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Characterization of Materials for a Reactive Transport Model Validation Experiment: Interim Report on the Caisson Experiment

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Characterization of Materials for a Reactive Transport Model Validation Experiment:

Interim Report on the Caisson Experiment

M. D. Siegel,¹ D. B. Ward,² C. R. Bryan,² and W. C. Cheng³

Abstract

A transport-model validation experiment, involving the migration of fluid and tracers (Li, Br, Ni) through a six-meter-tall sand column (caisson), is being carried out for the Yucca Mountain Site Characterization Project. The surfaces of the sand grains have been examined by a combination of wet chemical, microscopic, and spectroscopic techniques. X-ray diffraction and bulk chemical studies suggest that the sand is predominantly quartz; however, electron microscopy, X-ray photoelectron spectroscopy and leaching studies suggest that the surface of the quartz sand is partially covered by thin layers of Fe-oxyhydroxide and Ca-Mg carbonate and by flakes of kaolinite.

Adsorption of nickel, lithium and bromide by the sand were measured using batch techniques. The batch adsorption experiments show that Br does not adsorb and that Li adsorbs relatively slowly and weakly in the neutral pH range. For the pH range relevant to the caisson experiment (7 – 8.5), under CO₂-free to partially-equilibrated conditions, the measured Li K_d s range from approximately 0.05 to 0.25 ml/g (5% – 20% adsorption). The degree of adsorption is slightly dependent on the pH; reaching a maximum at near-neutral pH. Li batch isotherm data indicate stronger adsorption at lower concentrations and fit a Freundlich isotherm satisfactorily.

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Small column experiments were conducted to study the transport of Li and Br in saturated sand. Breakthrough curves for Br show a retardation factor slightly less than 1, indicating a small amount of anion exclusion, and were satisfactorily modeled by the equilibrium linear-adsorption isotherm convective-dispersive model of the CXTFIT code. The Li pulses could be adequately modeled by an equilibrium convective-dispersive model only using "effective" K_d s that are smaller than the lowest values measured in the batch experiments. The "effective" K_d s, equilibrium K_d s, and Li sorption rate constants measured in the batch experiments, however, are consistent with the value of "effective" retardation factors predicted with the kinetic model of Kuhn and Peters (1981). In addition, a single-site kinetic Li sorption model using an equilibrium K_d (0.15 ml/g) and a sorption rate constant similar to those measured in the laboratory batch experiments, gave a reasonable fit ($r^2 = 0.911$) to the experimental data.

Ni adsorption by the sand is rapid and is strongly pH-dependent, showing no adsorption at pH 5 and near-total adsorption at pH 7 ($K_d > \sim 50$ ml/g). The location of the adsorption edge is independent of ionic strength and concentration of dissolved Ni; it is shifted to slightly lower pH in the presence of CO_2 and to slightly higher pH by the presence of Li. Ni adsorption edges for goethite and quartz, two components of the sand, were also measured. Ni adsorption on pure quartz is only moderately pH-dependent and differs in shape and location from that of the sand, whereas Ni adsorption by goethite is strongly pH-dependent. A triple-layer surface-complexation model developed for goethite provides a good fit to the Ni-adsorption curve of the sand. Attempts to model the adsorption characteristics of the bulk sand in terms of the properties of pure end-member components suggest that much of the sand surface is inert. The Ni adsorption mechanisms have not been unambiguously identified; however, this preliminary adsorption model provides an initial set of parameters that can be used in transport calculations.

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Executive Summary

Models used in performance assessment and site characterization activities related to nuclear waste disposal rely on simplified representations of solute/rock interactions, hydrologic flow fields and the material properties of the rock layers surrounding the repository. A crucial element in the design and application of these models is the validity of these simplifying assumptions. An intermediate-scale experiment is being carried out by Los Alamos National Laboratory and Sandia National Laboratories for the Yucca Mountain Site Characterization Project to demonstrate a strategy to test key geochemical and hydrological assumptions in performance assessment models. The experiment is being carried out at the Experimental Engineered Test Facility at Los Alamos Laboratory. It involves the detection and prediction of the migration of fluid and tracers through a 6 m high x 3 m diameter caisson filled with a porous medium. Tracers were chosen for the experiment based on a range of sorption behavior, potential use in future field experiments and presence in nuclear waste. This report describes the geochemical characterization of the porous medium and tracers that was carried out as part of the design and detailed characterization phases of the experiment.

The caisson is filled with Wedron 510 sand, a commercially available silica sand (Wedron Silica, Wedron, IL 60557). The surfaces of the sand grains have been examined by a combination of wet chemical, microscopic, and spectroscopic techniques. Although X-ray diffraction and bulk chemical studies suggest that the sand is predominantly quartz, other minerals are present in non-trivial amounts. Electron microscopy, X-ray photoelectron spectroscopy and leaching studies suggest that the surface of the quartz sand is partially covered by thin layers of Fe-oxyhydroxide and Ca-Mg carbonate and by flakes of kaolinite.

Adsorption of nickel, lithium and bromide by the sand were measured using batch techniques. The batch adsorption experiments show that Br does not adsorb and that Li adsorbs relatively slowly and weakly in the neutral pH range. For the pH range relevant to the caisson experiment (7–8.5), under CO₂-free to partially-equilibrated conditions, the measured K_d s for Li range from approximately 0.05 to 0.25 ml/g (5%–20% adsorption). The degree of adsorption is slightly dependent on the pH; reaching a maximum at near-neutral pH. Li batch isotherm data indicate stronger sorption at lower concentrations and satisfactorily fit a Freundlich isotherm.

Small column experiments were conducted to study the transport of Li and Br in saturated Wedron 510 sand. Breakthrough curves for Br show a retardation factor slightly less than 1, indicating a small amount of anion exclusion, and were satisfactorily modeled by the equilibrium linear-adsorption isotherm convective-dispersive model of the CXTFIT code. The Li pulses could be adequately modeled by the equilibrium convective-dispersive model using "effective" K_d s that are smaller than the lowest values measured in the batch experiments. The "effective" K_d s, and the equilibrium K_d s and sorption rate constants measured in the batch experiments, however, are consistent with the value of "effective" retardation factors predicted with the kinetic model of Kuhn and Peters (1981). In

addition, a single site kinetic model using a K_d (0.15 ml/g) and k (0.00012 min^{-1}) values similar to those measured in the laboratory batch experiments, gave a reasonable fit ($r^2 = 0.911$) to the experimental data. Given the non-linear sorption behavior determined from the batch studies, it is likely that a set of transport equations including non-linear effects would model the Li effluent curves better. However, even without explicit inclusion of these effects, this analysis probably provides reasonable order-of-magnitude estimates of the Li sorption and kinetic parameters.

Ni adsorption by the sand is rapid and is strongly pH-dependent, showing no adsorption at pH 5 and near-total adsorption at pH 7 ($K_d > \sim 50 \text{ ml/g}$). The location of the adsorption edge is independent of ionic strength and concentration of dissolved Ni; it is shifted to slightly lower pH with higher P_{CO_2} and to slightly higher pH by competition with Li. Ni adsorption edges for goethite and quartz, two components of the sand, were also measured. Ni adsorption on pure quartz is only moderately pH-dependent and differs in shape and location from that of the sand, whereas Ni adsorption by goethite is strongly pH-dependent. A triple-layer surface-complexation model developed for goethite provides a good fit to the Ni-adsorption curve of the sand. Attempts to model the adsorption characteristics of the bulk sand in terms of the properties of pure end member components suggest that much of the sand surface is inert. The Ni adsorption mechanisms have not been unambiguously identified; however, this preliminary adsorption model provides an initial set of parameters that can be used in transport calculations.

The results of this experiment could be used to establish criteria for the *validation* of transport models used in performance assessment calculations for Yucca Mountain. Validation of contaminant transport models involves comparison of calculated and observed tracer elution curves. The agreement between experimental data and model predictions will not be perfect because of uncertainties in tracer detection and the accuracy of model assumptions. Criteria for acceptable agreement must be formulated as part of a model validation test and must reflect various sources of uncertainty in the experimental and model designs. The caisson experiment described in this report was designed to provide well-controlled conditions and a well-characterized geomedia to allow separation of uncertainties due to chemical and physical processes. The objective of the materials characterization studies was to obtain sufficient information for comparison of the robustness of several different transport models in of light the uncertainties in geochemical data and models.

I. Introduction

Models used in performance assessment and site characterization activities related to nuclear waste disposal rely on simplified representations of solute/rock interactions, hydrologic flow fields and the material properties of the rock layers surrounding the repository. A crucial element in the design of these models is the validity of these simplifying assumptions. An intermediate-scale experiment is being carried out at the Experimental Engineered Test Facility at Los Alamos Laboratory by the Los Alamos and Sandia National Laboratories to develop a strategy to validate key geochemical and hydrological assumptions in performance assessment models used by the Yucca Mountain Site Characterization Project. The overall objectives and plan for the experiment are described in Siegel et al. (1992).

The experiment involves the prediction and detection of the migration of fluid and tracers through a 6 m high x 3 m diameter caisson filled with a porous medium. An overview of the mechanical design of the caisson, characterization of the hydraulic properties of the porous medium and a description of transport calculations used in the design are given by Springer et al. (1993) which is included as Appendix D to this report. This report describes the geochemical characterization of the porous medium and tracers that was carried out as part of the design and detailed characterization phases of the experiment.

The caisson is filled with Wedron 510 sand, a commercially available silica sand (Wedron Silica, Wedron, IL 60557). According to its bulk chemistry and mineralogy, Wedron 510 sand is nearly pure quartz, but preliminary characterization suggested that it contains at least three other chemically reactive components: carbonate, iron oxyhydroxide, and kaolinite. Of particular interest are several questions related to the nature of these minor phases: 1. What role do they play in the overall sorption behavior of the sand? 2. Are the minor phases present as surface coatings or discrete mineral grains? 3. What will be the effects of dissolution of the quartz and the minor minerals on the chemical compositions of the pore water and mineral surfaces and on the behavior of the tracers?

Choice of tracers for the caisson experiment was based on geochemical, regulatory and programmatic considerations (Siegel et al., 1992; Siegel et al., 1993). Such constraints are related to specific conditions of the test site and to available technology for monitoring the fluid flow and tracer migration, and include:

1. The need to ensure that the test will not present a hazard to the environment;
2. The requirement that the travel times for the water and conservative tracers are long enough to allow detection with sufficient resolution for the model comparison (approximately 1 to 4 days); and

3. The requirement that the travel times for the reactive tracers are short enough to allow detection before winter weather makes monitoring impossible (approximately 4 to 6 months).

In addition to these model-validation questions and site-specific criteria, the choice of tracers was constrained by instrumental considerations such as detection limits and precisions of analytical techniques used to measure tracer concentrations.

The suite of tracers, which spans a variety of chemical behaviors, includes: 1. bromide, a conservative tracer that can be used to track the movement of water in the caisson, 2. lithium, a tracer that forms relatively weak surface complexes, and 3. nickel, a transition metal that forms strong surface complexes with geologic materials. The results of the transport experiments with these tracers and minerals will have applications to other studies in the Yucca Mountain Site Characterization Project (YMSCP). Lithium is important because of its potential use in field experiments. Nickel is representative of transition metal radionuclides released from the structural components of the spent fuel rods in high-level waste and is considered an important waste element due its relatively low retardation in Yucca Mountain tuffs. The component minerals of the caisson sand (quartz, calcite and iron oxyhydroxides) are present in fractures in Yucca Mountain tuffs.

For the purpose of design of the caisson experiment, laboratory studies were conducted to examine the most important influences on sorption for each tracer. Based on a review of the literature and preliminary experiments (Siegel et al., 1992), it was proposed that sorption of lithium by the sand would be influenced by tracer concentration and that sorption of Ni would be sensitive to solution pH. Data describing these behaviors are presented in this report. In addition, interactions between the tracers and solution sampling equipment were studied to estimate uncertainties in measurements of the time-dependent tracer concentration profiles within the caisson.

This report describes progress in formulation of a framework that supports the long-term objectives of the Reactive Transport Model Validation project carried out at Sandia National Laboratories for the Yucca Mountain Project. The goal of this work is the validation of geochemical approximations used in models of reactive transport for performance assessment. The work presented in this report represents the product of the *design and detailed characterization* phases of the caisson experiment. During the latter phase, data describing the interactions between each tracer and the sand, among the tracers, and among the tracers and the other solutes in the pore water of the sand are being collected to allow application of several models of geochemical retardation. These include K_d s, sorption isotherms and surface-complexation constants. In the *predictive modeling* and *flow and transport test* phases of the caisson experiment, tracer transport will be calculated with these data with the LEHGC version of the HYDROGEOCHEM code (Yeh and Tripathi, 1990) and then compared to the results of the caisson experiment.

II. Methods

A. Overview

One of the primary objectives of this work is the identification and characterization of the minerals that will most strongly affect the transport of aqueous species of lithium and nickel in the caisson. The minerals will affect tracer transport either directly through adsorption or coprecipitation or indirectly through solid/solution reactions that alter the bulk chemistry of the solution in the caisson. In this study, the surface of the porous medium in the caisson (Wedron 510 sand from Wedron Silica Corp., Wedron, IL 60557) has been characterized by a variety of chemical, mineralogical, and physical methods. The properties of the mineral coatings that armor much of the surface of the sand grains may be very different from those of the minerals that make up the bulk of the sand. Such surface coatings may be only a few nanometers thick and are difficult to identify directly. Instead, their identities must be inferred from leachable components and reactions with species in solution. In order to compare the properties of the surface coatings to those of the underlying minerals, several cleaning procedures were employed to strip the sand of its coatings to varying degrees. These ranged from complete removal of all coatings, exposing a quartz surface, to selective removal of carbonate coatings, which leave clay and Fe-oxyhydroxide coatings intact.

Potentiometric titrations are used to determine equilibrium constants for surface deprotonation and for surface complexation of pure minerals with electrolyte cations. One of the long-term objectives of the study described in this interim report is to determine if these techniques are applicable to natural materials composed of mixtures of several minerals. This is being accomplished by comparing titration curves of the bulk sand, acid-stripped sand and individual components of the sand. In this study, Min-U-Sil 5 (US Silica Co., formerly Pennsylvania Glass Sand Corp.) is used as an α -quartz reference material.

Batch adsorption studies were conducted to characterize the adsorption properties of Wedron 510 sand with respect to Ni, Li, and Br, the elements of interest in the caisson experiment. The goals of these experiments were to determine the pH dependence of adsorption for these elements in the sand/aqueous electrolyte system, and to determine the adsorption properties of the several mineral phases in the sand. Adsorption of Ni by Wedron sand was examined under a variety of adsorption times, atmospheric conditions, Ni concentrations and concentrations of competing cations. Adsorption experiments were also carried out on a quartz standard (Min-U-Sil 5) and synthetic goethite to examine the potential importance of these phases to Ni adsorption.

The investigations described in this report included microscopic and surface characterization studies, dissolution studies, sorption and solubility studies, and transport studies. They are classified in Table 1 according to the analytical methods used and the type of information provided.

Table 1. Summary of characterization studies (acronyms are defined in the subsection for each method)

Type of study	Type of information
<i>Mineralogic and Surface Studies</i>	
Optical Microscopy	Mineralogy Physical: grain morphology Physical/chemical: observations of colors of surface coatings
Sieving	Particle-size distribution
XRD	Mineralogy
SEM	Physical morphology
SEM/EDS	Chemical composition of outer $\sim 1 \mu\text{m}$ of grains
BET	Surface area
XPS	Chemical composition of outer $< 5 \text{ nm}$ of grains
<i>Dissolution Studies</i>	
HF Dissolution	Bulk chemical composition
Selective Leaching in Batch Systems	Surface chemical composition
Selective Leaching in Unsaturated Column	Surface chemical composition
<i>Potentiometric Titrations</i>	
Batch and Continuous Titrations of Slurries	Acidity and complexation strength of surface sites of solid
<i>Solubility and Adsorption Studies</i>	
Batch Solubility	Solubilities of phases precipitating from batch systems
Batch Adsorption	K_d s or surface complexation constants; effects of competition and complexation on adsorption
Isotherm	Isotherm parameters for nonlinear or linear adsorption
Kinetic	Rates of adsorption reactions
<i>Transport Studies</i>	
Column studies	Physical parameters: dispersivity, porosity Chemical parameters: retardation factors, reaction rate constants

B. Mineralogic and Surface Analysis

The mineralogy of the Wedron 510 sand was characterized by powder X-ray diffraction with a Scintag diffractometer. Morphologies of sand grains and surface coatings were examined by petrographic microscope and scanning electron microscopy with energy dispersive analysis. The surface area was measured with the BET method (Brunauer et al., 1938).

Both untreated and acid-leached grains of Wedron 510 sand were examined by X-ray photoelectron spectroscopy (XPS). Mounts were prepared by densely packing grains on a platform coated with double-sided tape; samples were exposed to Al K α X-rays under vacuum. The methods are described in more detail in Appendix A of this report.

For surface and potentiometric studies described below, acid-leached samples were prepared by boiling raw Wedron 510 sand or Min-U-Sil 5 quartz in 6 N HCl for 4 h to clean surfaces of all carbonate and Fe-oxyhydroxide coatings. After cooling, the supernatant solution was decanted, and the samples were rinsed repeatedly with air-saturated water (conductivity > 10 M Ω before adding air) until the pH of the rinse water reached 5.6. Finely powdered samples were stored as suspensions in deionized water, whereas granular samples were dried. Results of the mineralogic and surface studies are described in Section III.A of this report.

C. Dissolution Studies of Bulk and Surface Composition

A representative ~100 g sample of Wedron 510 sand was obtained with a splitter, loaded into a sieve stack and placed on a Pulverit Vibrator. Chemical analyses of bulk compositions and surface coatings were made of several particle size fractions. Subsamples for bulk analysis were digested in HF and HNO $_3$, evaporated to dryness, spiked with Be, Sc, and In to act as internal standards for mass spectrometric analysis and then taken up in 100 ml 1% nitric acid solution. Surface coatings were assumed to be represented by components leachable in boiling 6 N HCl. After boiling the sand, the leachate was evaporated to dryness, redissolved in 2 ml 50% nitric acid, diluted to 50 ml with D.I. water, filtered through Whatman #42 filter paper, spiked with Be, Sc, and In, and diluted to 100 ml with deionized water. Both sets of samples were analyzed for major and minor elements on the VG Instruments Plasmaquad ICP-MS (Inductively-coupled-plasma mass spectrometer). For Ca and Si analysis, 50 ml of the sample solutions was evaporated to dryness, taken up in a few ml of 2% HNO $_3$, and analyzed by atomic absorption (AA). Blanks consisting of acid and electrolyte filtered through the Whatman #42 paper were analyzed for both sets of samples. The methods are described in more detail in Appendix A of this report, and the results in Section III.B.

D. Unsaturated Column Leaching Experiments

Small-scale column experiments were carried out to study the changes in the pH and composition of leachable components of Wedron 510 sand in dilute NaCl electrolyte as functions of time and saturation state. A schematic of the column apparatus is shown in

Figure 1. NaCl solutions (0.01 M or 0.001 M NaCl, $\text{pH} \approx 6$) were pumped through columns (7 cm I.D. $\times$ 24 cm) filled with Wedron 510 sand. The pore volume of the column was approximately 180 mL. The flow rate and bottom boundary suction was varied to control the degree of saturation (50% - 100%). The pH of the influent solution was measured in a top reservoir and also in a flow-through cell just prior to entry into the column. The pH of the effluent solution was measured in a flow-through cell as it exits the column and after it was collected in an open vessel. In experiments with 0.001 M NaCl influent, samples of effluent were acidified (1% HNO_3) and analyzed for Al, Ca, Mg, Li, Ni, and Br by ICP-MS. Si was determined for each sample by atomic absorption as described for bulk analysis. The methods are described in more detail in Appendix A of this report, and the results in Section III.C.

Figure 1. Experimental apparatus for unsaturated flow sand column leaching studies.

E. Potentiometric Titrations

Potentiometric surface titrations were carried out with both batch and continuous titration methods. Detailed description of the methods and results are found in Appendices A and E.6. To evaluate the effects of mineral surface coatings, titration curves were obtained on the sand and Min-U-Sil 5 in both raw and surface-cleaned states. Surface coatings were removed from the Wedron sand and the Min-U-Sil 5 using a cleaning procedure described above.

In the batch experiments, acidimetric-alkalimetric titration data for Wedron 510 sand and Min-U-Sil 5, a reference α -quartz from the Pennsylvania Glass Corp. (Pittsburgh, PA), were obtained over the pH range 2.65 to 10 at increments of ~ 1 pH unit. Aliquots of HCl and NaOH were added to batch systems consisting of 15-20 ml 0.01 M NaCl electrolyte and 15 g sand or 0.53 g silica (sorbent surface area = 3.15 m^2) in 50 ml polyallomar (PA) centrifuge tubes. In kinetic studies, periodic pH measurements were made at intervals of 0, 3.0, 5.8, and 31 days. CO_2 -free conditions were maintained by preparing solutions from boiled deionized water, purging the headspace of all vessels with Ar and carrying out pH measurements under Ar purge as described below and in Appendix E.1.

Continuous titrations were carried out in a 250 ml reactor with an automated prototype/limited-production instrument (made by G. Redden, Stanford University). Computer-controlled 2.5 ml micrometer syringes added acid or base to a stirred 250 ml polypropylene reactor vessel. The pH was monitored by a combination electrode located in the reactor. When analyzing coarse materials that settled rapidly (i.e., sand), the electrode was shielded from the direct flow to avoid discrepancies induced by the sedimentation potential. The pH was considered to be stable when six pairs of readings differing by $< 0.15 \text{ mV}$ had been accumulated. The headspaces of the reactor and the basic reagent bottle were continuously purged with de-acidified and humidified Ar; the reactor temperature was the same as the ambient laboratory temperature ($23 - 25^\circ\text{C}$).

After vigorously stirring the suspension for at least 45 min while under Ar purge to remove all dissolved CO_2 , acid was added (if necessary) to provide an initial pH near 4. The suspension was then incrementally titrated to an endpoint of pH 9 using 0.05 M NaOH, and the ionic strength at the endpoint was measured by comparing conductivity with NaCl standards. Acid was then added to return the suspension to its initial pH, solid NaCl was added to raise the ionic strength, the suspension was stirred vigorously for 10 min to flush out any CO_2 that may have entered, and the incremental titration was repeated. Corrections to the experimental data for total electrolyte volume and ionic strength were calculated at each step of a titration.

A system consisting of 150 g acid-washed Wedron 510 sand and 150 ml electrolyte was titrated over the pH range 4.5 – 9 at ionic strengths ranging from 0.0003 to 0.096 M. Potentiometric titrations of acid-washed Min-U-Sil 5 α -quartz were also carried out to provide a baseline for validating the experimental procedure and to provide a point of reference for titrations on acid-washed Wedron sand. The titrated system consisted of 4.534 g HCl-washed Min-U-Sil 5 and 150 ml NaCl electrolyte. It was continuously titrated

over the pH range 4.2 – 9 at ionic strengths ranging from 0.0003 to 0.096 M. The methods used in the potentiometric titration studies are described in more detail in Appendix A of this report, and the results in Section III.D.

F. Batch Solubility and Adsorption Experiments

1. LiBr Batch Adsorption Studies

Batch studies of sorption of lithium and bromide by Wedron 510 sand in 0.001 M NaCl solutions under both nominally-CO₂-free and atmospheric conditions were carried out in 50 ml PC centrifuge tubes (the meanings of “nominally-CO₂-free” and “atmospheric conditions” are discussed below in the section on Ni adsorption studies). Experimental conditions are summarized in Table 2. Reagent grade lithium bromide (LiBr) was used as the source for both lithium and bromine. Li adsorption as functions of pH, time and concentration were carried out. Solution:sand ratios of approximately 1:1, 5:1, and 10:1, and lithium and bromine concentrations $1.44 \cdot 10^{-5}$ to $1.44 \cdot 10^{-1}$ M were used. Many of the techniques used for Li and Br adsorption studies are the same as those used for the Ni adsorption studies described below. The procedure used to adjust the pH and the solution-solid separation procedures are the same as those for nickel described below and in Appendix E.3. The samples were allowed to pre-equilibrate for two to six days and to equilibrate for up to seven days after tracer addition, while being continuously stirred on a hematology mixer. The samples were then analyzed for lithium by atomic adsorption and for bromine by ion-specific electrode as described below and in Appendices E.4 and E.5. The results of these studies are described in Section III.E of this report.

Table 2. Batch studies of Li adsorption by Wedron 510 sand

Data set	Total Li conc.	Ni conc.	P_{CO_2}	Comments
1	10 ppm	100 ppb	CO ₂ -free	K_d study
2	10 ppm	0	CO ₂ -free	K_d study
3	17 ppm	200 ppb	atmos.	K_d study
4	10 ppm	0	CO ₂ -free	K_d study
5	10 ppm	0	atmos.	K_d study
6	5 ppm	0	n/a	Kinetic study with NaHCO ₃ buffer
7	17.4 ppm	0	n/a	Kinetic study with NaHCO ₃ buffer
8	0.1 - 10 ppm	0	atmos.	Isotherm study with variable concentrations and solid/solution ratios
9	1-1000 ppm	0	atmos.	Isotherm study

2. Batch Solubility Studies of Ni Hydroxides

Total dissolved Ni was measured as a function of pH in nominally CO₂-free supersaturated batch systems lacking adsorbent to determine the solubility of Ni(OH)₂ in the background electrolyte. Batch systems containing 30 ml 0.001 M NaCl electrolyte and 1 – 7600 µg/ml ($1.7 \cdot 10^{-5}$ to $1.3 \cdot 10^{-1}$ M) total Ni were equilibrated for 14 days over the pH range 7 – 10 in 50 ml polyallomar centrifuge tubes. To obtain reliable and consistent pH values, CO₂-free conditions were maintained during preparation, equilibration, and measurement of the batch systems.

Systems were initially supersaturated with respect to amorphous Ni(OH)₂ by at least a factor of three, based on the equilibrium constants of Baeyens and McKinley (1989). For systems with a target pH of less than 8, Ni was added as NiCl₂ · 6H₂O to provide initial concentrations in the range 760 – 7600 µg/ml (0.013 – 0.13 M). For more alkaline systems (pH > 8), an aliquot of 1000 ppm Ni standard was added to provide an initial concentration of 1 µg/ml ($1.7 \cdot 10^{-5}$ M). Nickel concentrations were determined by GFAA as described in Section II.H and Appendix E.3.

Macroscopic quantities of precipitate formed in tubes with the highest Ni concentrations (pH < 8). The precipitate was collected by vacuum filtration on a 0.4 µm polycarbonate membrane filter and washed with a few ml of methanol before air-drying. It was analyzed by X-ray diffraction using a powder mount on an oriented quartz crystal scanned over a 2θ range of 5°–65°. Phase identification was accomplished visually by overlaying the diffractogram with a stick-figure representation of the expected maxima for candidate minerals.

Results of the Ni solubility studies are described in Section III.F of this report.

3. Batch Ni Adsorption Studies

Batch adsorption studies were carried out in 0.001 M NaCl electrolyte using substrates of Wedron 510 sand (Wedron Silica, Wedron, IL), synthesized goethite or Min-U-Sil 5 α-quartz. Experimental conditions are summarized in Table 3. Reaction vessels were 50 ml Oak Ridge-style centrifuge tubes made of either polyallomar or polycarbonate with polypropylene screw caps. Batch systems consisted of 20 ml electrolyte and 20 g sand, 0.4467 g Min-U-Sil, or 2.353 mg goethite.

For studies of adsorption as a function of pH, the pH of each suspension was adjusted using dilute HNO₃ and NaOH solutions prior to addition of adsorbate. The batch systems were equilibrated for 2 – 3 days. The suspensions were then spiked with a neutral-pH Ni solution and re-equilibrated for 2 – 4 days. After the equilibration period, the pH in each vessel was measured as described in Appendix E.1-- *pH Measurements Under Atmospheric and CO₂-free Conditions*. An aliquot of electrolyte was collected, filtered through a 0.2 µm filter, and analyzed for the element of interest. The batch adsorption procedure used in this study is described in detail in Appendix E.2--*Batch Adsorption Experiments Under*

Table 3. Experimental conditions for batch Ni adsorption studies

Substrate	Electrolyte (NaCl conc.)	Atmospheric conditions	Ni added, ng/ml	Li added, mg/ml
Wedron 510	0.001 M	CO ₂ -free	100	0
Wedron 510	0.001 M	CO ₂ -free (N ₂)	100	0
Wedron 510	0.1 M	CO ₂ -free (N ₂)	100	0
Wedron 510	0.001 M	Atmosphere	100	0
Wedron 510	0.001 M	Atmosphere	200	0
Wedron 510	0.001 M	CO ₂ -free	100	10
Wedron 510	0.001 M	Atmosphere	200	17
Goethite	0.001 M	Atmosphere	100	0
Min-U-Sil	0.001 M	CO ₂ -free (N ₂)	100	0

Atmospheric and CO₂-free Conditions. The procedures for Ni analysis are described in Appendix E.3, *Ni Analysis by Graphite Furnace Atomic Absorption*.

Total added Ni concentrations were 100 – 200 ng/ml ($1.7 - 3.4 \cdot 10^{-6}$ M). In two sets, Li was also added as a pH-neutral LiBr solution; total added Li concentrations were 10 – 17 µg/ml ($1.4 - 2.5 \cdot 10^{-3}$ M). Kinetic studies of rates of Ni adsorption by Wedron 510 sand were carried out in 0.001 M NaCl - 0.0001M NaHCO₃ solution at pH approximately 7.6.

In CO₂-free experiments, the electrolyte was sparged with Ar, the headspace in the centrifuge tubes was filled with Ar, and pH was measured under Ar atmosphere. The tubes were equilibrated in either the ambient atmosphere, or under N₂ in a glove box. In other experiments that were partially equilibrated with atmospheric CO₂ (described as “atmospheric conditions” in this report), initial pH adjustment was carried out under ambient atmosphere followed by sparging with air for 10 – 15 min, equilibration for two days, and then sparging again before Ni was added. The batch systems were equilibrated in closed tubes in the ambient atmosphere, and final pH measurements were made under a static Ar atmosphere.

Results of the Ni batch adsorption studies are described in Section III.G of this report.

G. Column Studies

Figure 2 illustrates the experimental setup used for saturated transport column experiments. The columns were 5.1 cm in diameter and 30 cm tall. The saturated runs were conducted in a manner described in Appendices C and E.7 using a 30 cm column of

Figure 2. Experimental set-up for saturated column experiments.

sand. The influent solutions consisted of 17.4 ppm Li and 200 ppm Br in a background solution of consisting of $9 \cdot 10^{-5}$ M NaHCO_3 and 0.001 M NaCl with a pH of approximately 7. Both micro-layered and homogeneous sand columns were prepared in order to evaluate hydrological effects due to potential heterogeneities in the sand bed. Results of these studies are described in Section III.H of this report.

H. Chemical Analyses

Aliquots for Ni analysis were filtered through a $0.2 \mu\text{m}$ nylon syringe filter and acidified to 2% (0.32 M) HNO_3 . Nickel concentrations were determined using graphite-furnace atomic absorption spectroscopy (GFAA) on a Perkin-Elmer 5000 instrument with HGA-500 graphite-furnace controller and AS-1 auto-sampler. The data-reduction scheme fit a quadratic curve to the absorbance data and applied corrections for carryover of Ni in the furnace tube and for evaporation from the auto-sampler vials to achieve better than $\pm 1.8\%$ (1 s.d.) precision over a dynamic range of 0 – 200 ng/ml, with a limit of detection of 0.2 ng/ml. Additional details may be found in Appendix E.3.

Lithium analyses were obtained using air-acetylene flame atomic absorption (AA) spectrophotometry on the Perkin-Elmer HGA-5000. The samples were drawn directly from the polyethylene vials at approximately 4.1 ml/min. A calibration curve was derived from a quadratic fit to the absorbance data using measurements made on blanks (0.001 M NaCl electrolyte) and standards of 1 $\mu\text{g/ml}$, 5 $\mu\text{g/ml}$, 10 $\mu\text{g/ml}$, and 20 $\mu\text{g/ml}$ Li. Samples with

higher Li concentrations were diluted with 0.001 M NaCl to fall within this range. Additional details may be found in Appendix E.4.

Br was analyzed with an ORION 94300 Br ion-specific electrode with a ORION 900100 single junction reference electrode. pH measurements were made with an Orion ROSS #8102 combination electrode connected to an Orion 940 pH meter. The electrode was calibrated against pH 4, 7, and 10 buffers (the actual values entered in the meter were corrected for the ambient temperature) using the Orion's internal 3-point calibration routine. Internal precision of the pH calibration is ± 0.03 pH units. Additional details may be found in Appendix E.5.

Because samples typically contained a partial pressure of CO₂ less than atmospheric, the headspace of each sample vessel was purged with Ar before pH measurement. The Ar was cleaned and humidified prior to use by passing through a two-stage scrubber; the first scrubber was filled with 0.5 M NaOH to remove an acidic contaminant in the Ar (probably CO₂ or HCl); the second stage contained boiled deionized water to remove NaOH aerosol. Actual pH measurements were performed under a static Ar atmosphere while the samples were being agitated on an orbital mixer. The electrode was allowed to equilibrate with the solution being measured until the electrode drift rate was less than 2 mV/min. In the Ni solubility studies, pH readings were taken after allowing the electrode to stabilize for 4 minutes. Additional details may be found in Appendix E.1.

Major and minor elements in leachates from batch and column leaching studies were analyzed on a VG Instruments Plasmaquad ICP-MS. An aliquot of each sample was spiked with 1000 ng/ml each of Be, Sc, and In, and run along with prepared standards, which defined the calibration curve. The standards were run again as unknowns to determine the detection limits and errors for each element. Additional details may be found in Appendix A.

III. Results

A. Mineralogic and Surface Studies

1. Mineralogy

The bulk mineralogy of the sand was determined by X-ray diffraction; the patterns show significant diffraction maxima for quartz only. A detailed examination of the XRD pattern for minor peaks between 6° and 64° fails to reveal any sign of carbonate, but shows traces of kaolinite as well as four unidentified peaks. A colloidal fraction of the sand (0.05% by weight), which remains dispersed at $\text{pH} > 8.5$, was also analyzed by XRD. It shows clear diffraction maxima for quartz and kaolinite, and again lacks any sign of carbonate. Observations using SEM revealed a collection of ragged fragments whose EDS spectra were dominated by subequal intensities of Al and Si X-rays with lower intensity (usually) of O X-rays. No fragments of quartz were observed, implying that quartz constitutes probably no more than 10% of the colloidal fraction. Studies of thin-sections under an optical microscope reveal that the sand grains are coated with a yellowish material suggesting that Fe is likely to be present as a thin coating of hematite and/or goethite on the sand grains.

2. Particle Size Distribution and Surface Area

The size analysis of the Wedron 510 sand obtained by dry sieving is shown in Table 4. Surface area was measured by N_2 BET on an aliquot of the sand, giving a value of $0.118 \text{ m}^2/\text{g}$. Although N_2 isotherms become problematic for specific surface areas of less than $1 \text{ m}^2/\text{g}$, measurements on NBS standards of similar specific area deviate from the nominal values by no more than $+0.02$. Applying this correction to the sand would lower its value to $0.098 \text{ m}^2/\text{g}$. Additional information about the BET measurements is given in Appendix A.

Table 4. Sieve results for Wedron 510 sand

U.S. sieve #	Size fraction	Weight % of total
50	fr. $> 295 \mu\text{m}$	8.91
70	$295 \mu\text{m} > \text{fr.} > 212 \mu\text{m}$	39.55
100	$212 \mu\text{m} > \text{fr.} > 150 \mu\text{m}$	27.74
140	$150 \mu\text{m} > \text{fr.} > 106 \mu\text{m}$	16.63
200	$106 \mu\text{m} > \text{fr.} > 74 \mu\text{m}$	6.42
Pan	$74 \mu\text{m} > \text{fr.}$	0.75

3. X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) provides information about elemental composition and chemical speciation for a thin (~5 nm) surface layer. X-ray photoelectron spectra were acquired on both untreated and acid-washed sand. The acid-washed sand had also been used in a titration experiment; a colloidal component (presumably kaolinite) was liberated at high pH and subsequently rinsed away. For the untreated sand, Si was the dominant cation, followed by Al (0.28 abundance relative to Si), and subequal amounts of Ca and Mg (0.02 – 0.03 abundance relative to Si). Reducing the slit width showed that the minor phases must have been uniformly distributed rather than occurring as rare large single grains. The acid-washed sand had 90% less Al and no Ca or Mg. Interfering peaks from the mounting tape obscured the possible presence of Fe and CO_3^{2-} in both samples.

In the untreated sand, apparent surface coverage of quartz by minor Al- and Ca+Mg-bearing phases was calculated according to a monolayer model and a discrete particle model as discussed in Appendix A. For Al present as kaolinite ($\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$), monolayer coverage implied a uniform coating 2.5 nm thick, but this accounts for less than 1% of the total Al in the sand measured by bulk dissolution. The discrete-particle model implied that approximately half of the surface area was covered by kaolinite flakes. Although surface coverage evident in SEM photomicrographs appeared to be much lower (5 – 10%), mass balance for Al was within an order of magnitude. These discrepancies are acceptable given the semi-quantitative nature of this model.

For Ca+Mg, the discrete particle model requires 4% surface coverage. Because Ca+Mg constitutes only ~0.008% of the bulk sand, however, mass-balance requires that Ca+Mg must be concentrated at the grain surfaces, either as a coating or as tiny particles, and cannot be present as individual sand-sized grains of carbonate. SEM/EDS observations provide additional support for the coating hypothesis, as no grains rich in Ca+Mg were detected.

B. Bulk Composition and Surface Leaching Experiments

Chemical analyses of the bulk chemical samples (dissolvable in concentrated HF and HNO_3) and surface leachates (dissolvable in hot 6 N HCl) from an unsieved sample and two particle size fractions are shown in Table 5. Surface concentrations are expressed as the mass of the element in the leachate divided by the weight of the sand sample. No values are given for Br in the surface chemistry samples because the Br contamination from the HCl was too high (6 – 10 μg per sample). Values of Si concentration are close to 100 wt.%. The composition of the 212 μm – 150 μm fraction was similar to that of the 295 μm – 212 μm fraction shown in the table. The bulk analyses of the finer size fractions that are not tabulated (150 μm – 106 μm and 106 μm – 74 μm) were more enriched in all of the minor and trace metals compared to the coarser fractions.

The bulk analysis of the finest size fraction and the surface coatings of all size fractions contain high concentrations of Al, Fe, Ca, and Mg. This suggests that the finest size fraction contains fragments of sand grain coatings composed of calcite, dolomite, iron

oxyhydroxide and clay minerals. Table 6 tabulates the fractions of total element mass contained in the surface coating and indicates that the surface coatings contain significant fractions of the Mg, Ca, Fe and Ni in all size fractions.

Table 5. Chemical analysis of Wedron 510 sand*

Element	Size Fraction					
	unsplit sand		295 μm - 212 μm		< 74 μm	
	bulk	surf.	bulk	surf.	bulk	surf.
Li	1.54	0.05	1.70	0.06	2.47	0.06
Na	1.67	<0.20	1.00	<0.20	9.59	0.86
Mg	24.7	10.92	23.0	13.7	118	84.6
Al	2820	482	2290	579	11300	1200
Si	**	5.4	**	5.4	**	18.4
K	2.52	0.51	1.40	<0.20	20.1	1.10
Ca	55	23	46	26	222	198
Ti	83.1	2.55	61.1	2.35	892	13.2
Fe	242	80.0	128	39.0	2280	1180
Ni	0.18	0.14	0.09	0.09	2.08	0.90
Br	1.68	***	<0.75	***	<0.75	***

*Values in $\mu\text{g/g}$.

**SiO₂ content was $\approx 100\%$.

***Analyses not reliable due to contamination.

Table 6. Ratios of surface/total concentrations

Element	Size Fraction		
	unsplit sand	295 μm > fr > 212 μm	< 74 μm
Li	0.03	0.03	0.02
Na	0.12	0.20	0.09
Mg	0.44	0.59	0.72
Al	0.17	0.25	0.11
K	0.20	0.14	0.05
Ca	0.42	0.57	0.89
Ti	0.03	0.04	0.01
Mn	0.33	0.21	1.46
Fe	0.33	0.30	0.52
Ni	0.78	0.92	0.43

C. Unsaturated Column Leaching Experiments

The results of the unsaturated leaching experiments are shown in Figure 3. The column effluent contains measurable concentrations of the major components of the sand (Ca, Mg, Si) and of the tracers (Ni, Br, Li) that will be used in the caisson experiment. The initial spike in the concentrations may be due to transient increase in the level of saturation during elution of the first 3 pore volumes; the concentration appeared to approach a steady state thereafter.

Under unsaturated conditions the effluent pH dropped to a steady-state range of 7.2 to 7.5 after elution of approximately 5 pore volumes. In preliminary saturated-condition experiments (not shown), the pH of the effluent was initially neutral, rose to > 8.7 , and then reached a steady-state value of approximately 8.2 after 6 pore volumes (approximately 1*l*) had been eluted from the column.

Figure 3. pH and compositions of effluent samples from unsaturated flow sand column leaching experiments (column pore volume = 180 ml and DL = estimated detection limits for the ICP-MS). Data below the DL are plotted as measured rather than set to the DL in order to provide a visual representation of the analytical scatter.

D. Potentiometric Surface Titrations

1. Batch Titrations

Titration curves for Wedron 510 sand at intervals of 0, 3.0, 5.8, and 31 days over the pH range 2.65 to 10 are shown in Figure 4. Readings at low pH (<4) became less acidic by ~1.5 pH units within the first three days and then were stable. Readings at pH > 9 continued to drift with time, and near-neutral pH readings revealed the development of a buffering plateau. The pH shifts for pH < 9 are consistent with the dissolution of carbonate-bearing minerals. A material-balance calculation for the most acidic batch system provides an estimate of the minimum carbonate content of the sand; the observed shift between 0 and 3 days of pH 2.76 to 4.33 requires an alkalinity of 1.93 $\mu\text{eq/g}$ sand, corresponding to 0.96 $\mu\text{moles/g}$ of carbonate.

Titration curves for acid-washed sand and acid-washed Min-U-Sil 5 silica show no time dependence except at very high pH (>10). In Figure 5, titration curves for these two systems are compared to the 31 day titration curve for unwashed Wedron 510 sand and to theoretical and experimental curves for 0.001 M electrolyte alone. The model titration curve for the electrolyte was adjusted to pass through the experimental data points at low pH. Titration curves for both acid-washed materials are essentially identical.

At low pH, the acid-washed curves are coincident with the curve for electrolyte alone. When CO_2 -free D. I. water is added to acid-washed sand (0 $\mu\text{equivalents}$ added acid), the pH drops from neutral to ~5.2 in both sand and silica systems. Under basic conditions, the

Figure 4. Potentiometric titration of Wedron 510 sand under CO_2 -free conditions.

Figure 5. Potentiometric titration of raw and acid-washed Wedron 510 sand, acid-washed Min-U-Sil 5 silica, and 0.001 M NaCl electrolyte under CO_2 -free conditions.

titration curves fall well below that for electrolyte alone due to the combined effects of silica dissolution and surface ionization. At high pH, the titration curve for raw sand lies above its acid-washed counterpart, indicating that the quartz-grain surfaces are armored with phases that are comparatively insoluble at high pH.

2. Continuous Titrations

Potentiometric titrations on quartz provide two input values for a triple-layer model of surface complexation (Yates et al., 1974; Kent et al., 1988) — the intrinsic equilibrium constant for proton loss by the surface (K_{a2}), and the intrinsic stability constant for complexation of the background-electrolyte cation (K_{Na}):

$$K_{a2} \equiv \text{SOH} \rightleftharpoons \text{SO}^- + \text{H}^+, \text{ and} \quad (1)$$

$$K_{Na} \equiv \text{SOH} + \text{Na}^+ \rightleftharpoons \text{SO}^- \text{Na}^+ + \text{H}^+; \quad (2)$$

where S represents a surface site. Potentiometric titrations were performed on acid-washed Wedron 510 sand and acid-washed Min-U-Sil 5 α -quartz. Raw Wedron sand could not be potentiometrically titrated because of its carbonate content, which strongly affects the system pH as it dissolves and thus obscures the contribution of surface interactions.

