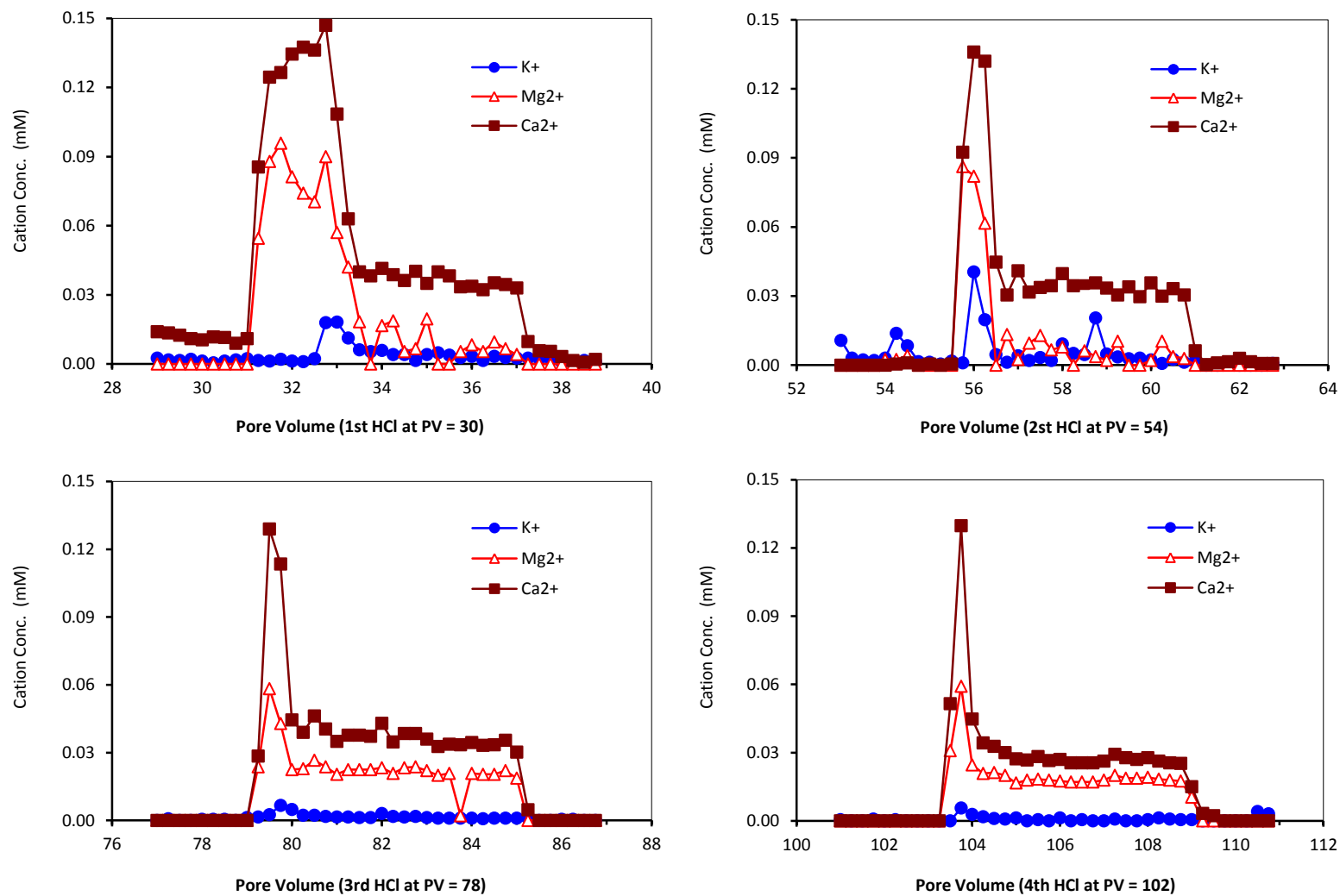


Figure 10. The cation concentration released during the HCl treatments over a time course expressed in pore volume.