Data Reduction. Data reduction followed the double-extrapolation method (Davis et al., 1978; Kent et al., 1988). The surface charge, σ , was calculated from charge balance considerations for the electrolyte as discussed in Appendix A. Double-extrapolations were performed graphically on a semi-log plot of the apparent equilibrium constant (Q) versus a linear combination of α_- (the fraction of deprotonated sites), and the ionic strength (I).

Here

$$\alpha_- = \frac{-\sigma}{N_s} \cdot b, \quad (3)$$

where N_s is the site density in sites/nm² and b is a conversion factor = 0.06239 relating sites/nm² to $\mu\text{C}/\text{cm}^2$. For K_{a2} and K_{Na} , the respective expressions for Q_{a2} and Q_{Na} are

$$pQ_{a2} = \text{pH} - \log \frac{\alpha_-}{1 - \alpha_-}, \text{ and} \quad (4)$$

$$pQ_{Na} = \text{pH} - \log \frac{\alpha_-}{1 - \alpha_-} + \log[\text{Na}^+]. \quad (5)$$

To find pK_{a2} , pQ_{a2} was plotted vs. $\alpha_- + c\sqrt{I}$, where I is the ionic strength and c is an adjustable parameter. Each titration curve was first extrapolated to $\alpha_- = 0$, and then the resulting array of points was extrapolated to the pQ_{a2} axis, where $\alpha_- = I = 0$ and $pK_{a2} = pQ_{a2}$. The data were also extrapolated to $I = 0$ and then to $\alpha_- = 0$. A similar procedure was followed to find pK_{Na} , except that pQ_{a2} was first substituted for pQ_{Na} (allowable because $pQ_{Na} = pQ_{a2}$ when $[\text{Na}^+] = 1 \text{ M}$ and $\log I = 0$) to provide increased dispersion, and then pQ_{a2} was plotted vs. $\alpha_- + c \log I$. Finally, contour lines were double-extrapolated to $\alpha_- = 0$ and $\log I = 0$, where $pK_{Na} = pQ_{a2} = pQ_{Na}$. Precision of extrapolations for pK_{a2} is better than ± 0.2 units, and is controlled mainly by the low I data. Precision for pK_{Na} is only ± 0.4 for data with maximum $I = 0.1 \text{ M}$.

Results for Acid-Washed Min-U-Sil and Wedron 510 Sand. Double-extrapolation plots for the intrinsic acidity and Na-association constants (K_{a2} and K_{Na} , respectively) for acid washed Min-U-Sil 5 are shown in Figure 6. Surface-charge calculations assumed a specific surface area of 5.95 m²/g (multi-point Kr BET) (Kohler and Leckie, 1991), and a site density of 6 nm⁻². Points below pH ~4.75 were excluded because of probable systematic errors implied by the erratic trends of surface charge vs. pH. The extrapolated values at zero surface charge and zero ionic strength or $\log I = 0$ are $K_{a2} = 7.8$ and $K_{Na} = 5.6$, respectively. The K_{a2} value is typical of quartz, but K_{Na} is slightly lower than normal.

Intrinsic acidity and Na-association constants (K_{a2} and K_{Na} , respectively) for acid-washed Wedron 510 sand, extracted from the titration data by the double-extrapolation method, are plotted in Figure 7. Surface-charge calculations assumed a specific surface area of 0.12 m²/g, (N_2 -BET) and a site density of 6 nm⁻², matching that of the Min-U-Sil.

Figure 6. Double-extrapolation plots for HCl-washed Min-U-Sil 5: (a) Extrapolation for pK_{a2} , giving a value of 7.8, and (b) Extrapolation for pK_{Na} , giving a value of 5.6.

Figure 7. Double-extrapolation plots for acid-washed Wedron 510 sand: (a) Extrapolation for pK_{a2} , giving a value of 5.5, and (b) Extrapolation for pK_{Na} , giving a value of 4.8.

The extrapolated values at zero surface charge and zero ionic strength are $K_{a2} = 5.5$ and $K_{Na} = 4.8$, much lower than typically seen for quartz.

E. Adsorption of Lithium and Bromide by Wedron 510 Sand

1. Equilibrium Adsorption

Bromide adsorption by sand was negligible over the pH range studied. A plot of the amount of Br adsorption as a function of pH can be found in Appendix C.

Figure 8 compares Li adsorption under several experimental conditions from the K_d data sets that are considered to be the most reliable at this time. K_d s were calculated from the amount of adsorbed Li and the solution to solid ratio of the experiments as discussed in Appendix E.2. For the pH range relevant to the caisson experiment (7- 8.5) under CO_2 -free to partially-equilibrated conditions, the measured K_d s range from approximately about 0.05 to 0.25 ml/g (5% - 20% adsorption). The degree of adsorption in all data sets is dependent on the pH; reaching a maxima at near-neutral pH. As discussed in Appendix C, Data Sets 4 and 5 are considered the most reliable of the available data. They show no dependence of adsorption on the amount of CO_2 present in the batch system.

Kinetic Studies. Figure 9 shows the aqueous concentration of Li as a function of time for a kinetic batch sorption experiment under atmospheric conditions. The total Li

Figure 8. Comparison of Li sorption data sets.

Figure 9. Li kinetic batch adsorption experiment (total Li (C_0)=17.4 ppm, calculated $k = 0.0012 \text{ min}^{-1}$).

concentration was 17.4 ppm, and the pH varied from 7.6 to 7.7. The initial values of [Li] are anomalously and inexplicably low, however, the rate constant as derived from the data in Appendix C was only slightly influenced by these low values. The rate constant for the adsorption reaction calculated from these data is 0.0012 min^{-1} . The rate constant calculated from the second kinetic experiment ($C_0 = 5 \text{ ppm}$) is 0.0004 min^{-1} . The plots of dimensionless driving force used to calculate the rate constants are found in Appendix C (Fig. C.4-4 and C.4-6).

Isotherm Studies. The results from initial lithium sorption isotherm measurements (Data Set 8) are summarized in Table 7. The data show that the measured K_d depended on both the tracer concentration and the solution:solid ratio. Attempts to fit these data to a Langmuir isotherm using a least squares analysis showed that the relationship between sorption and tracer concentration was different for each solution:solid ratio and that the scatter was unacceptably large at the two higher solution:solid ratios.

Figure 10 shows the adsorption isotherms obtained from Data Set 9. The data is best described by a Freundlich isotherm rather than a linear (K_d) or a Langmuir isotherm. The Freundlich equation is:

$$\ln S = \ln K + n \ln C \quad (6)$$

Table 7. Summary of Lithium K_d s

Total Li ($\mu\text{g/ml}$)	Solution/Solid Ratio (K_d , ml/g)					
	1		5		10	
	mean	σ	mean	σ	mean	σ
0.10	13	2.2	37	7.3	18	4.7
1	0.16	0.15	0.80	0.08	0.89	0.05
10	0.20	0.01	0.18	0.13	0.46	0.17

Figure 10. Li adsorption isotherm plots for Wedron 510 sand. Concentrations of Li (S , C) are in parts per million.

where S is the concentration of adsorbed Li, and the isotherm parameters $\ln K = 0.0878$ and $n = 0.5674$ were obtained from the intercept and slope of the isotherm plot respectively.

F. Solubility of Ni Hydroxides

The solubility-limited Ni concentration in batch adsorption systems must be known so that decreases in dissolved Ni due to precipitation are not attributed mistakenly to adsorption. Initially- CO_2 -free batch systems without adsorbent were equilibrated for 14 days in air. Dissolved Ni decreased significantly in all systems, indicating approach to

equilibrium from supersaturation. A precipitate was visible in those systems with initial $\text{Ni} > 10^{-2} \text{ M}$ (initial $\text{pH} < 8.5$); more alkaline systems lacked sufficient Ni to produce observable precipitate. The mineralogy of the precipitate, determined by X-ray diffraction, was poorly crystalline theophrastite ($\text{Ni}(\text{OH})_2$).

Figure 11 compares the dissolved Ni concentrations in CO_2 -free batch-adsorption experiments with the experimental $\text{Ni}(\text{OH})_2$ solubility curve and curves calculated using HYDRAQL (Papelis et al., 1989) with thermodynamic data given by Baeyens and McKinley (1989). Most batch-adsorption systems were quite undersaturated with respect to Ni hydroxide. In these systems, decreases in dissolved Ni must have been due to adsorption. At pH values > 9 , however, adsorption experiments were oversaturated with respect to crystalline $\text{Ni}(\text{OH})_2$ but not with respect to amorphous $\text{Ni}(\text{OH})_2$. Kinetics of precipitation of crystalline $\text{Ni}(\text{OH})_2$, however, are slow enough as to preclude precipitates during the 3-day batch adsorption experiments. Unfortunately, because of unquantified diffusion of CO_2 into the reaction tubes in these experiments, there may be no clear means of discriminating between adsorption, precipitation of amorphous $\text{Ni}(\text{OH})_2$, and carbonate-complexation effects.

Figure 11. Comparison of final Ni concentrations in batch adsorption experiments with measured Ni solubility (—) and calculated stability limits for crystalline (---) and amorphous (—) $\text{Ni}(\text{OH})_2$.

G. Batch Ni Adsorption Studies

1. Potential Sorption of Tracers by Plastic Labware, Solution Samplers and the Caisson Walls

Studies of tracer migration in the caisson and systematic laboratory studies of adsorption of tracers by sand will rely primarily on measurements of the concentration of the tracers in solutions. Direct measurements of the concentrations of tracers adsorbed to the solids will not be made routinely; therefore, any adsorption of the tracers by solution samplers or plastic labware must be accounted for in calculations of sorption partition coefficients (K_d s, isotherm parameters or surface complexation constants) or retardation factors. Appendix F describes studies of the adsorption of Ni as a function of pH by several kinds of labware used for sample collection tubes, syringes and centrifuge tubes. These include low-density polyethylene (LDPE), polypropylene (PP), polyallomer (PA), and polycarbonate (PC). These experiments were designed to maximize the amount of tracer adsorption by the plastics and tracer concentrations used in these experiments were similar to those expected for the batch, column and caisson experiments. The results indicate that even at high plastic surface area:solution ratios, less than 20% of the tracer was lost to the plastic under neutral and alkaline conditions. Because the surface area of the minerals in the batch, column and caisson experiments will be much higher than the surface areas of the plastics, sorption by the plastics will be relatively small and can be ignored in the sorption and solubility experiments. These studies also indicate that all of the plastics are suitable for use as geochemical sampling vessels for acidified solutions.

Uptake of tracers by the solution samplers will also introduce errors in estimation of breakthrough times in the caisson. Appendix F describes studies of the adsorption of the tracers by hollow fiber and ceramic samplers in static and flowing systems. The results indicate that the hollow fiber samplers do not adsorb any of the tracers but that the ceramic samplers will adsorb Ni and may be sources for Li and Br. At least 1 l of solution must pass through the sampler before the Ni concentrations of the influent and effluent become equal.

The effects of interaction between the caisson material and tracers is assumed to be negligible for the following reasons: 1) The interior walls of the caisson were coated with Teflon paint to prevent potential leaching of Ni, Br or Li from the metal walls. Laboratory studies of sorption of tracers by various plastics as described above suggest that sorption would be negligible by Teflon at the near-neutral pH expected for the caisson pore waters. 2) The effects of any potential sorption of the tracers by the Teflon coating would be localized to the outer ring of the sand if hydrologic flow within the caisson is essentially 1-dimensional as designed. Any such sorption would not effect the chemistry of solutions sampled in the interior of the caisson. 3) It is also unlikely that such interactions would effect the integrated tracer discharge (measured at the bottom of the caisson).

2. Results of Systematic Adsorption Studies

Results of Ni adsorption experiments on Wedron 510 sand, goethite, and Min-U-Sil 5 quartz showing the effects of pH, variations in P_{CO_2} and total Ni, the effects of competition with Li, and the effects of variations in ionic strength are shown in Figures 12 –16. Scales showing the effective batch distribution coefficient (K_d , in ml/g) have been calculated as described in Appendix E.2 and plotted in the figures. For Wedron sand systems, measurements on blanks showed that the sand contained ~34 ng/g exchangeable Ni, which has been included in total soluble Ni for adsorption calculations.

Figure 12 displays two sets of adsorption data for Wedron sand collected under nominally CO_2 -free conditions with 100 ng/ml added Ni. Both sets were initially CO_2 -free, sealed and then allowed to reach sorption equilibria. One set of sealed tubes (*air-equilibrated*) was equilibrated on the lab bench in air, so ambient CO_2 may have diffused into the containers through the seals. The other set of closed tubes was equilibrated in a nitrogen atmosphere glove box. Both data sets define the same adsorption edge, located at pH 6 – 7. However, at pH 10, the N_2 -equilibrated systems showed greater sorption (~95%) than the air-equilibrated systems (~88%).

Variations in adsorption due to differences in total Ni and P_{CO_2} are described in Figure 13. Two data sets, collected under atmospheric conditions with added Ni of 100 ng/ml or 200 ng/ml, define an adsorption edge which is offset slightly toward lower pH in comparison with N_2 -equilibrated CO_2 -free data. Both sets appear to lie on the same curve, suggesting that the available adsorption sites were not saturated at the higher Ni

Figure 12. Adsorption of Ni by Wedron 510 sand under initially CO_2 -free conditions, 100 ng/ml added Ni, in 0.001 M NaCl (o = sealed and then equilibrated in air; ● = sealed and then equilibrated in N_2 atmosphere).

concentration. At higher pH (>9) the data at atmospheric conditions show lower adsorption than the CO₂-free data, consistent with the trend noted in Figure 12 of decreasing adsorption with increasing P_{CO_2} . At low to intermediate pH values (4.5 – 9), adsorption is slightly higher under atmospheric conditions.

The competitive effect of Li on Ni adsorption is illustrated in Figure 14. These samples were run with 100 ng/ml added Ni and 10 µg/ml (0.0014 M) added Li under CO₂-free conditions, or with 200 ng/ml added Ni and 17.4 µg/ml (0.0025 M) added Li under atmospheric conditions. Li was added as LiBr. In both cases, the adsorption edge was slightly broader than for Li-free conditions and was displaced slightly toward higher pH. The second set, with higher Li under atmospheric conditions, is indistinguishable from the first.

The effect of ionic strength on Ni adsorption is shown in Figure 15. Ni adsorption in 0.1 M NaCl appeared to be essentially identical to adsorption in 0.001 M NaCl for CO₂-free systems.

Adsorption of Ni onto pure quartz and goethite surfaces is shown in Figure 16. Min-U-Sil 5 α-quartz was acid-washed prior to use. Batch systems containing 0.4467 g Min-U-Sil were run under CO₂-free protocol and were equilibrated under N₂. Although the surface area of the Min-U-Sil systems was similar to that of the Wedron systems (163 vs. 118 m²/l), the data differ markedly. The Ni adsorption edge for Min-U-Sil exhibits a low

Figure 13. Adsorption of Ni by Wedron 510 sand under atmospheric conditions (■ = 100 ng/ml Ni, □ = 200 ng/ml Ni, and — = N₂-equilibrated CO₂-free data from Figure 12, connected by a solid line).

Figure 14. Adsorption of Ni by Wedron 510 sand in the presence of Li ($\blacklozenge$ = 100 ng/ml Ni, 10 μ g/ml Li, CO_2 -free and $\square$ = 200 ng/ml Ni, 17 mg/ml Li, atmospheric conditions. Data collected under CO_2 -free conditions (—), and atmospheric conditions (---) from Figures 12 and 13 are connected by lines for reference).

Figure 15. Adsorption of Ni by Wedron 510 sand in 0.1 M NaCl, CO_2 -free conditions, N_2 atmosphere ($\square$ = 100 ng/ml Ni. Adsorption curve for 0.001 M NaCl under CO_2 -free conditions from Figure 12 is shown for reference).

Figure 16. Adsorption of Ni onto Min-U-Sil quartz ($\square$) and synthesized goethite ($\blacksquare$) (Experimental conditions are described in Table 3. Wedron 510 CO_2 -free adsorption curve (—) is shown for reference).

slope; adsorption increases approximately linearly with pH over the range 4.5–9. There was 20% adsorption at pH 5, a pH at which Wedron sand showed no significant adsorption.

In the batch sorption experiments using synthesized goethite, the amount of goethite (2.353 g) added to 20 ml 0.001 M NaCl was equivalent to the quantity of Fe that could be leached with 6 N HCl from 20 g sand. The resulting systems contained a surface area of $5.59 \text{ m}^2/\text{l}$ and a site concentration of $2.15 \cdot 10^{-5} \text{ M}$. These systems were partially equilibrated with atmospheric CO_2 during preparation by sparging with air for about 4 minutes. At pH values less than ~ 7.5 , equilibrium with CO_2 was probably closely approached, resulting in a partial pressure of CO_2 of nearly $10^{-3.5} \text{ atm}$, whereas at higher pH values the systems probably remained highly undersaturated due to the high solubility of CO_2 . Although the upper portion of the adsorption edge is poorly constrained, the Ni-adsorption curve appears to be similar in shape but less steep than the curve for Wedron sand.

3. Models for Ni Adsorption by Wedron 510 Sand

The adsorption of Ni^{2+} onto Wedron sand closely resembles that of synthesized goethite, suggesting that goethite alone may serve as an analog for the complicated sand for modeling purposes. Modeling was performed using the triple-layer model (Yates et al., 1974; Balistrieri and Murray, 1981) (TLM) as implemented in the HYDRAQL code (Papelis et al., 1988). Parameters for the goethite TLM were obtained from the literature and are summarized in part 1 of Table 8. The HYDRAQL thermodynamic database was

Table 8. Parameters held constant for modeling Ni adsorption onto synthesized goethite and Wedron sand using the triple-layer model (K_{int} = intrinsic equilibrium constant, S = surface site)

1. Properties of goethite	Value*	Reference
Specific surface area	48.5 m ² /g	Balistreri and Murray (1981)
Site density	2.31 sites/nm ²	Davis and Kent (1990)
Inner-layer capacitance	0.8 F/m ²	Papelis et al. (1988)
Outer-layer capacitance	0.2 F/m ²	James and Parks (1982)
2. Speciation of Ni²⁺	log K	Reference
$\text{Ni}^{2+} + \text{Cl}^- = \text{NiCl}^+$	0.4*	Ball et al. (1980)
$\text{Ni}^{2+} + 2\text{Cl}^- = \text{NiCl}_2$	0.96*	Ball et al. (1980)
$\text{Ni}^{2+} + \text{H}^+ = \text{NiOH}^+ + \text{H}_2\text{O}$	-9.71	Baeyens and McKinley (1989)
$\text{Ni}^{2+} + 2\text{H}^+ = \text{Ni(OH)}_2 + 2\text{H}_2\text{O}$	-20*	Smith and Martell (1976)
$\text{Ni}^{2+} + 3\text{H}^+ = \text{Ni(OH)}_3^- + 3\text{H}_2\text{O}$	-30*	Baes and Mesmer (1976)
$\text{Ni}^{2+} + 4\text{H}^+ = \text{Ni(OH)}_4^{2-} + 4\text{H}_2\text{O}$	-44*	Baes and Mesmer (1976)
$2\text{Ni}^{2+} + 3\text{H}^+ = \text{Ni}_2(\text{OH})_3^+ + 3\text{H}_2\text{O}$	-10.7*	Baes and Mesmer (1976)
$4\text{Ni}^{2+} + 4\text{H}^+ = \text{Ni}_4(\text{OH})_4^{4+} + 4\text{H}_2\text{O}$	-27.74*	Baes and Mesmer (1976)
$\text{Ni}^{2+} + \text{CO}_3^{2-} = \text{NiCO}_3$	6.87*	Ball et al. (1980)
$\text{Ni}^{2+} + 2\text{CO}_3^{2-} = \text{Ni(CO}_3)_2^{2-}$	10.11*	Ball et al. (1980)
$\text{Ni}^{2+} + \text{HCO}_3^- = \text{NiHCO}_3^+$	12.47*	Ball et al. (1980)
3. Surface complexes	log K_{int}	Reference
$\text{SOH} = \text{SO}^- + \text{H}^+$	-9.52	Balistreri and Murray (1981)
$\text{SOH} + \text{H}^+ = \text{SOH}_2^+$	5.57	Balistreri and Murray (1981)
$\text{SO}^- + \text{Na}^+ = \text{SO-Na}$	-8.4	Balistreri and Murray (1981)
$\text{SOH}_2^+ + \text{Cl}^- = \text{SOH}_2\text{-Cl}$	7	Balistreri and Murray (1981)

*Values recommended by Baeyens and McKinley (1989). Original sources are cited here.

augmented by more detailed Ni speciation data from a variety of sources, as presented in the part 2 of Table 8. These data were critically evaluated by Baeyens and McKinley (1989) for internal consistency and sound experimental design. Note that the speciation reactions correspond to the log K values as written and are consistent with the HYDRAQL input format. Where needed, these log K values have been calculated from log K values in cited references by adding the log K for the formation of water (or multiples thereof).

The experimental adsorption data for goethite were modeled by assuming one or more surface-complexation reactions between dissolved species and a surface site, and then adjusting the intrinsic equilibrium constants to obtain a good visual fit. This set of parameters was then used to model the experimental observations on the sand by adjusting the solid specific surface area (and hence the site concentration in solution) to again obtain a good visual fit. Finally, the effects of ionic strength were examined by comparing model predictions to experimental data on sand in 0.1 M NaCl.

HYDRAQL was used to calculate Ni speciation in 0.001 to 0.1 M NaCl solutions in the absence of adsorbent under both atmospheric CO_2 conditions ($P_{\text{CO}_2} = 10^{-3.5}$ atm) and very low CO_2 , where $P_{\text{CO}_2} = 10^{-6}$ atm. Results for 0.001 M NaCl solutions are shown in Figure 17. Under atmospheric conditions (Figure 17a), Ni-carbonato complexes predominate at pH values above 7.5, where Ni is strongly sorbed. Under low- CO_2 conditions ($P_{\text{CO}_2} = 10^{-6}$ atm, figure 17b), however, the predominance of Ni-carbonato complexes occurs only above pH 8.5, and the abundance of Ni-hydroxyl complexes is much greater. At higher NaCl concentrations, the concentration of NiCl^+ increases. (However, Ni sorption is not affected significantly because the Ni^{2+} is still the predominant species in the pH range over which sorption occurs, as discussed below). These differences in speciation are critical to developing a realistic model of the experimental data.

A range of possible surface complexes were modeled, as summarized in Table 9. Both monodentate (complexation to a single site) and bidentate (complexation to two sites) adsorption were considered. Possible sorbing species included Ni^{2+} or NiOH^+ as either inner-sphere or outer-sphere complexes, and various Ni-carbonato species as outer-sphere complexes.

Models of adsorption of the Ni-carbonato species were unable to reproduce the experimental data. Curves for two possible adsorbed Ni-carbonato complexes are shown in Figure 18 for atmospheric CO_2 ($P_{\text{CO}_2} = 10^{-3.5}$ atm). The calculated abundance of the SONiCO_3^- complex depends only on the concentration of the reactants, SO^- and NiCO_3^0 , and is unaffected by surface charge. The sorption edge for this reaction is located where NiCO_3^0 becomes the dominant Ni species. Formation of the $\text{SONi(CO}_3)_2^{3-}$ requires that the chemical interaction be strong enough to overcome a countervailing electrostatic contribution above the pH of zero net surface charge, resulting in a very broad sorption edge at low pH. For the curves shown, binding constants were adjusted to reproduce the adsorption edge. Increasing the binding constant (K_{int}) increases the maximum adsorption but shifts the adsorption edge to lower pH, resulting in poorer fits.

Figure 17. Nickel speciation [(a) $P_{CO_2} = 10^{-3.5} \text{ atm}$ and (b) $P_{CO_2} = 10^{-6} \text{ atm}$].

Table 9. Investigated surface complexes

Sorbing species	Surface sites	
	SO^-	$(\text{SO}^-)_2$
<i>Inner Sphere</i>		
Ni^{2+}	X	X
NiOH^+	X	
<i>Outer Sphere</i>		
Ni^{2+}	X	X
NiOH^+	X	
NiCO_3^0	X	
$\text{Ni}(\text{CO}_3)_2^{2-}$	X	
NiHCO_3^+	X	
$\text{NiH}_2\text{CO}_3^{2+}$	X

Figure 18. Calculated adsorption of Ni-carbonato complexes onto synthesized goethite at $P_{\text{CO}_2} = 10^{-3.5}$ atm (Experimental data (■) are the same as in Figure 16. Experimental conditions: surface area = 5.59 m²/liter; electrolyte = 0.001 M NaCl; total Ni = 100 ng/ml ($1.7 \cdot 10^{-6}$ M); partially equilibrated with atmospheric CO₂).

The most successful model involved the formation of an inner-sphere complex between Ni^{2+} and a single SO^- site, with an intrinsic equilibrium constant of 10^{-1} . This is also the stoichiometry recommended by Dzombak and Morel (1990). Results are shown in Figure 19 for $P_{\text{CO}_2} = 10^{-3.5}$ and 10^{-6} atm. At low pH, the calculated adsorption curves are insensitive to variations in P_{CO_2} , but at $\text{pH} > 7$ the calculated curves begin to diverge. At atmospheric CO_2 , adsorption reaches a maximum of only 83% at $\text{pH} 8.2$ and then shows decreasing sorption at higher pH due to formation of stable Ni-carbonato complexes in solution. Maximum calculated adsorption could be increased by postulating a larger intrinsic equilibrium constant, but this would also shift the calculated adsorption edge to lower pH. A more satisfactory alternative is to assume that the batch systems at high pH were greatly undersaturated with respect to CO_2 . A CO_2 partial pressure of 10^{-6} atm is the maximum CO_2 level compatible with the experimental data; at higher CO_2 levels, the calculated curve begins to show declining adsorption at high pH.

Application of this model using low P_{CO_2} to experimental data for Wedron sand is shown in Figure 20. Good agreement is obtained by setting the goethite surface area to $65 \text{ m}^2/\text{l}$. Increasing the ionic strength in the calculations by two orders of magnitude to 0.1 M shifts the calculated sorption edge to higher pH by only 0.2 pH units. This small shift is due to placement of Ni^{2+} in the 0 plane, where it forms an inner-sphere complex and is unaffected by competition with Na^+ for sorption sites. The calculated sorption edge is consistent with experimental observations; the increase in abundance of NiCl^+ at higher ionic strengths may also play a minor role in the slight shift in the adsorption edge. In contrast, outer-sphere complexes are quite sensitive to variations in ionic strength; all

Figure 19. Calculated adsorption of Ni^{2+} onto synthesized goethite for two partial pressures of CO_2 (Experimental data (■) are the same as in Figure 18).

Figure 20. HYDRAQL modeling of Ni sorption onto Wedron 510 sand using TLM parameters for goethite. (Model curves: — = 0.001 M NaCl, — — = 0.1 M NaCl. Experimental data (■) are the same as in Figure 13. Experimental conditions: surface area = 120 m²/l; total Ni = 135 ng/ml (2.3 · 10⁻⁶ M); partially equilibrated with atmospheric CO₂).

outer-sphere models of Ni complexation showed much greater shifts in the opposite direction, leading to their rejection. The behavior of Ni in the presence of Li lends further support to the inner-sphere hypothesis. Although Li was present at molar concentrations greater than Ni by a factor of 1000, it competed only weakly with Ni for adsorption sites. Lithium probably forms an outer-sphere complex with the sand, consistent with its comparatively weak adsorption. If Ni had formed an outer-sphere complex, it would have been displaced more readily by Li.

The specific surface area of the Fe-bearing phase postulated for the sand is quite high — the amount of Fe which gave a goethite surface area of 5.59 m²/l must be spread thinly enough to provide 65 m²/l. The estimated specific surface area is: 48.5 m²/g · (65 m²/l / 5.59 m²/l) = ~560 m²/g. Such a value is probably inconsistent with occurrence as goethite, but both ferrihydrite and amorphous Fe(OH)₃ can have such high specific surface areas, and have surface complexation constants similar to those of goethite (Dzombak and Morel, 1990).

The total surface area of the Wedron sand in the batch systems is estimated to have been ~120 m²/l by the N₂ BET data. Thus the postulated Fe oxyhydroxide phase with a surface area of 65 m²/l would account for 54% of the available surface area. It is possible

that Fe-oxyhydroxides coat most of the surfaces in the sand and hence dominate the adsorptive properties. Alternatively, the actual surface area of the sand available for sorption may be much greater as suggested by the potentiometric titrations described above. Another possibility is that the bulk adsorptive behavior of the sand is due to adsorption onto at least three types of surfaces: Fe-oxyhydroxide, kaolinite, and quartz.

H. Transport Studies

The results of column experiments for transport of pulses of LiBr through micro-layered and homogeneously-packed columns of Wedron 510 sand are described in detail in Appendix C. In the following section the experimental results are compared to model predictions using several alternative equilibrium and kinetic models. The values of geochemical parameters (sorption coefficients and reaction rate constants) obtained in batch studies and those calculated from the fits to the breakthrough curves (BTCs) using the CXTFIT (Parker and van Genuchten, 1984) computer code are also compared.

Calculated BTCs are compared to experimental data for Br transport in the homogeneously-packed and micro-layered beds in Figure 21. Dispersion coefficients (D) of 0.0023 and 0.0041 cm^2/min and retardation factors (R) 0.96 and 0.98 were obtained from the microlayered and homogeneously-packed columns, respectively. The retardation factor less than 1 for Br can be attributed to anion exclusion. This effect can be conceptualized as

Figure 21. Comparison of Br pulses through micro-layered and homogeneously-packed Wedron 510 sand.

a reduction of the effective cross-sectional area for the flow of Br^- ions caused by the repulsion of Br^- from the negatively charged sand surfaces and a concomitant increase in the average tracer velocity. Comparison of the results of the two columns shows that the differences in packing do not significantly affect the transport of Br. A similar insensitivity is shown for lithium in Appendix C.

It was assumed that the dispersivity of Li would be similar to that of Br in initial calculations of Li transport. Figure 22 compares calculated BTCs in the micro-layered sand bed column for the equilibrium and kinetic models. In both models, $D = 0.0023 \text{ cm}^2/\text{min}$ (the value for Br) and $K_d = 0.15 \text{ ml/g}$ (the value suggested by the batch sorption data at near-neutral pH in Wedron 510 sand in Figure 8). The analytical solution of Lapidus and Amundson (1952) was used for the equilibrium model. The solution predicts that for pore volumes larger than the pulse pore volume and initial concentration of zero,

$$C(x,t) = C_0 [A(x,t) - A(x,t-t_0)] , \quad (7)$$

$$\text{where} \quad A(x,t) = \frac{1}{2} \text{erfc} \left[\frac{Rx - vt}{2(DRt)^{1/2}} \right] + \frac{1}{2} \exp\left(\frac{vx}{D}\right) \text{erfc} \left[\frac{Rx + vt}{2(DRt)^{1/2}} \right] . \quad (8)$$

Here $C(x,t)$ is the concentration at time t and distance x , t_0 is the duration of the column pulse, D is the dispersion coefficient, R is the retardation factor, and v is the pore water velocity.

Figure 22 clearly shows that the equilibrium model does not accurately predict the column breakthrough pulse; the calculated pulse breakthrough occurs at 1.9 pore volumes ($R = 1.9$). CXTFIT was used to calculate the BTC for a single-sorption-site kinetic model; the fit by this model ($r^2 = 0.911$) is much better than that of the equilibrium model. The rate constant determined from CXTFIT is $k = 0.0013 \text{ min}^{-1}$. This value is in the same order of magnitude as that determined from the batch kinetic Li sorption experiments, ($k = 0.0004$ to 0.0012 min^{-1}) as discussed previously.

Kinetic effects can be represented in equilibrium transport models by use of an "apparent" or "effective" retardation factor (Relyea, 1982). Figure 23 compares the experimental breakthrough curves for Li and Br to the calculated BTCs for an equilibrium linear sorption isotherm model for transport through a micro-layered Wedron 510 sand bed. The CXTFIT code was used to optimize the fit by adjusting both R and D ; the $r^2 = 0.933$ for the Li curve. The experimental data and predicted BTC for Br were discussed previously (Figure 21). The Li pulse is broader than the Br pulse and has a pronounced tail which may indicate kinetic effects. The calculated dispersion coefficients are 0.017 and $0.0023 \text{ cm}^2/\text{min}$ for Li and Br, respectively and the retardation factors are 1.06 and 0.96 for Li and Br, respectively.

The value of the "effective" retardation factor for Li calculated by CXTFIT ($R = 1.06$) can be compared to that calculated using the analysis of Kuhn and Peters (1981) as described in Appendix C. They obtained an expression for R/R_{equil} , the ratio of the apparent

Figure 22. Comparison of kinetic and equilibrium models for fixed K_d and fixed D .

Figure 23. Experimental data and modeled pulses for Li and Br, through saturated, micro-layered Wedron 510 sand.

retardation factor under a given flow condition to the retardation factor assuming equilibrium sorption, as a function of the number of mass transfer units. The number of mass transfer units, n , is given by:

$$n = \frac{\rho_b K_d L}{\varepsilon v} \quad (9)$$

where ρ_b is the bulk density, K_d is the equilibrium K_d , L is the length of the column, ε is the porosity, v is the pore water velocity and k is the first order sorption rate constant. Using the expression for the retardation factor, $R = 1 + \rho_b K_d / \varepsilon$, and assuming ρ_b is 1.8 g/cm³, ε is 0.3, and K_d is 0.15 ml/g (the value from batch adsorption experiments), the value of R/R_{equil} can be plotted as a function of n for columns of Wedron 510 sand as shown in Figure 24. A discussion of the relationship between R/R_{equil} and n is found in Appendix C.

For the column experiments described previously, L is 30 cm, and v is 0.074 min⁻¹. Using the results of the batch adsorption experiments (K_d is 0.15 ml/g, and k is 0.0012 min⁻¹), the calculated values of n and R_{equil} are 0.44 and 1.9, respectively. The corresponding value of R/R_{equil} from Figure 24 is approximately 0.56 and the predicted effective retardation factor is 1.06, in excellent agreement with the value calculated with CXTFIT for the Li breakthrough curve.

Better fits of the experimental data can be obtained if CXTFIT is used to solve for several parameters simultaneously. The CXTFIT code was also used to extract best fit

Figure 24. Retardation factor ratio as a function of the number of transfer units.

parameters from the Li and Br BTCs for a two-site non-equilibrium (kinetic) sorption model. The parameter values obtained from best fit curves are summarized in Appendix C, Table C.4.6. The best fits ($r^2 = 0.976$) were obtained for models in which CXTFIT was used to calculate four best-fit parameters in the kinetic model simultaneously. The calculated dispersion coefficients are close to those of the Br breakthrough curves, however, the calculated K_d s for Li are low. The calculated rate constants, k , are significantly larger than those measured in the kinetic batch experiments. Additional discussion of the sensitivity analyses is found in Appendix C.

The study described helps to formulate acceptance criteria for validation tests by indicating reasonable expectations for agreement between predictions and measurements. These criteria should be based **in part** on goodness-of-fit criteria for breakthrough curves. The calculations with CXTFIT illustrate the interdependence of the values of the transport parameters chosen for the fits. The goodness of fit depends on the choice of adjustable parameters to include in the model, the initial guesses for the transport parameters, and other assumptions about the detailed nature of transport mechanisms. These column studies show that in some cases, excellent fits required assumptions that conflicted with experimental data collected in batch systems or with chemical intuition. In these cases the **preferred** fit may not be the curve with best goodness-of-fit statistics.

IV. Discussion: Application of Results of Material Characterization to the Caisson Experiment

A. Introduction: Relevance of Caisson to Validation Studies

Validation of contaminant transport models involves comparison of calculated and observed tracer elution curves. The agreement between model predictions and experimental data will not be perfect because of uncertainties in tracer detection and the accuracy of model assumptions. Criteria for acceptable agreement must be formulated as part of a model validation test and must reflect various sources of uncertainty in the experimental and model designs. The caisson experiment described in this report was designed to provide well-controlled conditions and a well-characterized geomeedia to allow separation of uncertainties due to chemical and physical processes.

The Wedron 510 sand was chosen for the porous matrix, because compared to other natural materials, it is relatively chemically and physically homogeneous. The hydrological properties of the sand are described in Appendix D. Detailed characterization of its geochemical properties revealed that the sand is a mixture of several reactive phases. It is likely that chemical reactions involving the surfaces of the minerals, solutes in the pore fluids, atmospheric gases, the tracers, and the solution samplers will introduce uncertainties into the interpretation of the observed tracer breakthrough curves. The objective of the materials characterization studies is to obtain sufficient data describing these interactions to allow for comparison of the robustness of several different transport models with respect to this uncertainty. In this section the sources of uncertainty and the alternative geochemical models are described.

B. Uncertainties in Applying Lab Characterization Studies to Field Tests

Characterization studies designed to support efforts to validate models of contaminant transport must address the following question: how do the properties of geomeedia measured in the laboratory differ from those that would be present under natural conditions? Valid application of measurements made in the laboratory to prediction of transport in the field requires (1) assurance that the material studied in the laboratory is representative of the material expected to be in contact with groundwaters in the study area and (2) assurance that the procedures used to characterize the natural or analog material have not altered its properties in ways important to transport.

The caisson experiment shares a fundamental uncertainty with tracer field studies. As in aquifers, the properties of the exposed surfaces that interact with the tracers in groundwaters may be very different from those of the minerals that make up the bulk of the rock. Although the bulk mineralogy of Wedron 510 sand is dominated by quartz, several studies revealed that mineral coatings armor much of the surface area of the sand grains. Several different leaching techniques were used to expose the underlying minerals surfaces for further characterization, to obtain the composition of the coatings, and to evaluate the potential dissolution of the coatings during batch sorption experiments,

during potentiometric surface titrations and during the caisson experiment. The compositions of the leachates and the resultant mineral surfaces provide a basis for determining if the properties of the mineral surfaces are changed in ways that invalidate the results of sorption experiments.

A comparison of batch titration curves for raw Wedron 510 sand, acid-washed Wedron 510 sand, and acid-washed Min-U-Sil 5 α -quartz suggested that the potentiometric titration curves of the raw sand were dominated by the effects of carbonate dissolution and CO₂ uptake. Washing in boiling HCl stripped the sand grains of their coatings, resulting in a batch titration curve that qualitatively resembled that for acid-washed Min-U-Sil 5 quartz.

Potentiometric titrations and related surface-charge calculations for acid-washed Min-U-Sil 5 provided a standard for surface properties expected for quartz. Double-extrapolation plots and derived values (pK_{a2} and pK_{Na}) for Min-U-Sil 5 are within the range of values reported in the literature for this material and other forms of silica (see Table A.10, Appendix A). In contrast, surface-charge calculations and double-extrapolation plots for Wedron sand give very different results. Calculated charge density was unusually high for all ionic strengths. The intrinsic association constants, K_{a2} and K_{Na} , were much greater than those for Min-U-Sil 5; $\log K_{a2} = 5.5$ vs. 7.8 and $\log K_{Na} = 4.8$ vs. 5.6 respectively. These results suggest that the surface area may have been much larger than the N₂-BET value. A source of additional surface area may have been the colloidal suspension of kaolinite that appeared as the pH was increased. Assuming a specific surface area for the kaolinite of 101 m²/g (Xie and Walther, 1992) and a site density of 6 nm⁻² (for consistency with the double-extrapolation calculations), the equivalent surface area for this kaolinite would be 333 m²/g. Because kaolinite constitutes ~0.05% by weight of the sand it could contribute 0.17 m² per gram of bulk sand, more than doubling the estimated surface area in contact with the solution.

The potentiometric titrations show that development of surface charge on the sand is only poorly understood. In spite of acid-washing for quantitative removal of carbonate and Fe-oxyhydroxide phases, the average surface of Wedron sand did not resemble quartz but instead must have included a variety of sites, with poorly constrained site density and effective surface area. Such complexity will be difficult to unravel by potentiometric titration.

C. Uncertainties in Prediction of Chemical Conditions in the Caisson and Effects on Tracer Sorption

1. Uncertainties in the Compositions of Pore Fluids

The leaching tests described previously indicate that significant amounts of the Li, Ni and Br will not be leached from the sand and interfere with the tracer tests. The studies also indicate, however, that the sand will not be chemically inert during the caisson experiment. Detectable amounts of Ca, Mg, and Si were observed in both batch and flowing systems at low and near neutral pH. Significant pH shifts were observed and were

dependent on the degree of hydraulic saturation in the unsaturated column leach tests. The surface titration curves shown in Figure 5 indicate that the sand contains minerals whose slow dissolution will affect the solution pH. The existence of other potentially reactive minor minerals was indicated by analysis using X-ray diffraction, petrographic microscopy and scanning electron microscopy.

These data suggest that the chemical composition of pore fluids within the caisson will be controlled by dissolution of quartz, carbonate cement, diffusion of atmospheric CO_2 into pore fluids, and deprotonation of silanol (SiOH) groups (see Figure 25). It is anticipated that chemical conditions within the caisson will initially be transient but that a steady-state chemical profile may eventually develop. The degree of hydraulic saturation, the flow velocity, the dissolution rate of carbonate cement and the CO_2 diffusion rate will control the approach to a steady-state pH profile in the caisson; the amount of carbonate cement will determine the lifetime of the steady-state profile.

Figure 25. Factors potentially affecting pH in a column filled with Wedron 510 sand.

2. Evaluation of Robustness of Alternative Models for Adsorption With Respect to Uncertainty in Composition of Pore Fluids

The potential uncertainty in the composition of the solutions and solid surfaces within the caisson leads to uncertainties in the degree of sorption of each of the tracers.

Adsorption of solutes by mineral surfaces can potentially be affected by many properties of the adsorbent and adsorbate including: the surface area and charge of the adsorbent, the speciation and concentration of the adsorbate, and competition for sorption sites between the adsorbate and other solutes. The abilities of several different models of equilibrium sorption to predict transport of the tracers in the caisson are being examined. In order of increasing complexity and robustness they are:

1. Linear sorption (distribution constant or K_d),
2. Non-linear sorption (Langmuir and other isotherms),
3. Ion exchange, and
4. Triple-layer surface complexation models.

The simplest model (linear sorption) requires a single constant (K_d) that is valid only for the physicochemical conditions of a particular experiment. In contrast, the triple-layer model (TLM) requires several adjustable parameters describing surface complexation of cations and anions, surface hydrolysis, electrostatic properties of the mineral surface double layer, and the density of surface sites. The complexation constants are valid over a wider range of conditions than K_d s, however, considerably more experimental data must be gathered to obtain values for the adjustable parameters.

Bromide Transport. The most appropriate adsorption model for each tracer depends on its specific chemistry. The pH_{ZPC} of quartz is $\cong 2$; under the near-neutral conditions of the caisson, the surface of the sand should be negatively charged. Bromine is present in natural waters as Br^- and should not be adsorbed by the sand; this was confirmed by batch adsorption experiments. The column experiments revealed the effects of anion exclusion. Thus bromine will not behave as perfect conservative tracer; uncertainties in its elution curve should be attributed to both hydrological effects and the degree of anion exclusion.

Lithium Transport. Lithium is present in natural waters as Li^+ , a simple cation; therefore, adsorption by the sand at near-neutral pH should be sensitive primarily to the surface area of the adsorbent, competition with other cations for sorption sites, and Li concentration. The data described in Table 7 indicate that Li sorption is nonlinear (i.e. K_d is a function of Li concentration and solution:solid ratio); over the range of interest (1 – 1000 $\mu\text{g/ml}$, Li; 1:1 ml/g) sorption is low and fairly constant ($K_d < 0.2 \text{ ml/g}$). The degree of adsorption is slightly dependent on the pH, reaching a maxima at near-neutral pH.

Batch and column studies were used to evaluate potential uncertainties due to kinetic effects. There is uncertainty in the values for the rate constants for Li sorption. The calculated batch rate constants were $k=0.0004$ and 0.0012 min^{-1} for initial Li concentrations of 5 and 17.4 ppm respectively. A single site kinetic model for the column data was calculated with CXTFIT using K_d (0.15 ml/g) and k (0.00012 min^{-1}) values similar

to those measured in the laboratory batch experiments. A two-site kinetic model with simultaneous calculation of D , R , k (first order sorption rate constant) and F (fraction of sites assumed to be in equilibrium) improved the fit significantly to account for the sharper leading edge and the tail. Although the best fit statistic (r^2) is highest for this model, the values of R and k are not consistent with the experimental data.

Although a kinetic model was required to model the laboratory column data, an equilibrium model may be sufficient for the caisson experiments. The Li breakthrough curves in saturated columns of Wedron 510 sand pulses could be adequately modeled by the equilibrium convective-dispersive model with an "effective" K_d of about 0.01 ml/g. The "effective" K_d is smaller than the lowest values measured in the batch experiments, and the dispersivities calculated with CXTFIT are one order of magnitude higher than that for Br. However, the "effective" K_d , and the equilibrium K_d and sorption rate constant measured in the batch experiments, are consistent with the value of "effective" retardation factors predicted with the model of Kuhn and Peters (1981). The same analysis shows that if the flow rate in the 600 cm caisson at Los Alamos is the same as in the laboratory column (0.074 cm^{-1}), then the predicted value of the effective retardation factor is 90% of the equilibrium retardation factor (1.9). Therefore, the solutions sampled from the bottom of the caisson should represent near-equilibrium conditions given the assumptions stated above. The contribution of geochemical effects to the uncertainty in the lithium breakthrough should be small and could be minimized by use of the appropriate nonlinear (isotherm) model for adsorption in an advective-dispersion equation for transport.

Ni Adsorption. The chemical speciation of Ni is considerably more complex than that of lithium or bromine because it forms complexes with OH^- and CO_3^{2-} . Figure 12 indicates that Ni sorption by Wedron 510 sand is very sensitive to pH under near-neutral conditions. The results of the unsaturated column experiments suggest that the pH in the caisson could be as high as 8.2 or as low as 7.2. Figure 12 shows that nickel adsorption ranged from about 20% to almost 100% for experiments with solution:solid ratios of about 1:1 ml/g. The corresponding range in calculated K_d is 15 - 90 ml/g. The uncertainty in tracer retardation is nearly proportional to the K_d ; if the classical advective-dispersive equation is used to model transport, the error in predictions of breakthrough times for Ni due to the uncertainty in pH could be as much as 600%. In the variably saturated caisson, the solution/solid ratio will be less than that of the batch sorption experiments; any additional associated error in the predicted Ni retardation factor for the caisson is not known at this time.

Doubling the amount of total Ni added (from 100 ppb to 200 ppb) had no measurable effect on the shape or the location of the adsorption edge; neither did increasing the ionic strength by a factor of 100 from 0.001 M to 0.1 M. These observations suggest that only a small fraction of the available sites are occupied by Ni, and that competition with Na for sites is not a significant factor determining Ni adsorption. Addition of 0.0014 - 0.0025 M Li as LiBr interfered with Ni sorption, shifting the sorption edge toward higher pH by ~0.2 pH units for 0.0014 M Li. At relatively low Li concentrations, Ni-Li interactions probably do not have to be included in transport calculations; however, if high Li concentrations (>

0.01 M Li) are used, Ni sorption may be affected. Such interactions can be modeled using surface complexation models.

A surface-complexation model of Ni adsorption by the sand was formulated for use in transport calculations using the LEHGC code. The data describing Ni adsorption onto goethite were examined to obtain the stoichiometries of possible adsorption reactions and associated binding constants. The most important system parameter appears to be pH, followed by surface area (and hence site concentration). These results were applied to the data for Ni sorption onto Wedron sand, where the model fit to the observations was optimized by adjusting the postulated surface area of goethite. The model successfully reproduced the adsorption edge observed for the sand. Adsorption was independent of ionic strength, and was enhanced by higher levels of CO₂ below pH 8. At higher pH values, higher levels of CO₂ appeared to stabilize Ni in solution. High concentrations of Li, a weakly adsorbing cation, reduced Ni adsorption slightly. This modeling exercise shows that the Triple Layer Model can successfully simulate the adsorptive behavior of Wedron sand with respect to Ni in a simple batch system with a single adsorbate. Although the model is not rigorously based on the behaviors of the constituent components of the sand, it does simulate the aggregate behavior of the bulk sand and may be useful for transport calculations.

D. Future Work and Relation to Transport Model Validation

In heterogeneous groundwater systems, adsorption may be controlled by trace amounts of reactive minerals or coatings of inert materials that are preferentially concentrated along flow paths or other structural features. Studies of metal adsorption by bulk rocks may not provide information about the most important adsorption sites. It is important for performance assessment calculations to determine if radionuclide discharges could be substantially different from those calculated using K_d values obtained from the bulk rock.

The caisson experiment provides an opportunity to evaluate alternative approaches to predict the sorption properties of natural mineral mixtures. The studies described in this report indicate that the trace components of Wedron 510 sand will exert significant if not dominant controls on the transport of the tracers in the caisson experiment; in addition, dissolution of minor mineral phases may affect the pH of the pore solutions. The mineral surfaces that interact with the tracers used in the caisson experiment cannot be represented by pure quartz reference standards. Additional studies of the properties of the minor components of the sand may be required to obtain effective values of the surface acidity and complexation constants for the bulk sand and to formulate a mineral-mixtures model for the surface properties of the sand.

The dependence of lithium sorption on concentrations of the tracer and the solids suggests that an isotherm sorption model may be required to predict Li transport. Additional data describing these relationships will be obtained to allow comparison of the applicability of the Freundlich, Langmuir and other isotherm models to lithium transport.

The data for Ni sorption suggest that a model describing the changes of pH and the concentrations of other solution species as a function of time and position within the caisson and the concomitant effects on Ni sorption may be required for accurate predictions of Ni transport. Data will be collected within the framework of the triple-layer model to allow inclusion of these effects in the Ni transport calculations with the LEHGC version of the HYDROGEOCHEM code (Yeh and Tripathi, 1990). Sorption data will also be collected and analyzed within the framework of ion-exchange theory. Ion-exchange experiments will be carried out for Ni-Na, Ni-Li and Li-Na exchange. Values of the ion-exchange equilibrium constants will be calculated and the robustness of the ion-exchange model will be compared to that of the isotherm model for lithium and that of the TLM model for nickel. The different approaches will be used to simulate transport of the tracers in the caisson; the validities of the sorption models for the conditions of the caisson experiment will be evaluated by comparing predicted and measured elution curves.

The caisson experiment is being used to develop a strategy to apply the results of laboratory-scale experiments to prediction of transport at the field scale. A comparison between the elution curves observed in the caisson and elution curves calculated from laboratory data will be made. Parameter values for transport models are being obtained independently from several kinds of studies: 1) batch studies are used to obtain equilibrium K_d s, surface complexation constants, and sorption rate constants; and 2) laboratory and large-scale (caisson) column studies with the conservative tracer (Br) are used to obtain hydrologic parameters such as dispersivity. In this experiment, parameter values are determined sequentially proceeding from batch experiments to column experiments to the caisson. Although it was demonstrated that codes like CXTFIT can be used to fit a large number of transport parameters simultaneously, the strategy adopted in this work emphasizes the use of the parameter values obtained from the batch experiments as constants in the fitting procedure. Similarly, the scale-dependent parameter dispersivity will be obtained directly from the caisson by analysis of the Br pulse. This value will be then combined with results of batch experiments to calculate the transport of the sorbing tracers.

The results of this experiment will be used to establish criteria for validation of transport models used for performance assessment of Yucca Mountain. Current high-level waste performance assessment codes use either K_d s or simple isotherms to represent retardation. These models are not *structurally* valid, i.e. they do not accurately describe retardation mechanisms. However, if they can be shown to be *predictively* valid in the appropriate experimental frames (i.e. predict the results of new experiments under a range of relevant physicochemical conditions), then they can be used in performance assessment calculations.

V. Summary

The surface of the porous medium in the caisson (Wedron 510 sand from Wedron Silica Corp., Wedron, IL 60557) has been characterized by a variety of chemical, mineralogical, and physical methods. The primary objective of the work described in this report is the identification and characterization of the minerals in the caisson that will most strongly affect tracer transport. These minerals will affect tracer transport either directly through sorption or coprecipitation or indirectly through solid/solution reactions that affect the bulk chemistry of the solution in the caisson.

It is proposed that the chemical composition of pore fluids and tracer sorption within the caisson will be controlled by dissolution of quartz, carbonate cement, diffusion of atmospheric CO_2 into pore fluids, hydrolysis of silanol (SiOH) groups and hydrolysis of FeOOH surface groups. It is anticipated that chemical conditions within the caisson will initially be transient but that a steady-state chemical profile will eventually develop.

Calcium, Mg, Al, and Fe were the elements most abundantly leached from Wedron 510 sand in boiling HCl . Dissolved Mg was always correlated with Ca, and both were strongly correlated with pH shifts in column and batch tests, leading to the conclusion that the host mineral phase was a Ca,Mg-carbonate. Iron readily dissolved under strongly acidic conditions, implying its presence as Fe-oxyhydroxide rather than hematite. The sand contains small amounts of tracers being used in the caisson. Total acid-leachable Ni was 140 ng/g, and Li was 50 ng/g. Leachable Ni averaged near 1 ng/g in effluent from an unsaturated column, and leachable Li and Br declined to this level after a dozen pore volumes.

Batch titration curves for raw Wedron 510 sand apparently are dominated by carbonate dissolution and CO_2 uptake. Washing in boiling HCl stripped the sand grains of their coatings, resulting in a titration curve that qualitatively resembled that for HCl -washed Min-U-Sil 5. Surface acidity and complexation constants, obtained with the double extrapolation (DE) method, however, suggest that the HCl -washed Wedron 510 sand has a much greater tendency to give up protons (K_{a2}) and form complexes with electrolyte cations (K_{Na}) than other "quartz" surfaces. The causes of differences in the constants for the HCl -washed Wedron sand, HCl -washed Min-U-Sil 5 and HClO_4 -washed Min-U-Sil 5 are unknown at this time. They may be due to low estimates of surface area, differences in the washing procedures and/or the inherent imprecision of the DE method itself. Potentiometric titrations on the sand differ from those of pure quartz and suggest that the effective surface area of the sand measured by N_2 -BET gas adsorption ($0.118 \text{ m}^2/\text{g}$) may seriously underestimate the actual area exposed to solutions. The untreated sand is probably too complex to investigate using potentiometric titrations.

Studies by SEM failed to reveal any grains or particles rich in Fe or Ca+Mg, even in the colloidal fraction, implying that the sources of these elements (Fe-oxyhydroxide and carbonate) occur as thin coatings or as fine particles adhering to the grains of sand. Modeled distributions of Ca and Mg based on XPS data favor an extremely dispersed mode of occurrence as well. In order to account for the observed surface concentration of Ca and

Mg while observing mass balance constraints (acid-leachable Ca+Mg is only 1.03 $\mu\text{mole/g}$), Ca and Mg must be concentrated at the immediate surface of the sand grains, either as a coating or as particles much less than 500 nm in large dimension (otherwise they would have been detected by SEM/EDS). The Al in kaolinite was also detected by XPS. The intense signal implied that as much as half the available surface might be covered by kaolinite flakes. Such a distribution is consistent with SEM observations on the morphology of the colloidal fraction and accounts for the Al content of the sand.

Adsorption of nickel, lithium and bromide by the sand were measured using batch techniques. The batch adsorption experiments show that Br does not adsorb and that Li adsorbs relatively slowly and weakly in the neutral pH range. For the pH range relevant to the caisson experiment (7- 8.5), under CO_2 -free to partially-equilibrated conditions, the measured Li K_d s range from approximately 0.05 to 0.25 ml/g (5% - 20% adsorption). The degree of adsorption is slightly dependent on the pH, reaching a maxima at near-neutral pH. Li batch isotherm data indicate stronger sorption at lower concentrations; the data are fit satisfactorily by a Freundlich isotherm.

Small column experiments were conducted to transport of Li and Br in saturated Wedron 510 sand. Breakthrough curves for Br show a retardation factor slightly less than 1, indicating a small amount of anion exclusion, and were satisfactorily modeled by the equilibrium linear isotherm adsorption convective-dispersive model of the CXTFIT code. The Li pulses could be adequately modeled by the equilibrium convective-dispersive model using "effective" K_d s that are smaller than the lowest values measured in the batch experiments. The "effective" K_d s, and the equilibrium K_d s and sorption rate constants measured in the batch experiments, however, are consistent with the value of "effective" retardation factors predicted with the kinetic model of Kuhn and Peters (1981). Given the non-linear sorption behavior determined from the batch studies, it is likely that a set of transport equations including non-linear isotherms would model the Li effluent curves better. However, even without explicit inclusion these effects, this analysis probably provides reasonable order-of-magnitude estimates of the Li sorption and kinetic parameters. For the longer residence times in the caisson at Los Alamos, it is expected that nearly equilibrium conditions will be present.

A surface-complexation model of Ni adsorption by the sand has been formulated for use in transport calculations using the LEHGC code. Batch adsorption studies show that Ni adsorption is strongly pH-dependent, changing from 20% adsorbed at pH 6 to complete adsorption at pH 7. Adsorption was independent of ionic strength, and was enhanced by higher levels of CO_2 below pH 8. At higher pH values, higher levels of CO_2 appeared to stabilize Ni in solution. High concentrations of Li, a weakly adsorbing cation, reduced Ni adsorption slightly. Ni adsorption edges for goethite and quartz, two components of the sand, were also measured. Ni adsorption on pure quartz is only moderately pH-dependent and differs in shape and location from that of the sand, whereas Ni adsorption by goethite is strongly pH-dependent.

Triple-layer surface-complexation model constants were obtained from the adsorption data for goethite using the HYDRAQL speciation code. Attempts to model the adsorption

characteristics of the bulk sand in terms of the properties of pure end-member components suggested that much of the sand surface is inert. The goethite model provides a good fit to the Ni-adsorption curve of the sand when the specific surface area of the Fe-oxyhydroxide coating on the sand is assumed to be $\sim 560 \text{ m}^2/\text{g}$, compatible with its occurrence as amorphous Fe-oxyhydroxide. Ni adsorption mechanisms have not been unambiguously identified; however, this preliminary adsorption model provides an initial set of parameters that can be used in transport calculations.

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Appendix A

Characterization of Wedron 510 Sand for the Intermediate-Scale (Caisson) Transport Experiment

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A.1 Objectives

The primary objective of the work described in this appendix is the identification and characterization of the minerals that will most strongly affect the transport of aqueous species of lithium and nickel in the caisson. The minerals will affect tracer transport either directly through adsorption or coprecipitation or indirectly through solid/solution reactions that alter the bulk chemistry of the solution in the caisson. In this study, the surface of the porous medium in the caisson (Wedron 510 sand from Wedron Silica Corp., Wedron, IL 60557) has been characterized by a variety of chemical, mineralogical, and physical methods. Determination of the bulk composition and mineralogy provide a starting point for inferring surface composition and mineralogy, but other studies reveal that mineral coatings armor much of the surface area of the sand grains. The properties of the phases exposed to solutions may be very different from those of the minerals that make up the bulk of the sand. Such surface coatings may be only a few nanometers thick and are difficult to identify directly. Instead, their identities must be inferred from leachable components and reactions with species in solution. In order to compare the properties of the surface coatings to those of the underlying minerals, several cleaning procedures were employed to strip the sand of its coatings to varying degrees. These ranged from complete removal of all coatings, exposing a quartz surface, to selective removal of carbonate coatings, which leave clay and Fe-oxyhydroxide coatings intact.

Potentiometric titrations have been used by other workers to determine equilibrium constants for surface deprotonation and for surface complexation of pure minerals with electrolyte cations (for example, see Kent et al. 1988, and Davis and Kent 1990). One of the long-term objectives of the study described in this interim report is to determine if these techniques are applicable to natural materials composed of mixtures of several minerals. This is being accomplished by comparing titration curves of the bulk sand, acid-stripped sand and individual components of the sand. In this study, Min-U-Sil 5 (U.S. Silica Co., formerly Pennsylvania Glass Sand Corp.) is used as an α -quartz reference material. The work described in this appendix provides the foundation for studies to determine if the behavior of the bulk sand can be predicted from those of synthetic mixtures of its constituent components. Further discussion of this "building-block" approach and its applicability to transport problems in the caisson are beyond the scope of this appendix. The focus of this appendix is a summary of progress in the development of techniques used to characterize the sand, and a description of interim results.

A.2 Methods

Characterization methods employed in this study may be subdivided into microscopic and surface methods, and wet chemical methods. They are summarized in Table A.1 according to sensitivity to surface composition and type of information (physical, chemical, or mineralogical) provided by each.

Table A.1. Analytical methods (Acronyms are defined in the subsection for each method)

Analytical method	Sensitivity	Type of information
<i>Microscopic and Surface Methods</i>		
Optical microscopy	Bulk	Mineralogical Physical: grain morphology
	Surface	Physical/chemical: observations of colors of surface coatings
Sieving	Bulk	Physical: particle-size distribution
XRD	Bulk	Mineralogical
XRD with pre-treatment	Near-surface	Mineralogical
SEM	Bulk	Physical: morphology
SEM/EDS	Semi-bulk	Chemical: composition of outer $\sim 1 \mu\text{m}$ of grains
BET	Bulk	Physical: surface area
XPS	Near-surface	Chemical: composition of outer $< 5 \text{ nm}$ of grains
<i>Wet-Chemical Methods</i>		
HF dissolution	Bulk	Chemical
Selective leaching	Surface	Chemical
Potentiometric titration	Surface	Chemical

A.2.1 Microscopic and Surface Methods

A.2.1.1 Optical Microscopy

Sand grains were examined by eye and binocular microscope before and after the cleaning procedures described in later sections of this appendix. Three thin sections of Wedron 510 sand were made. Two were standard grain mounts, and the third was cut using standard rock-sectioning techniques from a cured slurry of sand and epoxy. A significant amount of material was rubbed out of the grain mounts during polishing, whereas the other section cracked due to differential expansion upon heating while being glued to a petrographic slide. Thin sections were examined by petrographic microscope to obtain an estimate of the bulk mineralogy, including trace constituents.

A.2.1.2 Particle-Size Distribution by Sieving

An aliquot of sand (100 g) was placed in the uppermost sieve of a stack arranged in order of decreasing size from top to bottom. Seven sieves were used, with U.S. Standard

Mesh sizes of 50, 70, 100, 140, and 200, corresponding to openings of 295, 212, 150, 106, and 75 μm , respectively. The stack was shaken on a Pulverit Vibrator for a total of 45 minutes during which it was tilted and rotated by hand every 10 minutes to spread out the sand. Afterwards, the stack was disassembled, and the material remaining on each sieve and in the collection pan at the bottom was weighed to ± 0.01 g.

A.2.1.3 X-ray Diffraction (XRD)

X-ray diffraction data were obtained on an automated Scintag X-ray diffractometer. Packed powder mounts were used for samples of 0.5 g or larger; otherwise a thin layer was spread on an oriented slab from a quartz crystal (cut so that no diffraction maxima from the slab would be observed). The goniometer was scanned over the range $2\theta = 5\text{--}65^\circ$; instrument settings are summarized in Table A.2. Background correction and 40-point boxcar smoothing was performed using Scintag software. Phase identification was accomplished visually, using the TC9 software package to overlay the diffractogram with a stick-figure representation of the expected maxima for candidate minerals.

A.2.1.4 Scanning-Electron Microscopy With Energy-Dispersive Spectrometry (SEM/EDS)

Mounts were prepared by sprinkling a few grains onto a mounting stub that was coated with wet carbon paint. After drying, the mounted grains were carbon-coated to inhibit charge build-up during analysis. Observations were performed on a scanning electron microscope fitted with a solid-state X-ray spectrometer for semi-quantitative measurement of secondary characteristic X-rays, providing approximate elemental abundances of the area being swept by the electron beam. Incident electrons were accelerated through a potential difference of 15 kV. Grains were photographed at magnifications ranging from 75x to 10,000x to show features ranging from overall

Table A.2. Operating parameters for the Scintag X-ray diffractometer and software

Parameter I.D.	Value
X-ray tube	Cu
Filter	Ni
Incident slits	2° , 4°
Analyzer slits	1° , 0.3°
2θ range	$5 - 65^\circ$
Scan type	Step scan
Step size	0.05°
Preset time	6 s

morphology to surface details as small as 50 nm. EDS spectra were acquired at single points as well as over broad areas to aid mineral identification.

A.2.1.5 Surface Area by Gas Adsorption [Brunauer-Emmett-Teller (BET) method]

Surface area measurements were performed using a Quantachrome Autosorb-6. Operating parameters are summarized in Table A.3. Experimental isotherms consist of measurements of the amount of gas adsorbed at the boiling temperature of liquid N₂ (-196 °C) as the pressure of the gas varies from 0 to its equilibrium vapor pressure, p^0 . The measurements are analyzed by the BET method (Brunauer et al., 1938; Lowell, 1979) as described in Attachment 1 to this appendix.

A.2.1.6 X-ray Photoelectron Spectroscopy (XPS)

Both untreated and leached grains of Wedron 510 sand were examined by XPS. Surface coatings of the leached grains were removed by boiling in HCl according to procedures in section A.2.2.1 *Batch Dissolution for Bulk and Surficial Analysis*. Mounts for XPS were prepared by densely packing grains on a platform coated with double-sided tape. The platform was placed in the vacuum chamber of the instrument for exposure to Al K_α X-rays, and energies of secondary photoelectrons were measured. The photoelectrons have a mean free path of only a few nanometers, so the effective sampling depth is probably less than 5 nm (Koppelman and Dillard, 1977). Photoelectron energy is a function of both atomic number and oxidation state. Thus, XPS provides information about elemental composition and chemical speciation for a surface layer, much thinner than that sampled by SEM/EDS.

Table A.3. Operating parameters for BET measurements on the Quantachrome Autosorb-6

Parameter I.D.	Value
Gas type and molecular weight	N ₂ @ 28.0134 g/mole
Cross-sectional area (a_m)	16.2 Å
Correction factor	$6.580 \cdot 10^{-5}$
p/p^0 tolerance	4 torr(?)
Equilibration time	2 min(?)
Sample size	4.5 g or ~5 m ² , whichever is larger.
Outgas time and temperature	14 h @ 100°C
Approximate run time	6 h

A.2.2 Dissolution and Leaching Techniques

A.2.2.1 Batch Dissolution for Bulk and Surficial Analyses

Bulk Dissolution. Samples for bulk analysis were digested in 40 ml teflon screw-cap jars using HF and HNO₃ (0.5 g sample, 10 ml 48% HF and 3 ml 6 N HNO₃). Caps were screwed on loosely and the jars were placed on a hotplate set to ~80 °C to react overnight. Next, the caps were removed and the samples evaporated to dryness. The samples were redissolved in 4 ml 6 N HNO₃ and filtered into 100 ml volumetric flasks using Whatman #42 paper. For ICP-MS (inductively-coupled plasma mass spectrometry) analysis, they were then spiked with internal intensity standards and taken up in 100 ml 1% nitric acid solution. For Ca and Si analysis by AA, 50 ml of the ICP-MS solutions was evaporated to dryness, taken up in 5 ml of 2% HNO₃, and analyzed by AA.

Dissolution of Surface Coatings in Boiling HCl. Samples for surface analysis were leached using boiling HCl. 1.0 g samples were weighed into 40 ml glass beakers with magnetic stirring bars, 20 ml 6 N low-temperature distilled (LTD) HCl was added, and they were placed on a stirring hotplate to stir and simmer for 1 hr. After cooling, the supernate was filtered using Whatman #42 paper into a clean 40 ml glass beaker and evaporated to dryness. They were redissolved in 4 ml 6 N LTD HCl, transferred to 100 ml volumetric flasks, spiked with internal intensity standards for ICP-MS analysis, and brought up to volume with deionized water. For Ca and Si analysis by AA (atomic absorption spectrometry), 50 ml of the ICP-MS solutions was evaporated to dryness, taken up in 5 ml of 2% HNO₃, and analyzed by AA.

Dissolution in Near-Neutral, Weakly Acidic or Alkaline Solutions. In batch systems consisting of 100 ml 0.01 M NaCl and 50 g untreated sand, pH was adjusted by addition of weak HCl or NaOH to range from 6.7 to 8.0. Concentrations of Ca and Mg were monitored over a two-week period. Aliquots were taken for AA analysis at 0.67 days, 1.60 days, and 15.2 days, and pH was recorded at the same time. pH measurements were made under ambient atmospheric conditions. Between samplings, the bottles were agitated on a shaker table.

In a second study, batch systems consisting of 15 g untreated sand and 15 ml 0.01 M NaCl were equilibrated for 31 days under nominally CO₂-free conditions in 50-ml polyallomer centrifuge tubes. Initial pH values were adjusted to cover the range 2.75 – 11 using 0.05 M HNO₃ or NaOH. Measurements of pH were made under Ar atmosphere, obtained by purging the headspace of each tube with Ar for ~30s (Ar flow rate = ~1 l/min), then shutting off the Ar flow and recording the pH when the electrode drift rate decreased to less than 3 mV/min. A close-fitting cap with holes for the electrode and Ar supply lines prevented intrusion of the ambient atmosphere. Each tube was gently swirled during pH measurement. Between measurements, the tubes were rolled and tilted on hematology mixers, providing gentle agitation.

A.2.2.2 Leaching in an Unsaturated Column

Small-scale column experiments were carried out to study the changes in the pH and composition of leachable components of Wedron 510 sand in dilute NaCl electrolyte as functions of time under conditions of partial hydraulic saturation. A schematic of the column apparatus is shown in Figure A.1. NaCl solutions (0.01 M or 0.001 M NaCl, pH $\approx$ 6) were pumped through columns (7 cm dia. x 24 cm high) filled with Wedron 510 sand. The pore volume of the column was approximately 180 ml. The flow rate and bottom-boundary suction was adjusted to provide $\sim$ 50% saturation. The applied suction at the porous plate constituting the bottom boundary was always less than its bubble point, so no air was drawn through the column. Flow rate and saturation averaged $\sim$ 0.4 ml/min and

Figure A.1. Experimental apparatus for leaching studies under unsaturated flow conditions in a column of Wedron 510 sand.

60%, respectively, during most of the experiments. Thus the column contained 108 ml pore fluid, with a fluid residence time of 4.5 h (i.e., $108 \text{ ml} / 0.4 \text{ ml/min} = 270 \text{ min}$).

The pH of the influent solution was measured in a top reservoir and also in a flow-through cell just prior to entry into the column. The pH of the effluent solution was measured in a flow-through cell as it exited the column and after it was collected in an open vessel. These measurements were taken using standard combination reference-pH electrodes and Orion 940 pH meters. The electrodes were calibrated every three hours with commercial buffer solutions of pH 7 and 10. Reported effluent pH values are from the flow-through cell, where exchange with atmospheric CO_2 was assumed to be negligible.

For an experiment with 0.001 M NaCl influent, samples of effluent were acidified by adding 1% by volume concentrated HNO_3 , and were analyzed for Al, Ca, Mg, Li, Ni, and Br by ICP-MS. Si was determined for each sample by atomic absorption as described for bulk analysis.

A.2.3 Analysis of Aqueous Solutions

Analysis of solutions prepared by wet-chemical methods was accomplished either by inductively-coupled plasma mass spectrometry (ICP-MS) for most major, minor, and trace elements, or by atomic absorption spectrometry (AA) for selected elements where higher precision or only a few elements were required. Silicon was analyzed either by AA or the molybdate-blue method. Two techniques are described elsewhere: Br analyses are described in Appendix E.5 *Br Analysis by Ion-Specific Electrode (ISE)*, and measurement of pH in batch systems is described in Appendix E.1 *pH Measurement Under Atmospheric and CO_2 -free Conditions*.

A.2.3.1 Inductively-Coupled Plasma Mass Spectrometry (ICP-MS)

Major and minor elements in leachates from batch and column studies and in residues from bulk dissolutions were analyzed on a VG Instruments Plasmaquad ICP-MS. The specific isotope analyzed for each measured element is listed in Table A.4. Prior to analysis, samples were spiked with 1000 ng/ml each of Be, Sc, and In to provide internal intensity standards. Analyses of standard solutions interspersed with the samples defined the calibration curve for each element. The standards were also run as unknowns to determine the detection limit and precision for each element, which are listed in Table A.5. Surface analyses were twice as sensitive as bulk analyses because twice as much sample

Table A.4. Isotopes used for ICP-MS analysis

^7Li	^{27}Al	^{47}Ti	^{55}Mn	^{60}Ni	^{90}Zr	^{238}U
^{23}Na	^{39}K	^{49}Ti	^{56}Fe		^{91}Zr	
^{24}Mg		^{50}Ti	^{57}Fe		^{92}Zr	

Table A.5. Detection limits and precisions ($\pm 1\sigma$ errors) for ICP-MS analyses using bulk and surface-analysis dissolution procedures

Element	detection limit ($\mu\text{g/g}$)		minimum error ($\mu\text{g/g}$)		maximum error (%)	Typical blank ($\mu\text{g/g}$)	
	bulk	surface	bulk	surface		bulk	surface
Li	0.05	0.02	0.05	0.02	2	0.02	0.02
Na	0.5	0.2	0.3	0.1	2	0.11	0.00
Mg	0.5	0.2	0.13	0.05	2	0.28	0.21
Al	0.5	0.2	0.3	0.1	2	4.6	2.0
K	0.5	0.2	0.5	0.2	5	0.00	0.00
Ti	0.3	0.1	0.3	0.1	2	0.22	0.00
Mn	0.05	0.02	0.05	0.02	2	0.26	0.00
Fe	1.3	0.5	0.5	0.2	2	0.63	0.12
Ni	0.08	0.03	0.05	0.02	2	0.02	0.03
Zr	1.3	0.5	0.3	0.1	2	0.36	0.19
U	0.03	0.01	0.03	0.01	1	0.00	0.00

was used. Typical blank levels for both surface and bulk analyses are also listed in Table A.5.

A.2.3.2 Atomic Absorption Spectrometry (AA)

Nickel concentrations were determined using graphite-furnace atomic absorption spectroscopy (GFAA) on a Perkin-Elmer 5000 with HGA 500 graphite-furnace programmer and AS-1 auto-sampler. Analytical details are described in Appendix E.3 *Ni Analysis by Graphite Furnace Atomic Absorption*. Analyses for Li, Ca, Mg, Si, and Fe were obtained using air-acetylene or nitrous oxide-acetylene flame AA on the Perkin-Elmer 5000. Fuel mixtures followed Perkin-Elmer's recommendations, and analytical details were similar to those described in Appendix E.4 *Li Analysis by Flame Atomic Absorption*.

A.2.3.3 Dissolved Silica by Molybdate Blue

Dissolved silica was analyzed colorimetrically by the molybdate blue method (Brown et al., 1970). Briefly, dissolved silica reacts with ammonium molybdate at low pH to form a yellow silicomolybdate complex, which is then reduced by sodium sulfite to form the molybdate blue color. With 1 cm cells, the method can accommodate concentrations as high as 20 $\mu\text{g/g}$ (absorbance = 0.8), with a limit of detection near 20 ppb. Precision is estimated to be better than 1% or 40 ppb, whichever is greater. Samples with concentrations higher than 20 $\mu\text{g/g}$ were diluted volumetrically by a factor of 10,

introducing a small additional uncertainty. Samples with concentrations less than 5 $\mu\text{g/g}$ were measured in 3 cm cells, providing a 50% increase in sensitivity.

A.2.4 Potentiometric Titrations

Potentiometric titrations provide insight into the bulk interaction between adsorbing surfaces and ions in solution. Measurements consist of pH readings on systems of known composition (electrolyte volume, ionic strength, mass of sand, amount of added acid or base). Because it is a weak acid and will alter the pH of the system, CO_2 must be excluded from the titration. The resulting titration curve of pH vs. added acid (or base) is compared with the curve for electrolyte alone; differences between the two are attributable to uptake or release of protons by the surfaces. If the surface area and sorption site density are known, then the surface charge may be calculated. Finally, if titration data is collected at several ionic strengths, a double-extrapolation (DE) to zero ionic strength and zero surface charge can estimate the intrinsic acidity of the surface and the intrinsic stability of complexes between the surface and electrolyte ions. See sections 5 and 6 of Appendix E.6 *Potentiometric Titrations to Determine Surface Charge* for a more detailed discussion of the calculation of surface charge and the extrapolations to obtain intrinsic acidity and association constants.

A.2.4.1 Surface Preparation

Two techniques were employed to clean sample surfaces. The goal of these harsh methods was to strip the grains of all coatings, exposing the underlying quartz surface.

Ignition/boiling HClO_4 . This cleaning procedure was adapted from MacNaughton and James (1974). The samples were ignited for 48 h at 550 $^\circ\text{C}$ to remove organics, and then refluxed in 4M HClO_4 for 4 h followed by rinsing to pH 3. The reflux/rinse cycle was repeated two more times. The pH was raised to ~ 9.1 by the dropwise addition of dilute NaOH, and finally the sample was thoroughly rinsed with $> 10\text{ M}\Omega$ deionized water. Finely powdered samples were stored as suspensions in deionized water, whereas granular samples were dried. During ignition, the samples acquired a pinkish hue presumably due to conversion of Fe-oxyhydroxides to hematite that was not entirely removed by the HClO_4 reflux.

Boiling HCl. Samples were boiled in 6 N HCl for 4 h. After cooling, the supernate was decanted (and saved for analysis, if so desired), and the sample was rinsed repeatedly with air-saturated water (conductivity $> 10\text{ M}\Omega$ before adding air) until the pH of the rinse water reached 5.6. Finely powdered samples were stored as suspensions in deionized water, whereas granular samples were dried. This procedure leaves the sample colorless and appears to leave any clays intact.

A.2.4.2 Batch Method

Batch titrations were performed under CO_2 -free conditions in 50 ml polyallomar centrifuge tubes containing 15 or 20 ml 0.01 M NaCl electrolyte for 15 g Wedron sand or

0.53 g Min-U-Sil 5, respectively. The adsorbent surface area ranged from 1.80 – 3.15 m². The pH was adjusted by adding 49 mM HCl or 37 mM NaOH to obtain values in the range 3 – 10 at intervals of ~1 pH unit. Systems with untreated adsorbents were equilibrated for 5.8 days for Wedron sand and 5 days for Min-U-Sil 5, whereas systems with HClO₄-washed adsorbents were equilibrated for 2 days. A batch titration of electrolyte alone was equilibrated for only a few minutes before pH measurement. During equilibration, the centrifuge tubes were continuously agitated by hematology mixers which provided a gentle, eccentric rolling motion. Periodic pH measurements were made at elapsed times of up to 31 days to monitor the pH effects of the dissolution of sparingly soluble phases. CO₂-free conditions were maintained by preparing solutions from boiled deionized water, purging the headspace of all vessels with Ar and carrying out pH measurements under Ar atmosphere.

A.2.4.3 Continuous Method

Continuous titrations of Min-U-Sil 5 and Wedron 510 sand were performed with an automated titrator using a 250 ml polyethylene reaction vessel containing 150 ml electrolyte and ~20 m² surface area. The goals of these titrations were to validate the methods used here by comparing the values obtained on a standard reference material (Min-U-Sil 5) with those from the literature and to obtain a measurement of the surface properties of the grains themselves after they had been stripped of all armoring phases by the boiling-HCl treatment described above. Systems were titrated in step-wise fashion by adding a precise amount of acid or base, waiting for equilibrium (i.e., a stable pH measurement), recording the pH, adding another aliquot of acid or base, and so on. Two systems were studied: (1) a system consisting of 4.534 g HCl-washed Min-U-Sil 5 α -quartz and 150 ml NaCl electrolyte which was continuously titrated over the pH range 4.2 – 9 at ionic strengths ranging from 0.0003 to 0.096 M and (2) a system consisting of 150 g HCl-washed Wedron 510 sand and 150 ml electrolyte which was continuously titrated over the pH range 4.5 – 9 at ionic strengths ranging from 0.0003 to 0.096 M.

Electrolyte and adsorbent equilibrated rapidly after addition of acid or base under CO₂-free conditions in the absence of dissolution reactions. A titration curve could be acquired from a single system in about an hour; additional curves on the same system were acquired by returning to the starting pH, adding salt to increase the ionic strength, and repeating the measurement process. Details of the titration procedure and of data processing for the extraction of intrinsic stability and association constants are described in Appendix E.6 *Potentiometric Titrations to Determine Surface Charge*.

A.3 Results

A.3.1 Bulk Composition

A.3.1.1 Optical Microscopy

Quartz dominates the mineralogical mode, with an abundance of well over 99%. Grains range in size between 0.1 and 0.5 mm, and are subrounded to rounded, with a few percent subangular grains. Most quartz shows uniform extinction indicating minimal strain, but 5 – 10% of quartz grains are strained, showing undulose extinction, and a few (< 1%) are polycrystalline, characteristic of metamorphic origins. A majority of the grains are sparsely and irregularly coated by tiny (1 – 3 μm) granular minerals, too small for optical identification, that comprise less than 0.1% of the mode. Depending on the nature of the coatings, the grains range in color from clear to yellow brown to pink. As described in Section A.2.4.1 above, grain samples that were ignited for 48 h at 550 °C acquired a pinkish hue presumably due to conversion of Fe-oxyhydroxides to hematite. Some grains contain trains of inclusions 0.5 – 3 μm in size, which were also too small to identify. Very rarely, quartz grains contain small honey-brown inclusions (sphene?), and lath-shaped brown birefringent inclusions (biotite?). Rare heavy minerals include tourmaline and zircon.

A.3.1.2 Particle-Size Distribution and Surface Area

The size analysis of the Wedron 510 sand obtained by dry sieving is shown in Table A.6 and Figure A.2.

Surface area was measured by N_2 BET on an aliquot of the sand, giving a value of 0.118 m^2/g . Additional parameters, providing information about the quality of the run, include an acceptable C_{BET} value of 5.04, and a correlation coefficient of 0.971. The

Table A.6. Nominal and measured size distribution for Wedron 510 sand

U.S. sieve #	Size fraction (μm)	Nominal distribution* (% retained)	Measured distribution (% retained)
50	> 295	8	8.9
70	212 – 295	36	39.6
100	150 – 212	34	27.7
140	106 – 150	15	16.6
200	74 – 106	6	6.4
Pan	< 74	1	0.8

*Particle-size distribution by Wedron Silica Corporation (Wedron, IL 60557).

Figure A.2. Nominal and measured size distribution for Wedron 510 sand.

monolayer quantity, W_m , was not evaluated because the isotherm did not begin at low enough values of p/p^0 . Analytical data and results are tabulated in Table A.7 and displayed graphically in Figure A.3. Although N_2 isotherms become problematic for specific surface areas of less than $1 \text{ m}^2/\text{g}$, measurements on NBS standards of similar specific area deviate from the nominal values by no more than $+0.02$. Applying this correction to the sand would lower its value to $0.098 \text{ m}^2/\text{g}$. Additional information about the BET method is given in Attachment 1 to this appendix.

A.3.1.3 X-ray Diffraction

An x-ray diffraction pattern for untreated sand crushed to -200 mesh showed significant maxima for quartz only (Figure A.4a). A detailed examination of the pattern for minor peaks, reveals several small peaks attributable to kaolinite, as well as several unattributable peaks. None of these coincide with peak positions expected for carbonate minerals.

Table A.7. Multi-point N_2 BET surface area measurements and results for Wedron 510 sand (symbols are defined in section A.2.1.5)

p/p^0	V' (ml/g @ STP)	W (g/g)	$1/W(p^0/p - 1)$	Results
0.1113	0.01236	$1.545 \cdot 10^{-5}$	$0.8108 \cdot 10^4$	Area: $0.1184 \text{ m}^2/\text{g}$
0.1628	0.01492	$1.864 \cdot 10^{-5}$	$1.043 \cdot 10^4$	Slope: $2.358 \cdot 10^4$
0.2142	0.02056	$2.569 \cdot 10^{-5}$	$1.061 \cdot 10^4$	y-intercept: $0.5838 \cdot 10^4$
0.2649	0.02442	$3.051 \cdot 10^{-5}$	$1.181 \cdot 10^4$	Correlation coeff. (r): 0.9713
0.3154	0.02745	$3.430 \cdot 10^{-5}$	$1.343 \cdot 10^4$	C_{BET} : 5.039

Figure A.3. Linear-regression analysis of multi-point N₂ BET measurements.

A colloidal fraction of the sand (0.05% by weight) which remained dispersed in solution at pH > 8.5 was decanted, centrifuged, filtered, and dried. The XRD pattern (Figure A.4b) shows clear diffraction maxima for quartz and kaolinite, along with several unidentified peaks of low intensity. The packed powder mount exhibited a high degree of preferred orientation, greatly accentuating the intensity of the 7 Å basal diffraction for kaolinite. A qualitative comparison of the kaolinite and quartz peaks near $2\theta = 25^\circ$ shows that kaolinite must comprise a major fraction of the colloid, subequal in abundance relative to quartz. The kaolinite has a high degree of crystallinity, as indicated by the narrow peaks, indicating a detrital rather than authigenic origin.

A.3.1.4 Scanning-Electron Microscopy with Energy-Dispersive Spectrometry

Scanning electron microscopy provided detailed views of surface morphology (Figure A.5a), and revealed surfaces dominated by abrasion steps and randomly adhering particles (Figure 5b). Other than sieving, these grains were untreated. Colloidal particles released from grain surfaces at high pH were also examined, as shown in Figure A.5c. These are presumed to be analogous to the adhering particles seen in the previous figure (Figure A.5b). Most colloidal particles appear platy, with ragged edges, implying some mechanical damage. These particles could be detrital, as the XRD evidence suggests, or the ragged edges could have been created during agitation of the bulk sand before the colloids were decanted.

Figure A.5. SEM photomicrographs of Wedron 510 sand (scale bars are in μm): (a) Grains from the $> 295 \mu\text{m}$ fraction showing rounded to subrounded morphology; (b) Surface detail of a grain from the $74 - 106 \mu\text{m}$ fraction showing abrasion steps and adhering fragments; (c) Colloidal particles released from grain surfaces at high pH.

Figure A.6. SEM/EDS spectra showing approximate proportions of O, Mg, Al, Si, S, K, and Ca in the outer 1 μm of the examined area (samples are carbon-coated so C peak is meaningless): (a) Typical of quartz grains in Figure A.5a; (b) From one of the steps in Figure A.5b; (c) Broad-area scan of many colloidal grains in Figure A.5c.

Energy-dispersive spectrometry was used to provide qualitative estimates of compositions in the outer 1 μm of the grains. This layer appears to be nearly pure quartz in all grains examined. A typical EDS pattern is shown in Figure A.6a, in which Si is the dominant cation, with barely detectable amounts of Al and Mg. Small regions ($\sim 1 \mu\text{m}^2$) exist on individual grains that are richer in Al, as shown in Figure A.6b. Colloidal particles (Figure A.6c) are notably different in composition, with subequal amounts of Si and Al, and traces of Na, Fe, and Ti. These elemental abundances and the XRD data described previously suggest that kaolinite is the major constituent of the colloids. As discussed in Section A.3.2.2, surface leachates of the sand contained significant amounts of Ca, Fe and Mg. In spite of intensive search, no carbonate phases (distinguished by $\text{Ca} \pm \text{Mg}$ as the dominant cations) could be identified. Similarly, no Fe-oxyhydroxides (Fe as the dominant cation) could be found. However, it is important to note that the electron beam induces emission of secondary x-rays from up to 1 μm below the surface. If present, the Fe, Ca and Mg-bearing phases must be flakes or surface coatings significantly less than 1 μm thick and thus all but invisible to EDS.