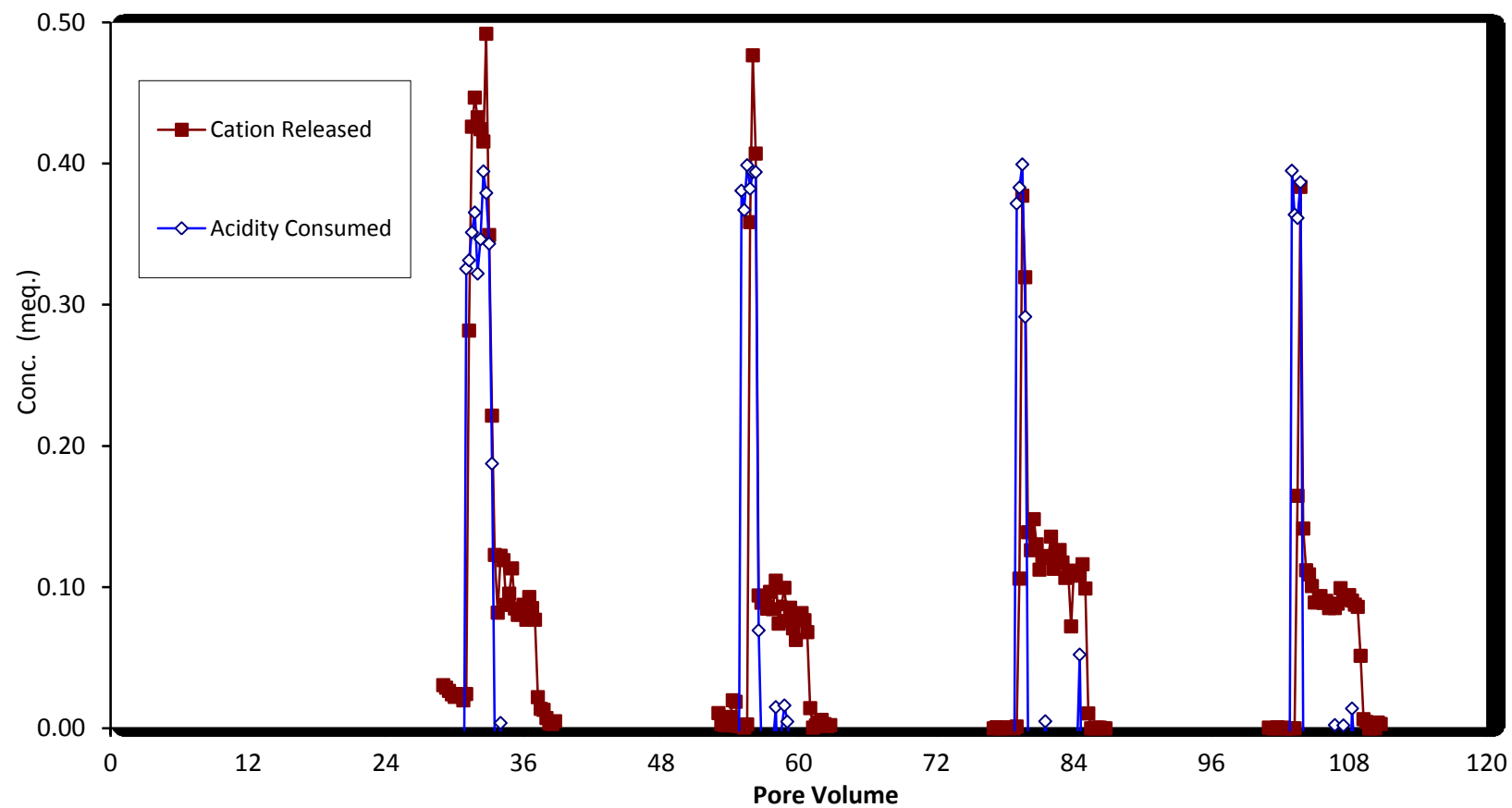


Figure 11. The total concentration of cations released and acidity consumed over a time course expressed in pore volume.

## 3.2 Citric Acid Test Results

### 3.2.1 Turbidity Release

The citric acid tests were conducted with the similar methods and material as the HCl tests. Though the results of both the citric and hydrochloric acid tests were similar, there were important differences. During the first injection of NaCl, from 0 to 6 PV, the turbidities measured in the effluent were trivial and only ranged between 2 to 4 mg/L. When the first round of NaOH, from 6 to 12 PV, was introduced into the system there was an immediate release of colloids. The release had an initial steep spike climbing to 236 mg/L that quickly subsided; by the end of the injection the turbidity had dropped below 40 mg/L. These rates were significantly higher than those of the HCl test. This could have occurred due to the initial condition of the sand. When the next injection of NaCl came, from 12 to 18 PV, the turbidity returned to below 3 mg/L. The second dose of NaOH, from 18-24 PV, released an intermediate quantity of colloids. The peak turbidity for this round only reached 33 mg/L. The total mass of colloids released from this phase was 115 mg. This mass was higher than the HCl test which only had a total colloid mass released of 84 mg. Figures 12 and 13 show the changes in turbidity and pH, respectively, compared to time shown in pore volume. The vertical lines indicate the beginning of an injection with NaCl in grey, NaOH in blue, and citric acid in red.

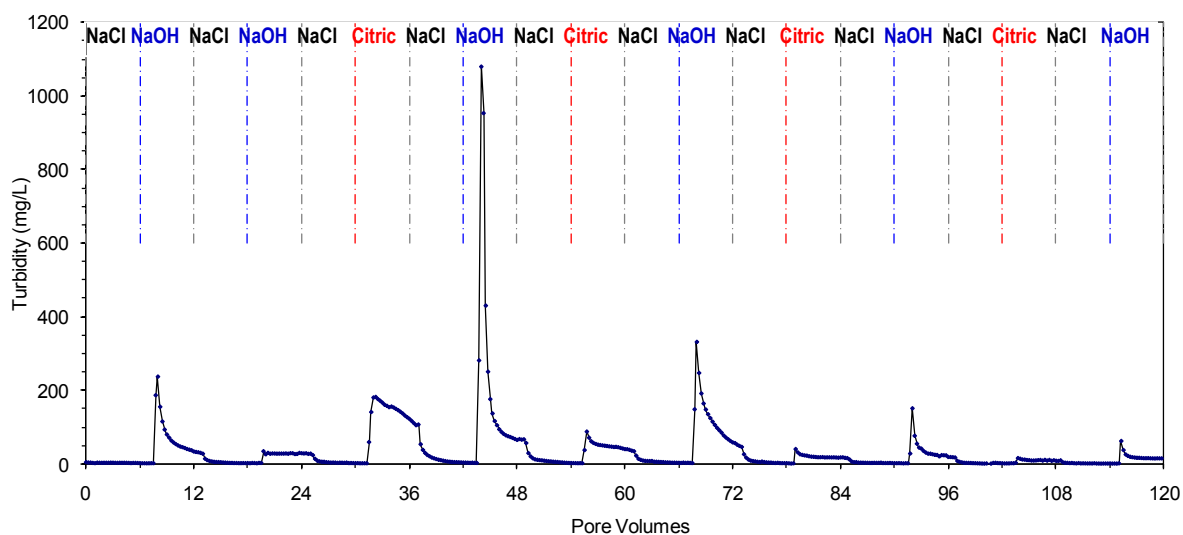


Figure 12. Turbidity measured in mg/L over time, expressed in PV, during the citric acid test. The vertical lines indicate the beginning of an injection with NaCl in grey, NaOH in blue, and HCl in red.

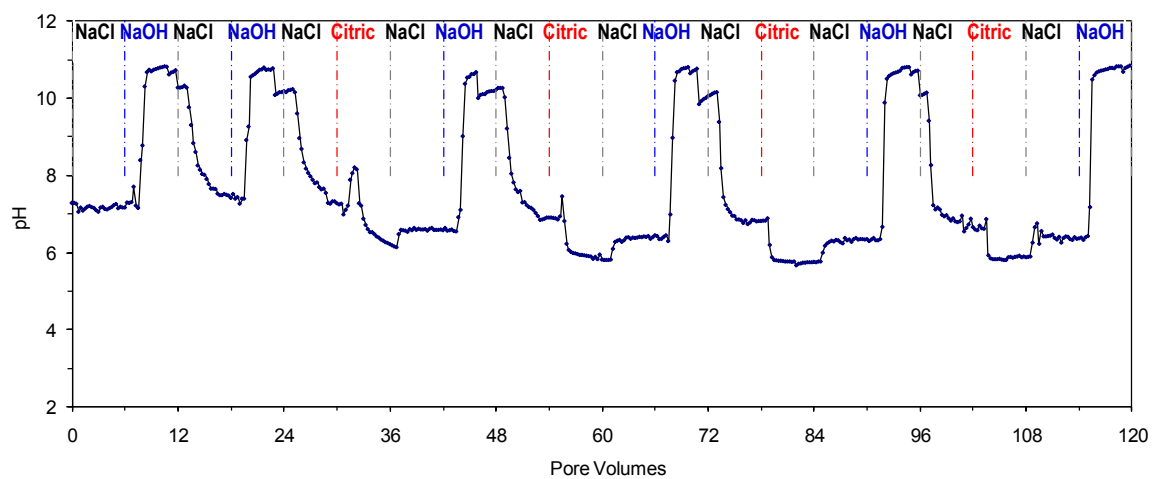


Figure 13. The fluctuation in pH over time, expressed in PV, during the citric acid test. The vertical lines indicate the beginning of an injection with NaCl in grey, NaOH in blue, and HCl in red.

Phase II, started with the NaCl buffer, from 24-30 PV, releasing the baseline of less than 3 mg/L. At 30 PV, the first cycle with citric acid was introduced into the sand column. The turbidity immediately jumped up to over 180 mg/L, by the end of the injection the turbidity was still over 120 mg/L. This tailing effect of the turbidity continued on into the injections of NaCl which never reached below 3 mg/L, from 36-42 PV. When the first dose of NaOH came in phase II there was again an instantaneous release of high quantity of clay colloids. The peak of this dose reached 1079 mg/L, almost five times higher than that of the first dose before citric acid was introduced. This showed that the higher pH of the citric solution and weaker acid did not affect the treatment's ability to mobilize surface colloids.

### **3.2.2 Acidity Consumption**

As a reminder, the acidity of phase I was not recorded because there was no acidity added to the system until phase II. It was apparent that large quantities of acidity were consumed in the first injection of citric acid (Figure 14). There are multiple differences between acidity results in HCl and citric acid. The first item to notice is that citric acid has a much higher peak acidity ranging from about 37-38 mg/L. Next, the first injection of citric acid never reaches this peak acidity; it only climbs to about 24 mg/L. This means that a substantial quantity of the first cycle of citric acid was consumed. Like HCl the first real increase in acidity came around 3 PV, which means that during the first two PV of the cycle, the acidity of citric acid was almost completely consumed. The acidity then slowly climbs up to the first injection's maximum of 24 mg/L. It can be observed that when the acidity was consumed during the first injection



there is an apparent increase in pH after the acid was introduced. The pH of the effluent increased to more than 8. In cases like this one, a base treatment might not be needed to aid in the removal of the colloids because the  $H^+$  consumption was able to raise the pH enough. The consumption of  $H^+$  could be the factor behind both the increase in pH and the lag in acidity. The total acidity consumed in the first dose of HCl was 0.174 m mole.