A.3.2 Surface Composition

A.3.2.1 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectra were acquired on both untreated and acid-washed (boiling-HCl method) sand. The acid-washed sand had also been used in a titration experiment; a colloidal component (presumably kaolinite) was liberated at high pH and subsequently rinsed away. For the untreated sand, Si was the dominant cation (1.00 relative abundance), followed by Al (0.28 relative abundance), and subequal amounts of Ca and Mg (0.02 – 0.03 relative abundance). Reducing the slit width from 2 mm to 1 mm merely reduced the intensity of all peaks, indicating that minor phases are uniformly distributed rather than occurring as rare large single grains. The acid-washed sand had 90% less Al and no Ca or Mg. Interfering peaks from the mounting tape obscured the possible presence of Fe and CO_3^{2-} in both samples.

Models of the distribution of the element within the surface layer are based on quantitative data (the intensity of photoelectron emission and known calibration curves) and qualitative assumptions about the nature of the surface. For example, an element could be present as a constituent of a monolayer coating all surfaces, or it could be present in thick discrete particles covering only a small portion of the available area. Other data, such as that from SEM (presence and morphology of discrete particles) or XRD (mineralogy of the finest size-fraction), is required in order to constrain the choice of model.

In the untreated sand, apparent surface coverage of quartz by minor Al- and Ca+Mg-bearing phases was calculated according to two different models, illustrated schematically in Figure A.7. In the first, layer-by-layer coverage was assumed; monolayers covering the entire available surface were added until the calculated relative intensities of diagnostic elements reproduced the XPS spectra. In the second, the minor phase of interest was assumed to occur as discrete particles that are opaque to XPS, obscuring that part of the quartz surface upon which they rest. A thickness of 500 nm was assumed, based on SEM

Figure A.7. Models used to calculate apparent coverage of a smooth horizontal surface by a minor phase (e.g., kaolinite) from XPS data. Probable effects of grain morphology are illustrated schematically.

observations of particles adhering to grain surfaces. Both models assumed that the sample surface was a smooth horizontal plane. No corrections were made for surface roughness or grain morphology. Deviations from the horizontal should lead to over-estimates of the proportion of the minor phase for both models.

For Al present as kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_2$), layer-by-layer coverage implied a uniform coating 2.5 nm thick, but this accounts for an unacceptably small fraction (less than 1%) of the total Al in the sand measured by bulk dissolution. (Surface-leaching analyses were not sensitive to structural Al contained in flakes of kaolinite and thus underestimate the quantity of Al accessible to XPS.)

The discrete-particle model implied that approximately half of the surface area was covered by kaolinite flakes. Although surface coverage evident in SEM photomicrographs appeared to be much lower (5 – 10%), mass balance for Al was within an order of magnitude. These discrepancies are acceptable given the semi-quantitative nature of this model.

For Ca+Mg abundance, the discrete particle model requires 4% surface coverage. Because Ca+Mg constitutes only ~0.008% of the bulk sand, however, mass-balance requires that Ca+Mg must be concentrated at the grain surfaces, either as a coating or as tiny particles, and cannot be present as individual sand-sized grains of carbonate. As discussed above, SEM/EDS observations provide additional support for the coating hypothesis, because no grains rich in Ca+Mg were detected.

A.3.2.2 Chemical Analyses of Bulk Composition and Acid-Leachable Components

Chemical analyses of the bulk composition and surface leachates from a bulk (unsplit) sample and five sieve fractions are shown in Table A.8. Surface concentrations are expressed as the mass of the element in the leachate divided by the mass of the sand leached. No values are given for Br in the leachates because blank levels due to Br in the HCl were too high. High blank levels also plagued the bulk Mn analysis. Values of bulk Si concentration were close to 100 wt.%. The finer size fractions (106 – 150 μm and 74 – 106 μm) were more enriched in all of the minor and trace metals compared to the coarser fractions.

The highly enriched nature of the finest size fraction becomes quite apparent when its bulk concentrations are divided by corresponding concentrations in the unsplit sand, giving the enrichment factors tabulated in Table A.9a. The most dramatic enrichments are seen for Zr and U, and to a lesser extent in Ni, Ti, and Fe. The bulk of Zr and U is probably contained in zircon; Ni, Ti, and Fe may be controlled by ilmenite and/or Fe-oxyhydroxide. The surface-leaching data, summarized in Table A.9b, indicate that in spite of their comparative enrichment in the finest size fraction, Zr and U are not leachable by the comparatively inert solutions likely to be used in transport experiments. Titanium is similarly unreactive, as is Li, whose host phase is probably tourmaline. Sodium, K and Al show moderate bulk enrichment but decreasing leachability in the finest fraction, suggesting that a greater proportion of these elements is immobilized in clay, kaolinite, or authigenic feldspar in the finest fraction.

Both the bulk analyses of the finest size fraction and surface leachings of all size fractions reveal high concentrations of Al, Fe, Ca, and Mg relative to the unsplit sand.

Table A.8. Bulk and surface composition of Wedron 510 sand inferred from dissolution experiments (Concentrations normalized to weight of sand as $\mu\text{g/g}$ sand)

	unsplit		>295 μm		-212 to 295 μm		150 to 212 μm	
	bulk	leachate	bulk	leachate	bulk	leachate	bulk	leachate
Li	1.54	0.05	1.91	0.06	1.70	0.06	1.43	0.05
Na	1.67	<0.20	1.15	<0.20	1.00	<0.20	1.08	<0.20
Mg	24.7	10.92	9.73	3.25	23.0	13.7	27.2	13.4
Al	2820	482	2150	447	2290	579	2310	663
Si	*	5.4	*	6.9	*	5.4	*	5.4
K	2.52	0.51	1.30	0.86	1.40	<0.20	0.92	<0.20
Ca	55	23	47	6.9	46	26	44	22
Ti	83.1	2.55	55.9	2.26	61.1	2.35	65.8	3.25
Mn	1.11	0.36	0.79	0.06	0.99	0.21	0.85	0.14
Fe	242	80.0	83.4	45.6	128	39.0	121	77.4
Ni	0.18	0.14	0.08	0.06	0.09	0.09	0.13	0.15
Br	1.68	**	2.84	**	<0.75	**	3.01	**
Zr	192	0.49	35.7	0.24	35.8	0.28	30.1	0.42
U	0.73	0.02	0.21	0.02	0.22	0.01	0.21	0.02

	106 to 150 μm		74 to 106 μm		<74 μm	
	bulk	leachate	bulk	leachate	bulk	leachate
Li	1.30	0.06	1.41	0.05	2.47	0.06
Na	1.33	0.41	3.36	0.52	9.59	0.86
Mg	40.6	13.5	113	29.4	118	84.6
Al	3120	756	5430	884	11300	1200
Si	*	5.4	*	7.8	*	18.4
K	1.73	0.34	1.97	0.33	20.1	1.10
Ca	52	33	90	60	222	198
Ti	85.4	4.15	152	6.06	892	13.2
Mn	1.04	0.30	1.76	0.53	2	2.89
Fe	186	116	441	229	2280	1180
Ni	0.16	0.14	0.35	0.23	2.08	0.90
Br	2.84	**	2.86	**	<0.75	**
Zr	116	0.59	712	1.53	9450***	7.93
U	0.56	0.02	2.11	0.07	20.2**	0.37

* SiO_2 content was @100%.

** Analysis impractical due to high blank.

***3.5% insoluble residue appeared to be zircon. Thus, total Zr may be 27,230 mg/g, and U may be 58.2 $\mu\text{g/g}$ (calculated using Zr abundance and U/Zr ratio from coarser fractions).

Table A.9. Relative enrichments: (a) Enrichment in bulk concentration of the finest fraction ($< 74 \mu\text{m}$) relative to bulk (unsplit) sand and (b) Contribution of leachable component to bulk (total) concentration in three size fractions (Elements preferentially enriched in the finest-fraction leachate relative to the coarser size fractions are *emphasized*)

(a)		(b)			
bulk enrichment		leachable proportion by size fraction			
Element	$< 74 \mu\text{m} / \text{unsplit}$	Element	unsplit	$212 - 295 \mu\text{m}$	$< 74 \mu\text{m}$
Li	1.6	Li	0.03	0.03	0.02
Na	5.7	Na	0.12	0.20	0.09
Mg	4.8	<i>Mg</i>	<i>0.44</i>	<i>0.59</i>	<i>0.72</i>
Al	4.0	Al	0.17	0.25	0.11
K	8.0	K	0.20	0.14	0.05
Ca	4.0	<i>Ca</i>	<i>0.42</i>	<i>0.57</i>	<i>0.89</i>
Ti	10.7	Ti	0.03	0.04	0.01
Mn	1.8	<i>Mn</i>	<i>0.33</i>	<i>0.21</i>	<i>1</i>
Fe	9.4	<i>Fe</i>	<i>0.33</i>	<i>0.30</i>	<i>0.52</i>
Ni	11.6	Ni	0.78	0.92	0.43
Zr	49	Zr	0.0025	0.0078	0.00084
U	28	U	0.027	0.045	0.018

This suggests that the finest size fraction is composed in large part of fragments of the coatings present on larger grains. Four elements show increased leachability in the finest fraction: Mg, Ca, Fe, and Mn. Highly leachable Ca and Mg is readily explained by the presence of a carbonate phase, which is also needed to explain the observed solution chemistry (to be discussed later). Carbonate probably occurs abundantly in the finest fraction as chips of cement that have been knocked off larger sand grains. The putative carbonate appears to have a Ca:Mg mole ratio of 1:1, consistent with either dolomite or high-Mg calcite. A similar scenario explains enhanced Fe and Mn leachability. Iron-Mn oxyhydroxide coatings, ubiquitous in the near-surface terrestrial environment, probably thinly coat all of the surfaces of the sand. Because the specific surface area (e.g., m^2/g) increases with decreasing grain size, the leachable proportion of Fe and Mn should also increase if they are present predominantly as coatings. Leachable Fe is almost two orders of magnitude more abundant than leachable Mn, so the putative coating may be Fe-oxyhydroxide with a trace of Mn.

A.3.2.3 Surface Leaching in Near-Neutral, Weakly Acidic, or Alkaline Solutions

Leaching of trace constituents from untreated sand in weakly acidic, near-neutral pH or alkaline solutions was examined in closed system (batch) and open-system (column) experiments (Section A.3.3.4). These experiments were carried out to gain insights into potential dissolution, exchange, or desorption of components that will be mobile under conditions expected in the caisson, and to investigate possible interferences with proposed tracers.

Leaching in Near-Neutral Solutions. In the first batch study, concentrations of Ca and Mg and pH were monitored over a two-week period in batch systems consisting of 100 ml 0.01 M NaCl and 50 g untreated sand and an initial pH range of 6.7 to 8.0. Calcium concentrations (referenced to the mass of sand, not electrolyte) at 0.67 days decreased from 6 $\mu\text{g/g}$ at pH 6.7 to 4 $\mu\text{g/g}$ at pH 8. At the same time, Mg decreased from 2 $\mu\text{g/g}$ to 1 $\mu\text{g/g}$. After two weeks, the pH range had narrowed to only 7.2 – 7.5 due to uptake of CO_2 from the atmosphere and the buffering effect of the sand (presumably due to Ca+Mg carbonate dissolution). Final Ca concentrations decreased from 7.5 $\mu\text{g/g}$ at pH 7.2 to 6 $\mu\text{g/g}$ at pH 7.5, and Mg decreased from 4 $\mu\text{g/g}$ to 3 $\mu\text{g/g}$ over the same pH range.

Leaching in Mildly Acidic and Alkaline Solutions. In the second batch study (15 g untreated sand, 15 ml 0.01 M NaCl in 50-ml polyallomar centrifuge tubes, nominally CO_2 -free conditions), initial pH values were adjusted to cover the range 2.75 – 11. Results of pH measurements made after elapsed times of < 0.02, 3.0, 5.8, and 31 days are displayed in Figure. A.8 as titration curves (i.e., pH vs. μeq added acid/g sand.) Most of the systems did not reach steady-state, but evolution towards a buffered system was evident in the measurements on day 3, with the development of a hump in the titration curve at $\sim 1 \mu\text{eq/g}$ added acid and pH 7 – 8. A plausible buffer candidate is the carbonate-bicarbonate system.

The initial pH deviated only slightly from that expected for the electrolyte alone. At acidic pH, this was a consequence of partial dissolution of the Ca+Mg carbonate before the pH could be measured. At high pH, deviations were initially due to surface reactions between the sand and H^+ , OH^- , Na^+ , and Cl^- in solution. After 3 days elapsed, pH stabilized in batch systems with pH < 5, whereas the others continued to evolve. Two mechanisms account for the observed trends. Firstly, continuing dissolution of carbonate provided a sink for H^+ , causing the pH to rise. This was essentially complete within three days for the most acidic batches, and within 5.8 days for the remaining batches. The observed pH shift at 3.25 $\mu\text{eq/g}$ added acid would be produced by dissolution of 1.03 μmoles carbonate/g sand, calculated from mass balance considerations and assuming carbonate speciation as predominantly H_2CO_3 . Secondly, CO_2 diffused into each system through the containers' seals or walls, forming carbonic acid and hence a source for H^+ , causing the pH to decrease. This process was evident at high pH at 3 days, and became evident at pH 5 – 7 at 31 days. At 1.25 μmoles added base (-1.25 μmoles added acid), diffusion of $\sim 3 \cdot 10^{-14}$ moles/day CO_2 into this batch system could produce the observed decrease in pH with time.

Figure A.8. Evolution of pH with time in batch titrations of Wedron 510 sand under nominally CO₂-free conditions.

At the end of the 31-day equilibration period, each batch system was sampled for determination of dissolved Ca, Mg, and Si by AA. Results are graphed in Figure A.9. Calcium and magnesium concentrations were essentially constant under acidic conditions (pH < 6.5), and decreased under more alkaline conditions; the average Ca/Mg molar ratio of the leachate was 1.33. The relationship between Ca and Mg suggests that both were dissolving from the same solid phase, probably high-Mg calcite. Dissolved Si showed a U-shaped pattern, reaching ~2.1 μmoles/g solution (corresponding to 60 μg/g sand) at both pH 4.33 and 10, with a minimum of 0.31 μmoles/g solution (9 μg/g sand) at pH 6.5 – 7.5. High values at high pH are consistent with the increasing solubility of SiO₂ polymorphs and with a possible colloidal component due to dispersion of clays. High values at low pH are not understood at this time. In comparison, Si concentrations of only ~5 μg/g solution were measured in the acidic surface leaching experiments (Table A.8). There appears to have been excess dissolved Si at neutral pH also—the solubility of quartz in pure water is ~5 μg/g solution, but ~9 μg/g solution was measured here.

Mass balance for Ca and Mg versus carbonate is problematic here. Total carbonate inferred from the decrease in pH under acidic conditions was at least 1.03 μmoles/g sand (Figure A.8), a value consistent with leachable Ca and Mg observed in the bulk (unsplit) sand (Table A.8). In contrast, the Ca+Mg measured here implies a carbonate content of only 0.75 μmoles/g sand, a discrepancy much larger than can be accounted for by analytical precision limits. One source of systematic error may be the low-ionic strength standards

Figure A.9. Soluble Ca, Mg, and Si vs. pH in batch systems equilibrated for 31 days.

used for these AA analyses. High chloride in the samples may have complexed with Ca and Mg, reducing the proportion of neutral Ca and Mg atoms in the AA flame, and hence reducing sensitivity relative to the standards.

A.3.2.4 Leaching Under Open-System Conditions

Leaching under open-system conditions was investigated in an unsaturated column experiment eluted with 0.001 M NaCl, as described in section A.2.2.2, with results shown in Figure A.10. Except for an initial increase in saturation (up to ~ 100%) during the elution of the first three pore volumes (540 ml), the column was 60% saturated. The column effluent contains measurable concentrations of the major leachable components of the sand (Ca, Mg, Si) and of the proposed tracers (Ni, Br, Li). The initial spike in the concentrations is probably related to dissolution of the finest particles in the sand. After these dissolved, the available surface area was lower, reducing the total rate of dissolution. Near steady-state conditions appear to have been achieved for most solutes after the elution of 6 pore volumes (~1000 ml), although Ca, Mg, Li, and Br concentrations continued to decrease slowly with further elution.

The pH history of the eluate is explained by dissolution of Ca+Mg carbonate coupled with variable partial pressure of CO_2 (P_{CO_2}). As saturation increased in the early part of the run, air was progressively excluded from the column, reducing the degree of communication between the pore fluid and the atmosphere. At the same time, carbonate was dissolving and driving up the pH by consuming protons as carbonate equilibrated to bicarbonate: $\text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{OH}^-$. The maximum pH observed here did not exceed 8.0 because partial equilibration with the atmosphere was still possible; a preliminary

Figure A.10. pH and compositions of effluent samples from unsaturated flow sand column leaching experiments (column pore volume = 180 ml, average saturation = 60%, and flow rate = 0.4 ml/min; DL = estimated detection limits; estimated analytical precisions were Si – 15 ng/g; Al, Mg, and Ca – 2%; Li and Ni – 0.3 ng/g; Br – 10%). Data below the DL are plotted as measured rather than set to the DL in order to provide a visual representation of the analytical scatter.

experiment under completely saturated conditions reached a pH of at least 8.7 before stabilizing at pH ~8.2 after elution of 6 pore volumes.

The similarity of the trends observed for pH, Ca, and Mg are consistent with control by carbonate dissolution. Lithium appears to have been contained in a phase that dissolved more rapidly than carbonate, as evidenced by its more rapidly declining concentration relative to Ca and Mg.

The other measured components (Al, Si, and Ni) quickly reach steady-state in ~1 pore volume (~200 ml), suggesting that they are present in sparingly soluble phases whose surface areas did not significantly change during the course of the experiment. The magnitude of dissolved Al and Si is too high to be controlled by equilibrium with crystalline

phases (i.e., gibbsite and quartz, respectively, or possibly kaolinite). Equilibrium with amorphous silica produces dissolved Si in the range observed here, suggesting that the sand surface may contain amorphous silica. These may have been mechanically produced during mining and processing by the supplier (Wedron Silica), analogous to the well-known amorphization that may occur when samples are powdered for x-ray diffraction analysis.

A.3.3 Potentiometric Titrations

Potentiometric titrations were performed on samples of raw and acid-washed (boiling-HCl or HClO₄) Wedron 510 sand and Min-U-Sil 5 that were prepared as described in Section A.2.4.1. The latter is a widely used α -quartz reference material obtained from U.S. Silica Co. (formerly Pennsylvania Glass Sand Corp.) Other studies examining the surface properties of Min-U-Sil 5 include MacNaughton and James (1974), Benjamin and Leckie (1980), and Kohler and Leckie (1991). Batch-system titrations of the raw sand were compared with those of with the other materials. Meaningful continuous titrations of raw sand could not be obtained, however, because its carbonate component strongly affects the system pH and obscures the contribution of surface interactions to the titration curve. Harshly cleaned sand lacked carbonate or Fe-oxyhydroxide coatings. It could thus be continuously titrated for comparison with the α -quartz standard.

A.3.3.1 Preliminary Batch Titrations on Raw and HClO₄-Washed Surfaces

Results of batch titrations performed under CO₂-free conditions on raw and HClO₄-cleaned Wedron sand or Min-U-Sil 5 are presented in Figure A.11. A titration curve for electrolyte alone coincides closely with the curve ["H₂O (model)"] predicted from an acid-base equilibrium model using the Debye-Hückel equation (constants taken from Drever, 1982). This titration indicates that the container does not affect the acid-base chemistry of the solution.

The curves for raw Wedron sand and Min-U-Sil 5 show little resemblance to each other or to the curves for the HClO₄-cleaned materials. Deviations of the curve for raw Wedron sand from the electrolyte curve are attributable in large part to the carbonate content of the sand and diffusion of CO₂ into the systems at high pH (see section A.3.2.3). The curve for raw Min-U-Sil 5 resembles its cleaned counterpart at high pH, but crosses the electrolyte curve at pH 8.2. Curves for HClO₄-cleaned Wedron sand and Min-U-Sil 5 are essentially identical, suggesting that the cleaning procedure has stripped away any surface coatings to reveal a similar surface on both materials. These curves are consistent with a quartz surface (pH_{ZPC} = ~2). At low pH, the quartz surface is weakly charged and has little effect on solution pH. Because of the logarithmic nature of the pH scale, deviations from the electrolyte curve are apparent only for pH > 5. Under basic conditions, the titration curves fall well below that for electrolyte alone due to the combined effects of silica dissolution and surface ionization. At high pH, the titration curve for acid-washed sand lies below its untreated counterpart, providing additional evidence that exposed quartz surfaces in the untreated sand are rare.

Figure A.11. Representative batch titration curves for raw and HClO₄-cleaned Wedron 510 sand and Min-U-Sil 5 quartz.

A.3.3.2 Continuous Titrations of HCl-Washed Min-U-Sil and Wedron 510 Sand

The results of continuous titrations of HCl-washed Min-U-Sil 5 and HCl-washed Wedron 510 sand performed with an automated titrator are shown in Figures A.12 to Figure A.15. Calculated surface charge for the acid-washed Min-U-Sil 5 as a function of pH and I is shown in Figure A.12. For these calculations a specific surface area of 5.95 m²/g was used (multi-point Kr BET determination, Kohler and Leckie, 1991), and the site density was assumed to be 6 nm⁻². Points below pH ~4.75 are excluded from further consideration because of probable systematic errors implied by the erratic trends. Intrinsic acidity and Na-association constants (K_{a2} and K_{Na} , respectively), extracted from the titration data by the double-extrapolation (DE) method, are plotted in Figure A.15. The extrapolated values at zero surface charge and zero ionic strength are $K_{a2} = 7.8$ and $K_{Na} = 5.6$. The K_{a2} value is typical of quartz, but K_{Na} is slightly lower than normal.

Calculated surface charge on the HCl-washed Wedron 510 sand as a function of pH and I is shown in Figure A.14. The specific surface area was assumed to be 0.12 m²/g, from N₂ BET determinations, and the site density was assumed to be 6 nm⁻². These curves only vaguely resemble those for HCl-washed Min-U-Sil 5 (Figure A.12). Calculated charge density is unusually high for all ionic strengths; the position of the curves can be shifted

Figure A.12. Surface charge vs. pH for titrations of HCl-washed Min-U-Sil 5 α -quartz (the curve for 0.0004 – 0.0006 M is slightly concave downward at pH 6 because ionic strength increased during the titration from low to high pH as base was added).

vertically by assuming a different surface area, but their shapes and relative positions are constant.

Intrinsic acidity and Na-association constants (K_{a2} and K_{Na} , respectively), extracted from the titration data by the double-extrapolation method, are plotted in Figure A.15. The extrapolated values at zero surface charge and zero ionic strength are $K_{a2} = 5.5$ and $K_{Na} = 4.8$, values lower than are typically seen for quartz. These peculiarities, combined with the high calculated surface charge noted above, suggest that the surface area may have been much larger than the BET value. A source of additional surface area is the colloidal suspension of kaolinite that appears as the pH is increased, however, because it constitutes only 0.05% by weight of the sand, however, it probably could not contribute enough additional surface area. The causes of the differences between the shapes of the double extrapolation curves and the derived property values for Wedron 510 and Min-U-Sil 5 are not known at this time.

Figure A.13. Double-extrapolation plots for HCl-washed Min-U-Sil 5: (a) Extrapolation for $\text{p}K_{a2}$, giving a value of 7.8 and (b) Extrapolation for $\text{p}K_{\text{Na}}$, giving a value of 5.6.

Figure A.14. Surface charge vs. pH for titrations of HCl-washed Wedron 510 sand (data are plotted at the same scale as in Figure A.12 to emphasize the relative differences).

A.4 Discussion

A.4.1 Surface Characteristics Implied by Potentiometric Titrations

Potentiometric titrations of the acid-washed quartz reference (Min-U-Sil 5) over a range of ionic strengths potentially provide information on the effect of various leaching procedures on the characteristics of silica surfaces. Table A.10 compares the calculated surface acidity and Na complexation constants for the HCl-washed Min-U-Sil 5 and Wedron 510 sand, obtained in this study, to values for silica polymorphs reported in the literature. The results of measurements made at the British Geological Survey (BGS) on HClO_4 -washed Min-U-Sil 5 are also included. The BGS cleaning procedure is based on the method of MacNaughton and James (1974) and is similar to that described in Section A.2.4.1 above. It involved heating the sample at 500°C , refluxing in 4 M HClO_4 , soaking first in dilute HNO_3 and then in alkaline (pH 10) waters and final storage as a slurry at near-neutral pH. The BGS data were used to calculate intrinsic acidity (K_{a2}) and affinity for electrolyte cations (K_{Na}) with the double-extrapolation (DE) method (Ward, 1994). A specific surface area of $4.4 \text{ m}^2/\text{g}$ (single-point N_2 BET measurement provided by the BGS) and a site density of 6 nm^{-2} were assumed. Double-extrapolation plots for the BGS data appear qualitatively different from those of the HCl-washed Min-U-Sil 5 obtained in this study; the surface of the BGS samples reach much greater degrees of ionization at low ionic strength than do the HCl-washed Min-U-Sil 5.

Figure A.15. Double-extrapolation plots for HCl-washed Wedron 510 sand (I = ionic strength and $\alpha_- = \alpha_s$, the fraction of sites which have been ionized): (a) Extrapolation for pK_{a2} , giving a value of 5.5 and (b) Extrapolation for pK_{Na} , giving a value of 4.8.

Table A.10. Intrinsic acidity and association constants for Wedron 510 sand and other silica polymorphs

Material	pK_{a2}	pK_{Na}	A_{sp} (m^2/g)	N_s (sites/ nm^2)	Comments
Wedron 510 Sand (HCl-washed)	5.5	4.8	0.12	6*	This study. Charge density ~10x of quartz
Min-U-Sil 5 (HCl-washed)	7.8	5.6	5.95	6*	This study. Low charge at low I , higher affinity for Na.
Min-U-Sil 5 ($HClO_4$ -washed)	6.8	6.4	4.4	6*	Calculated from data provided by the British Geological Survey (Ward and Siegel, 1994).
Min-U-Sil ($HClO_4$ -washed)	7.5	6.7	5.95	6*	Kohler et al., 1991
Ludox silica	6.4 – 7.9	6.4 – 7.1	180	2.5-4.5	Range of values obtained by Kent et al. (1988) from data of Bolt (1957) using DE and HYDRAQL
Amorphous silica and quartz	7.2	6.7	170	5	Rea and Parks (1990), Davis et al. 1978.

*value used in calculation of K_{a2} and K_{Na} , but not determined experimentally.

The significance of differences in the constants for the HCl- washed Wedron sand, HCl-washed Min-U-Sil 5 and $HClO_4$ -washed Min-U-Sil 5 is unclear at this time. If correct, the calculated constants indicate that that the HCl-washed Wedron 510 sand has a much greater tendency to give up protons (K_{a2}) and form complexes with electrolyte cations (K_{Na}) than other “quartz” surfaces. Alternatively, the constants for the HCl-washed Wedron 510 and Min-U-Sil 5 may differ because the surface presented by the HCl-washed sand is not quartz and/or the surface area estimate for the HCl-washed sand is too low. There are experimental observations to support this suggestion: in spite of the washing procedure, a colloidal component (probably kaolinite) appeared in the Wedron sand system as it was titrated to high pH. The colloid may also serve to increase the effective surface area of the sand.

Constants for HCl-washed and $HClO_4$ -washed Min-U-Sil 5 may differ because the different acid-washing procedures may alter the properties of the quartz surfaces in different ways. As discussed previously, when the $HClO_4$ -washing procedure of MacNaughton and James (1974) was used at Sandia, the samples acquired a pinkish hue during ignition, presumably due to conversion of Fe-oxyhydroxides to hematite that was not entirely removed by the $HClO_4$ reflux. It was hoped that the BGS data set on $HClO_4$ -washed Min-U-Sil 5 would provide an independent check on experimental technique by allowing comparison of surface-charge and double-extrapolation plots with those obtained on Min-U-Sil 5 in this study. However, the value of the BGS data set as a validation tool is

ambiguous; washing procedures were different, and the quality of the raw data collected by the BGS is unknown.

A.4.2 Applicability of Laboratory Characterization Studies to Field Tests

Characterization studies designed to support efforts to validate models of contaminant transport must address the following question: how do the properties of geomedia measured in the laboratory differ from those that would be present under natural conditions? Valid application of measurements made in the laboratory to prediction of transport in the field requires (1) assurance that the material studied in the laboratory is representative of the material expected to be in contact with groundwaters in the study area and (2) assurance that the procedures used to characterize the natural or analog material have not altered its properties in ways important to transport.

The caisson experiment shares a fundamental uncertainty with other tracer field studies. As in aquifers, the properties of the surfaces exposed to groundwaters and interact with the tracers may be very different from those of the minerals that make up the bulk of the rock. Although the bulk mineralogy of Wedron 510 sand is dominated by quartz, several studies revealed that mineral coatings armor much of the surface area of the sand grains. Several different leaching techniques were used to expose the underlying mineral surfaces for further characterization, to obtain the composition of the coatings, and to evaluate the potential dissolution of the coatings during batch sorption experiments, potentiometric surface titrations and during the caisson experiment. The compositions of the leachates and the resultant mineral surfaces provide a basis for determining if the properties of the mineral surfaces are changed in ways that invalidate the results of sorption experiments described in Appendix B.

A number of additional experimental studies and numerical analyses are required to understand the nature of the surface of the Wedron 510 sand. Some of these studies provide essential information to conducting the caisson experiment and are discussed in the Summary chapter of this report. Other studies are not required specifically for the caisson experiment but would provide basic understanding of mineral surfaces and would facilitate application of the results of the caisson experiment to future model validation studies involving tuff. These studies would support development of a model for multicomponent sorption by mixtures of minerals for use in transport modeling. Areas requiring further work include:

1. Understanding the contribution of individual minerals to the composite surface characteristics of the sand. Studies in support of this objective include:
 - Determining the role of Fe-oxyhydroxides and kaolinite in the development of surface charge, and
 - Determining the role of Ca+Mg carbonate in the development of surface charge.
2. Determination of the importance of colloidal coatings to the surface chemistry of the sand. Studies in support of this objective include:
 - Identification of colloids formed during titration of HCl-washed sand,

- Improved surface-area measurements on sand (using Kr) and on colloidal phase (using N₂), and
 - Determining the source of high dissolved Si at low pH. Is this merely an analytical artifact, or is a metastable silicate phase dissolving?
3. Examining the effect of surface leaching procedures on the sand. Studies in support of this objective include:
- Titration of HClO₄-washed Min-U-Sil 5 to investigate differences in shape between titration curves for HCl-washed Min-U-Sil 5 (this study) and HClO₄-washed Min-U-Sil 5 (BGS).
 - Titration of kaolinite and titration of carbonate-stripped sand.
 - Investigation of alternative leaching procedures for removal of carbonate (e.g., EDTA, acetate) and Fe-Mn oxyhydroxides (e.g., oxalate, citrate).

Finally, it is likely that the equilibrium constants obtained by the double extrapolation are too imprecise to allow quantitative comparisons. The technique involves visual extrapolation of curves around corners to obtain the intrinsic acidity and complexation constants (see Appendix E.6). The FITEQL code (Westall, 1982) which can be used to calculate the constants directly using chemical equilibrium equations and regression analysis will be used in future studies.

A.5 Summary

The surface of the porous medium in the caisson (Wedron 510 sand from Wedron Silica Corp., Wedron, IL 60557) has been characterized by a variety of chemical, mineralogical, and physical methods. The primary objective of the work described in this appendix is the identification and characterization of the minerals in the caisson that will most strongly affect tracer transport. These minerals will affect tracer transport either directly through sorption or coprecipitation or indirectly through solid/solution reactions that affect the bulk chemistry of the solution in the caisson. Calcium, Mg, Al, and Fe were the elements most abundantly leached from Wedron 510 sand in boiling HCl. Dissolved Mg was always correlated with Ca, and both were strongly correlated with pH shifts in column and batch tests, leading to the conclusion that the host mineral phase was a Ca,Mg-carbonate. Iron readily dissolved under strongly acidic conditions, implying its presence as Fe-oxyhydroxide rather than hematite. Measured concentrations of Si and Al varied sympathetically and were surprisingly high in a column test, suggesting equilibration with an amorphous rather than crystalline phase. Such an amorphous phase could have been produced during mining and processing of the sand by the supplier. Alternatively, a colloidal component may have been present in the aliquots analyzed by AA in spite of filtering efforts.

Examination of the sand by SEM failed to reveal any grains or particles rich in Fe or Ca+Mg, even in the colloidal fraction, implying that the sources of these elements (Fe-oxyhydroxide and carbonate) occur as thin coatings or as fine particles adhering to the grains of sand. Simple geometrical models based on XPS data for Ca and Mg favor an

extremely dispersed mode of occurrence as well. The observed surface concentration of Ca and Mg and mass balance constraints (acid-leachable Ca+Mg is only $1.03 \mu\text{mole/g}$) suggest that Ca and Mg must be concentrated at the immediate surface of the sand grains, either as a coating or as particles much less than 500 nm in large dimension (otherwise they would have been detected by SEM/EDS).

In batch systems, a colloidal component becomes dispersed at $\text{pH} > 8.5$; analysis of XRD data suggest that is composed predominantly of kaolinite and quartz. No other surface minerals could be detected. The Al in kaolinite was also detected by XPS. The intense signal implied that as much as half the available surface might be covered by kaolinite flakes. A flaky distribution is consistent with SEM observations on the morphology of the colloidal fraction, whereas a dispersed mode of occurrence would not account for most of the Al present.

The sand contains small amounts of tracers being used in the caisson. Total acid-leachable Ni was 140 ng/g, and Li was 50 ng/g. Leachable Ni averaged near 1 ng/g in effluent from an unsaturated column, and leachable Li and Br declined to this level after a dozen pore volumes.

Batch titration curves for raw Wedron 510 sand apparently are dominated by carbonate dissolution and CO_2 uptake. Washing in boiling HCl stripped the sand grains of their coatings, resulting in a titration curve that qualitatively resembled that for HCl-washed Min-U-Sil 5. Surface acidity and complexation constants, obtained with the double extrapolation method, however, suggest that the HCl-washed Wedron 510 sand has a much greater tendency to give up protons (K_{a2}) and form complexes with electrolyte cations (K_{Na}) than other "quartz" surfaces. The causes of differences in the constants for the HCl-washed Wedron sand, HCl-washed Min-U-Sil 5 and HClO_4 -washed Min-U-Sil 5 are unknown at this time. They may be due to low estimates of surface area, differences in the washing procedures and/or the inherent imprecision of the DE method itself.

The studies described in this appendix and other portions of this report indicate that the trace components of Wedron 510 sand will exert significant if not dominant controls on the transport of the tracers in the caisson experiment. Simple leaching experiments indicate that the sand will not be a source of significant amounts of the tracers used in the experiment. However, dissolution of minor mineral phases may affect the pH of the pore solutions. The mineral surfaces that interact with the tracers used in the caisson experiment cannot be represented by pure quartz reference standards. Additional studies of the properties of the minor components of the sand may be required to obtain effective values of the surface acidity and complexation constants for the bulk sand and to formulate a mineral mixtures model for the surface properties of the sand. However, such studies may not be required for the transport calculations that will be carried out as part of the transport model validation experiment described in the main text of this report.

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ATTACHMENT 1:

Surface Area by Gas Adsorption

[Brunauer-Emmett-Teller (BET) method]

Experimental isotherms obtained for analysis of surface area by the BET method (Brunauer *et al.*, 1938; Lowell, 1979). consist of measurements of the amount of gas adsorbed at the boiling temperature of liquid N₂ (−196 °C) as the pressure of the gas varies from 0 to its equilibrium vapor pressure, p^0 . Experimental measurements are reported as relative pressures (p/p^0) paired with a quantity of adsorbed gas, expressed as a volume per unit mass of sample under conditions of 298 K and 1 atm. Corrections are made for non-ideal behavior (cf. Lowell, 1979), giving a corrected adsorbed volume which can be used in the ideal gas law to calculate the mass of adsorbed gas:

$$W = \frac{PV'}{RT} \cdot MW_{gas} \quad , \quad (1)$$

where

W = mass of gas absorbed per unit mass of sample (g/g; effectively dimensionless),

P = pressure at STP (i.e., 1 atm),

V' = volume adsorbed, corrected for non-ideal behavior (ml/g),

R = ideal gas constant (82.06 ml · atm · mole^{−1} · K^{−1}), and

MW_{gas} = molecular weight of the adsorbing gas.

Adsorbed mass as a function of the relative pressure is analyzed using the BET equation:

$$\frac{1}{W(p^0/p - 1)} = \frac{1}{W_m \cdot C_{BET}} + \frac{(C_{BET} - 1)}{W_m \cdot C_{BET}} \cdot p/p^0 \quad , \quad (2)$$

where

W_m = monolayer capacity (same dimensions as W),

p/p^0 = relative pressure of the adsorbing gas as a fraction of its equilibrium vapor pressure, and

C_{BET} = a function of the difference between the heat of adsorption onto the first layer and the heat of condensation (dimensionless).

Equation 2 is linear, of the form $y = mx + b$. The entire left side of Eqn. 2 is equated with y , and p/p^0 is equated with x , permitting determination of slope m and intercept b by least-squares linear regression. The correlation coefficient, r , provides an indication of the quality of the data. Then, W_m and C_{BET} are calculated according to:

$$W_m = \frac{1}{m+b} \quad , \quad \text{and} \quad C_{BET} = \frac{m}{b} + 1 \quad (3)$$

Finally, the area, A , is calculated from W_m by:

$$A = (W_m / MW_{gas}) \cdot \alpha_m \cdot L \quad (4)$$

where α_m is the cross-sectional of a molecule of the adsorbing gas in a completed monolayer, and L is a conversion factor that depends on the units of W_m and α_m .

Appendix B

Ni Sorption and Solubility Studies

C. R. Bryan, D. B. Ward, and M. D. Siegel

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B.1 Introduction

Batch adsorption studies were conducted to characterize the adsorption properties of Wedron 510 sand with respect to Ni, Li, and Br, the elements of interest in the caisson experiment. The goals of these experiments were to determine the pH dependence of adsorption for these elements in the sand/aqueous electrolyte system, and to determine the adsorption properties of the several mineral phases in the sand. Adsorption of Ni by Wedron sand was examined under a variety of conditions. Experiments were run under both nominally CO₂-free and nominally atmospheric conditions, at Ni concentrations of 100 and 200 ng/ml ($1.7 - 3.4 \cdot 10^{-6}$ M). Adsorption of Ni was also examined in the presence of Li (10 – 17 µg/ml; $1.4 - 2.5 \cdot 10^{-3}$ M) and over a range of concentrations of Na (0.001 M – 0.1 M) to examine the effects of competition for adsorption sites.

Although Wedron 510 is dominantly a quartz sand, it does contain minor amounts of iron oxyhydroxide. The iron-bearing phase occurs as surface coatings on the grains, and may contribute much more to the surface area and surface properties of the system than its abundance (~80 ppm Fe) would suggest. Adsorption experiments were carried out on a quartz standard (Min-U-Sil 5) and synthetic goethite to examine the potential importance of these phases to Ni adsorption.

B.2 Summary of Experimental Designs and Methods

B.2.1 Studies of Ni(OH)₂ Solubility

Batch systems containing 30 ml 0.001 M NaCl electrolyte and 1 – 7600 µg/ml ($1.7 \cdot 10^{-5}$ to $1.3 \cdot 10^{-1}$ M) total Ni were equilibrated for 14 days over the pH range 7 – 10 in 40 ml polyallomar centrifuge tubes. To obtain reliable and consistent pH values, CO₂-free conditions were maintained as much as possible during preparation, equilibration, and measurement of the batch systems. Experimental procedures are described in Appendix E.2 *Batch Adsorption Measurements Under Atmospheric and CO₂-free Conditions* for preparation of reagents and electrolytes and Appendix E.1 *pH Measurement Under Atmospheric and CO₂-free Conditions* for measurement of pH.

Enough Ni was added to provide initial supersaturation with respect to amorphous Ni(OH)₂ by at least a factor of three, based on the equilibrium constants of Baeyens and McKinley (1989). For systems with target pH < 8, Ni was added as NiCl₂ · 6H₂O to provide initial concentrations in the range 760 – 7600 µg/ml (0.013 – 0.13 M). For more alkaline systems (pH > 8), an aliquot of 1000 ppm Ni standard was added to provide an initial concentration of 1 µg/ml ($1.7 \cdot 10^{-5}$ M).

Nickel concentrations were determined according to the method described in Appendix E.3 *Ni Analysis by Graphite Furnace Atomic Absorption*. Concentrated samples were diluted to fall within the range 50 – 200 ng/ml ($8.5 \cdot 10^{-7}$ – $3.4 \cdot 10^{-6}$ M) Ni as follows. An aliquot from each tube was passed through a 0.2 µm Gelman Acrodisc filter to remove

any fine suspended precipitate. Dilutions were performed gravimetrically using an electronic balance to record solution masses to within ± 0.1 mg. Up to three dilution stages were required for the most concentrated samples. Dilution for an individual stage consisted of adding 50 – 200 mg sample to 5 g acidified 0.001 M NaCl; the dilution factor was always less than 100 in order to prevent loss of precision. Assuming dilution errors of 1% per stage and an analytical error of 1%, overall precision was $\pm 4\%$ or better, and was not a critical factor in interpreting the results.

Macroscopic quantities of precipitate formed in tubes with the highest Ni concentrations ($\text{pH} < 8$). The precipitate was collected by vacuum filtration on a $0.4 \mu\text{m}$ polycarbonate membrane filter and washed with a few ml of methanol before air-drying. This was collected for phase identification by X-ray diffraction as described in Appendix A *Characterization of the Surface of Wedron 510 Sand*, section 2.1.6.

B.2.2 Batch Adsorption Studies

Batch adsorption studies were run under a variety of experimental conditions, summarized in Table B.1. All experiments were carried out with 20 ml 0.001M NaCl solutions in 50 ml polyallomar or polycarbonate screw-cap centrifuge tubes, using substrates of Wedron 510 sand, synthetic goethite or Min-U-Sil 5, a powdered quartz obtained from U.S. Silica (Berkeley Springs, WV).

Prior to addition of the tracers, the pH of the samples was adjusted using dilute HNO_3 and NaOH solutions, and the samples were equilibrated for 2–3 days. The samples were then spiked with 200 – 400 μl of 10 $\mu\text{g/ml}$ ($\sim 1.70 \cdot 10^{-4}$ M) Ni solution and allowed to re-equilibrate for 2 – 4 days. Final total Ni concentrations were 100 – 200 ng/ml Ni ($1.7 \cdot 10^{-6}$ – $3.4 \cdot 10^{-6}$ M).

Table B.1. Experimental conditions for batch adsorption studies

Substrate	Electrolyte (NaCl conc.)	Atmospheric conditions	Ni added, ng/ml	Li added, $\mu\text{g/ml}$
Wedron 510	0.001 M	CO_2 -free	100	0
Wedron 510	0.001 M	CO_2 -free (N_2)	100	0
Wedron 510	0.1 M	CO_2 -free (N_2)	100	0
Wedron 510	0.001 M	Atmosphere	100	0
Wedron 510	0.001 M	Atmosphere	200	0
Wedron 510	0.001 M	CO_2 -free	100	10
Wedron 510	0.001 M	Atmosphere	200	17
Goethite	0.001 M	Atmosphere	100	0
Min-U-Sil	0.001 M	CO_2 -free (N_2)	100	0

Adsorption experiments were carried out under CO₂-free atmosphere or in partial equilibrium with atmospheric CO₂. In most of the experiments carried out in the absence of atmospheric CO₂, Ar-purged electrolyte was used, and the headspace in the centrifuge tubes was filled with Ar. The samples were not actually CO₂-free, however, as carbonate phases within the sand released CO₂ upon dissolution, and atmospheric CO₂ probably diffused through the cap seal and into the sample during the 3 day equilibration step. In an attempt to evaluate the importance of the latter process, a single sample set was equilibrated in a N₂-filled glove box. In another set of experiments, Li was added to two sets of samples as 1000 µg/ml Li (0.144 M LiBr); final total Li concentrations ranged from 10 – 17 µg/ml Li (1.4 – 2.5 · 10⁻³ M).