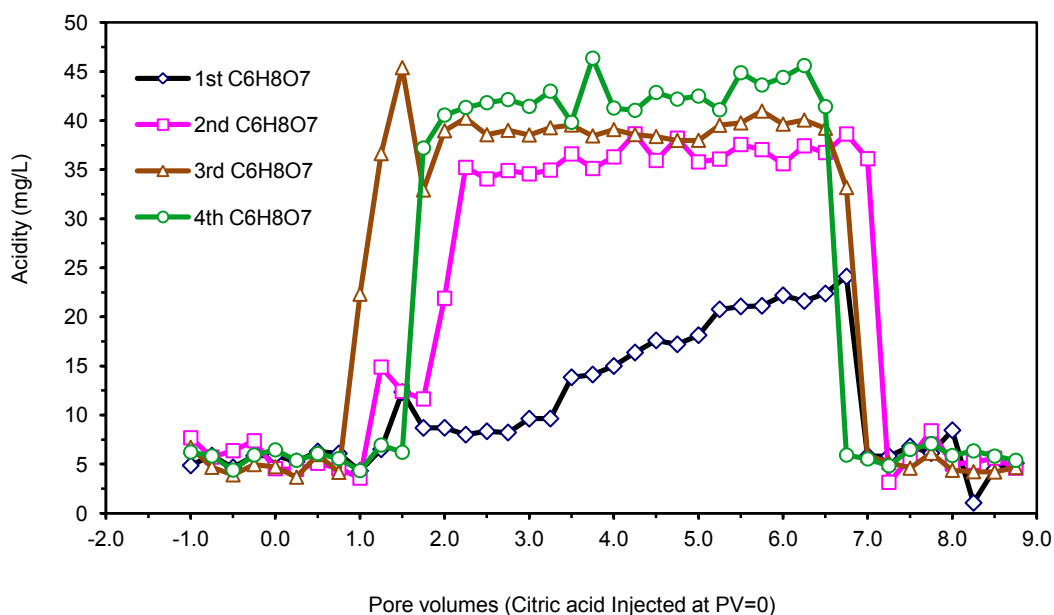


Figure 14. The acidity in the effluent in relation to time expressed in pore volume. The injection time of the citric acid is offset to when PV is 0 so that the four cycles of citric acid could be compared.

The second injection of citric acid also revealed a slight lag in acidity. This lag, however, was not as long as the first injection and the acidity consumed in the second injection was much less than that of the first. The lag time for the third cycle was longer than the second cycle but the acidity is even higher. This shows that even less acidity

was consumed in the third cycle. The fourth cycle as expected had only a slight lag time but did have a higher acidity. As seen with the HCl, the consumption of acidity is lowered after each cycle.

### 3.2.3 Cation Release

During phase I there were no significant quantities of  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  discovered in the effluent of the column. A small amount of  $\text{K}^{+}$  was released, while  $\text{Na}^{+}$  concentration did not change from the carboy to the test tube. When phase II began the amount of cations released began to increase drastically. The results from the first injection of citric acid showed a drastic increase in  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  cation concentrations, as can be seen in Figure 15. The increase in these cation releases corresponds to when the  $\text{H}^{+}$  was consumed in the column. These elevated cation releases lasted the majority of the first cycle. There was no significant amount of  $\text{Na}^{+}$  throughout any of phase II.

During the second injection of citric acid both the acidity consumed and the release of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  both decreased slightly. The main difference between the first injection of citric acid and the second injection of citric acid is that the  $\text{K}^{+}$  cation release increased and continued to increase throughout the remaining cycles.

Overall the trends in cation and anion release are similar to the HCl test (Figure 16). The main difference between citric acid and HCl is the  $\text{K}^{+}$  ion release observed in the fourth cycle of citric acid treatment. This could be because there was  $\text{K}^{+}$  sealed by the surface colloid coating so after the initial citric acid removed much of the surface clay coating, the underlying  $\text{K}^{+}$  could be exposed and subsequently released in the 4th cycle.

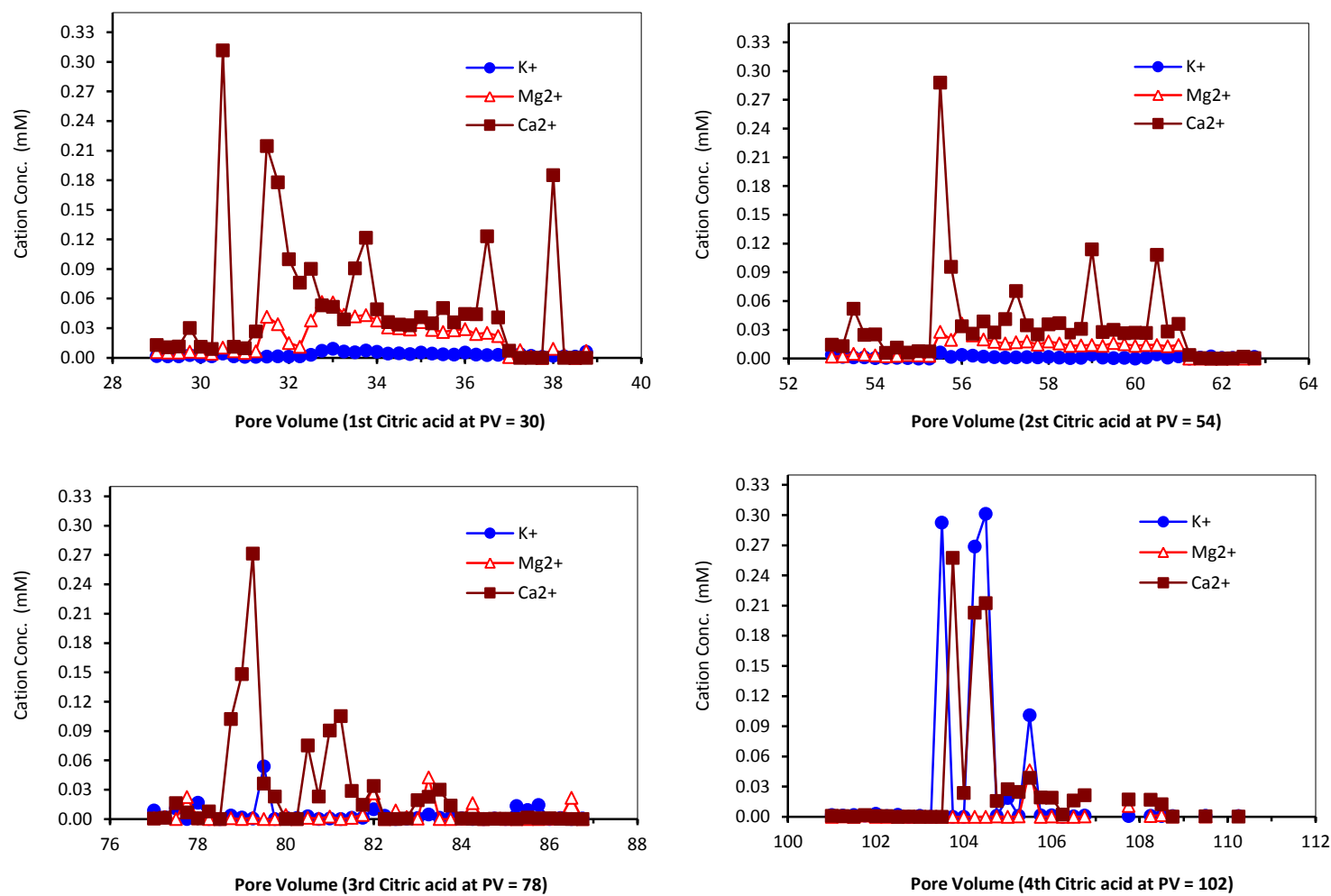


Figure 15. The cation concentration released during the citric acid treatments over a time course expressed in pore volume.