After a 3-day equilibration period, the pH in each vessel was measured as described in Appendix E.1 *pH Measurements Under Atmospheric and CO₂-free Conditions*. An aliquot of electrolyte was collected, filtered through a 0.2 µm filter, and analyzed for the element of interest. The batch adsorption procedure used in this study is described in detail in Appendix E.2 *Batch Adsorption Experiments Under Atmospheric and CO₂-free Conditions*. The procedures for Ni analysis are described in Appendix E.3 *Ni Analysis by Graphite Furnace Atomic Absorption*.

Ni adsorption by quartz and iron oxyhydroxide, two of the major mineral components in the sand, was also examined. In these experiments, the surface area of the pure mineral used was equivalent to the estimated surface area of the corresponding component present in the natural sand. Min-U-Sil-5, which had been boiled in 6 N HCl to remove Fe oxide/hydroxide coatings, was used as the quartz component. The specific surface area of Min-U-Sil 5 is approximately 6 m²/g (see Appendix A, this report). To obtain a surface area equivalent to that of the 20 g of sand used in the Wedron 510 adsorption experiments, 0.4467 g of Min-U-Sil was added to CO₂-free 0.001M NaCl solutions as a neutral pH aqueous slurry. The Min-U-Sil/solution ratio was 27 mg/ml. The calculated surface area was 0.162 m²/ml.

Goethite was used to represent the iron oxyhydroxide component of the Wedron 510 sand. It was synthesized from ferric nitrate solution, using the method described by Atkinson et al. (1967) and Tripathi (1983). The specific surface area of goethite synthesized in this way is approximately 50 m²/g (Balistrieri and Murray, 1979; Tripathi, 1983). It was assumed that the iron hydroxide component of the sand had the same specific surface area as the synthetic goethite. An amount equivalent to the amount of leachable Fe in 20 g Wedron 510 sand (2.54 mg) was added as neutral pH aqueous slurry to 0.001 M NaCl under atmospheric conditions to produce a final solid/solution ratio of 0.127 mg/ml, with a corresponding surface area of 6.35 · 10⁻³ m²/ml.

A third group of adsorption experiments was conducted using the procedure developed by Los Alamos National Laboratories for the Yucca Mountain Project (procedure # TWS-INC-DP-05, R2), hereafter referred to as the LANL procedure. This method was developed for work with ash-flow tuff samples from the Yucca Mountain site, using natural groundwater from that location as an electrolyte, and differs from the method described in Appendix E.2. The typical solution/solid ratio in the LANL method is 20 ml/1 g (as opposed

to 20 ml/20 g in Appendix E.2) and, in the LANL method, after the electrolyte is added to the rock and allowed to equilibrate, it is *poured off*, and fresh electrolyte, spiked with the element of interest, is added. The samples are not pH-adjusted; the final pH is determined by surface reactions between the substrate and the electrolyte. In the experiments with tuff (for example, see Triay et al., 1993), the pH changes only slightly, because the groundwater used as electrolyte may be nearly in equilibrium with the rock. Separation of solid and liquid phases is accomplished by either ultracentrifugation (centrifuging for 12 hours at 25,000 rpm) or ultrafiltration (using membrane filters with a 30,000 MW pore size). Samples are run in duplicate, and the K_d s produced must agree to within a factor of two to be acceptable.

Comparative experiments were run using modifications of the LANL method and the method described in Appendix E.2 (see Table B.2). Solution/solid (0.001 M NaCl/Wedron sand) ratios of 20/1 and 1/1 were examined; five replicates were run under each set of conditions. A separate sample set was run using a modified version of the LANL method; the slurry was centrifuged prior to pouring off the first batch of electrolyte, to minimize loss of fine-grained material (Method E in Table B.2).

Table B.2. Sand/electrolyte ratios used in the comparison study of SNL and LANL batch adsorption procedures

Method	Sand:electrolyte ratio	Procedure used
A	20 g / 20 ml	SNL
B	1 g / 20 ml	SNL
C	20 g / 20 ml	LANL
D	1 g / 20 ml	LANL
E	1 g / 20 ml	LANL*

* Samples centrifuged prior to pouring off first batch of electrolyte.

B.3 Results

B.3.1 Preliminary Studies

B.3.1.1 Preliminary Solubility Studies

It is important to insure that precipitation of Ni-containing solids does not occur in batch adsorption experiments. Total dissolved Ni was measured as a function of pH in nominally CO₂-free supersaturated batch systems lacking adsorbent to determine the solubility of Ni(OH)₂ in the background electrolyte. Experimental data are summarized in Table B.3 and plotted in Figure B.1.

Table B.3. Measurements of Ni stability in solution*

$\text{pH}_{\text{initial}}$	pH_{final}	$\text{Ni}_{\text{initial}}$ (log M)	Ni_{final} (log M)
7.22	6.96	-0.85	-0.91
7.72	7.13	-1.56	-1.59
7.91	7.28	-1.83	-1.87
7.86	7.41	-1.82	-1.83
7.99	7.28	-1.85	-2.05
8.3	7.48	-1.83	-2.68
9.4	8.48	-4.77	-4.99
9.8	9.46	-4.85	-6.55
10.24	10.15	-4.85	-7.07

* Precision of pH measurements is ± 0.1 pH units or better, and Ni concentrations are precise to $\pm 5\%$ or better.

Figure B.1. Ni concentrations in batch system initially supersaturated with respect to $\text{Ni}(\text{OH})_2$ [tie lines connect initial conditions (open symbols) to measurements made after two weeks equilibration (filled symbols) for each system; visible precipitate formed in systems with greater than 10^{-2} M initial Ni, whereas precipitation is inferred from the shift in Ni concentrations in the more dilute systems; the heavy lines are calculated stability limits for amorphous and crystalline $\text{Ni}(\text{OH})_2$ as discussed in the text].

After 14 days, dissolved Ni decreased significantly in all systems, indicating approach to equilibrium from supersaturation. A precipitate was visible in those systems with initial Ni > 10^{-2} M (initial pH < 8.5); more alkaline systems lacked sufficient total Ni to produce observable precipitate. Data from preliminary experiments equilibrated near pH 7 for only 7 days are concordant with the 14-day results, suggesting that metastable equilibrium is achieved in less than a week at this pH. Ionic strength is different for each system. The background electrolyte was 10^{-2} M NaCl, but at low pH the addition of large amounts of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ raised the ionic strength to as much as 0.4 M (an initial Ni concentration of 0.13 M).

Solubility curves for amorphous and crystalline $\text{Ni}(\text{OH})_2$, calculated for CO_2 -free conditions using HYDRAQL (Papelis, 1988) with thermodynamic data given by Baeyens and McKinley (1989) are also shown in Figure B.1. These thermodynamic data also indicate that Ni may complex with CO_3^{2-} , leading to greatly enhanced solubility at high pH if equilibrium is achieved with atmospheric CO_2 . Unfortunately the partial pressure of CO_2 in the batch systems is not known precisely, preventing rigorous evaluation of the solubility measurements. In the nominally- CO_2 -free systems the P_{CO_2} was much less than atmospheric, but batch titration experiments in identical vessels (see Appendix A, section 3.2.3) revealed diffusion of CO_2 into the containers during the equilibration period. The solutions appear to have been supersaturated relative to crystalline $\text{Ni}(\text{OH})_2$ but undersaturated with respect to the amorphous phase (except at the five lowest pH values, where the system appears to have been in metastable equilibrium with amorphous $\text{Ni}(\text{OH})_2$). It may be that at pH > 8.5, the activity of dissolved Ni^{2+} was controlled by the solubility of crystalline $\text{Ni}(\text{OH})_2$, but total dissolved Ni included a significant component complexed by carbonate. Speciation calculations, using the thermodynamic data in Baeyens and McKinley (1989) and discussed in the main section of this report, suggest that at near-neutral pH, the contribution of NiCO_3^0 to the total dissolved Ni is negligible and that the aqueous Ni concentration is controlled by amorphous- $\text{Ni}(\text{OH})_2$ alone.

The mineralogy of the precipitate formed at pH < 8 was determined by X-ray diffraction. The diffraction pattern, reproduced in Figure B.2, shows clear maxima for theophrastrite [crystalline $\text{Ni}(\text{OH})_2$]. Crystallite size was small, as evidenced by the relatively broad peaks. The low background intensities suggest that amorphous $\text{Ni}(\text{OH})_2$ is not the dominant component of the precipitate. However, the solubility data in Figure B.1 suggest that it may still be present in sufficient quantity to control dissolved Ni for pH < 8.

The Ni solubility data and calculations described above can be used to discriminate among batch-adsorption experiments in which the aqueous concentration of Ni was probably controlled by adsorption and those in which precipitation effects must also be considered. In Figure B.3, the dissolved Ni concentrations in CO_2 -free batch-adsorption experiments are compared with the $\text{Ni}(\text{OH})_2$ solubility curves calculated with HYDRAQL. Most batch-adsorption experiments were run under pH and dissolved Ni conditions far below saturation with respect to Ni hydroxide or Ni carbonate solids. All adsorption experiments for pH < 9.0 were undersaturated with respect to crystalline $\text{Ni}(\text{OH})_2$. At greater pH values, adsorption experiments were oversaturated with respect to crystalline $\text{Ni}(\text{OH})_2$ but not with respect to amorphous $\text{Ni}(\text{OH})_2$. Because of potential diffusion of CO_2

Figure B.2. X-ray diffraction pattern from Ni precipitate formed in batch systems with pH < 8, showing clear maxima for theophrastrite [crystalline $\text{Ni}(\text{OH})_2$] (powder mount on oriented quartz crystal, maximum intensity = 3149 counts/sec).

Figure B.3. Comparison of final Ni concentrations in batch adsorption experiments with calculated stability limits for amorphous and crystalline $\text{Ni}(\text{OH})_2$.

into the reaction tubes in these experiments, there is no clear means of discriminating between adsorption, precipitation, and carbonate-complexation effects. A few samples at pH 10.1 lie on the supersaturation boundary for amorphous $\text{Ni}(\text{OH})_2$, and thus precipitation as well as adsorption may have occurred in these samples.

B.3.1.2 Adsorption of Ni on Labware Used in the Adsorption Studies

Prior to starting the adsorption experiments with the Wedron 510 sand, the plastic centrifuge tubes were tested for Ni adsorption as described in Appendix F *Studies Of Adsorption of Ni, Li, and Br by Synthetic Materials Used in the Caisson Tests*. Ni adsorption onto the walls of the vessels was examined and found to be minimal over the pH range of interest (5 – 10); it was only a few percent at pH = 7. The labware washing procedure, which includes soaking the centrifuge tubes in 10% HNO_3 , apparently removes adsorbed Ni from the container walls. An electrolyte blank study showed that Ni carry-over between experiments was negligible with respect to the objectives of this study; blank levels were consistently less than 1 ng/ml. Subsequent electrolyte blanks, run with each set of samples to monitor reagent contamination, were also less than 1 ng/ml.

B.3.1.3 Correction to Calculated Adsorption for Ni Content of Raw Sand

Bulk chemical analysis of Wedron 510 sand indicated that about 180 ng/g Ni is present in the sand. Most of this (~140 ng/g) can be leached with hot 6 N HCl (cf. Table A.8, Appendix A, this report). Release of this Ni fraction is due to desorption of Ni from surfaces and/or dissolution of minor mineral phases. A study of the leaching of Ni from raw Wedron 510 sand as function of pH over a pH range 5-10 was carried out. The measured aqueous Ni concentrations reflect a combination of the total Ni available for exchange and the extent of Ni adsorption at a given pH. An empirical Ni adsorption curve was derived from data collected under similar experimental conditions (described in the next section), and was used to calculate the total exchangeable Ni from the measured aqueous Ni concentrations as:

$$Ni_{\text{exchangeable}} \text{ ng / ml} = Ni_{\text{meas.}} * \left[\frac{100}{(100 - \% \text{ sorbed})} \right] \quad (\text{B.1})$$

While the experiment was nominally 1 g sand/1 ml electrolyte, the actual amount of electrolyte varied by as much as 5% due to the acid or base added to adjust the pH. Exchangeable Ni per mass of sand is calculated from:

$$Ni_{\text{exchangeable}} \text{ ng / g} = Ni_{\text{exchangeable}} \text{ ng / ml} * \left(\frac{\text{vol}_{\text{solution}}, \text{ ml}}{\text{mass}_{\text{sand}}, \text{ g}} \right) \quad (\text{B.2})$$

The results are shown in Table B.4 and Figure B.4. Although the concentration of dissolved Ni varies from 1 to 38 ng/ml over the pH range of 4.5 to 10, the total amount of Ni available for exchange (adsorbed plus dissolved), calculated using the concentration

values and % sorbed values derived from the empirical adsorption curve, is approximately 35 ng Ni/g sand over the entire pH range of interest. This portion of the total Ni in the sand must be included in the adsorption calculations. The distribution of Ni in Wedron sand appears to uniform; 20 g sand blanks included with each sample set have given very similar results.

Table B.4. Exchangeable Ni in Wedron 510 sand*

pH	Ni in solution, ng/ml	% sorbed, from adsorption curve	Exchangeable Ni, ng/ml	Exchangeable Ni in sand, ng/g
4.70	33.4	0.0	33.4	34.7
4.72	32.7	0.0	32.7	34.0
4.84	33.2	0.0	33.2	34.6
4.88	38.0	0.0	38.0	39.5
4.88	34.4	0.0	34.4	35.8
4.96	35.7	0.0	35.7	37.1
5.28	32.3	6.5	34.6	36.0
5.47	30.0	8.4	32.8	34.1
6.81	3.4	94.0	<i>57.1</i>	<i>57.9</i>
6.91	2.3	94.8	<i>44.2</i>	<i>44.8</i>
6.92	2.4	94.8	<i>45.2</i>	<i>45.8</i>
6.97	1.3	96.0	32.4	32.8
6.98	1.3	96.0	31.4	31.8
6.98	1.3	96.0	32.4	32.9
7.01	1.1	96.0	27.0	27.4
7.01	1.3	96.0	32.6	33.1
9.82	3.4	88.0	28.1	28.8
9.83	4.7	88.0	39.5	40.5
9.88	4.2	88.0	35.1	36.0
9.89	4.9	88.0	41.1	42.1
9.89	3.4	88.0	28.2	28.9
9.96	4.0	88.0	33.2	34.0
9.98	4.1	88.0	34.4	35.3
10.02	5.1	88.0	42.3	<u>43.3</u>
Average (excluding italicized data) =				34.9

* The pH measurements are accurate to ± 0.1 ; precision of Ni concentrations is 0.3 ng/ml or 1% (whichever is larger); precision of % sorbed is $\sim 1\%$. Italicized data were excluded because they fell on the steepest part of the adsorption curve; the percent adsorption was too sensitive to pH to be accurately predicted.

Figure B.4. Concentration of Ni in electrolyte in equilibrium with Wedron sand, in batch systems with 1 g sand/1 ml electrolyte (filled symbols).

B.3.1.4 Adsorption Kinetics

A study was conducted to determine the time necessary for the batch adsorption experiments to reach steady state. The results (Table B.5 and Figure B.5) indicate that Ni adsorption by Wedron 510 sand is very rapid, with 90% of the adsorption occurring in the first 1/2 hour; equilibrium is reached within 4 hours.

The % sorbed is calculated using the following equation:

$$\% \text{ sorbed} = \frac{[Ni_{\text{total}} - (Ni_{\text{meas.}} * vol_{\text{solution}})]}{Ni_{\text{total}}} * 100 \quad (\text{B.3})$$

where Ni_{total} is the total available Ni, $Ni_{\text{meas.}}$ is the measured Ni concentration in the electrolyte in ng/ml, and vol_{solution} is the volume of electrolyte in ml. Note that the amount of Ni adsorbed is calculated assuming that 35 ng/g Ni in the raw sand is available for exchange in addition to the added Ni spike.

Table B.5. Results of adsorption kinetics study¹

Time(hrs)	pH	Ni meas. x vol.		% sorbed ³
		ng/ml	ng ²	
0.50	7.60	8.2	164	93.8
0.53	7.70	8.2	165	93.7
0.55	7.64	7.5	152	94.3
1.00	7.63	5.6	112	95.8
1.03	7.46	4.1	83.2	96.8
1.05	7.57	5.2	105	96.0
2.12	7.69	3.1	62.2	97.6
2.13	7.66	2.1	42.3	98.4
2.17	7.65	2.5	51.1	98.1
3.90	7.63	1.4	27.1	99.0
3.92	7.63	1.6	32.7	98.8
3.93	7.66	1.5	30.4	98.8
7.88	7.72	1.4	27.9	98.9
7.92	7.60	0.8	16.0	99.4
7.95	7.69	0.9	18.5	99.3
23.27	7.75	1.6	32.9	98.8
23.30	7.75	2.0	40.0	98.5
23.35	7.46	0.4	7.2	99.7
48.23	7.70	1.5	29.2	98.9
48.23	7.83	2.0	40.0	98.5
48.23	7.79	0.8	15.2	99.4
Sand blank	7.52	1.2	23.2	
Sand blank	7.85	0.8	15.0	
Acid blank		2.7	52.9	
Acid blank		0.1	2.6	
Spike added (average of 2)		96.1	1930	
Exchangeable Ni in sand			700	
Total available Ni (Ni _{total})			2630	

¹ The pH measurements are accurate to ± 0.1 ; precision of Ni concentrations is 0.3 ng/ml or 1% (whichever is larger); precision of % sorbed is $\sim 1\%$.

² Total Ni in solution, $Ni_{sol'n}$.

³ %sorbed = $(Ni_{total} - Ni_{sol'n})/Ni_{total} \times 100$.

B.3.2 Systematic Ni Adsorption Studies

B.3.2.1 Effect of Ni Concentration and P_{CO_2} on Ni Adsorption

Results of Ni adsorption experiments for different total Ni concentrations and different partial pressures of CO_2 are shown in Figures B.5 and B.6 and Tables B.6 and B.7.

Figure B.5. Time-dependent adsorption of Ni onto Wedron 510 sand (at a pH of 7.6 ± 0.1 , 90% of the available Ni is adsorbed in the first 1/2 hour; steady state is reached within 4 hours).

Figure B.6. Adsorption of Ni by Wedron 510 sand under CO₂-free conditions [all samples run using spikes of 100 ng/ml Ni and 20 g sand/ 20 ml electrolyte; two data sets (filled and shaded symbols) equilibrated in sealed containers, but under ambient atmospheric conditions (CO₂ may have diffused through the container walls and into the samples; the third (open symbols) equilibrated in an inert (N₂) atmosphere).

Table B.6. Adsorption of Ni by Wedron 510 sand, under nominally CO₂-free conditions¹

concentrations					concentrations				
pH	Ni in solution		K _d ²	% sorbed ³	pH	Ni in solution		K _d ²	% sorbed ³
	ng/ml	total ng				ng/ml	total ng		
<i>Data set #1, 100 ng/ml Ni added</i>					<i>Data set #2, 100 ng/ml Ni added</i>				
4.59	126.8	2670	0.00	1.1	6.13	73.9	1520	0.83	44.5
4.63	120.9	2540	0.01	5.7	6.24	64.6	1330	1.1	51.5
4.64	127.6	2680	0.00	0.6	6.51	31.1	640	3.4	76.7
5.34	120.0	2500	0.02	7.3	6.80	8.1	167	16	93.9
5.44	119.0	2480	0.02	8.1	6.80	7.9	162	17	94.1
5.67	111.0	2310	0.05	14.3	6.87	7.4	152	18	94.5
5.98	94.4	1960	0.11	27.5	7.00	5.6	114	24	95.8
6.00	101.4	2100	0.09	22.1	7.02	4.5	91.0	30	96.7
6.11	87.8	1820	0.15	32.6	6.25	13.8	281	Sand blank	
7.17	3.0	61.0	16	97.7	7.11	1.6	31.5	Sand blank	
7.18	2.9	58.3	16	97.8	6.10	1.0	19.8	Electrolyte blank	
7.23	3.1	62.4	15	97.7	7.00	2.9	59.2	Electrolyte blank	
7.69	1.8	35.4	29	98.7		101.7	2050	Spike, average of 2	
7.73	0.3	6.0	170	99.8			700	Ni available in sand	
7.81	2.6	52.2	20	98.1			2750	Total available Ni	
8.12	0.4	7.8	140	99.7					
8.18	0.1	1.7	670	99.9					
8.28	0.6	11.8	95	99.6					
8.45	-0.1	-2.1	-550	100.1					
8.62	1.5	30.2	38	98.9					
8.75	0.5	9.3	130	99.7					
9.13	4.1	83.9	14	96.9					
9.20	7.1	144	8.2	94.7					
9.30	8.2	168	7.0	93.8					
10.04	15.4	317	3.8	88.3					
10.12	15.1	311	3.9	88.5					
10.20	18.1	372	3.2	86.2					
4.45	31.2	650	Sand blank		<i>Data set #3, 100 ng/ml Ni, equilibrated in nitrogen</i>				
4.82	33.2	691	Sand blank		6.08	86.0	1800	0.35	25.0
7.17	0.2	4.7	Sand blank		6.16	85.7	1800	0.54	34.1
7.17	1.0	19.7	Sand blank		6.16	85.7	1800	0.55	34.3
9.93	2.1	42.9	Sand blank		7.07	3.1	62.4	44	97.7
9.94	0.7	14.0	Sand blank		7.09	3.0	60.4	45	97.8
4.60	0.6	12.1	Electrolyte blank		7.14	2.5	50.6	54	98.2
4.60	0.9	18.5	Electrolyte blank		10.13	5.3	109	25	96.0
7.20	0.8	16.6	Electrolyte blank		10.18	6.0	124	22	95.5
7.20	0.2	4.5	Electrolyte blank		10.20	5.0	104	26	96.2
10.00	-0.4	-7.3	Electrolyte blank			100.9	2030	Spike, average of 2	
10.00	-0.5	-9.6	Electrolyte blank				700	Ni available in sand	
	99.2	2000	Spike, average of 2				2730	Total available Ni	
		700	Ni available in sand						
		2700	Total available Ni						

¹ The pH measurements are accurate to ±0.1; precision of Ni concentrations is 0.3 ng/ml or 1% (whichever is larger); precision of % sorbed is ~1%. Errors for K_ds are proportional to K_d and are distributed asymmetrically about the reported value. For example, for K_d = 80 ml/g, the ±1s range is 57–135 ml/g, and for K_d = 5 ml/g, the ±1s range is 4.8–5.2 ml/g. K_ds are reported to two significant figures.

² K_d calculated by Eq. B.4.

³ %sorbed calculated by Eq. B.3.

Table B.7. Adsorption of Ni by Wedron 510 sand under conditions of partial equilibrium with atmospheric CO₂¹

Ni in solution					Ni in solution				
pH	ng/ml	total ng	K _d ²	% sorbed ³	pH	ng/ml	total ng	K _d ²	% sorbed ³
<i>Data set #1, 100 ng/ml Ni added</i>					<i>Data set #2, 200 ng/ml Ni added</i>				
4.53	120.9	2530	0.09	8.2	4.60	221.5	4630	0.04	3.6
4.55	122.7	2570	0.08	6.8	4.67	220.3	4610	0.05	4.1
4.63	124.4	2600	0.06	5.5	4.97	217.6	4550	0.06	5.3
5.68	102.3	2120	0.31	23.0	5.40	200.3	4150	0.16	13.7
6.01	70.5	1460	0.92	46.9	5.91	156.4	3240	0.50	32.6
6.18	51.3	1060	1.7	61.4	5.97	161.5	3350	0.45	30.4
6.60	11.6	237	11	91.4	6.45	34.5	707	6.0	85.3
6.61	10.4	214	12	92.2	6.47	37.0	759	5.5	84.2
6.62	9.6	197	13	92.9	6.48	38.2	785	5.3	83.7
7.06	2.3	46.9	59	98.3	6.84	7.7	157	30	96.7
7.09	3.1	62.0	44	97.8	6.93	5.9	119	40	97.5
7.09	1.6	32.8	85	98.8	6.97	5.3	107	45	97.8
7.53	1.6	31.2	88	98.9	7.49	2.5	50.7	95	99.0
7.59	1.3	26.5	100	99.0	7.50	2.7	54.2	89	98.9
7.62	1.1	21.4	130	99.2	7.51	1.9	38.2	130	99.2
8.15	0.1	2.1	1400	99.9	8.16	2.1	42.0	120	99.1
8.19	0.8	15.5	180	99.4	8.35	0.5	11.0	450	99.8
8.29	2.0	39.9	69	98.6	8.71	0.4	7.7	640	99.8
8.66	0.3	6.0	470	99.8	9.00	3.3	67.3	72	98.6
8.83	1.0	20.0	140	99.3	9.02	5.0	101	48	97.9
8.87	1.6	32.0	87	98.8	9.08	2.3	47.4	100	99.0
8.96	3.9	80.6	34	97.1	9.47	14.3	294	16	93.9
8.97	3.0	60.4	46	97.8	9.52	12.9	264	18	94.5
9.17	2.7	54.3	56	98.0	9.60	12.7	260	18	94.6
9.99	10.3	214	12	92.2	10.33	22.8	472	9.6	90.2
10.04	8.6	178	15	93.5	10.40	17.0	352	13	92.7
10.13	10.8	224	12	91.9	10.40	14.3	296	16	93.8
4.56	25.2	522	Sand blank		4.90	29.3	608	Sand blank	
4.73	23.5	488	Sand blank		4.91	31.1	645	Sand blank	
7.16	0.3	5.8	Sand blank		7.03	2.1	41.5	Sand blank	
7.26	0.7	13.1	Sand blank		7.04	0.7	14.2	Sand blank	
9.88	2.1	43.6	Sand blank		10.37	1.0	21.0	Sand blank	
10.01	3.9	80.1	Sand blank		10.39	3.3	67.7	Sand blank	
4.60	0.2	3.4	Electrolyte blank		4.90	2.0	42.1	Electrolyte blank	
4.60	0.2	3.2	Electrolyte blank		4.90	0.1	2.5	Electrolyte blank	
7.20	0.1	2.9	Electrolyte blank		7.03	0.0	0.8	Electrolyte blank	
7.20	0.9	17.9	Electrolyte blank		7.03	0.0	0.0	Electrolyte blank	
9.95	-0.01	-0.2	Electrolyte blank		10.38	0.9	18.0	Electrolyte blank	
9.95	-0.03	-0.6	Electrolyte blank		10.38	-0.02	-0.4	Electrolyte blank	
	102.1	2050	Spike, average of 2			204.1	4110	Spike, average of 2	
		700	Ni available in sand				700	Ni available in sand	
		2750	Total available Ni				4810	Total available Ni	

¹ The pH measurements are accurate to ± 0.1 ; precision of Ni concentrations is 0.3 ng/ml or 1% (whichever is larger); precision of % sorbed is $\sim 1\%$. Errors for K_ds are proportional to K_d and are distributed asymmetrically about the reported value, as discussed in Table B.6. K_ds are reported to two significant figures.

² K_d calculated by Eq. B.4.

³ %sorbed calculated by Eq. B.3.

The K_d s are calculated from the % sorbed (Eq. B.3) using:

$$K_d, ml/g = \left\{ \frac{1000 * \%sorbed}{\left[(100 - \%sorbed) * \left(\frac{mass_{sand}, g}{vol_{solution}, ml} \right) \right]} \right\} \quad (B.4)$$

Under both atmospheric P_{CO_2} and CO_2 -free conditions, Ni is not adsorbed appreciably by the Wedron 510 sand below a pH of 5. Adsorption increases with pH, with a steep adsorption edge between 6.0 and 7.0; by pH = 7, adsorption is 99+ %. Nearly all Ni is adsorbed from pH 7.0 to 9.0; as pH increases above 9.0, adsorption slowly decreases.

In Figure B.6, three data sets collected under nominally CO_2 -free conditions, using spikes of 100 ng/ml Ni, are illustrated. Each set was initially CO_2 -free, but two of the sample sets were equilibrated on hematology mixers in an open room, and atmospheric CO_2 may have diffused through the container walls and into the samples. The third was equilibrated in a nitrogen-filled glove box. Results from all three sample sets are coincident below pH = 9; at higher pH, they diverge. Adsorption decreases to about 95% at pH 10 for the samples equilibrated in the glove box, and to about 88 % for the other samples.

In Figure B.7, two data sets collected under atmospheric conditions, using spikes of 100 ng/ml and 200 ng/ml Ni, are illustrated. They coincide, suggesting that the available adsorption sites are not saturated at the higher Ni concentration.

The effect of P_{CO_2} on Ni adsorption is unclear at this time. At pH < 7, Ni adsorption is somewhat higher at any given pH under atmospheric conditions than under CO_2 -free conditions. (Figure B.7). At higher pH, adsorption is lower for samples under atmospheric conditions than for CO_2 -free samples equilibrated in the nitrogen-filled glove box. However, it is higher under atmospheric conditions than under the nominally CO_2 -free conditions without the glove box.

B.3.2.2 Effect of Ionic Strength and Competing Cations (Li, Na) on Ni Adsorption

Results of Ni adsorption experiments carried out in the presence of competing cations (Li and Na) are summarized in Tables B.8 and B.9. The effect of added Li is illustrated in Figure B.8. Samples were run using spikes of 100 ng/ml Ni with 10 $\mu g/ml$ Li, and 200 ng/ml Ni with 17.4 $\mu g/ml$ Li, under CO_2 -free and atmospheric conditions, respectively. In both cases, the adsorption edge is broader than the Li-free conditions, and at any given pH, the % sorbed is lower. It seems that, under conditions when Li concentrations are orders of magnitude larger than those for Ni, site competition may have a slight but measurable effect on Ni adsorption. The effect of increased Na concentration on Ni adsorption is shown in Figure B.9. The Ni adsorption curve in a 0.1 M NaCl background electrolyte is identical

Figure B.7. Adsorption of Ni by Wedron 510 sand under atmospheric conditions [two sample sets were run using spikes of 100 ng/ml Ni and 200 ng/ml Ni (shaded and open symbols, respectively) and 20 g sand/20 ml electrolyte; the heavy line is data collected under CO₂-free conditions from Figure B.6 above (the high pH end of the curve was drawn using samples equilibrated in a nitrogen-filled glove box)].

to that derived from the experiments conducted in 0.001 M NaCl. This may indicate that Na does not compete effectively with Ni for adsorption sites on the Wedron 510 sand.

B.3.2.3 Other Effects

In all of the Wedron 510 sand experiments, Ni adsorption decreased at high pH. For most sample sets, this drop was ~10%, from 99+% adsorption at pH 9 to about 90% adsorption at pH 10. However, for CO₂-free samples equilibrated in a nitrogen-filled glove box, the magnitude of the drop was only about ~5%. This suggests that the presence of CO₂ causes a decrease in adsorption, perhaps through formation of a relatively stable Ni-carbonate complex or by enhancement of the stability of colloidal material at high pH. There is some evidence that colloids may be involved; samples run under atmospheric conditions using 20 g sand/20 ml electrolyte, and spiked with 200 ng/ml Ni and 17 µg/ml Li (Table B.8, data set 2) were then filtered through 25,000 molecular weight membrane ultrafilters and resampled. The ultrafiltered samples contained less Ni (Table B.10, and Figure B.10), suggesting that Ni-bearing colloidal material (goethite?) is passing through the standard 0.2 µm filters (Ni adsorption by the ultrafilters was tested and found to be

Table B.8. Adsorption of Ni by Wedron 510 sand in the presence of Li¹

Ni in solution					Ni in solution				
pH	ng/ml	total ng	K _d ²	% sorbed ³	pH	ng/ml	total ng	K _d ²	% sorbed ³
Data set #1, 100 ng/ml Ni and 10 mg/ml Li added, CO2-free cond.					Data set #2, 200 ng/ml Ni and 17 mg/ml Li added, Atmos. cond.				
5.55	111.7	2350	0.22	17.1	4.56	219.4	4660	0.02	1.4
5.71	114.5	2410	0.19	15.0	4.61	215.8	4580	0.03	3.0
6.22	87.4	1830	0.58	35.5	4.75	216.5	4590	0.03	2.8
6.23	87.6	1850	0.57	35.0	5.08	210.8	4440	0.07	5.9
6.36	77.8	1630	0.78	42.6	5.24	210.3	4430	0.07	6.2
6.38	69.1	1450	1.0	49.0	5.42	205.5	4330	0.10	8.3
6.46	63.0	1320	1.2	53.6	6.10	152.5	3180	0.51	32.6
6.47	60.1	1260	1.3	55.7	6.23	135.2	2820	0.71	40.2
6.53	38.4	803	2.7	71.7	6.47	94.2	1950	1.5	58.8
6.81	45.5	948	2.1	66.6	6.48	92.6	1930	1.5	59.1
6.83	43.5	907	2.2	68.1	6.79	58.2	1200	3.0	74.5
6.87	49.3	1030	1.9	63.8	6.86	31.5	650	6.5	86.2
7.26	26.4	546	4.4	80.8	7.46	5.2	107	44	97.7
7.49	16.7	345	7.5	87.9	7.52	4.0	82.7	58	98.3
7.80	22.6	468	5.3	83.5	7.58	3.9	80.0	60	98.3
8.16	2.2	43.9	65	98.5	8.21	2.4	48.7	99	99.0
8.16	3.0	60.3	47	97.9	8.22	0.5	9.9	490	99.8
8.20	2.7	55.1	52	98.1	8.26	0.4	8.6	570	99.8
8.42	0.3	5.8	500	99.8	8.77	1.3	27.2	180	99.4
8.42	0.1	2.7	1100	99.9	8.80	0.5	9.7	500	99.8
8.45	0.1	2.5	1200	99.9	8.84	0.7	15.4	320	99.7
8.60	0.1	2.3	1300	99.9	9.17	8.4	175	27	96.3
8.70	0.4	7.1	410	99.8	9.23	7.1	148	32	96.9
8.93	0.4	7.3	400	99.7	9.23	5.2	109	44	97.7
9.17	2.7	56.6	51	98.0	9.64	14.3	300	16	93.7
9.17	3.4	69.6	41	97.6	9.94	20.6	432	10	90.9
9.33	3.4	69.6	41	97.6	10.06	9.2	194	25	95.9
6.13	12.9	267	Sand blank		4.56	21.2	439	Sand blank	
6.24	14.0	290	Sand blank		4.59	21.4	442	Sand blank	
6.65	3.4	69.7	Sand blank		7.12	0.7	14.4	Sand blank	
6.89	3.7	74.9	Sand blank		7.22	0.7	14.8	Sand blank	
9.26	0.9	18.8	Sand blank		10.11	1.3	26.9	Sand blank	
9.27	2.0	40.0	Sand blank		10.12	1.5	31.3	Sand blank	
6.20	0.0	0.2	Electrolyte blank		4.58	1.3	27.0	Electrolyte blank	
6.20	1.2	25.8	Electrolyte blank		4.58	0.4	8.7	Electrolyte blank	
6.80	-0.1	-1.1	Electrolyte blank		7.17	0.0	0.2	Electrolyte blank	
6.80	0.8	17.2	Electrolyte blank		7.17	0.4	7.6	Electrolyte blank	
9.20	-0.1	-1.9	Electrolyte blank		10.11	0.1	2.5	Electrolyte blank	
9.20	0.1	1.9	Electrolyte blank		10.11	0.5	9.8	Electrolyte blank	
	106.3	2140	Spike, average of 4			196.5	4020	Spike, average of 2	
		700	Ni available in sand				700	Ni available in sand	
		2840	Total available Ni				4720	Total available Ni	

¹ The pH measurements are accurate to ± 0.1 ; precision of Ni concentrations is 0.3 ng/ml or 1% (whichever is larger); precision of % sorbed is $\sim 1\%$. Errors for K_ds are proportional to K_d and are distributed asymmetrically about the reported value (see Table B.6). Data in italics are of poor quality. K_ds are reported to two significant figures.

² K_d calculated by Eq. B.4.

³ %sorbed calculated by Eq. B.3.

Table B.9. Adsorption of Ni by Wedron 510 sand in 0.1 M NaCl¹

pH	Ni in solution		K _d ²	% sorbed ³
	ng/ml	total ng		
<i>Data set #1, 100 ng/ml Ni, CO2-free cond.</i>				
4.69	112.3	2360	0.04	3.3
5.04	113.0	2380	0.03	2.7
5.09	111.2	2340	0.05	4.2
6.12	76.7	1590	0.55	34.9
6.33	75.9	1570	0.57	35.6
6.47	44.4	922	1.7	62.3
6.52	44.1	910	1.7	62.7
6.58	36.2	748	2.3	69.4
6.59	32.1	663	2.8	72.9
6.79	9.5	195	12	92.0
6.84	7.6	155	15	93.7
6.97	7.8	160	15	93.5
7.20	3.5	69.9	34	97.1
7.29	3.1	63.1	38	97.4
7.33	4.0	80.5	30	96.7
7.55	2.5	51.2	47	97.9
7.56	2.6	52.0	47	97.9
7.60	2.1	42.1	58	98.3
7.83	2.2	45.4	54	98.1
7.86	1.9	39.6	62	98.4
7.90	6.4	130	18	94.7
8.18	1.8	35.9	69	98.5
8.31	1.7	35.1	70	98.6
8.31	1.7	35.5	69	98.6
9.35	2.2	45.0	55	98.2
9.45	1.9	38.7	64	98.4
9.47	2.2	45.9	54	98.1
4.95	29.2	608	Sand blank	
5.01	28.8	600	Sand blank	
7.04	2.5	49.9	Sand blank	
7.08	2.3	45.8	Sand blank	
9.27	1.5	30.4	Sand blank	
9.35	1.4	28.2	Sand blank	
6.20	3.1	65.3	Electrolyte blank	
6.20	1.5	30.8	Electrolyte blank	
6.80	1.2	25.0	Electrolyte blank	
6.80	1.7	33.6	Electrolyte blank	
9.20	1.5	31.4	Electrolyte blank	
9.20	1.1	23.5	Electrolyte blank	
	89.8	1820	Spike, average of 4	
		625	Ni available in sand	
		2445	Total available Ni	

¹ The pH measurements are accurate to ± 0.1 ; precision of Ni concentrations is 0.3 ng/ml or 1% (whichever is larger); precision of % sorbed is $\sim 1\%$. Errors for K_ds are proportional to K_d and are distributed asymmetrically about the reported value (see Table B.6). K_ds are reported to two significant figures.

² K_d values calculated by Eq. B.4.

³ %sorbed calculated by Eq. B.3.

Figure B.8. Adsorption of Ni by Wedron 510 sand in the presence of Li [two sample sets were run using spikes of 100 ng/ml Ni and 10 µg/ml Li (filled symbols), and 200 ng/ml Ni and 17 µg/ml Li (shaded and open symbols; open symbols are questionable data) and 20 g sand/20 ml electrolyte; data collected under CO₂-free conditions (solid line; the high pH end was drawn using the samples equilibrated in the nitrogen-filled glove box), and atmospheric conditions (shaded line) from Figure B.6 and B.7 are shown for reference]

Table B.10. Effect of ultrafiltration on the apparent % Ni sorbed at high pH*

pH	Ni in solution, ng/ml		Ni % sorbed	
	0.2 mm filter	ultrafilter	0.2 mm filter	ultrafilter
10.06	9.2	2.2	95.9	99.0
9.64	14.3	6.5	93.7	97.1
9.94	20.6	1.3	90.9	99.4

* The pH measurements are accurate to ±0.1; precision of Ni concentrations is 0.3 ng/ml or 1% (whichever is larger); precision of % sorbed is ~1%.

Figure B.9. Adsorption of Ni by Wedron 510 sand in 0.1M NaCl [experiment was run under CO_2 -free conditions, using 20 g sand/20 ml electrolyte; samples were spiked with 100 ng/ml Ni, and equilibrated in a nitrogen-filled glovebox; adsorption curve for Wedron in 0.001 M NaCl under CO_2 -free conditions (solid line) from Figure B.6 is shown for reference].

Figure B.10. Effect of ultrafiltration on apparent Ni adsorption [filled symbols are samples filtered through standard 0.2 μm filter (complete data set is shown in Figure B.9); open symbols are ultrafiltered samples].

negligible). This agrees with the empirical observation that the fines in the samples do not flocculate above a pH of ~9 (for samples above this pH, the electrolyte is commonly cloudy after centrifuging, and the 0.2 μm filters clog while filtering).

B.3.3 Adsorption Experiments With Pure Minerals

The results of Ni adsorption by Min-U-Sil 5 which had been cleaned in boiling 6N HCl- (see Appendix A for cleaning procedure), are given in Table B.11. The experiment was run under CO_2 -free conditions (in a N_2 -filled glove box; see Table B.1 for experimental parameters). K_{ds} were normalized to 1 g/ml Wedron sand (by assuming a substrate mass of 20 g when calculating the K_{ds} in Eq. B.4 rather than the actual mass of Min-U-Sil used), so that they could be compared directly with the K_{ds} for the Wedron sand. The data differ markedly from the Ni adsorption curve obtained for Wedron 510 under similar conditions (Figure B.11.) The adsorption of Ni by Min-U-Sil increases linearly with pH, and exhibits a very broad adsorption edge. There is 20 % adsorption at a pH of 5, a pH at which the Wedron showed no significant adsorption.

A Ni adsorption experiment with goethite was run under atmospheric conditions (see Table B.1). The results are given in Table B.11 and compared to Ni adsorption by Wedron 510 sand and Min-U-Sil 5 in Figure B.10. As with the Min-U-Sil data, the K_{ds} are normalized to 1g/ml Wedron sand for comparison purposes. The S-shaped curve for Ni adsorption by goethite is generally similar in shape but less steep than the curve derived for the Wedron sand.

B.3.4 Comparison of Batch Adsorption Methods

A study on Ni adsorption by Wedron sand was run to compare results obtained using the batch adsorption procedure described in Los Alamos Procedure # TWS-INC-DP-05, R2 to those obtained using the method described in Appendix E.2. The experiment is described in Table B.2.

Adsorption distribution coefficients determined by both procedures on samples run under similar conditions are listed in Table B.12 and illustrated in Figure B.12. The K_{ds} were calculated as described in section B.3.2.1. The K_{ds} differ for the two procedures; the Los Alamos procedure seems to result in lower adsorption than the SNL procedure. However, pH has not been considered; when the electrolyte is poured off and replaced per the LANL procedure, it re-equilibrates at a lower pH. When the results of this study are plotted against an experimentally derived pH/adsorption curve (Figure B.13), it is apparent that the LANL procedure actually predicts *higher* K_{ds} at a given pH than the method used in this study.