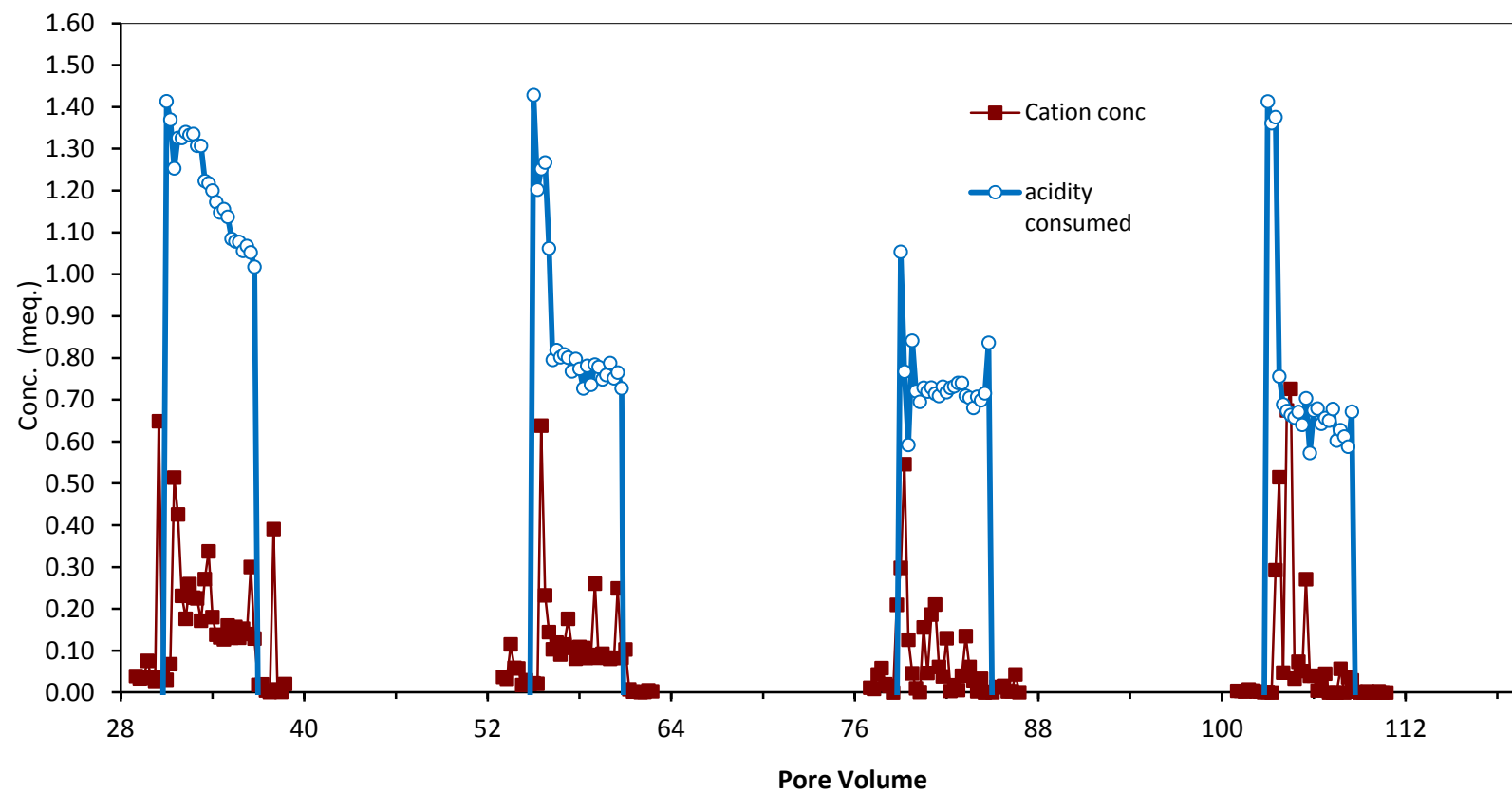


Figure 16. The total concentration of cations released and acidity consumed over a time course expressed in pore volume.

### 3.3 Hypothesis Results and Models

Figure 17 displays a conceptual model that demonstrates how the cyclical process removed loosely bound particles and  $H^+$  is substituted for the  $Ca^{II}$  which is released as  $Ca^{2+}$ . The natural sand in the column was cyclically treated with weak acid and base solutions to increase mobilized colloids. The loosely bound particles could be removed by rinsing with a weak alkaline solution to create an electrostatic condition favorable for colloid mobilization. A weak acid solution was injected into the column. A dynamic protonation/ deprotonation process could then allow  $H^+$  to transfer from  $H_2O$  molecular sites and the sands surface absorption sites.  $H^+$  size aided the ion in infusing deep into crevices. The  $Ca^{2+}$  and  $Mg^{2+}$  ions that were chemically bonded to the natural grain surface were replaced by  $H^+$ . This substitution allowed for a release of over 1 kg of surface clay per 1 mole of  $H^+$  that was consumed. The colloids were layered on the grain surface and the  $H^+$  could only react with the outer colloids. Therefore, multiple cycles of acid/base had to be injected so that the colloids could be removed layer by layer.