There are several possible reasons for the the difference in K_{ds} . When the first electrolyte is poured off in the LANL procedure, fine material in the sand is lost, and, unlike the tuff studies for which the procedure was written, this fine material is chemically different from the bulk of the sand. It contains the clay fraction, and possibly some

Table B.11. Adsorption of Ni by "cleaned" Min-U-Sil 5 and synthetic goethite¹

pH	Ni in solution		Normed		pH	Ni in solution		Normed	
	ng/ml	total ng	K_d^2	% sorbed ³		ng/ml	total ng	K_d^2	% sorbed ³
<i>Min-U-Sil, 100 ng/ml Ni added, CO₂-free cond.</i>					<i>Goethite data, 100 ng/ml Ni added, Atmos. cond.</i>				
4.50	74.8	1490	0.29	22.7	3.85	98.7	1990	0.03	3.2
4.77	73.9	1470	0.31	23.7	3.94	101.2	2050	0.00	0.3
4.83	69.7	1390	0.39	28.1	4.01	101.8	2060	0.00	-0.1
4.87	75.0	1490	0.29	22.6	4.23	101.5	2050	0.00	0.3
5.10	64.6	1290	0.50	33.3	4.23	101.6	2050	0.00	0.4
5.68	57.9	1150	0.67	40.2	4.35	102.3	2060	0.00	-0.3
6.28	58.5	1170	0.65	39.5	4.81	100.8	2040	0.01	1.1
6.42	54.6	1090	0.77	43.6	4.83	101.0	2040	0.01	0.9
6.67	53.0	1060	0.83	45.3	4.84	98.8	1990	0.03	3.1
6.81	47.7	952	1.0	50.7	5.20	100.4	2030	0.02	1.6
7.31	39.9	797	1.4	58.7	5.38	101.0	2040	0.01	1.0
7.32	42.1	839	1.3	56.5	5.52	94.2	1900	0.08	7.7
7.41	39.6	790	1.4	59.1	5.66	199.0	4050	0.02	1.5
7.80	28.6	570	2.4	70.5	5.91	83.3	1680	0.23	18.3
7.85	26.5	529	2.7	72.6	6.65	62.9	1270	0.63	38.3
7.92	26.5	530	2.7	72.6	6.72	57.3	1160	0.79	43.7
8.15	20.7	413	3.7	78.6	7.00	39.8	803	1.6	61.0
8.18	19.4	388	4.0	79.9	7.17	27.3	552	2.8	73.2
8.46	14.8	296	5.5	84.7	7.20	44.6	904	1.3	56.1
8.46	14.5	289	5.7	85.0	7.21	43.0	867	1.4	57.8
8.56	14.5	291	5.7	85.0	7.59	27.4	556	2.8	73.0
8.99	9.0	182	9.7	90.6	8.95	1.9	39.2	53	98.1
9.04	5.1	102	18.1	94.7	9.43	0.2	3.3	630	99.8
9.09	5.1	102	18.1	94.7	9.62	3.4	69.2	30	96.6
4.77	0.1	2.4	Min-U-Sil blank		9.66	0.2	4.2	510	99.8
4.85	0.4	7.5	Min-U-Sil blank		10.02	0.3	6.9	310	99.7
6.54	0.9	17.1	Min-U-Sil blank		10.51	0.7	13.8	150	99.3
6.70	1.6	31.1	Min-U-Sil blank		10.66	0.4	8.0	270	99.6
9.06	1.6	31.5	Min-U-Sil blank		4.93	1.4	27.9	Goethite blank	
9.10	2.0	40.9	Min-U-Sil blank		4.89	0.8	15.7	Goethite blank	
4.91	0.3	4.8	Electrolyte blank		6.65	0.3	5.3	Goethite blank	
4.93	0.8	14.7	Electrolyte blank		6.71	0.3	5.7	Goethite blank	
9.72	-0.1	-1.6	Electrolyte blank		10.83	2.4	49.7	Goethite blank	
	102.0	1930	Spike, average of 4		10.76	0.6	12.8	Goethite blank	
		0	Ni available in smple		4.80	0.6	12.0	Electrolyte blank	
		1930	Total available Ni		4.80	0.0	0.4	Electrolyte blank	
					6.70	0.3	5.5	Electrolyte blank	
					6.70	1.6	30.9	Electrolyte blank	
					10.75	1.7	36.1	Electrolyte blank	
					10.75	0.2	3.4	Electrolyte blank	
						99.8	2010	Spike, average of 2	
							50	Ni available in goeth.	
							2060	Total available Ni	

¹ The pH measurements are accurate to ± 0.1 ; precision of Ni concentrations is 0.3 ng/ml or 1% (whichever is larger); precision of % sorbed is $\sim 1\%$. Errors for K_d s are proportional to K_d and are distributed asymmetrically about the reported value (see Table B.6). K_d s are reported to two significant figures.

² K_d values calculated by Eq. B.4.

³ %sorbed calculated by Eq. B.3.

Figure B.11. Adsorption of Ni onto Min-U-Sil quartz (open symbols) and synthetic goethite (filled symbols) [experimental conditions are described in Table B.1; Wedron 510 CO₂-free adsorption curve (shaded line, from Figure B.5) is shown for reference].

colloidal iron hydroxide, important phases in terms of the adsorption properties of the sand. Also, the electrolyte, 0.001M NaCl, is not initially in equilibrium with the sand.

B.4 Discussion

One of the objectives of this work is the formulation of a strategy to model sorption of Ni by naturally occurring mixtures of minerals. Two possible approaches include: (1) treating the natural material as a single phase in Ni adsorption experiments; and (2) obtaining Ni adsorption data on synthetic or natural analogs for the individual components of the natural material and then predicting Ni adsorption by the natural material using a mixtures model. In this study, both approaches are being pursued simultaneously. Ni adsorption by the raw Wedron sand has been compared to that by both an acid-washed quartz (Min-U-Sil-5) and synthetic goethite. At present, we have no data describing the nature of the sites in Wedron 510 sand, goethite and Min-U-Sil 5 at which adsorption is occurring. It is possible that neither the Min-U-Sil 5 or the synthetic goethite are good analogs for the quartz and iron oxyhydroxide components of the Wedron 510 sand. If the acid-washed Min-U-Sil-5 is representative of pure quartz, then the Ni adsorption experiments with the Min-U-Sil-5 suggest that quartz is not the dominant adsorbing phase

Table B.12. Comparison of SNL and LANL batch adsorption procedures (methods A-E are as described in Figure B.12)*

pH	Ni in solution		K _d
	ng/ml	total ng	
<i>Method A</i>			
7.26	1.1	22.2	120
7.27	1.6	31.2	88
7.25	2.2	43.3	63
7.28	0.7	13.6	200
7.27	1.1	21.4	130
		Average	120
		St. Dev.	48
<i>Method B</i>			
7.02	21.7	436	76
7.23	13.2	267	140
7.11	13.1	264	140
7.20	11.7	235	160
6.72	33.3	670	42
		Average	110
		St. Dev.	44
<i>Method C</i>			
7.54	3.0	60.0	45
7.76	3.0	60.8	45
7.47	2.2	45.0	61
7.45	1.9	37.6	73
7.48	2.5	49.7	55
		Average	56
		St. Dev.	10
<i>Method D</i>			
5.58	69.9	1410	9.6
5.96	61.8	1240	14
5.87	68.3	1380	10
5.84	67.3	1350	11
6.90	37.5	755	35
		Average	16
		St. Dev.	9.8
<i>Method E</i>			
6.04	50.1	1010	21
6.07	50.5	1020	21
5.80	57.2	1150	16
6.46	32.3	650	44
		Average	26
		St. Dev.	11

* The pH measurements are accurate to ± 0.1 ; precision of Ni concentrations is 0.3 ng/ml or 1% (whichever is larger); precision of % sorbed is $\sim 1\%$. Errors for K_ds are distributed asymmetrically about the reported value. K_ds are reported to two significant figures.

Figure B.12. Comparison of Ni K_d s for Wedron sand determined by different batch adsorption procedures and the LANL procedure (methods A through E are as described in Table B.2; the samples were not pH-adjusted).

Figure B.13. A plot of K_d vs pH for the results of the batch adsorption procedure comparison study described in Table B.2 and Figure B.12 [the filled squares and diamonds are the results for methods A and B, as described in Figure B.12; the open squares and diamonds are method C and D results, respectively; and the shaded diamonds are method E results; the X's are the Wedron sand adsorption data (Table B.7, data set #1) obtained under similar experimental conditions (Method A)].

in Wedron 510. It is probable that sorption of Ni by an iron oxyhydroxide occurs in Wedron 510; experiments with synthetic goethite produced an adsorption curve that is at least broadly similar to the Wedron curve. The roles of kaolinite and carbonate, other minor phases in the sand, have yet to be examined.

The role of CO_2 in Ni adsorption is poorly understood. Empirically, near neutral pH, adsorption is somewhat higher in the presence of CO_2 . This may be due to the adsorption of molecular CO_2 by the goethite coatings on the sand grains. It has been shown (Russell et al., 1975) that the linear CO_2 molecule deforms when it is adsorbed by weakly bonding with an oxygen atom in the goethite structure. This produces a localized surface charge imbalance, and might effectively increase the number of sites available for adsorption. If adsorption of Ni by the sand occurs on iron hydroxide coatings, then this effect may lead to the observed increase of adsorption in the presence of CO_2 .

Under alkaline conditions, the presence of CO_2 causes a drop in the amount of Ni adsorbed. The ultrafiltration study suggests that Ni may be passing through the standard filters adsorbed onto colloidal particles or as colloidal $\text{Ni}(\text{OH})_2$; CO_2 present as an aqueous carbonate phase may inhibit flocculation and enhance this effect. Alternatively, Ni may form a stable aqueous Ni-carbonate complex at high pH, resulting in decreased adsorption.

Another question which has not been addressed fully is the effect of competing ions on Ni adsorption. Na has been shown to have little effect, even at extremely high concentrations ($>2000 \text{ mg/ml}$), but Li, at concentrations of $10\text{-}20 \text{ mg/ml}$, causes a measurable decrease in Ni adsorption at near-neutral pH. Li^+ is somewhat smaller than Na^+ , and is similar in size to Ni^{2+} ; and may compete for Ni adsorption sites.

The presence of other exchangeable metal cations, such as Cr, Co, or V, in the Wedron 510 sand must also be considered. If present in sufficient quantities, these elements could compete with Ni for adsorption sites. The overlap of the 100 ng/ml and the 200 ng/ml Ni adsorption curves (Figure B.6) suggests that the available Ni adsorption sites are not saturated at these concentrations; hence, site competition with other naturally metal ions may not be an important process.

In applying these static batch adsorption results to caisson transport experiments, adsorption reaction rates must be considered. If adsorption kinetics are slow relative to transport experiment durations, then Ni retardation in the caisson will be less than that predicted by the batch experiments. The adsorption rate study discussed earlier (Table B.3 and Figure B.5) indicates that Ni adsorption by Wedron sand is very rapid; hence, adsorption data obtained from batch experiments should be directly applicable to the caisson studies.

A second objective of this study is the determination of the validities of alternative models for adsorption. The adsorption data collected in this study will be used to calculate both K_d s and surface complexation constants for solute transport models. The K_d data can be used in existing transport codes such as FEHM (Zyvoloski et al., 1991). Additional modeling and data collection are required before the surface complexation constants can be obtained. Adsorption curves similar to that shown in Figure B.6 will be

used to obtain surface complexation constants describing adsorption of Ni by Wedron 510 sand under CO₂-free conditions. Ni adsorption in the presence of CO₂, Li and higher concentrations of Na will then be calculated using the HYDRAQL code and compared to adsorption curves in Figures B.7–B.9. Prior to execution of these calculations, additional data for Li and Na adsorption by the Wedron 510 sand at several constant values of total CO₂ will be obtained. When both data sets are complete, predictive modeling of Ni transport in the caisson will be carried out with the FEHM and LEHGC version of the HYDROGEOCHEM code (Yeh and Tripathi, 1990) respectively.

B.5 Conclusion

Progress in the collection of data required to predict the retardation of Ni under conditions relevant to the joint LANL/SNL caisson experiments is described in this appendix. The pH-dependence of Ni adsorption onto Wedron 510 sand has been examined under a variety of experimental conditions. Interpretation of the batch adsorption data and extrapolation to natural conditions are still difficult; several important questions remain to be answered. Data have been collected in ways suitable for the calculations of surface complexation models as well as according to procedures developed by the Yucca Mountain Site Characterization project for measurement of K_d s. Studies of Ni adsorption by the labware, leaching of Ni from the sand by the background electrolyte and the rate of Ni adsorption were carried out prior to initiation of systematic experiments. These systematic experiments examined the effect of various solution parameters on Ni adsorption. The effect of pH, presence of atmospheric CO₂, competition for adsorption sites by Li and Na were examined. Ni hydroxide solubility data were obtained to discriminate among batch-adsorption experiments in which the aqueous concentration of Ni was probably controlled by adsorption and those in which precipitation effects must also be considered. The data described in the Appendix will be combined with additional data to form the basis for future modeling efforts in support of the caisson experiment. These modeling exercises will compare the relative merits of alternative models for sorption (K_d vs. surface complexation models) and alternative approaches to predicting the sorption properties of complex multiphase natural materials.

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Appendix C

Column Studies in Support of the Caisson Experiments: Design and Preliminary Results for Li and Br

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C.1 Introduction

C.1.1 Objectives

The development of techniques for the study of the transport of tracers in saturated and unsaturated soil columns in support of model validation studies is documented in this appendix. Batch adsorption and column transport studies were carried out to estimate breakthrough curves (BTC's) for Li and Br through saturated Wedron 510 sand as part of the design and detailed characterization phases of the caisson experiment. Several issues were addressed in this study. The simplest task was to compare the accuracies of a simple K_d model and a simple first order rate model for descriptions of Li and Br transport in the lab-scale columns. If adsorption rates are fast and mass transfer resistances are relatively small, then equilibrium adsorption (K_d) will be sufficient for describing the BTC. However, if reaction rates are slow, then a model including a rate expression will be required for describing the breakthrough curves.

This appendix provides a summary of progress in the development of one component of a framework to validate reactive transport models. The long term objective of this portion of the work is to evaluate experimental and theoretical limitations on the measurement of a self-consistent set of transport parameters from batch and column experiments for a relatively simple chemical and hydrological system. The parameters measured in batch sorption experiments included adsorption coefficients and adsorption rate constants. Parameters, measured directly or obtained by numerical fits to BTC's obtained in column experiments, include dispersivity, adsorption rate constants and retardation factors. The values of reaction rate constants obtained from the batch and column experiments can be compared directly; a K_d calculated from the retardation factor measured in the column experiment could be compared to that measured in the batch experiment using assumed values of porosity and bulk density of the sand. This work demonstrates the complementary nature of batch and column studies in attempts to extrapolate parameters measured in the laboratory to the intermediate-scale caisson experiment or other field sites. This study provides a partial basis for the formulation of criteria for validation tests by indicating reasonable expectations for agreement between predictions and measurements of transport of reactive tracers.

C.1.2 Previous Work

C.1.2.1 Batch Sorption Studies

Lithium is commonly used in column and field tracer studies for several reasons. Both of its readily available solids, Li_2CO_3 and LiCl are soluble at high concentrations. Lithium does not form strong aqueous or surface complexes or undergo microbial conversion. Lithium has a large hydrated radius, high hydration energy and a very low polarizability (Anderson et al., 1989). These characteristics make lithium the hardest acid among the alkali cations, i.e. it has the least ability to exchange its solvent water molecules for the oxygen ions (soft base) in surface functional groups.

A general selectivity sequence of most common cations by general-purpose cation exchangers (Fuentes et al., 1989) shows lithium with the lowest preference:

Several studies of Li adsorption by the minerals similar to those present in the caisson have been reported. Abendroth (1970) found that the affinities of cations for pyrogenic silica increase in the order: $\text{Cs}^+ > \text{K}^+ > \text{Li}^+$. Chardymyskaya et al. (1987) found that Li adsorption by quartz in LiCl solutions was low in the neutral pH region, whereas for $\text{pH} > 7$, it rose sharply. He also found that the amount of adsorption and surface charge increased as the solution's ionic strength increased.

Ardizzone et al. (1982) examined the behavior of the surface of lepidocrocite ($\gamma\text{-FeOOH}$) in LiCl solutions. He found a well-defined pH_{ZPC} of 7 which was lower than that found for NaCl and other solutions. He also found that the sequence of interaction of monovalent cations with the surface was $\text{K}^+ < \text{Na}^+ < \text{Li}^+$. Na^+ showed a very strong adsorption while Cl^- showed an absence of specific interactions.

Nir et al. (1986) examined Li-Na adsorption by montmorillonite clay. He found that Na-Li exchange was not appreciably sensitive to ionic strength because their binding affinities were similar ($K_{\text{Li}} = 0.6 \text{ M}^{-1}$ vs. $K_{\text{Na}} = 1 \text{ M}^{-1}$). Anderson et al. (1989) examined lithium adsorption in soils and clays. He did not find a lithium sorption maximum for any of the soils for total Li concentrations up to 1 mmol/l. The extent of sorption depended on the effective cation exchange capacity and not specifically on clay content or mineralogy. At the lowest total lithium concentration (0.005 mmol/l), more than 90% of the Li was removed from solution even though solution concentrations of potentially competing Na^+ , K^+ , Mg^{2+} , and Ca^{2+} ions were usually an order of magnitude or more greater. Anderson et al. (1989) found that most of the adsorbed Li was non-exchangeable and suggested that sites exist within soils, presumably within clay minerals, which are highly specific for lithium. Fletcher and Sposito (1989) reported that the ion-exchange affinities of sodium and lithium for clay surfaces were nearly the same. The value of the equilibrium exchange constant K_a for the reaction $\text{Li}^+ + \text{NaX} = \text{LiX} + \text{Na}^+$ is 0.95.

Lithium adsorption by tuff is relatively weak and reversible (Fuentes et al., 1989; Newman et al., 1991). The adsorption data were best fit with Langmuir and Modified Freundlich isotherms. In the linear range, the K_d s were approximately 0.4 ml/g. Adsorption kinetic experiments indicated that equilibrium was reached in about 1-2 hr.

C.1.2.2 Column Studies

The results of several previous studies provided information for the design of these column studies. Bowman (1982) conducted batch and saturated column experiments using Ni as a sorbing species and saturated soils from southwestern United States as the sorbing media. He described the use of activity-based Freundlich isotherms to model elution

curves. Liddle and Bowman (1990) conducted several breakthrough tests with Br in saturated and unsaturated tuff columns. He obtained retardation factors and dispersion coefficients using the equilibrium dispersion-convection model in the code CXTFIT of Parker and van Genuchten (1984). The retardation factors were calculated relative to tritium, a non-sorbing, non-charged species, in order to separate fluid-flow effects from chemical effects. For saturated columns the retardation factors ranged from 0.75 to 0.99 for Br. For unsaturated columns the retardation factors ranged from 0.64 to 0.97.

Newman et al. (1991) calculated breakthrough curves for total Li concentrations of 1 to 1000 ppm. It was found that the use of different isotherms resulted in very large differences in breakthrough curves. For an applied step input of 100 ppm Li, the Langmuir, Modified Freundlich and Freundlich isotherms resulted in 50% breakthroughs at 267%, 300% and 367%, respectively, of that calculated using a linear isotherm.

Kuhn and Peters (1981) and Relyea (1982) used the theoretical sorption rate analysis of Sherwood, Pigford and Wilke (1975) to relate the apparent retardation factor to the equilibrium retardation factor for columns in which sorption equilibrium was not attained. As noted by Kuhn and Peters (1981) and Relyea (1982), equilibrium is closely approached for fluid residence times typical in repositories; however, sorption kinetics must be considered in column experiments used to obtain retardation factors for use in performance assessment codes.

C.1.2.3 Summary of Properties of Wedron 510 Sand

Chemical properties of Wedron 510 sand are described in Appendix A of this report. Potentiometric titrations, acid leaching studies, and microscopic surface analysis of Wedron 510 sand suggest that carbonate minerals, clays and iron oxyhydroxides coat the sand surface. The effective surface area is about 0.12 m²/g, as determined from the BET (Brunauer, Emmett, and Teller, 1938) method.

Hydrologic characteristics of the sand have been previously described (Siegel et al. 1992, 1993). The particle size distribution of sand is described in Appendix A of this report. Figure C.1 shows the sand particle size distribution for Wedron 510 and perturbations expected due to micro-layering and cross-bedding heterogeneities created during caisson filling and packing.

C.2 Experimental Procedures for Batch and Column Studies

C.2.1 Batch Sorption Studies

Batch studies of sorption of lithium and bromide by Wedron 510 sand in 0.001 M NaCl were carried out under atmospheric and CO₂-free conditions in 50 ml polycarbonate centrifuge tubes. Reagent grade lithium bromide (LiBr) was used as the source for both

Figure C.1. Sand particle size distribution for Wedron 510 and perturbations expected due to micro-layering and cross-bedding heterogeneities created during caisson filling and packing [A=Wedron 510, B=slight narrowing, C=slight widening of grain size distribution, D and E=expected values due to the grading process causing micro-layering (after Siegel et al., 1992)].

lithium and bromine. Batch sorption procedures, including pre-equilibration and separation techniques, are similar to those described in Appendix E.2 of this report.

Tracers were added into the sample vials using automatic pipettes for all tests. For the tests in which the K_d s were reported in ml/g, the volume of added tracer was measured with an automatic pipette, whereas for tests in which the K_d s were reported in g/g, the amount of tracer added was determined by sample weight. Results from the methods are directly comparable for low tracer concentrations, due to the small deviation of the density of the solution from 1 g/ml. However, for isotherm experiments where the concentration of Li was as high as 1000 ppm and of Br as high as 10,000 ppm, the density difference should be considered when comparing K_d values obtained from data sets.

Procedures for measuring pH of solutions under atmospheric and CO_2 -free conditions are described in Appendix E.1.

C.2.1.1 Br Adsorption Studies

Equilibrium K_d values were determined for adsorption by Wedron 510 sand as a function of pH. A solution to sand ratio of 20 g of 0.001 M NaCl electrolyte to 20 g sand was used and allowed to pre-equilibrate for 2 days prior to the addition of 200 μl of $1.4 \cdot 10^{-3}$ M LiBr spike solution, which yielded a solution concentration of 114 ppm Br. The samples

were then put on mixers and allowed to equilibrate for 2-3 days. The study was performed under "CO₂-free" conditions and the final Br concentrations were measured with an ion specific electrode as described in Appendix E.5. The samples in this experiment are those from which the Li Data Set 2 was derived.

C.2.1.2 Li Equilibrium Batch Adsorption Studies

The adsorption experiments can be classified as K_d , isotherm, and kinetic experiments. The Li batch adsorption data sets are described in Table C.1. Li concentrations in the solutions were measured with flame atomic absorption as described in Appendix E.4. The use of KCl as an ionization suppressant affected the absolute values of measured Li concentrations. Data sets which were analyzed using this technique are identified in Table C.1 and are discussed in the Results section.

C.2.1.2.1 K_d experiments

Equilibrium K_d values for Li sorption by Wedron 510 were determined as a function of pH for total concentrations of 10 and 17 ppm Li under in CO₂-free batch systems and systems partially-equilibrated with atmospheric CO₂. For K_d experiments, the solution-to-sand ratio was 20 g of sand to 20 g of 0.001 M NaCl electrolyte. The solids and solutions were pre-equilibrated for 2 days, and then allowed to equilibrate for another 2 to 3 days after addition of the LiBr tracer. Batch systems described as "CO₂-free" were prepared

Table C.1. Li batch adsorption studies

Data set	Total Li conc.	Ni conc.	P _{CO₂} *	Comments
1	10 ppm	100 ppb	CO ₂ -free	K_d study, no KCl
2	10 ppm	0	CO ₂ -free	K_d study, no KCl
3	17 ppm	200 ppb	atmos	K_d study, samples analyzed twice to determine effect of KCl
4	10 ppm	0	CO ₂ -free	K_d study, with KCl
5	10 ppm	0	atmos.	K_d study, with KCl
6	5 ppm	0	n/a	Kinetic study with NaHCO ₃ buffer, no KCl
7	17.4 ppm	0	n/a	Kinetic study with NaHCO ₃ buffer, no KCl
8	0.1 - 10 ppm	0	atmos.	Isotherm study with variable concentrations and solid/solution ratios
9	1-1000 ppm	0	atmos.	Isotherm study, no KCl

* atmos = partially-equilibrated with atmospheric CO₂ as described in text.

with CO₂-free reagents, purged of CO₂ at various times, and equilibrated in closed centrifuge tubes on a lab bench, but were not kept in a controlled-atmosphere glove box. Some diffusion of CO₂ into the sealed centrifuge tubes may have occurred at high pH. Batch systems described as "partially-equilibrated with atmospheric CO₂" were aerated with air several times during the experiments, however, at high pH, it is unlikely that equilibrium with atmospheric CO₂ was attained.

C.2.1.2.2 Li kinetic adsorption experiments

Adsorption of Li as a function of time was studied in batch experiment under partially-equilibrated atmospheric conditions in a buffered solution consisting of $9 \cdot 10^{-5}$ M NaHCO₃ and 0.001 M NaCl. The total Li concentrations of the batch systems were 5 or 17.4 ppm. The sand samples were pre-equilibrated with the solutions for 8 hours and then sampled for periods of up to 1 week after addition of the LiBr tracer. Other experimental procedures were the same as those of the K_d experiments described above.

C.2.1.2.3 Li isotherm studies

Isotherm experiments were carried out at variable solution/solid ratios and variable total Li concentrations of 1 - 1000 ppm, at a pH of ~7.5. Solution:sand ratios of approximately 1:1, 5:1, and 10:1, and lithium and bromine concentrations of $1.44 \cdot 10^{-5}$, $1.44 \cdot 10^{-4}$ and $1.44 \cdot 10^{-3}$ M were used. The samples were allowed to pre-equilibrate for approximately six days and to equilibrate for approximately seven days after tracer addition while being continuously stirred on a hematology mixer. No attempt was made to control the pH during the isotherm experiments. Other experimental procedures were the same as those of the K_d experiments described above.

C.2.2 Column Experiments

Experimental procedures for column studies are described in detail in Appendix E.7 of this report; a summary is presented here.

C.2.2.1 Procedure to Pack Micro-Layered and Homogeneous Columns

The columns were packed in either one of two ways. In the first method, sand was poured down the column in small amounts (about 20 g) at a time. Clearly visible layers formed from the different portions poured; the resulting column was said to be "micro-layered." In the second method, sand was mixed using two screens as it fell into the column. Three columns were connected together with screens between the columns to mix the sand as it fell into the bottom column; the resulting sand column was referred to as a homogenous sand column. The procedure is described in more detail in Appendix E.7. A micro-layered and a homogenous column were prepared in order to determine if there were any hydrological effects due to potential heterogeneities in the sand bed.

C.2.2.2 Saturated Column Procedure

Figure C.2 illustrates the experimental setup used for saturated column experiments. The main components were a peristaltic pump, a feed scale, the column and a fraction collector. The columns were 5.1 cm in diameter and 30 cm tall. The saturated runs were conducted in a manner specified in Appendix E.7 using a 30 cm column of sand. The influent solutions consisted of 17.4 ppm Li and 200 ppm Br in a background solution of $9 \cdot 10^{-5}$ M NaHCO_3 and 0.001 M NaCl with a pH of approximately 7.

C.3 Modeling Techniques: The CXTFIT Model

C.3.1 Overview

The CXTFIT computer code (Parker and van Genuchten, 1984) uses least-squares analysis to fit breakthrough curves to analytical solutions for transport. The two models used for analysis of the breakthrough curves in this study are the linear equilibrium (K_d) and the two-site non-equilibrium (kinetic) sorption models.

Figure C.2. Experimental set-up for saturated column experiments.

These models can be derived from the basic one dimensional transport equation:

$$\frac{\rho}{\theta} \frac{\partial s}{\partial t} + \frac{\partial C_r}{\partial t} = D \frac{\partial^2 C_r}{\partial x^2} - v \frac{\partial C_r}{\partial x} - \mu_w C_r - \frac{\mu_s \rho s}{\theta} + \gamma_w + \frac{\gamma_s \rho}{\theta} \quad (\text{C.2})$$

where C_r and s are the concentrations of the tracer in the liquid and solid phases, respectively, ρ is the bulk density, v is the fluid velocity, D is the dispersion, θ is the water content (cm^3 water/ cm^3 total bed volume), and μ_w and μ_s are rate constants for first-order decay in the liquid and solid phases of the soil, respectively. The coefficients γ_w and γ_s represent similar rate constants for zero-order production in the two soil phases. The terms in Eq. C.2 describe change in tracer concentration in the solid phase (here assumed to be due to adsorption), change in tracer concentration in the liquid phase, dispersion, convection, decay in tracer concentration in the liquid phase, decay in tracer concentration in the solid phase, zeroth order tracer production in liquid phase and zeroth order tracer decay in the solid phase. When there is no decay or production, the transport equation reduces to:

$$\frac{\rho}{\theta} \frac{\partial s}{\partial t} + \frac{\partial C_r}{\partial t} = D \frac{\partial^2 C_r}{\partial x^2} - v \frac{\partial C_r}{\partial x} \quad (\text{C.3})$$

C.3.2 Equilibrium Linear Sorption Isotherm (K_d) Model

In the equilibrium linear sorption isotherm (K_d) model, the concentration of tracer on the solid phases, is represented as $K_d C_r$. Substitution into the left hand side of Eq. C.3 results in a combined term $(1 + \rho K_d / \theta) \partial C_r / \partial t$. The retardation factor, R , is defined as $1 + \rho K_d / \theta$. Thus, the transport equation, assuming equilibrium, reduces to:

$$R \frac{\partial C_r}{\partial t} = D \frac{\partial^2 C_r}{\partial x^2} - v \frac{\partial C_r}{\partial x} \quad (\text{C.4})$$

If there is no sorption, then the K_d is zero and the retardation factor is 1. For anionic species such as Br^- , it is possible for R to be less than 1, due to anion exclusion by repulsion of Br^- by negatively charged sites on the porous media (Gvirtzman et al., 1991). Input to CXTFIT consists of the relative (C/C_0) tracer concentration at the end of the column as a function of dimensionless time (i.e., pore volumes) and initial guesses of R and D . CXTFIT calculates the best-fit values of R and D , goodness of fit statistics and plots a theoretical breakthrough curve calculated from these parameters.

C.3.3 Non-Equilibrium Model

In the two-site/two-region non-equilibrium (kinetic) model, it is assumed that for a fraction F of the total sites, sorption equilibrium exists and for the fraction $1-F$ sorption is reaction-rate limited. For the non-equilibrium sites, it is assumed that the sorption rate is

proportional to the difference between the equilibrium tracer concentration on the surface corresponding to the actual liquid tracer concentration and the actual tracer concentration on the surface. If s_1 is the concentration of tracer on equilibrium sites and s_2 is the concentration of tracer on non-equilibrium sites, then the governing equations are:

$$\left(1 + \frac{F\rho K_d}{\theta}\right) \frac{\partial C_r}{\partial t} + \frac{\rho}{\theta} \frac{\partial s_2}{\partial t} = D \frac{\partial^2 C_r}{\partial x^2} - v \frac{\partial C_r}{\partial x} \quad (C.5)$$

$$\frac{\partial s_2}{\partial t} = k(s_2^* - s_2) \quad (C.6)$$

$$s_2^* = (1 - F) K_d C_r \quad (C.7)$$

where k is the first order rate constant.

Given input data consisting of liquid tracer concentration at the exit of the column as a function of pore volumes, and initial guesses of R , D , F and k , CXTFIT calculates best-fit values of R , D , F , and k along with a concentration versus pore volume profile based on these fitted parameters. Fixed values can be specified for any number of the parameters for a calculation.

C.3.4 Method of Solution

CXTFIT uses the maximum neighborhood method of Marquardt (1963) to minimize the sums of squares of the residuals between observed and calculated concentrations. Daniel and Wood (1973) give a detailed description of the method.

C.4 Results

The results presented in this chapter are in three parts. First, results of batch studies of bromide adsorption by Wedron 510 sand as a function of pH are presented. Next, the results of studies of adsorption of lithium by Wedron 510 sand as a function of pH, concentration, time, and atmospheric CO_2 conditions are described. Finally, breakthrough curves for the tracers Li and Br obtained from transport experiments through Wedron 510 sand columns are presented and then modeled using a linear equilibrium (K_d) model and a sorption rate (kinetic) model.

C.4.1 Bromide Analysis by Ion Specific Electrode

The results of the Br batch adsorption experiment are shown in Figure C.3. The Br analysis was done by Ion Specific Electrode as described in Appendix E.5. The data suggest that no significant sorption of Br occurs at any pH. The slight scattering may be attributed to a change in the Br^- electrode response with pH during analysis.

Figure C.3. Equilibrium K_d s from Br batch adsorption experiments.

C.4.2 Lithium Analysis by Flame Atomic Absorption

Lithium analyses by flame atomic absorption (AA) were obtained in support of batch adsorption experiments described in this subsection and in the column transport experiments described in the next section. During the approximately 2 years of measurements, it was determined that the precision and accuracy of Li AA analyses for solutions partially equilibrated with atmospheric CO_2 improved with the addition of KCl, an ionization suppressant, during the AA analysis. In particular, it was found that samples in Data Set 4 when re-analyzed with the KCl additive gave consistently lower Li concentration values and subsequently higher calculated K_d s.

Discussions of this effect and of verification of the AA analysis technique using the KCl additive are found in the Attachment to this appendix. Samples from several data sets collected early in this study were not re-analyzed using the new procedure. These include Data Sets 1, 2, 3, 7, 8, and 9 in Table C.1 and all of the solutions collected from the column transport studies. The data sets may contain errors due to the combination of competing cations, CO_2 and ionization suppression during the AA analysis, however, any such errors will not significantly affect the conclusions drawn from the experiments. As discussed in the attachment, the effect does not appear to be important for samples equilibrated at neutral pH under CO_2 -free conditions (Data Sets 2 and 3). In addition, the effect does not invalidate the results of isotherm studies (Data sets 1 and 7) because the isotherm constants are obtained from plots of relative changes in concentrations of adsorbed lithium. Finally, systematic errors due the omission of KCl in the AA analysis for Li, should not affect the determination of the breakthrough curves in column studies, which depends

upon the ratio of the effluent concentration to the initial concentration, C/C_0 , rather than on the absolute value of the effluent concentration.

C.4.3 Batch Experiments

C.4.3.1 Equilibrium Batch Sorption (K_d) Experiments

Figure C.4 compares Li adsorption under several experimental conditions from the K_d data sets that are considered to be the most reliable at this time. K_d s were calculated from the amount of adsorbed Li and the solution to solid ratio of the experiments as discussed in Appendix E.2. For the pH range relevant to the caisson experiment (7-8.5) under CO_2 free to partially-equilibrated conditions, the measured K_d s range from approximately 0.05 to 0.25 mL/g (5% - 20% adsorption). The degree of adsorption in all data sets is dependent on the pH; reaching a maxima at near neutral pH. As discussed in the Attachment, Data Sets 4 and 5 are considered the most reliable of the available data. They show no dependence of adsorption on the amount of CO_2 present in the batch system. This is not consistent with the values in Data Set 3, which show depressed levels of adsorption relative to results of the CO_2 -free experiments.

C.4.3.2 Kinetic Batch Sorption Experiments

Figure C.5 shows the aqueous concentration of Li as a function of time for a kinetic batch sorption experiment under atmospheric conditions. The initial Li concentration was 17.4 ppm, and the pH varied from 7.6 to 7.7. The increase in Li concentration in the first hour is puzzling. It does not necessarily indicate leaching of Li from the sand, because electrolyte solution was equilibrated with the sand for 8 hours before the Li tracer was added. Equilibrium appears to be reached within 25 – 30 hours.

Figure C.6 shows a plot of the dimensionless driving force, $(s^*-s)/(s^*-s_0)$, as a function of time. The absolute value of the slope of the plot is the first order reaction rate constant, k , of 0.0012 min^{-1} .

The results of the second kinetic adsorption experiment, with a total Li concentration of 5 ppm and pH range of 7 – 8, are shown in Figures C.7 and C.8. The same initial rise in Li concentration is observed during the first few hours. The first-order reaction rate constant is estimated at 0.0004 min^{-1} from Figure C.8. Equilibrium was reached in 80 – 100 hours in this experiment.

C.4.4 Li Isotherm Experiments

Table C.2 summarizes the results of Li batch adsorption tests under atmospheric conditions for several solution/solid ratios and total Li concentrations (Data Set 8). The calculated K_d depends on both the tracer concentration and the solution:solid ratio. Preliminary attempts to fit the data to a Langmuir isotherm using a least squares analysis showed that the relationship between amount of adsorption and tracer concentration was

Figure C.4. Comparison of Li sorption data sets.

Figure C.5. Li kinetic batch adsorption experiment [total Li (C_0)=17.4 ppm].

Figure C.6. Li adsorption rate plot ($C_0=17.4$ ppm).

Figure C.7. Li kinetic batch adsorption experiment ($C_0= 5$ ppm).

Figure C.8. Li adsorption rate plot ($C_0 = 5$ ppm).

Table C.2. Li sorption on Wedron 510, atmospheric conditions

Initial Li (mg/ml)	K_d (ml/g)					
	L/S =1		L/S =5		L/S =10	
	mean	s	mean	s	mean	s
0.10	13.00	2.20	37.00	7.30	18.00	4.70
1.00	0.16	0.15	0.80	0.08	0.89	0.05
10.00	0.20	0.01	0.18	0.13	0.46	0.17

different for each solution:solid ratio. Deviations of the experimental observations from calculated Langmuir isotherm plots were unacceptably large at the two higher solution:solid ratios.

Figure C.9 shows the relationship between the calculated K_d and the concentration of Li in solutions for Data Set 9. Figure C.10 shows the corresponding adsorption isotherm. Note that the values of K_d in Figure C.9 are plotted with units of g/g instead of ml/g because the tracer standard and the electrolyte were both weighed into the test tubes. Table C.3 shows the best-fit values of the Freundlich and Langmuir relations. The data is best described by a Freundlich isotherm rather than a linear (K_d) or a Langmuir isotherm.

Figure C.9. K_d s for Li adsorption by Wedron 510 sand under atmospheric conditions as function of concentration of Li in solution (KCl not added during AA analysis).

Figure C.10. Isotherm for Li sorption by Wedron 510 sand. Concentrations of Li (C,S) are in units of parts per million.

Table C.3. Isotherms for Li sorption onto Wedron 510 sand: 1 to 1000 ppm

Langmuir isotherm	Freundlich isotherm
$S = kbC/(1+kC)$	$\ln(S) = \ln(K) + n\ln(C)$
$k = 0.006131$	$\ln(K) = 0.0878$
$b = 69.06$	$n = 0.5674$

C.4.5 Transport of Li and Br Through Wedron 510 Sand Columns

The results of column experiments for transport of pulses of LiBr through micro-layered and homogeneously-packed columns of Wedron 510 sand are shown in Figures C.11 and C.12, respectively. In the following section the experimental results are compared to model predictions using several alternative equilibrium and kinetic models. The values of parameters obtained in batch studies and those calculated from the fits to the breakthrough curves (BTC's) are also compared. The parameter values obtained from best-fit curves with the CXTFIT (Parker and van Genuchten, 1984) computer model are summarized in Table C.4. Note that R, F, and the least-squares fit statistic r^2 are dimensionless.

Figure C.11. Experimental data and modeled breakthrough for Li and Br, through saturated, micro-layered Wedron 510 sand.

Figure C.12. Experimental data and modeled pulses of Li and Br, through saturated, homogeneously-packed Wedron 510 sand.

C.4.5.1 Experimental Data and Equilibrium Linear Sorption Isotherm Modeling

Figure C.11 compares the experimental breakthrough curves for Li and Br to the calculated BTC for an equilibrium linear sorption isotherm model (Models 3LiBr and 3LiBr -1, respectively) for transport through a micro-layered Wedron 510 sand bed. The Li pulse is broader than the Br pulse and has a pronounced tail. Analysis of the BTC's with CXTFIT yielded dispersion coefficients of 0.018 and 0.002 cm²/min for Li and Br, respectively and retardation factors, R's, for Li and Br of 1.060, and 0.964, respectively. The retardation factor of less than 1 for Br can be attributed to anion exclusion. This effect can be conceptualized as a reduction of the effective cross-sectional area for the flow of Br⁻ ions caused by the repulsion of Br⁻ from the negatively charged sand surfaces and a concomitant increase in the average tracer velocity.

Figure C.12 shows the breakthrough curves for Li and Br pulses through a homogeneously-packed Wedron 510 sand bed. Analysis of these BTC's (Models 5LiBr and 5LiBr -1, respectively) with CXTFIT yielded dispersion coefficients of 0.016 and 0.004 cm²/min for Li and Br, respectively and retardation factors, R's, for Li and Br of 1.082, and 0.979, respectively.

The values of the parameters obtained from CXTFIT indicate that the equilibrium sorption model is not appropriate for these column experiments. The large difference

Table C.4. Summary of CXTFIT calculations

Model	D (cm ² /min)	R	K _d (ml/g)	F	k (min ⁻¹)	r ²	Comments
<u>Micro-layered</u>							
Br pulse							
3LiBr-1	0.002	0.964	-0.006	-----	-----	0.997	Equilibrium Model, vary R and D.
Li pulse							
3LiBr	0.018	1.060	0.010	-----	-----	0.933	Equilibrium Model, vary R and D.
3LiBr-D	0.002	1.036	0.006	-----	-----	0.929	Equilibrium Model, fixed D, vary R.
3Li-3	0.002	1.900	0.150	0.0000	0.001	0.911	Kinetic Model, fixed D, R, and F, vary k.
3Li-2	0.002	1.156	0.026	0.006	0.011	0.976	Kinetic Model, fixed D, vary R, F, and k.
3Li-1	0.004	1.175	0.029	0.062	0.008	0.976	Kinetic Model, vary D, R, F, and k.
<u>Homogeneous</u>							
Br pulse							
5LiBr-1	0.004	0.979	-0.004	-----	-----	0.996	Equilibrium Model, vary R and D.
Li pulse							
5LiBr	0.016	1.082	0.014	-----	-----	0.911	Equilibrium Model, vary R and D.
5Li-3	0.004	1.142	0.024	0.148	0.014	0.973	Kinetic Model, fixed D, vary R, F, and k.
5Li-2	0.002	1.146	0.024	0.065	0.016	0.976	Kinetic Model, vary D, R, F, and k.
5Li-1	0.000	1.132	0.022	-0.057	0.022	0.984	Kinetic Model, bad initial guess, vary D, R, F, and k.

between the dispersions of Li and Br is surprising. Conceivably, the reduction in cross-sectional area due to anion exclusion of Br could affect its dispersion as well as its retardation factor. If the change in dispersion is proportional to the change in retardation factor, however, the former would increase by only about 2 – 3 %, rather than the differences of 400 – 700% suggested by the CXTFIT equilibrium sorption model.

The retardation factor of 1.082 for Li is equivalent to a K_d of 0.014 ml/g for a sand bed of bulk density 1.8 g/cm³ and liquid content of 0.3 cm³/cm³ bed volume. This K_d is somewhat smaller than the K_d of 0.05 to 0.25 shown in Figure C.3 from of Li batch adsorption experiments.

The effect of flow heterogeneities on the breakthrough curves can be evaluated from comparison of the results of the two columns. Comparison of the pulses for micro-layered

and homogeneous beds, as indicated in Figures C.13 and C.14, shows that the difference in packing does not significantly affect the transport of Br or Li.

Both Figures C.11 and Figure C.12 show tailing of the Li pulse but not of the Br pulse. Yu et al. (1986) have suggested that the tailing may be due to a number of possible factors. One factor is the effects of mass transfer (diffusion) between dead end pores and the bulk liquid flow. However, the fact that Br, a non-sorbing species, does not exhibit a tail indicates that mass transfer effects are not dominant.

Tailing may also indicate slow kinetics of adsorption and/or desorption. Fluid residence time in the columns was about 7 hours whereas the kinetic batch experiments (Section C.4.3.2) show that equilibration times of 24 to 80 hours are required to reach sorption equilibrium. The difference between the K_d s measured in batch adsorption tests (0.05 - 0.25 ml/g) and the equivalent K_d s for the flowing condition (0.014 ml/g) also suggest that the tailing is due to relatively slow sorption kinetics.

C.4.6 Kinetic Sorption Modeling

C.4.6.1 Kinetic Model Based on Batch Sorption Data

If it is assumed that the batch sorption data presented in Figure C.4 are reliable, then the K_d for Li sorption at near-neutral pH in Wedron 510 sand is approximately 0.15 ml/g. Figure C.15 compares calculated BTC's in the micro-layered sand bed column for the equilibrium and kinetic models for $D=0.002$ cm²/min (the value for Br) and $K_d=0.15$ ml/g. The analytical solution of Lapidus and Amundson (1952) was used for the equilibrium model. The solution for pore volumes larger than the pulse pore volume and initial concentration of zero is:

$$C(x,t) = C_0 [A(x,t) - A(x,t-t_0)] , \quad (7)$$

$$\text{where} \quad A(x,t) = \frac{1}{2} \operatorname{erfc} \left[\frac{Rx - vt}{2(DRt)^{1/2}} \right] + \frac{1}{2} \exp \left(\frac{vx}{D} \right) \operatorname{erfc} \left[\frac{Rx + vt}{2(DRt)^{1/2}} \right] . \quad (8)$$

Here $C(x,t)$ is the concentration at time t and distance x , t_0 is the duration of the column pulse, D is the dispersion coefficient, R is the retardation factor, and v is the pore water velocity.

Figure C.15 clearly shows that the equilibrium model does not accurately predict the column breakthrough pulse; the pulse breakthrough occurs at 1.9 pore volumes ($R = 1.9$).

A single sorption site ($F = 0$) was assumed for the kinetic model; the fit by this model is much better than that of the equilibrium model ($r^2 = 0.911$). As shown in Table C.4 (Model 3Li-3), the rate constant determined from CXTFIT assuming an R of 1.9 is $k = 0.001$ min⁻¹. This value is the same order of magnitude as that determined from the

Figure C.13. Comparison of Br breakthrough through micro-layered and homogeneously-packed Wedron 510 sand.

Figure C.14. Comparison of Li breakthrough curves through homogeneous and micro-layered Wedron 510 sand.

Figure C.15. Comparison of kinetic and equilibrium models of Lithium breakthrough curves for fixed K_d and fixed D .

batch kinetic sorption experiments, ($k=0.0004$ to 0.0012 min^{-1}) as discussed in Section C.4.3.2.

C.4.6.2 Sensitivity Analysis

The CXTFIT code was used to extract best fit parameters from the Li and Br BTC's for the two-site non-equilibrium (kinetic) sorption model described in Section C.3.3. CXTFIT can be used to calculate four best-fit parameters in the kinetic model simultaneously, or, up to three of the parameters can be fixed and the remaining one(s) calculated. As described above, the parameters are F , the fraction of sites assumed to be in equilibrium, k , the first-order sorption rate constant, D , the dispersion coefficient, and R , the retardation factor. Table C.4 summarizes the parameters calculated for the pulses through micro-layered and homogeneously-packed beds.

Figure C.16 compares experimental data to the best-fit equilibrium and kinetic models for transport of Li through the micro-layered sand bed. Equilibrium and kinetic models in which D is fixed at $0.002 \text{ cm}^2/\text{min}$, the dispersion coefficient for Br, are also shown. The model assumptions and results are summarized in Table C.4. It can be seen that the equilibrium (K_d) model with the fixed D (Model 3LiBr-D) gives a low calculated K_d and a poor fit to the experimental data. The kinetic model using the fixed D (Model 3Li-2) gives a better fit to the Li column data, however, the calculated k is 0.011 min^{-1} , an order of magnitude greater than that determined from batch kinetics experiments. Similar models

Figure C.16. Comparison of equilibrium and kinetic models for Li breakthrough curves, saturated micro-layered Wedron 510 sand column.

and experimental data for the homogeneously-packed sand bed are shown in Figure C.17 and described in Table C.4.

In Models 3Li-1 and 5Li-2 in Table C.4, CXTFIT was used to calculate four best-fit parameters in the kinetic model simultaneously. The calculated dispersion coefficients are close to those of the Br pulses (Models 3LiBr-1 and 5LiBr-1), however, the calculated K_d s are low. The calculated rate constants, k , are significantly larger than those measured in the kinetic batch experiments (0.0012 and 0.0004 min^{-1} for 17.4 and 5 ppm Li solutions, respectively).

The limited sensitivity analyses presented above do not provide a basis for choice of unique set of parameter values to describe Li transport in the Wedron sand. There is considerable uncertainty in the values for the rate constants, retardation factors and dispersivity for Li. Although the best fit statistic (r^2) is highest for Models 3Li-2 and 5Li-2, the values of R and k are not consistent with the experimental data. Additional discussion of the sensitivity analyses is found in Cheng (1993).

Figure C.17. Comparison of equilibrium and kinetic models for Li breakthrough curves, saturated, homogeneous Wedron 510 sand ($v = 0.074$ cm/min).

C.5 Discussion: Calculation of Effective Retardation Factor for Li Transport

The analyses of Kuhn and Peters (1981) and Relyea (1982) can be used to obtain an expression for R/R_{equil} , the ratio of the apparent retardation factor under a given flow condition to the retardation factor assuming equilibrium sorption, as a function of the number of transfer units. The number of transfer units is:

$$n = \frac{\rho_b K_d L}{\varepsilon v} k \quad (\text{C.10})$$

where ρ_b is the bulk density, K_d the equilibrium partition coefficient, L the length of the column, ε the porosity, v the interstitial fluid velocity and k the first order sorption rate constant. Figure C.18 shows the relationship of T vs. n obtained from the tabulation of Relyea (1982), assuming linear extrapolation to $n=0$, where

$$[\rho_b K_d / \varepsilon]_{\text{apparent}} = T[\rho_b K_d / \varepsilon] \quad (\text{C.11})$$

Note that Relyea (1982) erroneously identifies T as R/R_{equil} .

Figure C.18. Relationship between T and mass transfer units.

Using the expression for the retardation factor, $R = 1 + \rho_b K_d / \epsilon$, and assuming ρ_b is 1.8 g/cm³, ϵ is 0.3, and K_d is 0.15 ml/g, we can plot the value of R/R_{equil} as a function of n for columns of Wedron 510 sand as shown in Figure C.19.

For the column experiments described previously, ρ_b is 1.8 g/cm³, L is 30 cm, ϵ is 0.3 and v is 0.074 min⁻¹. Assuming K_d is 0.15 ml/g, and k is 0.0012 min⁻¹, n is 0.44, and R_{equil} is 1.9. The corresponding value of R/R_{equil} from Figure C.19 is approximately 0.56. The effective R values determined from the equilibrium sorption model ranged from 1.04 to 1.08 and R/R_{equil} ranged from 0.55 to 0.57.

For the caisson at Los Alamos, the height of the sand column is 600 cm. Using the same equilibrium and flow parameters as for the small column, n is 8.8. The corresponding value of R/R_{equil} in Figure C.19 is approximately 0.9, therefore this analysis suggest that the caisson should have an operating condition close to equilibrium.

C.6 Conclusions

Batch and small column experiments were conducted to analyze sorption and transport of Li and Br in saturated Wedron 510 sand. The batch adsorption experiments show that Br does not adsorb and that Li sorbs weakly in the neutral pH range. Li batch isotherm data indicate stronger sorption at lower concentrations; the data fit satisfactorily a Freundlich isotherm. The adsorption data sets may contain errors due to the combination of

Figure C.19. Retardation factor ratio as function of number of transfer units.

competing cations, CO_2 and ionization suppression during the AA analysis, however, any such errors will not significantly affect the conclusions drawn from the experiments. For the pH range relevant to the caisson experiment (7- 8.5), under CO_2 free to partially-equilibrated conditions, the measured K_d s range from approximately 0.05 to 0.25 ml/g (5% - 20% adsorption). The degree of adsorption is slightly dependent on the pH; reaching a maxima at near-neutral pH. There is also uncertainty in the values for the rate constants for Li sorption. An initial increase in Li concentration in the batch systems could not be explained. The calculated rate constants were $k=0.0004$ and 0.0012 min^{-1} for initial Li concentrations of 5 and 17.4 ppm, respectively.

Column breakthrough curves were determined for Li and Br. The Br pulses show a retardation factor slightly less than 1, indicating a small amount of anion exclusion, and were satisfactorily modeled by the equilibrium linear isotherm adsorption convective-dispersive model of the CXTFIT code.

The Li pulses were not adequately modeled by the equilibrium convective-dispersive model. In order to fit the Li column data using the equilibrium sorption model, CXTFIT calculated K_d s of about of 0.01 ml/g and D's in the range of $0.016 \text{ cm}^2/\text{min}$. These "effective" K_d s are smaller than the lowest values measured in the batch experiments, and the D's are one order of magnitude higher than that for Br. This value of "effective" K_d , and the equilibrium K_d and sorption rate constant measured in the batch experiments are consistent with the value of "effective" retardation factors predicted with the model of Kuhn and Peters (1981). In addition, a single site kinetic model was calculated with

CXTFIT using K_d (0.15 ml/g) and k (0.00012 min^{-1}) values similar to those measured in the laboratory batch experiments. This model gave a reasonable fit to the elution curve for the micro-layered sand column ($r^2 = 0.911$). A two-site kinetic model with simultaneous calculation of D , R , k (first order sorption rate constant) and F (fraction of sites assumed to be in equilibrium) improved the fit significantly to account for the sharper leading edge and the tail. Although the best fit statistic (r^2) is highest for Models 3Li-2 and 5Li-2, the values of R and k are not consistent with the experimental data. The value of the first-order kinetic parameter determined by CXTFIT was almost one order of magnitude greater than that determined from kinetic batch sorption experiments conducted for Li, and the equilibrium K_d calculated by CXTFIT was about 0.025 ml/g. This result gave confidence that the actual partition coefficient is in the range of 0.15 ml/g and that the kinetic mechanism was in effect.

The rate expression for the kinetics model includes a K_d to establish the equilibrium concentration in the solid phase. Since K_d depends on concentration, a set of transport equations allowing for a non-linear isotherm would model the Li effluent curves better. However, this analysis, which did not account for K_d varying with concentration does give some confidence as to the order of magnitude of the batch sorption and kinetic parameters. In a continuing study, an isotherm can be accounted for as an improvement.

For the larger residence times in the caisson at Los Alamos, it is expected that nearly equilibrium conditions will be present.

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Attachment 1

Batch sorption experiments were run to determine the variation in Li sorption onto Wedron 510 sand with pH. The experiments were run under "CO₂-free" and "atmospheric" conditions with varying Li concentrations as discussed previously. During Atomic Absorption (AA) analysis of the batch samples for Li, it was found that the addition of KCl improved the precision and accuracy for measurement of Li in solutions partially equilibrated with atmospheric CO₂. Verification of the AA analysis was done using Inductive Coupled Plasma (ICP), which showed close agreement with the AA readings in the neutral pH range.

Figure 1 shows the effect of adding 1000 ppm K as KCl in a 1:1 dilution to samples under atmospheric conditions prior to AA analysis. Data Set 3a was analyzed without KCl and Data Set 3b was analyzed with KCl. The addition of KCl acts as an ion suppressant, lowering the measured Li concentration values and giving higher calculated K_d values.

The results of the analysis by AA and ICP are shown in Figure 2 and Table 1. KCl was added to Data Sets 4 and 5. The K_d values at either end of the pH range for the ICP analysis were lower than those calculated by AA analysis. However in the neutral pH range the AA and ICP results are very close.

Figure 3 shows a comparison between the different batch experiments run under CO₂-free and atmospheric conditions. The first batch study, shown as data set 1, was run under CO₂-free conditions and the samples were spiked with ~100 ppb Ni and 10 ppm Li. The second experiment, shown as data set 2, was similar to the first but without the Ni addition. Data Set 2 shows less scatter and a lower range of K_d values, but the pattern is similar to data set 1. It is unclear if the addition of Ni, or errors in the experiment and/or analysis, cause the scatter in data set 1. The samples in Data Set 3b were spiked with Li and Ni under atmospheric conditions and KCl was added as an ion suppressant prior to AA analysis. Data Sets 4 and 5 are from runs under CO₂-free and atmospheric conditions respectively, and include the addition of KCl. Both data sets are close to data set 2 in the neutral pH range and give calculated K_d s in the range 0.16-0.21.

The offset between the atmospheric and CO₂-free data sets may be due to the presence of carbonate species in solution that effect the efficiency with which other elements being released from the sand suppress Li ionization during AA analysis. Perhaps the carbonate species present are bonding to surface sites on the sand, decreasing sorption of other elements, increasing their concentration in the electrolyte, and hence their ability to act as ionization suppressants.

Figure 1. Effect of KCl addition on measured Li sorption under atmospheric conditions.

Figure 2. Li sorption on Wedron 510 sand, analysis by AA and ICP.

Table 1. Comparison of AA and ICP readings for Li sorption experiments

pH	AA Li conc.	Total ug Li in sol'n	ICP Li conc.	Total ug Li in sol'n	AA Calc. Kd	AA % Li sorbed	ICP Calc. Kd	ICP % Li sorbed	Comments
5.00	0.00	0.00							Acid blank, atmos.
5.51	0.01	0.23							Sand blank, atmos.
5.02	8.44	177.20	8.70	182.70	0.124	10.54	0.010	0.96	Atmospheric
4.69	8.54	179.34	8.85	185.85	0.110	9.45	-0.008	-0.75	Atmospheric
4.73	8.59	180.41	8.92	187.32	0.103	8.91	-0.016	-1.55	Atmospheric
4.93	8.33	175.04	8.74	183.76	0.138	11.62	0.004	0.38	CO ₂ -free
4.88	8.25	173.55	8.69	182.71	0.149	12.38	0.010	0.95	CO ₂ -free
4.71	9.08	190.91	8.98	188.80	0.039	3.62	-0.024	-2.35	CO ₂ -free
7.00	0.00	0.00							Acid blank, atmos.
7.14	0.00	0.02							Sand blank, atmos.
6.98	8.32	169.43	7.90	160.96	0.172	14.46	0.149	12.74	Atmospheric
7.08	8.21	167.35	7.70	156.89	0.187	15.51	0.179	14.95	Atmospheric
6.97	8.09	164.86	7.58	154.44	0.205	16.77	0.198	16.28	Atmospheric
6.94	8.21	167.76	7.49	152.98	0.184	15.30	0.210	17.07	CO ₂ -free
7.12	8.37	170.89	7.47	152.57	0.162	13.72	0.213	17.29	CO ₂ -free
6.94	8.24	168.38	7.42	151.55	0.180	14.99	0.222	17.84	CO ₂ -free
9.90	0.00	0.00							Acid blank, atmos.
9.98	0.00	0.06							Sand blank, atmos.
9.93	9.17	190.33	8.97	186.13	0.042	3.91	-0.009	-0.90	Atmospheric
9.89	9.06	188.01	9.10	188.83	0.056	5.08	-0.024	-2.36	Atmospheric
9.03	8.89	184.41	8.84	183.43	0.077	6.90	0.006	0.56	Atmospheric
9.90	8.52	176.35	9.02	186.71	0.127	10.96	-0.012	-1.22	CO ₂ -free
9.89	8.81	182.27	9.00	186.30	0.090	7.98	-0.010	-0.99	CO ₂ -free
9.74	9.07	187.77	8.76	181.33	0.057	5.20	0.018	1.70	CO ₂ -free

Figure 3. Comparison of Li sorption data sets.

Appendix D

Testing Models of Flow and Transport in Unsaturated Porous Media

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TESTING MODELS OF FLOW AND TRANSPORT IN UNSATURATED POROUS MEDIA

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ABSTRACT

The design of an intermediate-scale flow and transport experiment in an unsaturated porous media is described. This experiment will be conducted a 3-m-diameter by 6-m-long caisson filled with silica sand. The study has been designed to minimize uncertainties in the conceptual model governing flow and transport of nonreactive tracers and to evaluate predictions of field tracer migration using laboratory data. Data from laboratory characterization of hydraulic and geochemical properties of the sand and tracer were used in preliminary modeling and sensitivity analyses to determine optimal fluid flux, influent tracer concentrations, and locations of sensors and sampling devices. Alternative approaches to compare observed and predicted data for model evaluation are discussed.

INTRODUCTION

The Yucca Mountain Site Characterization Project (YMP) is responsible for characterizing and assessing the suitability of Yucca Mountain, Nevada, for the siting of a potential high-level nuclear waste repository. Regulations governing the repository licensing process require assessments of potential radionuclide transport from the repository to the accessible environment for time periods up to 10000 years. Performance assessment will use subsurface flow and transport models or an appropriate abstraction of them in conjunction with data collected during site characterization to determine if the potential repository can meet the regulatory requirements. The validation step in the modeling process will consist of comparing predictions made using an independent data set to experimental results. This step is necessary to ensure

confidence in the computer codes used to support the license application for the potential high-level waste repository.

The term validation invokes a sense of certainty that is difficult to achieve with models of geological settings and the time frame required for repository assessment¹. Generic validation or validating of a model that will predict correctly under all conditions is impossible to achieve given current knowledge in the geosciences. Consequently, various approaches including laboratory, intermediate and field-scale experiments, and information from analogues will be used by the YMP for model validation. Advantages and disadvantages are associated with each approach, and no single one can satisfy all of the requirements for validation; however by employing all of the above approaches, it is possible to evaluate the models and their associated computer codes using data from a wide variety of conditions and achieve more accurate prediction.

This paper describes the status of an intermediate-scale experiment to test models of flow and transport through unsaturated porous media. The design described below was selected because porous material emplacement and boundary conditions can be well controlled, and point and total system tracer responses can be measured simultaneously. Models for both reactive and nonreactive tracers will be tested.

The intermediate-scale design was selected for nonreactive tracers because the underlying conceptual model governing water flow and tracer transport is a porous media continuum, which we have assured by constructing the porous medium and thus avoid introducing discontinuities that require consideration of

alternate conceptual models. Our objective is to reduce uncertainties associated with the model structure. The two sources of error that cannot be controlled are those associated with measurement and parameter heterogeneity. Measurement errors will be bounded by the choice of the instruments and procedures; and parameter heterogeneity will be introduced by packing the caisson with sand. The description of this experiment that follows discusses how parameter heterogeneity will be characterized.

Behavior of reactive tracers will be used to discriminate among alternate sorption models including K_d , or linear sorption, nonlinear sorption, ion exchange, and surface complexation models. Parameters for these models will be obtained using geochemical characterization described in a companion paper.² Predictions of tracer migration based on data from laboratory experiments will be compared to the results of this intermediate-scale experiment.

The highly controlled conditions and scale of this experiment provide an opportunity to evaluate predictive performance of transport models for conditions where three-dimensional flow and heterogeneities occur. These results are a valuable prerequisite for evaluating

field tests because better prediction of tracer migration cannot be expected when model structure is unknown and parameter heterogeneities and measurement errors are present. The measures of proposed criteria comparing predicted versus observed tracer migration from this study provide a foundation for gauging results from more complicated experiments.

DESCRIPTION OF THE ACTUAL WORK

Background

This intermediate-scale experiment will be carried out in a caisson, a corrugated, galvanized metal highway culvert set in a concrete base that is 6-m high by 3-m diameter³. Access ports are located at six different depths 75-cm apart to allow horizontal placement of instruments (Figure 1).

Siegel et al.⁴ presented an initial design for this experiment and indicated that the final design would require several iterations of preliminary calculations, simple laboratory experiments and prototype constructions. This initial design consisted of a relatively chemically inert material, Wedron 510 silica sand (Wedron Silica, Wedron, IL 60557), as the background

Caisson Geometry and Instrumentation

Figure 1. Schematic of the caisson showing locations of instrument.

porous matrix and a sorbing layer containing limonite. Characterization of the hydraulic properties of the porous medium and a description of transport calculations used in the design are presented below. A brief description of the chemical properties of the porous matrix is also given; details of the geochemical characterization studies are provided in a companion paper².

Studies of the hydraulic properties of the porous materials to be used in the caisson were carried out in laboratory columns and two-dimensional slabs filled with sand. The slab chambers are 60 x 30 x 1-cm so that high-resolution measurements can be made of moisture content or tracer concentration using either light transmission or x-ray. The two-dimensional slab chambers also can be used to develop scaling laws for effective media properties including the small-scale layering and cross-bedding that are expected to result from packing the caisson.

The geochemical properties of sand and limonite, which are important to tracer transport, were characterized to determine their suitability for the caisson experiment.² Samples of the limonite (Wards Earth Science) were characterized by x-ray diffraction and wet chemical analysis. The surfaces of the sand grains were examined using a combination of techniques including potentiometric titration, acid leaching, optical microscopy, and scanning electron microscopy with energy-dispersive spectroscopy. Chemical analyses of bulk compositions and acid-leachable components were made of several particle size fractions of the Wedron 510 sand. Small-scale column experiments were carried out to study the changes in the pH and composition of leachable components of the sand in dilute NaCl electrolyte as a function of time and water saturation. For the purpose of caisson design, experiments were conducted to examine the most important factors controlling sorption of each tracer. Nickel solubility as function of pH, and the adsorption of nickel (Ni), lithium (Li), and bromide (Br) on sand, limonite, and sand/limonite mixtures were measured using batch techniques. The batch experiments were conducted to bracket the ranges of solution pH values, tracer concentrations, and concentrations of competing anions and cations expected in the caisson experiment. The preliminary data were used for calculation of K_d 's; additional data will be collected and analyzed within the conceptual framework of nonlinear isotherms and surface-complexation models. In addition, interactions between the tracers and solution sampling equipment were studied to estimate uncertainties in measurements of the time-dependent tracer concentration profiles within the caisson.

Several models will be used to predict tracer transport in the caisson. The LEHGC version of the HYDROGEOCHEM⁵ coupled transport/geochemical code was used in this and the previous⁴ papers. Two three-dimensional flow and transport codes, TRACR3D⁶ and FEHMN⁷ will be used for tracers that exhibit nonlinear sorption.

A sensitivity analysis using LEHGC to simulate transport with linear sorption was performed to determine optimal flow conditions, solution sampler placement, and tracer input concentration. The response variable was depth of penetration of the solute front at concentrations 10 times current detection limits. Hydraulic parameters and sorption parameters from laboratory experiments were also used in this sensitivity analysis.

The experiment provides opportunities for development of criteria for testing model predictions against observed data, which has traditionally employed goodness-of-fit methods with a statement indicating the relative merit of the result. This experiment offers the advantage of point measurements from within the caisson and an integrated system response via the lower-boundary condition. Comparisons using these point and integrated data are being investigated for application to this experiment.

Bottom Boundary Condition

In previous caisson experiments^{8,9}, the bottom boundary was free drainage through a 15-cm diameter pipe connected to the central access caisson. This design is considered inadequate because of additional mixing caused by the convergence of the stream tubes and the presence of a locally saturated condition in the vicinity of the outlet. A design to provide a constant pressure boundary and to resolve the spatial distribution of solute transport has been developed. This design will use 268 ceramic porous cups that are vertically oriented and mounted on a plastic base. The tubing from each porous cup will be connected to a manifold that will allow an individual cup to be sampled, and suction will be supplied either by vacuum pumps or through a hanging water column arrangement.

Instrumentation

Figure 1 shows the location and type of measuring and sampling equipment that will be used.

Water content will be measured using both the neutron probe and time-domain reflectometry (TDR). Aluminum access tubes will be installed across the caisson at each caisson access port so that neutron probe measurements can be made. Neutron probe measurements are difficult to make near the air-soil interface because of the sphere of influence of the probe, and usually measurements are made at least 15 cm from any surface, so that measurement of the water content in the outer annulus region of the caisson with the neutron probe is prevented. This annular region is important because of potential wall effects or channeling of water at the boundary. TDR rods will be installed in the annular region to provide data on water content.

Solution samplers will be made from either ceramic cups or hollow-fiber porous membranes. Previous

caisson experiments³ identified interactions between the ceramic material of the porous cups and the sorbing tracers, and the hollow-fiber bundle was developed to circumvent problems related to tracer uptake and consequential errors in estimated breakthrough times. The solution samplers are actuated by applying a suction to the tubing and collecting a sample after a given number of sample system volumes have been discharged. One of the constraints on the hollow-fiber sampler, however, is the amount of suction that can be applied without collapsing the filter.

RESULTS

Hydraulic Properties

Laboratory studies have been conducted to determine the hydraulic properties of the Wedron silica sand that was selected as the porous medium. Using the two-dimensional glass slab chambers (60 x 30 x 1 cm), the Wedron sand was emplaced with a filling extension containing randomized screens.¹⁰ Although a homogeneous fill was desired, the pack did contain small-scale sinusoidal microlayering (Figure 2).

Transient moisture content of the slab for a series of wetting and drying events was followed using the light transmission technique.¹¹ Figure 3 shows the moisture profiles for the secondary wetting curve (Figure 3A) and primary drainage curve (Figure 3B). Moisture content was measured at 300 points across the width (30 cm) of the chamber at 0.1 mm resolution in height. Average moisture content was calculated for each height, which resulted in values for the average primary drainage, average secondary wetting, and drainage saturation and pressure relations given in Figure 4.

The sand exhibits substantial hysteresis and increased air entrapment within the material after primary wetting and drainage. This increased trapping caused a reduction in "saturated" moisture content of about 10% (from 0.34 to 0.31) and a reduction in "saturated" conductivity of about 65% (from 0.87 to 0.31 cm/min). These observations imply that it will be important to achieve a constant saturation throughout the caisson. The steady state flux rate will be established by filling the caisson with the background electrolyte solution from the bottom so that air can vent through the surface. After the caisson has been saturated, the lower-boundary condition will be applied and the surface-boundary flux, applied by a rotating spray system, will be adjusted to achieve a steady-state flux rate. In order to minimize the hysteresis effects, this procedure may be repeated three times.

The moisture characteristic relation, $\theta(\psi)$, can be described by any number of relationships. The equation for the moisture characteristic from Brooks and Corey¹² is

$$\theta(\psi) = \epsilon \left[\frac{|\psi_{ae}|}{|\psi|} \right]^\lambda \left[1 - \frac{|\psi_{ae}|}{|\psi|} \left[1 - \frac{\theta_s}{\epsilon} \right] \right], \psi < \psi_{ae} \quad (1)$$

$$\theta(\psi) = \theta_s, \psi > \psi_{ae} \quad (2)$$

where ϵ is the porosity; ψ_{ae} is the air entry or bubbling pressure; λ is the Brooks-Corey fitting parameter; and θ_s is the sand at saturation including entrapped air. Siegel et al.⁴ used the method of Haverkamp and Parlange¹³ and the Brooks-Corey relation to calculate the primary drainage curve of the Wedron sand from the grain size

Figure 2. Heterogeneity field within the "uniform" pack of Wedron 510 sand within a thin (1 cm) 30 x 60 cm slab chamber as illuminated with the light transmission technique. Dark zones denote regions of higher bulk density and smaller mean grain size; light zones denote regions of lower bulk density and larger mean grain size. Sinusoidal microlayers of about 0.1 to 1.0 cm in thickness run from side to side in the chamber. Also note light and dark bands that run from top to bottom of the chamber cross-cutting the microlayering.

Figure 3. Equilibrium moisture content fields for the Wedron 510 sand pack shown in Figure 2 as illuminated with the light transmission technique. Images are black and white reproductions of false colored saturation images so that dark and light bands do not reflect absolute values of moisture content. Image a) depicts the saturation field that determined the primary drainage curve and b) that for the secondary wetting curve. Note that the atmospheric pressure position was approximately the bottom of the image for a) and approximately 20 cm above the bottom of the image for b). Bands of light and dark running across the chamber denote zones of nearly the same moisture content. Figure 3 demonstrates the effects of both the microlayering and vertical heterogeneities shown in figure 2 to vary the local air entry values for the sand pack on the order of 25% of its average value. Higher percent changes are expected in the permeability field due to these variations. An additional feature to note is the entrapment of an air pocket seen the zone at the bottom of the chamber in figure 3b. The air pocket was entrapped after the chamber was drained to field capacity and resaturated by capillary rise as depicted in figure 3b. This demonstrates the effect of local heterogeneity in combination with boundary conditions to create structures that will add to larger scale macrodispersivity. Higher macrodispersivity for the entire system is expected than will be measured on small diameter core samples taken during the post mortem phase of the caisson experiment.

Figure 4: Measured moisture characteristic curves for the Wedron 510 sand. Primary wetting and secondary wetting and drainage curves were obtained from images such as those shown in figure 3a and 3b. Curves were averaged over the chamber to yield effective relations.

Distribution and bulk density. A comparison of this calculated curve with the measured primary drainage curve from the slab can be seen in Figure 5 and the predicted parameters for Equation 1 are given in Table 1. From Figure 5, it can be seen that the predicted ψ_{ae} from the approximation of Haverkamp and Parlange¹³ is reasonable, but the slope of the predicted drainage curve at higher values of pressure head reveal how poorly λ was estimated. Equations 1 and 2 were fitted to the primary drainage curve data (BC Fit in Figure 5) and the parameters are given in Table 1. The values for ψ_{ae} from the estimated and fitted curves are in reasonable agreement, but the difference between λ values is substantial.

Equations 1 and 2 are not continuous at the air entry value, ψ_{ae} ; therefore the moisture characteristic relationship from van Genuchten¹⁴ can be used to make numerical solution easier. The van Genuchten equation is

$$\theta(\psi) = \left[\frac{\theta_s - \theta_r}{(1 + |\alpha\psi|)^n} \right]^m + \theta_r, \psi < 0; \quad (3)$$

$$\theta(\psi) = \theta_s, \psi \geq 0; \quad (4)$$

where θ_r is the residual moisture content; and α and n are the van Genuchten fitting parameters with $m = 1 - 1/n$. The van Genuchten fit to the primary drainage curve and to the Brooks-Corey curve from the particle-size mapping⁴ can also be seen in Figure 5. Parameters for the van Genuchten fit can be found in Table 1. Again, note the agreement in the α values and the substantial change in the slope parameter, n , for the estimated and fitted Equation 3.

Geochemical Characterization of the Porous Matrix and Tracers

Limonite. Mineralogical and wet chemical analysis of three splits of the limonite revealed that the crushed 600-pound sample delivered for the caisson experiment (hereafter referred to as the "caisson limonite") contained much less iron than the limonite sample described in Siegel et al.⁴ (referred to as Wards limonite #1). The caisson limonite contained a mixture of goethite-coated sand, goethite grains, detrital aluminosilicates and amorphous phases. Leaching studies in near-neutral solutions yielded significant amounts (>1 ppm) of Ca, Mg, and Ni. Acid leaching studies indicated the presence of an acidic component; the pH of deionized water in contact with the samples (solution:solid = 20:1) was 3.0 - 3.3. Repeated rinsing and boiling with deionized water failed to remove the acidic component.

Figure 5: Moisture characteristic curve prediction. The primary drainage curve for the Wedron 510 sand is compared to the predictions based on the theory of Haverkamp and Parlange⁹ which maps grain size distribution and bulk density into the pressure saturation relation. Best fits to the data using the Brooks and Corey form (BC fit) and the van Genuchten form (VG fit) are also shown.

Table 1. Parameters for the Brooks-Corey¹² and van Genuchten¹⁴ moisture characteristic relationships for the Wedron 510 sand using the method of Haverkamp and Parlange¹³ to estimate based on particle size distribution and fitting these equation to the observed data for the primary drainage curve.

	Brooks-Corey		van Genuchten	
	ψ_{as} (cm)	λ	α (cm ⁻¹)	n
Estimated	40.75	2.09	.02	3.2
Fitted	42.0	5.0	.0125	18.0

Batch studies of sorption of Ni using mixtures of sand and Ward's limonite #1 (3% limonite: 97% sand) were carried out.^{4,15} Sorption ratios (K_d s) ranged from 4 ml/g to 175 ml/g over the pH range 6 - 7.75, respectively. The presence of the acidic component in the caisson-limonite, however, prevented similar experiments with this material at neutral pH. At the low pH characteristic of batch systems containing the caisson-limonite, Ni

sorption was negligible^{4,15}, therefore layers containing mixtures of the caisson-limonite and sand would not appreciably sorb nickel. The above characteristics of the caisson limonite introduced a level of complexity into the chemical component of the experiment that could compromise the attempt to develop a baseline for comparisons of the predictive capabilities of alternate sorption models. In addition, because the amount of limonite that was available was limited to 272 kg (600 lbs), the "sorbent" sand-limonite mixture would contain only 3% limonite and the difference in magnitude of sorption by the sorbent layer versus the "inert" sand layers would be relatively small. The required effect of a sorption layer might not be seen; therefore, the sand-limonite layer was removed from the experimental design.

Bulk and Surface Properties of Wedron 510 Sand.

According to its bulk chemistry and mineralogy, Wedron 510 sand is nearly pure quartz, but characterization of some of its surface properties as described in Siegel et al.² suggests that it contains at least four components: quartz, carbonate, iron oxyhydroxide, and kaolinite. A

titration curve for Wedron 510 sand obtained under CO₂-free conditions over the pH range 2.75 to 11 showed development of a buffering plateau, suggesting slow dissolution of a conjugate base, tentatively identified as a carbonate. Measurements of dissolved Ca and Mg leached from the sand in batch systems are consistent with a concentration of 0.75 - 0.80 μ moles of carbonate per gm sand. Significant Fe (0.575 μ moles/g) and trace amounts of Na and K were also leached. Studies of thin-sections under an optical microscope revealed that the sand grains are coated with a yellowish material; therefore the majority of the Fe is likely to be present as a thin coating of hematite and/or goethite on the sand grains. The bulk analysis of the finest size fraction and the analyses of the surface coatings of all size fractions suggest that the finest size fractions contains fragments of sand grain coatings composed of calcite, dolomite, iron oxyhydroxide and clay minerals.

The results of the leaching experiments are described in Siegel et al.² (their Figure 2). The column effluent contains measurable concentrations of the major components of the sand (Ca, Mg, Si) and of the tracers (Ni, Br, Li) that will be used in the caisson experiment. Under unsaturated conditions, the effluent pH dropped to a steady-state range of 7.2 to 7.5 after elution of approximately 5 pore volumes. In preliminary saturated-condition experiments (not shown), the pH of the effluent was initially neutral, rose to >8.7, and then reached a steady-state value of approximately 8.2 after elution of 6 pore volumes.

The above results suggest that significant amounts of the Li, Ni, and Br will not be leached from the sand and interfere with the tracer tests. The studies indicate, however, that the sand will not be chemically inert during the caisson experiment. The chemical composition of pore fluids within the caisson will be controlled by the following: dissolution of quartz, carbonate cement, diffusion of atmospheric CO₂ into pore fluids, and hydrolysis of silanol (SiOH) and FeOOH surface groups. It is anticipated that chemical conditions within the caisson will initially be transient, but a steady-state chemical profile may develop after elution of 6-10 pore volumes. The flow velocity, the dissolution rate of carbonate cement, and the CO₂ diffusion rate will control the approach to a steady-state pH profile in the caisson; the amount of carbonate cement will determine the lifetime of the steady-state profile.

Sorption of Tracers by Wedron 510 Sand. Ni sorption has been measured in batch experiments equilibrated for at least 48 hours at solid:solution ratios of 1:1 over the pH range 5 to 9.5. The pH - percent sorption curve (Siegel et al.², Figure 5) shows a distinct sorption edge at pH ~6.5, reaching maximum sorbance at pH 8.0, followed by slowly declining sorbance at higher pH. The equivalent K_ds range from approximately 0 ml/g (at pH = 5.5) to 80 ml/g (at pH = 8).

Batch studies of sorption of Li and Br by Wedron 510 sand were also carried out². Bromide sorption by sand was negligible over the pH range studied (6.2 - 7.3). Lithium K_ds' range from 0.16 to 0.89 ml/g over the same pH range; the Li concentration was 0.1 to 10 ppm and the solution:solid ratios were 1 - 10 ml/g. Data from lithium sorption measurements are summarized in Table 4 in [2] and show that the K_d depends on both the tracer concentration and the solution:solid ratio.

Instrumentation

Point measurements will be made throughout the caisson to complement the data provided by the exit samplers.

Appendix A in [2] describes studies of the adsorption of the tracers by hollow fiber and ceramic samplers in static and flowing systems. The results indicate that the hollow fiber samplers do not adsorb any of the tracers, but the ceramic samplers may be sources for trace Li and Br contamination and will adsorb nickel. The ceramic samplers cannot be used for Ni sampling because at least 1 l of solution must pass through the sampler before the Ni concentrations of the influent and effluent become equal. Appendix A in [2] also describes studies of the adsorption of Ni as a function of pH by several kinds of labware that could be used for sample collection tubes, syringes, and centrifuge tubes. These include low-density polyethylene, polypropylene, polyallomar, and polycarbonate. The results indicate that each of the plastics become a significant sorber of Ni under neutral and alkaline conditions; this effect will have to be accounted for in sorption and solubility experiments. These studies also indicate that all of the plastics are suitable for use as geochemical sampling vessels for acidified solutions.

Temperature fluctuations that might affect chemical reactions can be expected during the experiment so temperature will be measured at two depths in the caisson with a series of four thermocouples located across the caisson at each depth. Instrumentation will be emplaced during the filling of the caisson. To ensure good contact between instruments and porous material, instrument location is being optimized by preliminary modeling described below. The estimated depth of penetration of the tracers will be used to locate the samplers where they will be the most effective. For example, the hollow-fiber samplers should be located in the upper 300 cm of the caisson to track nickel migration rather than at the lower depths.

Preliminary Transport Modeling

The laboratory-scale hydraulic and geochemical data will be used to make predictions with several different flow and transport computer codes.

The flow problem was solved using the LLUVIA-II code.¹⁶ This version of the code uses the method-of-lines technique to solve the Richard's equation for two-dimensional, isothermal flow of liquid water through partially saturated porous media. Hydraulic properties were measured in the laboratory experiments described in the previous section. All simulations assumed a steady-state water flow that was specified by the pressure applied to the lower boundary and the parameters in either Equation 1 or 3. The computed moisture content and Darcy velocities were written to an external file for use in subsequent transport calculations.

The preliminary transport calculations were made using the LEHGC version of the HYDROGEOCHEM⁵ code. Transport of reactive tracers assuming linear sorption was simulated by scaling the capacitance and dispersion/diffusion terms of the transport equation by the retardation factor defined as

$$R = 1 + \frac{P_b K_d}{\theta} \quad (5)$$

where P_b is the bulk density, K_d is the equilibrium sorption coefficient; and θ is the water content. The range of K_d values were obtained from the batch sorption experiments. The θ values were supplied by the LLUVIA-II calculations. A dispersivity of 5 cm was assumed for the LEHGC calculations.

The effect of flux rate and sorption were examined in this series of simulations. The sensitivity studies in Siegel et al.⁴ assumed a ten-day pulse of tracer, a flux rate of 56 cm/day, and a lower-boundary condition of pressure head of -56 cm. From a logistics standpoint, the amount of water applied to the experiment is a consideration particularly if operations are maintained throughout the year. Therefore, a series of simulations were carried out assuming a -75 cm pressure head for the lower-boundary condition, reducing the steady-state flux to 12 cm/day, a ten-day pulse for lithium ($C_0 = 1$ mg/l), and a constant source for nickel ($C_0 = 0.1$ mg/l). Figure 6 shows the spatial distribution of Li and Ni with two different K_d values for several specified times. The calculations predict that the lithium concentration pulse breaks through at the outlet of the caisson after 25 days, and the nickel will migrate less than 200 cm at concentrations above the detection limit (1 ppb) in 200 days. Differences in transport of the lithium and the nickel are substantial and are expected given the difference in the K_d 's. The case where the K_d for nickel is 30 ml/g with a 56 cm/day water flux can be seen in Figure 7. This situation is more favorable, allowing detection of nickel near 300 cm at 100 days (Figure 7). This information along with other data on experimental duration and time constraints will determine the final water-flux rate.

Model Comparisons

Model testing will involve comparison of numerical predictions, such as those presented in Figures 6 and 7, with observed data. The design of the caisson experiment will allow collection of both point data from individual samplers and integrated total system response by the exit samplers. This provides an opportunity to test our ability of using point samples to estimate the total system response.

The microlayering in two-dimensional glass slab experiments (Figure 2) suggest that heterogeneity and variability will be present in the caisson; and the less controlled filling of the caisson will only exacerbate this situation. In the previous saturated flow caisson experiment (Fuentes et al.⁹), variability of solute breakthrough in the horizontal plane increased with transport distance. All pre-experiment calculations, such as those reported in this and the previous⁴ paper, assume homogeneous conditions. The uncertainty in solute migration can be addressed using a stochastic approach that requires assumptions about the mean, variance, and spatial correlation of the caisson hydrologic properties that control flow, and geochemical parameters controlling reactive transport. In a field experiment, the parameter statistics are obtained by sampling locations near the test volume and assuming a stationary random field. The test volume is minimally disturbed in this process, and this results in a minimum effect on the flow within the test region. The caisson presents a different problem because the variability in properties is a product of the filling process and is difficult to describe a priori. Disturbance of the test volume by introducing vertical or horizontal discontinuities through sampling may substantially alter the caisson flow and transport system. Post experiment sampling is the alternative that has been selected for characterizing the caisson. In this step, a number of samples will be removed, and their hydraulic and chemical properties will be characterized. By knowing the spatial location of the sample, the statistics that describe these parameter fields can be obtained. This information will be used for a new round of predictions to see if any improvement has been attained by the additional sampling.

Various objective functions for comparing observed and predicted hydrologic or chemical state variables can be defined. In many cases, these have been defined for model calibration exercises where goodness-of-fit is used to select a parameter set, boundary or initial condition, or source/sink term for a model. Other functions besides goodness-of-fit include comparing the temporal and/or spatial moments of predicted and observed concentration field. This approach has the advantage of providing an integrated quantity with a smoother response than the individual concentration measurements.

Figure 6. Concentration profiles for lithium and nickel for a water flux rate of 12 cm/day, a 10-day input pulse of lithium at an initial concentration of 1 mg/l, and a continuous input of nickel with an input concentration of 0.1 mg/l. The vertical line represents the detection limit for nickel.

The use of solute flux¹⁷ rather than breakthrough curves represents another mode of comparison. This approach was used in analysis of previous caisson experiments by Dagan et al.^{18,19} and Nguyen et al.²⁰ In these studies, the method was used to determine parameters for a stochastic model of the caisson under saturated conditions.^{18,20} Cvetkovic et al.¹⁷ derived the moments of the solute flux and cumulative solute flux for stratified, two-dimensional, and three dimensional porous media, and their results indicated that the solute flux is a robust state variable that can reduce uncertainty.

CONCLUSIONS

Model validation, or testing, is a critical issue for performance assessment of high-level nuclear waste disposal facilities. The proposed intermediate-scale experiment offers the advantage of exhibiting reduced uncertainty in the conceptual model governing water flow and nonreactive tracer transport, while using a porous medium that will be heterogeneous in physical and chemical properties. This combination will provide optimal conditions for prediction of flow and transport in

a three-dimensional, heterogeneous system. The results of the transport experiments with these tracers and minerals will have implications for other studies in the YMP. Lithium is an important tracer because of its potential use in field experiments. Nickel is representative of radionuclides released from the structural components of the spent fuel rods in high-level waste and is considered an important waste element due its relatively low retardation in Yucca Mountain tuffs.²¹ The component minerals of the caisson sand (quartz, calcite and iron oxyhydroxides) are present in fractures in Yucca Mountain tuffs.

The initial experimental design⁴ was modified by adding a constant-pressure lower boundary and eliminating the sorbing layer. The new boundary condition eliminates additional mixing caused in the past by the convergent flow at the point discharge boundary, and eliminating of the sorbing layer reduces uncertainty in geochemical behavior.

Characterization of the hydraulic properties has shown the difficulty in using surrogates such as particle size to predict hydraulic properties. Further comparisons

Figure 7. Concentration profiles of nickel in Wedron 510 sand for a water flux rate of 56 cm/day and a continuous input of nickel at a concentration of 0.1 mg/l.

will be made with samples collected from the caisson following the tracer tests.

Criteria to evaluate models represents a crucial element in this study. Questions such as, "What constitutes an adequate or defensible comparison between predicted and observed values?" must be addressed before moving on to field experiments.

Although far from complete, the caisson experiment has fostered the development of tools and procedures that will be needed in field experiments. This test does not, nor is it expected to, represent all of the conditions that will be found at Yucca Mountain. The results can temper expectations from any field experiments proposed for a high-level waste disposal site and provide a more pragmatic evaluation of predictive capability.

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Appendix E

Experimental Procedures Used in the Characterization Study

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Introduction

The following are detailed descriptions of the technical procedures used in this transport-model validation study for the Yucca Mountain Site Characterization Project. Included are experimental procedures for batch adsorption and column flow studies, and for potentiometric titration studies to determine the surface properties of the adsorption substrate. Also included are the analytical techniques used to measure pH, Ni, Li, and Br for these studies, and a rigorous labware washing procedure used to minimize contamination and carryover in these experiments.

E.1 Procedure for pH Measurement Under Atmospheric and CO₂-Free Conditions

E.1.1 Purpose

The purpose of this document is to describe the specific procedures required to measure the pH of test samples in support of the batch and column sorption studies.