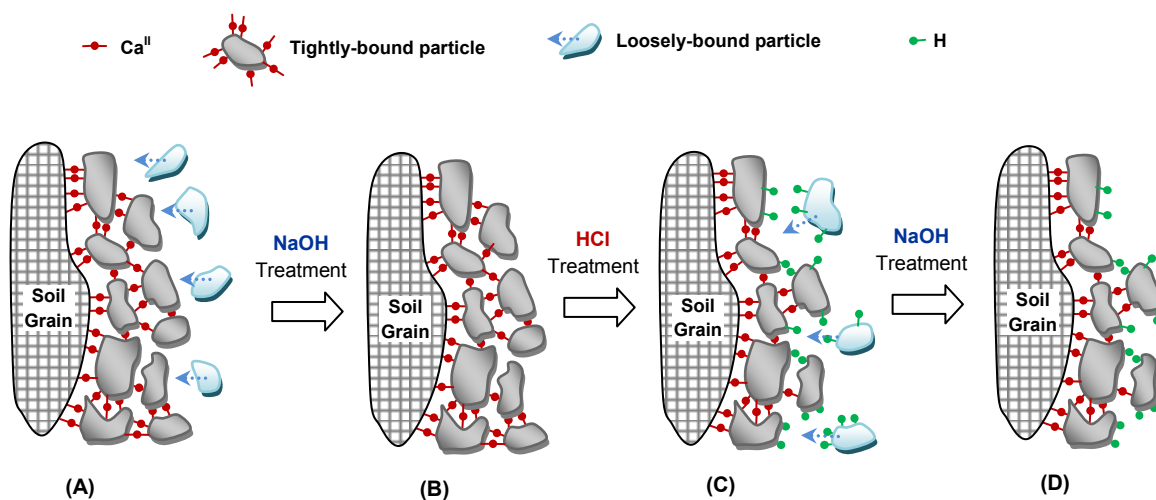


Figure 17. Schematics of the role of  $\text{H}^+$  in releasing colloid from the adhered surface. (A) Original sand surface covered with multiple layers of clay particles. Some of outer-sphere particles (in blue color) are loosely bound by attractive forces (e.g., van der Waals and other attractive electrostatic force); most of particles are tightly bound by chemical bonds (e.g.,  $\text{Ca}^{II}$  bonds); (B) With negative surface charge induced or strengthened by an elevated pH, the resultant repulsive force can overcome attractive forces and expel the loosened particles; (C) In the presence of  $\text{H}^+$ ,  $\text{Ca}^{II}$  can be replaced by two  $\text{H}^+$ . As  $\text{Ca}^{II}$  is replaced by two  $\text{H}^+$ , bonds are severed and the particle is loosened (but may still be held by a net attractive force); and (D) Repeated treatments of acid and base could remove surface-adhered colloids layer by layer.

## 4. CONCLUSION

### 4.1 Summary

Colloid mobilization in the subsurface environment has been increasingly recognized as a potential contributor to accelerating subsurface contaminant transport. In previous studies, it had been found that contaminants could be transported faster and further through the soil matrix when attached to a mobilized colloid particle. Over the years, various factors that may affect colloid mobilization have been extensively investigated, among which the role of pH has been repeatedly studied as a major contributor to colloid mobilization, if not the main contributor.

Through all the studies, the role of acidity has been inadequately researched in the area of colloidal science. Acidity, which denotes the amount of  $H^+$  available for reaction, has been over shadowed by the prominent role of pH, the concentration of  $H^+$ . This study was performed to investigate the important chemical role of acidity in mobilizing colloids from a natural sand grain surface and to establish a quantitative relationship between the amount of acidity consumed and colloids released in a system.

A sand column experiment was performed, where the column was cyclically eluted with weak acid and base solutions to increase colloid mobilization. The experiment demonstrated that a simple weak base could remove loosely bonded surface colloids but only those on the outer layer of the surface. The acid treatment could then sever the stronger chemical bonds by replacing  $Ca^{II}$  with two  $H^+$  ions and releasing  $Ca^{2+}$  ions. Though the smaller size of  $H^+$  suggest that it could be more effective than  $Na^+$  in ion exchange,  $H^+$  was still not able to penetrate to the under lying colloidal layers in a

single acid treatment. This is why cyclical elution of the sand column was needed to optimally remove surface colloids. Furthermore, the subsequent base treatments could expand remaining particle gaps to aid in  $H^+$  penetrating and releasing more chemically bonded colloids.

The study found that for the HCl test that 1 m mole acidity consumed could release 1175 mg of clay compared to 1021 mg clay released when using citric acid. In other words, the ratio of 1 m mole  $H^+$  to approximately 1 g of clay can be estimated from this study. Citric acid is a naturally found organic acid that plants produce through metabolism of the citric acid cycle. If 1 mole of citric acid, 3 mole  $H^+$ , was found in the environment it could cause 3 kg of clay colloids to be mobilized in the subsurface.

This study implies that acidity could have played a more important role in naturally occurring colloidal process than previously known. Though HCl is not found in natural systems, citric acids and other organic acids are common in these environments. This study can be used as a building block in understanding and estimating the role of acidity in mobilizing natural subsurface colloids. Additionally, the exchanges between acidity and labile Ca and Mg are likely to play a role in depositing clay colloids. Most importantly, this study demonstrated how chemicals with similar pH but different acidity could impact colloid mobilization differently. This could explain some discrepancies in previous results in literature that simply regarded the role of pH in colloid mobilization. Most importantly this study could aid in estimating transport in a subsurface environment that has been impacted by natural acidity.



## **4.2 Study Limitations**

The influent solutions that were stored in the carboys were not capped and the headspace filled with N<sub>2</sub> gas. This practice should have been used to minimize the influent solutions ability to react with the CO<sub>2</sub> in the air or volatilization of citric acid. This artifact has no major implication to the results.

The sand used during the study (0.25-0.42mm) is at least an order of magnitude larger than typical clay particle (0.001mm). This creates the possibility that the transport of clays could have been changed through size exclusion. However, upon further inspection during disassembling the sand column, no evidence of clay trapping was found.

## **4.3 Recommendations**

It is recommended that further studies be performed to describe more completely the impact of natural acidity and its relationship with cation release on colloid mobilization. Additional organic acids can be tested and compared to the results of the citric acid results to see if colloid release is consistent with the results from our study. Furthermore, additional sand sizes should be tested to see how the pore size of different soils will affect the effectiveness of acidity rinses on colloid release.

## **4.4 Final Evaluations**

This study is a first step in shedding light on the role of acidity facilitated colloid mobilization. It demonstrates that the roles of pH and acidity on colloidal transport should be differentiated and that acidity, though previously overlooked, might be playing

a more dominate role in environmental colloidal processes. These findings could prove beneficial when working on improvement with contaminated groundwater and soil management.

## REFERENCES

- American Public Health Association (APHA), American Water Works Association (AWWA), and Water Environment Federation (WEF) (1998), *Standard Methods for the Examination of Water and Wastewater*, 20<sup>th</sup> edition. Washington, DC, American Public Health Association.
- Francis, E. (2003) Brønsted-Lowery Concept. Clackamas Community College, 13 April 2011, <http://dl.clackamas.edu/ch105-04/bronsted.htm>.
- Bhattacharjee, S., M. Elimelech, and M. Borkovec (1998), DLVO Interaction between Colloidal Particles: Beyond Derjaguin's Approximation, *Croatica Chemica Acta*, 71(4), 883-903.
- Bunn, R.A., R.D. Magelky, J.N. Ryan, and M. Elimelech (2002), Mobilization of Natural Colloids from an Iron Oxide-Coated Sand Aquifer: Effect of pH and Ionic Strength, *Environ. Sci. Technol.*, 36(3), 314-332.
- Corapcioglu, M.Y. and H. Choi (1996), Modeling Colloid Transport in Unsaturated Porous Media and Validation with Laboratory Column Data, *Water Resour. Res.*, 32(12), 3437-3449.
- Derjaguin, B., and L. Landau (1941), Theory of the Stability of Strongly Charged Lyophobic Sols and of the Adhesion of Strongly Charged Particles in Solutions of Electrolytes, *Acta Physico Chemica URSS*, 14, 633-662.

- Flury, M. and H. Qui (2008), Modeling Colloid-Facilitated Contaminant Transport in the Vadose Zone, *Vadose Zone J.*, 7, 682-697.
- Hiemenz, P. and R. Rajagopalan, 1997, *Principles of Colloid and Surface Chemistry*, New York: Marcel Dekker.
- Hoek, E.M.V., and G.K. Agarwal (2006), Extended DLVO Interactions between Spherical Particles and Rough Surfaces, *J. Colloid Interface Sci.*, 298, 50-58.
- Kersting, A.B., D.W. Efur, D.L. Finnegan, D.J. Rokop, D.K. Smith, and J.L. Thompson (1999), Migration of Plutonium in Ground Water at the Nevada Test Site. *Nature*, 397, 56-59.
- Kolakowski, J.E. and E. Matijevic (1979), Particle Adhesion and Removal in Model Systems. *J. Chem. Soc., Faraday Transactions 1: Physical Chemistry in Condensed Phases*, 75, 65-78.
- Lenhart, J.J., and J.E. Saiers (2003), Colloid Mobilization in Water-Saturated Porous Media under Transient Chemical Conditions, *Environ. Sci. Technol.*, 37(12), 2780-2787.
- Luty, B.A. and W.F. van Gunsteren (1996), Calculating Electrostatic Interactions Using the Particle-Particle-Particle-Mesh Method with Nonperiodic Long-Range Interactions, *J. Phys. Chem.*, 100 (7), 2581-2587.
- Nightingale, H.I., and W.C. Bianchi (1977), Groundwater Chemical Quality Management by Artificial Recharge, *Ground Water*. 15(1), 15-22.

- Puls, R.W., and R.M. Powell (1992), Transport of Inorganic Colloids through Natural Aquifer Material: Implication for Contaminant Transport, *Environ. Sci. Technol.*, 26(3), 614-621.
- Ryan, J.N., and M. Elimelech (1996), Colloid Mobilization and Transport in Groundwater, *Colloids Surf. A: Physicochem. Eng. Aspects*, 107, 1-56.
- Ryan, J.N., and P. Gschwend (1994), Effects of Ionic Strength and Flow Rate on Colloid Release: Relating Kinetics to Intersurface Potential Energy, *J. Colloid Interface Sci.*, 164, 21-34.
- Saiers, J.E., and G.M. Hornberger (1996), The Role of Colloidal Kaolinite in the Transport of Cesium through Laboratory Sand Columns, *Water Resour. Res.*, 32(1), 33-41.
- Saiers, J.E., and J.J. Lenhart (2003), Ionic-strength Effects on Colloid Transport and Interfacial Reactions in Partially Saturated Porous Media, *Water Resour. Res.* 39(9): 1256.
- Swartz, C. H., and P.M. Gschwend (1998), Mechanisms Controlling Release of Colloids to Groundwater in a Southeastern Coastal Plain Aquifer Sand, *Environ. Sci. Technol.*, 32, 1779-1785.
- Thamburaj, P.K. (2007), Known-to-Unknown Approach to Teach about Coulomb's Law, *J. Chem. Educ.*, 84 (3), 438-439.

Verwey, E., and J. Overbeek (1948), *Theory of the Stability of Lyophobic Colloids*, Elsevier, Amsterdam.

Wan, J., T. Tokunaga, E. Saiz, J. Larsen, Z. Zheng, and R. Couture (2004), Colloid Formation at Waste Plume Fronts, *Environ. Sci. Technol.*, 38, 6066-6073.

Yotsumoto, H. and R.H. Yoon (1993), Application of Extended DLVO Theory, *J. Colloid Interface Sci.*, 157, 426-433.

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