E.1.2 Definitions

SLPM, SCFH: Standard Liter Per Minute and Standard Cubic Feet Per Hour, respectively. These are units of gas flow rate in terms of volume per unit time at standard temperature and pressure.

Snubber: A porous frit that permits only low flow rates, thus avoiding over-pressurization of downstream components in the Ar purge system.

Electrode Notebook: A notebook used to record the calibration history of an electrode.

E.1.3 Equipment And Software Resources

1. pH meter capable of 3-buffer calibration with user-specified pH values for the buffers. Meters presently available in the laboratory are the Orion 720a and the Orion 940.
2. Combination pH electrode — incorporates both the reference electrode and pH-sensitive glass membrane in one housing. Electrodes presently available in the laboratory include the Orion ROSS 8102, Orion ROSS 8104, and the Corning flat-surface electrode.
3. Electrode filling solution — proprietary solution for the Orion ROSS electrodes, Ag/AgCl for the Corning.
4. Electrode log book — maintained for each electrode, to record calibration parameters.
5. 10% HCl (1:10 dilution of 16M HCL) for electrode reconditioning.
6. Syringe with needle or capillary tube for draining electrodes.
7. Commercial certified buffers at pH 4, 7, and 10. For measurement of pH < 4 or > 10, additional buffers are required that bracket the range of interest.
8. Thermometer.

9. Ar gas purge system to purge headspace of vessels to exclude CO₂ or to sparge solutions to strip them of CO₂ (see Figure E.1).
10. No specific software is required for this TP.

Figure E.1. Ar gas purge system for pH measurements under CO₂-free conditions.

E.1.4 Procedures

E.1.4.1 Readyng the Electrode

Connect the electrode to the meter, remove the electrode from its storage solution, uncap the vent hole, and (if needed) add filling solution. Clean the electrode if necessary (see *Electrode Cleaning* below).

E.1.4.2 Electrode Calibration

A three-point calibration is employed, using the temperature-corrected pH for each of the three buffers. The buffers and the electrode should be at the same temperature as the samples. Measure this temperature and then refer to Figure E.2 to determine the effective pH for each buffer. Refer to the appropriate meter manual for detailed operating instructions during calibration. Measure the potential (see *Making a Measurement* below) for each buffer and enter it as a calibration point along with the effective pH. Wait for the READY indicator to signal stability. Record the potential (in mV) for each buffer in the

Figure E.2. Temperature dependence of pH for three common buffers (these curves were derived from data accompanying FisherBrand buffers without dyes, and applies to all standard pH 4, 7, and 10 buffers).

electrode logbook. Buffers are normally measured in the order 7, 10, 4, because there seems to be a conditioning effect due to the storage solution that is most evident if the pH 4 buffer is measured first.

E.1.4.3 Making a Measurement (atmospheric and CO₂-free conditions)

Refer to the appropriate meter manual for detailed operating procedure for pH measurements.

1. Rinse the electrode thoroughly with the background electrolyte used in the batch or column experiment and blot or wick dry with a fresh Kimwipe. Deionized water may also be used for the rinse, but can lead to slower electrode response.
2. a. Atmospheric conditions: Place the electrode in the solution to be measured and begin agitating.
- b. CO₂-free conditions: Set the Ar gas flow rate to ~1 SLPM. Insert the electrode into the Ar-purge cap and place the assembly on the sample vessel. Purge for 1 min, then turn Ar off and begin agitating.

3. Wait for the reading to stabilize. The stability criterion varies according to the requirements of the experiment, and should be recorded in the scientific notebook for the experiment. If CO₂ exchange is of concern, then a compromise must be struck between drift due to lack of equilibration and drift due to loss or gain of CO₂. Present experience indicates that an interval of 90 to 120 seconds is reasonable for Orion ROSS 8102 electrodes, whereas the Orion ROSS 8104 electrode requires 180 seconds to reach a similar degree of equilibration. The Corning electrode has not been studied under these conditions. If CO₂ exchange is of no concern, then one should wait for the READY indicator to appear steadily for at least 30 seconds, or when using an ORION 940 meter wait for the drift rate to fall below 3 mV/min.
4. Record the stable reading.

E.1.4.4 Electrode Storage

The ceramic junction on pH electrodes must never dry out; proper electrode response depends upon a small but continuous flow of filling solution through this junction and into the sample. Thus the electrode must be stored wet. A second consideration is that under long-term storage, the filling solution may become slightly contaminated with the storage solution as it diffuses into the electrode through the ceramic junction. Finally, the storage solution must not adversely affect the properties of the pH-sensitive glass bulb. Thus, the ideal storage solution should have neutral pH, low buffering capacity, bulk chemistry similar to that of the filling solution, and be non-corrosive.

Various commercial electrode storage solutions are available, but not all are suitable. The Orion storage solution meets the requirements, but FisherBrand storage solution is a KHPthalate buffer with a pH of less than 4, causing unacceptable contamination of the filling solution. For best results, follow the electrode manufacturer's recommendations.

For long-term storage, the vent hole should be capped. For short-term storage, especially in less-than-ideal storage solutions, it may be desirable to leave the vent hole uncapped to reduce the likelihood of contamination of the filling solution due to diffusion of the storage solution into the electrode.

E.1.4.5 Electrode Cleaning

Cleaning may become necessary due to accumulation of microscopic deposits on the glass bulb or ceramic junction, causing sluggish electrode response, or because of the possibility of cross-contamination of dilute samples after measuring very concentrated solutions. The electrodes should equilibrate in CO₂-free de-ionized water in approximately 1.5 minutes and 2.25 minutes for the 8102 and 8104 electrodes respectively. A longer response time is considered sluggish. The procedure described below is suitable for a very dirty, contaminated electrode, and may be abbreviated for less severe cases.

1. Add filling solution until its level reaches the vent hole.

2. Immerse in 10% HCl to within 2 cm of the vent hole for 30 min.
3. Thoroughly rinse the external surfaces of the electrode.
4. Drain the filling solution. A syringe with a needle or capillary tubing is essential.
5. Add a few ml of filling solution, swirl to completely wet the interior surfaces of the electrode, and drain. Repeat twice more.
6. Add filling solution until its level reaches the vent hole.

E.1.5 Records

The raw data collection form(s) and reduced data (including calibration curves) shall be collected and maintained in the appropriate data package per the draft technical procedure for the sorption experiment being run (e.g., appendices E.2 and E.7 of this report).

When calibrating the electrode, record the potential (in mV) for each buffer in the electrode logbook

E.1.6 References

See Section E.2 of this report, *Batch Sorption Experiments Under Atmospheric and CO₂-Free Conditions*.

See Section E.7 of this report, *Technical Procedures for Column Studies*.

Orion Research Inc., *Instruction Manual for Model EA 940 Expandable Ionanalyzer*.

Orion Research Inc., *Instruction Manual for Ross pH Electrode*.

E.2 Batch Adsorption Experiments Under Atmospheric and CO₂-Free Conditions

E.2.1 Purpose

This document describes the procedures used to carry out batch adsorption experiments at Sandia National Laboratories. These experiments were designed for determining the distribution of an element between crushed rock, soils, or powdered samples and aqueous solutions. The experiments are performed at varying pHs, and require 40 ml screw top centrifuge tubes, hematology mixers, a pH meter, a high speed centrifuge, and adjustable micropipettes of various sizes. After sampling, aliquots of the electrolyte are measured for the element of interest using GFAAS, Flame AAS, ISE and other techniques described elsewhere.

Although this is a general procedure, it was initially designed to determine adsorption of Ni, Li, and Br by Wedron 510 sand in contact with 0.001 M NaCl, in support of caisson transport experiments. Conditions specific to these experiments are given in Attachment 1.

Prior to using this technique, the user should familiarize himself with the technical procedure for pH measurements (appendix E.1), and the Orion 960 instrument manual.

E.2.2 Definitions

GFAAS: Graphite Furnace Atomic Absorption Spectroscopy.

AAS: Flame Atomic Absorption Spectroscopy.

ISE: Ion Specific Electrode.

PI: Principal Investigator.

TP: Technical Procedure.

Ultrafiltration: The use of a filter that retains >95% of molecules above 25,000 molecular weight.

Wedron 510 Sand: A medium grain quartz sand.

Sparge: To bubble a compressed gas through a liquid.

Aliquot: A representative portion of a solution.

E.2.3 Equipment and Software Resources

The batch experiments are carried out in 40 ml polycarbonate or polyallomar screw cap centrifuge tubes. A hematology mixer is used to agitate the samples during equilibration. A high speed centrifuge is used to separate solid and liquid phases after equilibration. An Orion 960 pH meter or equivalent, with a Ross 1802 or 1804 pH electrode, is necessary to determine the pH after equilibration. The pH electrode is inserted into a machined Lexan cap, which fits tightly over the mouth of each centrifuge tube, and connected to an Ar supply, so that the head space within the tube may be purged during pH measurements. Ten ml syringes and 0.2 micron filter packs are used to sample the electrolyte in the sample tubes after equilibration, and 7 ml leak-proof sample vials are needed to store the aliquots collected for analysis. Calibrated balances must be used for determining weights throughout the experiment, and calibrated adjustable micropipettes must be used for measuring volume quantities. The adjustable pipettes are calibrated to be accurate at their maximum delivery, and are systematically less accurate at lower capacities. Charts stored with the pipettes show the necessary corrections for any given delivery volume.

E.2.4 Procedures

E.2.4.1 Sample Parameters

Although this procedure was specifically designed for determining the pH-dependence of trace element adsorption coefficients using Wedron 510 sand and 0.001M NaCl electrolyte, it can be readily adapted for other experiments. A known weight of solid (substrate) and volume of electrolyte is put in each centrifuge tube, and acid or base is added, according to a predetermined titration curve, to achieve a specific pH. The samples are allowed to equilibrate, and then are spiked with a known amount of the trace element of interest, and allowed to re-equilibrate. The pH is then taken and the electrolyte in each tube is sampled and analyzed.

Samples are run in triplicate over a pH range from 5 to 10, with 2 electrolyte blanks and 2 unspiked substrate blanks run at pHs of 5, 7, and 10. The electrolyte blanks are run to insure that the electrolyte and the acid and base, used to adjust the pH, are uncontaminated, and to insure that contamination from poorly washed labware is minimal. The substrate blanks are run to determine the amount of the element of interest that is present naturally in the material and that is either soluble or exchangeable over the pH range being studied.

In addition, samples of the spike solution are collected at the beginning and at the end of the spiking procedure, and analyzed to determine the actual amount of the element added.

E.2.4.2 Step-by-Step Procedure

1. Clean the labware (see appendix E.8) to be used in the experiment. All labware is washed in soapy water, rinsed with deionized water, soaked in 10% HNO_3 for 1-2 hours, and then rinsed at least 7 times with $>18 \text{ M}\Omega$ ultrapure water and allowed to air-dry. The acid bath is necessary because some elements (i.e., Ni) sorb onto the plastic centrifuge tubes at moderate to high pH (higher than 7); soaking in acid causes these elements to desorb, eliminating a possible source of contamination.
2. Number the centrifuge tubes and lids, and record the sample number and target pH for each sample in the laboratory notebook. Weigh out and add to each of the sample and substrate blank tubes the appropriate amount of substrate, recording the weights in the laboratory notebook. If the substrate is being added as a dry crushed solid, then the weights should fall within 0.1 % of the target amount for each sample. The substrate can also be added as a neutral-pH aqueous slurry; in this case, the suspension must first be characterized to determine the density of the slurry and the weight of substrate present per gram of slurry. Each sample tube is tared on an analytical balance and the desired weight of slurry is added using a micropipette. Sample-to-sample variation is much larger than with a dry sample; an accuracy of 1 – 2 % is acceptable.
3. Fill a 1 liter bottle with electrolyte. All electrolyte used in the experiment will come from this bottle. If the experiment is being run under *CO_2 -free conditions*, then sparge the electrolyte for at least $\frac{1}{2}$ hour with Ar to remove CO_2 . The Ar is bubbled through 0.05 M NaOH and deionized water, to remove any acidic component. The pH of the electrolyte should be ~ 7 once CO_2 removal is complete, but may be as high as 7.5 if some NaOH aerosol is present in the Ar. If the buffering capacity of the solid is large, this is not critical.

If the experiment is being run under *ambient or atmospheric conditions*, then sparge the electrolyte with air for at least $\frac{1}{2}$ hour, using a small aquarium pump. This equilibrates the electrolyte with the atmosphere. Assuming an ambient temperature of $\sim 25^\circ\text{C}$, the pH should be ~ 5.6 once equilibrium is reached.

4. Add 20 ml of electrolyte to each of the centrifuge tubes, using a 5 ml adjustable pipette. If the experiment is being run under CO_2 -free conditions, purge the tubes with Ar before and after filling. Store the two spike sample tubes for later use.
5. Mix up 50 mM solutions of NaOH and HNO_3 , and for CO_2 -free experiments, sparge them with Ar. Use a predetermined titration curve for the solid/electrolyte ratio being examined to estimate the amount of acid or base to add to each sample to achieve the target pH, and add it using an adjustable micropipette (example titration curves for the 20 g Wedron/20 ml 0.001 M NaCl system are given in Attachment 1). The electrolyte blanks will not have the proper pH, of course, as there is no solid in them. Actual pH of the blanks is not important; of interest is

how much contamination could have been added to the samples in the acid or the base at each pH.

6. Make sure all of the tubes are tightly capped, and place the samples on the hematology mixer for 2 – 3 days. This pre-equilibration step allows grain surfaces to come in equilibrium with the electrolyte. In addition, any of the element of interest that is naturally present in the sand reaches equilibrium with respect to adsorption.
7. Mix up a spike solution of known concentration. Ideally the spike solution should be about 2 orders of magnitude as concentrated as the target concentration in the samples; however, make sure that the spike solution is undersaturated with respect to any solid phases. This may require calculation of solubilities of potential solids. If the solubility limits are high enough, and the target concentrations are low enough, adjust the pH of the spike to 7 using weak acid and base solutions. Although the pH adjustment slightly changes the volume, and hence the concentration, of the spike, this is not critical because all samples will be normalized to the measured spike samples. Remove the sample tubes from the mixer, and retrieve the two spike sample tubes from storage. Add a known amount of concentrated spike solution to the first spike (before) tube, to all of the samples, and then to the second spike (after) tube. **Do not** spike the electrolyte and sand blanks. Record the amount of spike solution added to each tube in the lab notebook. Immediately acidify the two spike samples with 408 μl concentrated trace metal grade HNO_3 and put aside.
8. Put the tubes back on the mixers and allow to re-equilibrate for 2 – 3 days (an adsorption rate study should have been made to determine the minimum length of time necessary for equilibration to be reached). Remove the samples from the mixer, and centrifuge for $\frac{1}{2}$ hour at 5000 rpm.
9. Measure the pH (see appendix E.1 for pH measurements) of each sample, using an Orion 960 pH meter and a Ross 8102 or 8104 pH electrode. The meter and electrode should be calibrated with three buffered pH standard solutions immediately prior to use.
10. Immediately after measuring the pH of each sample, label a clean 7 ml sample vial, place it on the balance, and tare it. Using a 10 ml disposable syringe, draw ~8 ml of the electrolyte out of the sample tube. Put a 0.2 μm filter pack onto the syringe, and push the plunger, forcing the sample through the filter and into the 7 ml sample vial. Continue until 5.00 ± 0.02 g of sample has been collected. Record the exact weight in the laboratory notebook.
11. Add 102 μl concentrated HNO_3 to the sample vial using an adjustable micropipette, and tightly cap the vial. The samples are acidified to prevent adsorption onto the walls of the vial.

E.2.4.3 Batch Adsorption Experiment Setup Form

The Batch Adsorption Experiment Setup (Attachment 2) form should be completed with the following information:

1. The starting date for the experiment.
2. The conditions under which the experiment was run--CO₂-free or atmospheric.
3. The composition and approximate specific surface area of the solid used (if known) and the composition and volume of electrolyte used.
4. The pre-equilibration and equilibration times allowed in the experiment.
5. The element of interest, its target concentration in the samples, and the concentration of the spike solution.
6. For each sample:
 - a. sample identification number.
 - b. weight of solid used, recorded to 0.1%, or 0.001 g, whichever is less.
 - c. the target pH.
 - d. the amount of NaOH/HCl added.
 - e. the volume of the spike solution added.
 - f. the pH at <2 mV/min drift rate.
 - g. the mass of the sample aliquot collected for analysis.

E.2.4.4 Data Reduction

Once the collected aliquots have been analyzed, the data may be used to calculate percent adsorption, adsorption density, or K_{ds} . The measured concentration on the element of interest in each sample is corrected for dilution during acidification, and then the total amount of that element that was in the electrolyte is calculated.

$$M_{(\text{liquid})}, \text{ ng} = [C], \text{ ng/ml} * V_{(\text{liquid})}, \text{ ml} \quad (\text{E.1})$$

where $M_{(\text{liquid})}$ is the mass of the element in solution, $[C]$ is the concentration of the element in the electrolyte, and $V_{(\text{liquid})}$ is the total electrolyte volume (initial volume (usually approximately 20 ml) + acid/base added + spike added).

The total exchangeable amount of the element in the closed system can also be calculated:

$$M_{(\text{total})}, \text{ ng} = M_{(\text{added})}, \text{ ng} + M_{(\text{blank})}, \text{ ng} \quad (\text{E.2})$$

where $M_{(added)}$ is estimated from the average concentrations of the two spike samples, and $M_{(blank)}$, the amount of exchangeable element of interest naturally present in the sand, is obtained from the sand blanks. For Ni adsorption in polycarbonate or polyallomar centrifuge tubes, no correction is made for adsorption of Ni by the containers. The importance of this effect must be evaluated for each element studied.

1. The percent of the element which is sorbed onto the sand in each sample can then be calculated:

$$\% \text{ sorbed} = (M_{(total), ng} - M_{(liquid), ng}) / M_{(total), ng} \times 100\% \quad (E.3)$$

2. The adsorption density (Γ) can be calculated as:

$$\Gamma = \frac{\text{Moles of Element Adsorbed}}{\text{Surface Area}} = \frac{M_{(total), ng} - M_{(liquid), ng}}{MW * 10^9 * SA} \quad (E.4)$$

Where: SA= Weight of solid * specific surface area.
MW= Atomic weight of element of interest.

3. The K_d can be calculated:

$$Kd \left(\frac{ml}{g} \right) = \frac{(1000 * \% \text{ sorbed})}{(100 - \% \text{ sorbed}) * \left(\frac{Mass_{sand}}{Volume_{liquid}} \right)} \quad (E.5)$$

E.2.4.5 Potential Sources of Error

Potential sources of error include the following:

1. Equipment malfunctions: balance out of calibration, or micropipettes out of calibration or leaking.
2. Contamination by improperly washed labware, or by improperly used pipettes. Contamination is monitored by running electrolyte blanks with each sample set.
3. Underestimation of the effect of container adsorption of the element of interest.
4. Incorrect estimation of the blank levels in the solid.
5. Underestimation of the necessary equilibration time.
6. Incomplete separation of the solid and liquid phases. This may be a serious problem; at pH >8, clay does not flocculate, and some passes through the 0.2 μm filter. The importance of this is currently being evaluated. It may be necessary to

use ultrafiltration to obtain accurate adsorption measurements under some conditions.

E.2.5 Records

The following records shall be collected and maintained in a data package for the batch adsorption experiments:

1. Batch Adsorption Experiment Setup form. See Attachment 2.
2. Raw data produced by the analysis of the samples using Graphite Furnace Atomic Absorption Spectroscopy, Flame Atomic Absorption Spectroscopy, or Ion Specific Electrode analysis. Refer to the appropriate Technical Procedures when performing the analyses (e.g., appendices E.3, E.4, and E.5).
3. All worksheets and graphs generated during the reduction of the raw analysis data.
4. Any plots, memos, correspondence, etc. concerning the adsorption experiment, or any deviations from the technical procedures used during the course of the experiment as recorded in a laboratory notebook.

E.2.6 References

See Section E.5 of this report, *Br⁻ Analysis by Ion-Specific Electrode*.

See Section E.4 of this report, *Operating Notes for Flame AAS on the Perkin-Elmer 5000 (using Li as an example)*.

See Section E.3 of this report, *Ni Analysis by Graphite-Furnace AAS*.

See Section E.1 of this report, *Procedure for pH Measurement Under Atmospheric and CO₂-Free Conditions*.

See Section E.8 of this report, *Procedure for Washing Glassware for Reactive Tracer Studies*.

E.2.7 Attachments

Attachment 1. Specific Conditions for Adsorption Experiments With Wedron 510 Sand in Support of Caisson Transport Experiments

Attachment 2. Batch Adsorption Experiment Setup Form

E.3 Ni Analysis by Graphite Furnace AAS

E.3.1 Purpose

The goal of this document is to describe the specific instrumental settings and procedures used to measure Ni concentrations in support of sorption studies at Sandia National Laboratories. Measurements are performed using a Perkin-Elmer 5000 AAS, HGA-500 Graphite Furnace Programmer, and AS-1 Auto-Sampler operated in a semi-manual mode. The present data-reduction algorithm can accommodate Ni concentrations in the analyte up to 200 ppb, with a limit of detection of less than 0.4 ppb. Internal precision (within a measurement series) is better than $\pm 0.5\%$, with an external precision of $\sim 2\%$ (2σ).

Concentrations are calculated from manually recorded run-time data using a spreadsheet (the provided example runs under Microsoft Excel 4.0) to fit a parabola to the observations on standards. Full calibration makes use of seven parameters: background, carryover and carryover decay, evaporation rate, and three quadratic constants. Background is determined by averaging; the others by summation minimization using Excel's solver.

A basic familiarity with the instrumentation and spreadsheet software is assumed; general operating procedures are described in the relevant Perkin-Elmer and Microsoft manuals.

E.3.2 Definitions

E.3.2.1 General Terms

AAS: atomic absorption spectrophotometry.

au: absorbance units (dimensionless).

Beer's Law: Each atom of vaporized Ni absorbs the same fraction of light incident upon it, regardless of the concentration of Ni in the vapor or the intensity of the incident light.

Calibration Standards: samples containing a known concentration of the element of interest, used to calibrate instrumental response characteristics.

Detection Limit: the point at which analytical scatter exceeds the measured concentration. In other words, the point at which the measured concentration is not statistically different from zero concentration.

External Precision: the precision calculated from separate, independent measurements on the same sample. Measurements are compared from separate data sets over a period of at least several days.

Gravimetric Dilution: solution quantities are measured by mass to at least four significant figures using an electronic balance. Precise dilution ratios ($\pm 0.2\%$ or better) are obtained in comparison to volumetric methods ($\pm 1.0\%$ or worse). Measurement of actual solution density in a pycnometer permits conversion from mass back to volume units.

Internal Precision: the precision calculated from the scatter of back-to-back readings on the same sample.

Ni: nickel.

ppb: parts per billion, e.g., ng/g. If the solution density = 1 g/ml, then ng/ml = ng/g = ppb. In this document, concentrations are given in units of ppb by way of example only. In practice, if solutions and standards have been prepared volumetrically, then use ng/ml.

rms: root mean square, as applied to a collection of values. Each value is squared, the mean of the resulting collection is calculated, and the square root of the mean is reported. When used as a quantity to be minimized mathematically, it is functionally equivalent to minimizing just the sum of the squares or the square root of the sum of the squares.

Terms Related to the Perkin-Elmer 5000: see the referenced Perkin-Elmer instruction manuals.

E.3.2.2 Variables Used in Data Reduction

a, b, c: coefficients for the quadratic response curve (units = ppb/cycle², ppb/cycle, and ppb, respectively).

Abs2_n: absorbance corrected for background and carryover of Ni from previous cycles for the *n*th furnace cycle (units = au).

AbsCorr_n: absorbance corrected for background and carryover of Ni from previous cycles and evaporation effects for the *n*th furnace cycle (units = au).

Abs_n: absorbance corrected for background for the *n*th furnace cycle (units = au).

Baseline_n: integrated absorbance reading taken during the baseline step after the furnace has cooled following the measurement step (units = au).

Bkg: the average absorbance recorded during the measurement step in the absence of a sample. It is measured after the furnace has been purged of residual Ni by cycling several times without adding a sample. A single value applies throughout a data set (units = au).

carryover: the fraction of Ni remaining in the furnace from the preceding cycle (dimensionless).

carryover_decay: the coefficient describing the decrease in carryover from second preceding cycle relative to the immediately preceding cycle (dimensionless).

evap_rate: the amount of sample that evaporates from the sample cup in the autosampler per furnace cycle (units = cycle⁻¹).

n: the cycle number. It is incremented each time the furnace is cycled (units = cycle).

[Ni]_n: calculated Ni concentration for the *n*th furnace cycle (units = ppb).

Sample_n: integrated absorbance reading taken during the measurement step of the analytical cycle for the furnace. It includes contributions from the sample and from the baseline of the instrument (units = au).

E.3.3 Equipment and Software Resources

The equipment required by this TP for the analysis of Ni includes:

1. Perkin-Elmer 5000 Atomic Absorption Spectrometer.
2. HGA-500 Graphite Furnace Programmer.
3. AS-1 Auto-Sampler attachments.
4. In addition a Microsoft Excel 4.0 workbook is used to calculate analyte concentrations.

E.3.4 Procedures

E.3.4.1 Instrumental Parameters

E.3.4.1.1 Perkin-Elmer 5000 AAS with HGA 500 graphite furnace and AS-1 auto-sampler attachments

Table E.1. AAS settings

Setting ID	Value	Function and procedure for setting
Wavelength (λ)	232.0 nm	The auto-peaking feature is sometimes unreliable, so the wavelength should be peaked manually. After the lamp is warmed up, choose the Setup mode and peak the wavelength using the + and – keys by counting short steps across the maximum energy plateau and then choosing the midpoint. The display should still show $\lambda = 232.0$ (or possibly 231.9); if it doesn't, a nearby peak has been found instead of the Ni peak.
Slit	L 0.2 nm	Use the “L” slits — these are short rather than tall, masking the beam shape to coincide with that of the graphite furnace.
Current	25 mA	Be sure the Ni lamp is selected. Warm it up for ~15 min. (30 mA is max for this lamp, but running at reduced current prolongs the lamp life and yields a more stable beam).
Expansion (Exp)	10	Scale expansion factor. Set it at 10 for samples with [Ni] ≤ 200 ppb Ni. At this level, the least significant figure is mostly noise.
Conc.	on	Set mode to Conc., not Abs.; otherwise the scale-expansion factor will not be used. (Conc. = Abs. $\cdot$ Exp.)
Peak Area	on	Choose peak area rather than peak height. This will integrate over the entire read period, a more accurate and less noisy method than just looking for the maximum signal.
Read	5 s	Set the read period to 5 s.
Print	on	Starts the printer, which will then record each reading (except for its sign, i.e., + or –).
<i>Check Value:</i>		
Energy	> 65	If the lamp is properly positioned and λ has been optimized, the beam energy will be 66.

E.3.4.1.2 Graphite furnace programmer

Table E.2. Standard settings (for samples with [Ni] ≤ 200 ppb)

	Step	Temp. (°C)	Ramp (s)	Hold (s)	Recor d	Read (s)	Interrupt flow
drying	1	110	1	15			
dehydrating	2	250	25	0			
charring	3	1400	10	4	10		
measuring	4	2600	0	6	yes	1	yes
purging	5	2700	1	4	yes		
baseline	6	110	1	9	yes	4	

The purpose of each step is:

Step 1: Drying. All free water evaporates during this step.

Step 2: Dehydration. Bound water is driven off during this step. With the above parameters, some hissing at ~180°C is audible; visually it is apparent that some boiling is occurring. A slower heating rate here might improve overall precision.

Step 3: Charring. All volatile components are vaporized during this step. The chart recorder is turned on when the temperature reaches 1400°C, monitoring the loss of volatiles. Increase the hold time if absorbance has not returned to zero by the end of this step.

Step 4: Measurement. Maximum-power mode is used (indicated by ramp time = 0), in which furnace temperature is measured by the optical pyrometer rather than the internal calibration of current vs. temperature in the furnace programmer. At the beginning of the step, internal gas flow is reduced to 50 ml/min for [Ni] < 100 ppb (interrupt flow = yes). Slightly more than one second elapses before the furnace reaches the preset temperature, so the 5 s reading is initiated after a delay of 1 s. The chart recorder remains on throughout this step.

Step 5: Purge. Most of the remaining sample is flushed from the furnace. The chart recorder continues to operate.

Step 6: Baseline. Once the furnace has cooled (after 4 s), a 5 s reading is initiated. This reading is used as the baseline for the preceding sample reading. This step continues 1 s beyond the end of the reading to avoid erratic behavior caused by the furnace programmer as it switches itself off.

E.3.4.1.3 Graphite furnace

The furnace should be aligned in the beam path so that light transmission is maximized (absorbance is minimized). To reposition the furnace, release the locking lever at its base; the furnace can now slide from side to side, with front-to-back and vertical positioning controlled by thumbwheels.

Pyrolytically coated graphite furnace tubes with L'vov platforms are used. For Ni analysis of clean samples, it appears that a tube may last for a thousand cycles or more. An old tube should be discarded when readings of a 20 μl aliquot of 50 ppb standard become erratic or give 10x absorbance values of less than 2.0.

A new tube must be preconditioned, which may be accomplished by manually cycling it to 2700°C ten times or so (or follow the recommendations accompanying the new tubes). This fuses the platform with the tube and conditions the surface so that little of a sample will be retained to contaminate subsequent runs. If a tube has been inadequately preconditioned, the platform may become unseated, producing low and erratic readings. A new tube and platform must then be installed.

E.3.4.1.4 Auto sampler

The Auto Sampler provides much more reproducible sample injections into the graphite-furnace tube than can be achieved manually using a micropipettor. Be sure the capillary tube lines up with the furnace hole. See the auto-sampler manual for adjustment procedure. Automatic sequencing and/or repeating features are not utilized; the 30-position turret is aligned manually to the desired sample location, and the repeat counter is set to zero. For standard analyses, the sampler pump is installed in the 20 μl position.

The teflon capillary should extend far enough from its teflon sleeve (12 mm) so that the sleeve does not come into contact with the opening in the furnace tube, and its holder should be positioned in the sampler arm so that immersion of the sleeve in the sample is avoided. The capillary tip should be trimmed with a razor blade at a 45° angle and positioned as shown. If the capillary becomes damaged, a fresh section of tubing can be pulled through the sleeve.

Evaporation during a series of analyses is significant, often averaging ~15% over the course of 100 readings. Although only 20 μl are needed for a reading, the volume of solution in the sampler vial should be maximized in order to reduce the magnitude of the correction for evaporation. A volume of 800 μl appears to be a good compromise between minimizing the effects of evaporation and avoiding immersion of the capillary sleeve in the solution.

E.3.4.1.5 Chart recorder

Turn power knob to SERVO, set chart speed to 20 mm/min, and set range to 2 mV (5 mV if [Ni] > 50). Adjust range as needed in order to avoid pinning the pen against the full-scale stop.

Figure E.3. Configuration of auto-sampler capillary

E.3.4.1.6 Optical pyrometer

This is calibrated against the internal current-to-temperature calibration of the furnace programmer as follows:

1. On the Furnace Programmer, enter "2600" on the keypad, then push and hold MANUAL.
2. Allow 4 or 5 seconds for the furnace temperature to stabilize, then adjust the potentiometer on the optical pyrometer so that both red and green LEDs are lit.
3. Release the MANUAL button within 10 to 15 seconds.
4. Repeat if necessary, rather than holding MANUAL for a longer period.

E.3.4.2 Sample Parameters

E.3.4.2.1 Matrix effects

The matrix recommended by Perkin-Elmer for Ni analyses is 2% (0.32 N) HNO_3 ; ionization suppressants are not needed. The presence of other ions in the matrix can have significant effects on measured absorbance, however. For example, the presence of 0.01 M NaCl suppresses absorbance by ~3% for samples with 30 ppb Ni. Thus standards should be prepared in the electrolyte used for sorption experiments. Furthermore, analyses from experiments involving solids that contribute significantly to the quantity of dissolved

species must be monitored carefully for incomplete loss of volatiles during the charring step; continued loss of volatiles during reading can produce falsely high absorbance. If uncorrected matrix effects are suspected, then either background correction or the standards-addition technique may be required (cf. Perkin-Elmer manuals for discussions of both procedures).

E.3.4.2.2 Blanks

Trace-metal-grade HNO_3 should be used for the preparation of all solutions. Early experience with reagent-grade HNO_3 indicated the presence of ~ 100 ppb Ni, resulting significant Ni in blank determinations. Blanks prepared with trace-metal-grade acid have no detectable Ni.

E.3.4.2.3 Normal samples

Normal samples are those with $10 \text{ ppb} \leq [\text{Ni}] \leq 200 \text{ ppb}$. The injection volume can be reduced to $10 \mu\text{l}$, extending this range to $\leq 400 \text{ ppb}$. Additionally, sensitivity may be reduced by maintaining Ar flow at the normal 300 ml/min , although accurate calibration under these conditions has not yet been investigated.

The matrix recommended in the Perkin-Elmer literature is 2% HNO_3 , which is interpreted here to mean a 2% solution (1:50 dilution) of concentrated ($\sim 16 \text{ N}$) HNO_3 . As concentrated HNO_3 is nominally 70% and 16 N , a 2% solution may be obtained by diluting 20 ml conc. HNO_3 to 1000 ml with deionized water, with a resulting concentration of 0.32 N .

AAS samples from dilute near-neutral solutions may be conveniently prepared by pipetting a 5 ml aliquot into a 7 ml vial and adding $102 \mu\text{l}$ conc. HNO_3 , resulting in a 2% HNO_3 matrix and a dilution factor of 1.020. Smaller volumes of sample and HNO_3 may be used, at the cost of some precision in acidification, but volumes smaller than 1 ml and $20.4 \mu\text{l}$, respectively, should probably be avoided.

Place $\sim 1 \text{ ml}$ of the prepared sample in a disposable auto-sampler vial and load into turret for analysis. Normally the Auto Sampler is set to inject a $20 \mu\text{l}$ aliquot, but this can be set to $10 \mu\text{l}$, permitting samples up to 400 ppb to be analyzed using standard parameters, or multiple aliquots can be injected, permitting increased sensitivity and precision for samples below 20 ppb . In any case, do not exceed a vol. * sample value of ($200 \text{ ppb} * 20 \mu\text{l} =$) $2000 \text{ ppb} \cdot \mu\text{l}$. To avoid uncertainties in matrix effects, the same aliquot size must be used for standards as well as samples.

E.3.4.2.4 Standards

Standards are prepared by diluting a commercially available Ni AA standard ($[\text{Ni}] = 1000 \text{ ppm}$) with 0.01 M NaCl , 2% HNO_3 blank solution (see above) to provide standards of 200, 100, 50, 20, 10, 5, 2, and 1 ppb. Gravimetric dilution is recommended in order to avoid inducing excessive uncertainty.

E.3.4.2.5 Low Ni samples

At concentrations below ~10 ppb, the calibration curve reverses curvature, becoming concave upward when absorbance is plotted vs. concentration. Thus it is not possible to accurately fit a parabola over the entire range of 0 – 200 ppb. Instead, two separate parabolas must be used: 0 – 10 ppb and 10 – 200 ppb.

The limit of detection may be lowered significantly by loading and drying multiple aliquots before charring and measuring. Three aliquots are a good compromise between increased sensitivity and diminishing returns. To eliminate matrix variations, suitably dilute standards should be loaded identically to the samples.

The standard settings for the Graphite Furnace Programmer are altered for convenience: For drying, save steps 1 and 2 as a separate program. Then analyze using steps 3 to 5, also saved as a separate program.

E.3.4.3 Data Collection

Because of evaporation effects, all samples and standards must be loaded into the auto-sampler at the same time (i.e., over a period of a few minutes; a sample added half an hour later cannot be easily corrected to account for the difference in evaporation between it and the standards).

E.3.4.3.1 To make a reading

1. Position the turret to the desired sample location and start the Auto Sampler. After the rinse cycle, very gently blot the capillary tube with a Kimwipe if there are any adhering water droplets (these would otherwise dilute the sample).
2. Wait . . . Position the turret for the next cycle.
3. Record the sample reading.
4. Record the baseline reading, then hit AZ (auto-zero) if significant drift has occurred (reading $> \pm 0.020$).
5. The Auto Sampler should begin cycling on its own. Be ready with the Kimwipe.
6. Subtract the baseline from the sample reading to give the net peak area (*Sample – Baseline*), which will be entered into the data reduction spreadsheet.

E.3.4.3.2 Measurement of standards and samples

Data is collected in pairs of measurements on each sample or standard, providing an immediate check on internal consistency after correction for sample carryover. Before beginning data collection, however, the baseline characteristics of the furnace tube must be established by taking readings in the absence of a sample.

After the instrument has warmed up for a few minutes and the operating parameters have been set, run several empty cycles (nothing injected into the furnace) until the peak shape as indicated on the chart recorder is flat or nearly so, and the *Sample - Baseline* value appears to be constant. Some conditioning of the furnace tube is required apparently after it has been idle for awhile (more than an hour or so). Record on the data form at least three consistent empty cycles. The stable value ranges from slightly positive due to residual Ni from very high Ni samples to slightly negative due to blackbody radiation (10x absorbance ranges from 0.050 to - 0.050). These *Sample - Baseline* readings are the background absorbance and are used to correct all subsequent readings.

Next, take a pair of readings on the 50 ppb standard: the 10x absorbance readings should be consistent and > 1.8 if the instrument has been properly set up and adjusted. If acceptable, then proceed to measure the other calibration standards. The calibration curve should be established by running at least three standards that cover the range of concentrations expected in the samples. For low-Ni samples, the high end of the calibration curve should be anchored by the 10 ppb standard even if the most concentrated sample is < 5 ppb; otherwise measurement uncertainties of lower standards will lead to erratic results.

As a minimum, calibration standards should be measured at the beginning and end of a series samples and after every fifteen unknowns. It is not necessary to measure the standards sequentially; it is equally effective to intersperse them randomly with the samples.

Carryover from one sample to the next must also be monitored. This is accomplished by running two empty cycles following measurement of the most concentrated standard.

E.3.4.3.3 Quality assurance

At least once during a day's analyses, a standard should be run as an unknown rather than as a calibration sample. If time permits, run multiple standards as unknowns. A more rigorous QA program would involve replicate analyses of the same unknowns during many different analytical sessions. Ideally, these unknowns would have concentrations intermediate to the standards used to establish the calibration curves.

E.3.4.3.4 Form for logging data

Use the attached *GFAA* form to record Conc. ($= \text{Abs.} \cdot \text{Exp}$) readings. Readings are also recorded by the printer, but signs (+ or -) are not, so the handwritten record is essential.

The *Sample* reading is obtained during Programmer Step 4, and the *Baseline* reading during Step 6. The net peak area (*Sample - Baseline*) is calculated manually by the operator while awaiting the next reading. Be sure to note the expansion factor in effect, as well as anything else that deviates from the norm, including peak shape on the chart recorder, aliquot size, strange noises emanating from the instrument, or any problems.

E.3.4.4 Data Reduction Theory

Data reduction for Ni is complicated by several factors: (1) some Ni is retained in the furnace from cycle to cycle, (2) a significant portion of the each sample evaporates from the cups in the autosampler during a series of runs, and (3) response is significantly non-linear (Beer's Law is not strictly valid). The mathematical forms of these corrections is discussed in the following paragraphs. Actual data reduction has been automated using an Excel 4.0 workbook, described in section 6.5.

E.3.4.4.1 Absorbance corrections

A measurement on a single solution consists of two furnace cycles, and each cycle consists of a sample reading (*Sample*) followed by a baseline reading (*Baseline*). For the n th cycle in a data set, the absorbance, Abs_n , is the difference between sample and baseline readings (correcting for drift in the zero-point of the detector) and the background of the furnace itself (correcting for blackbody radiation and Ni diffusing out of the graphite furnace tube):

$$Abs_n = (Sample_n - Baseline_n) - Bkg, \quad (E.6)$$

where Bkg is the average absorbance of the empty furnace tube when it has been purged of residual Ni.

Ni contamination from previous cycles is modeled as a geometrically decreasing contribution from the three previous readings:

$$Abs2_n = Abs_n - (carryover \cdot Abs_{n-1} + carryover \cdot carryover_decay \cdot Abs_{n-2} + carryover \cdot carryover_decay^2 \cdot Abs_{n-3}). \quad (E.7)$$

where *carryover* is the contribution from the immediately preceding reading, and *carryover_decay* provides decreasing weight to earlier readings. Both values are determined mathematically by minimizing the rms sum of the values of readings made on an empty tube that immediately followed readings on samples or standards with relatively high Ni. Ideally, an empty tube should give a corrected ($Abs2$) value of zero.

Correction for evaporation and other sources of monotonic drift are made using a mathematically determined slope (*evap_rate*) relating the increase in $Abs2$ values on standards to the run number (n). The value of *evap_rate* is determined during fitting of the calibration curve (see 6.4.2). The evaporation correction is assumed to be linear. For any measurement $Abs2_n$, it is expressed as:

$$AbsCorr_n = \frac{Abs2_n}{1 + n \cdot evap_rate}, \quad (E.8)$$

where $AbsCorr_n$ is the net absorbance that would have been observed in the absence of evaporation (i.e., the net absorbance that would have been observed had this been the initial cycle instead of the n th cycle). Because each $AbsCorr_n$ implicitly also includes

corrections for carryover of residual Ni and for baseline offsets, all of the *AbsCorr* values are directly comparable, with variations due solely to differences in Ni concentration in the samples themselves, not to instrumental or evaporation effects.

E.3.4.4.2 Calibration curve

Four assumptions are made in fitting a calibration curve to a set of data:

1. The drift rate is a linear function of run number and absorbance — drift is probably due to evaporation from the autosampler vials and changing sensitivity of the furnace tube.
2. The shape of the calibration curve is constant — it is not a function of run number.
3. The absorbance = 0 in the absence of Ni (i.e., electrolyte only) — the calibration curve passes through the origin.
4. The error induced by the regression model is negligible — the model assumes all of the error is in the concentrations, when in reality it is mostly in the absorbances.

Four adjustable parameters are used to describe the calibration curve: the *evap_rate* (previously described in Equation E.8) and the constants *a*, *b* and *c* from the equation for a parabola:

$$[Ni]_n = a \cdot (AbsCorr_n)^2 + b \cdot AbsCorr_n + c \quad (E.9)$$

All four parameters are determined mathematically for each data set by choosing values that minimize the rms scatter about the curve described by Equation E.9. The details of the fitting procedure are contained in the Excel 4.0 workbook GFAA_FRM.XLW, described in the next section.

The fitting parameters for the calibration curve may now be applied to the *AbsCorr* values to calculate concentrations. For the pair of measurement cycles on each solution, results are reported as the mean of the two calculated values $\pm$ one-half the absolute value of the difference.

E.3.4.5 Excel Spreadsheet for Fitted Parameters and Data Reduction

Applying the various corrections, fitting empirical calibration parameters, and calculating concentrations lends itself to automation by spreadsheet. A collection of spreadsheets found in the Microsoft Excel 4.0 workbook GFAA_FRM.XLW is used for this task. This workbook contains three bound worksheets: *data*, *calibration*, and *macros*. The following discussion assumes a working knowledge of Excel. The workbook is used as follows:

1. **Create a working copy.** Copy the workbook to a new name unique to the data set to be reduced. The date is a convenient identifier, and should be used in the form YYMMDDXX.xlw where XX are two extra characters used for distinguishing multiple data sets from the same day.
2. **Enter the raw data.** Open the *data* sheet and update its title. Insert or delete rows in the data area as required to match the data set. The formulas in each row (except the first) are identical, so an existing row should be copied into any newly inserted blank rows. The run # is automatically numbered sequentially; fields always requiring data entry are **I.D.** and **Sample - Baseline**. Fields that may require data entry are:
 - a. Dil. Ratio — the dilution ratio. The default formula here is equal to 1.00 for numeric sample IDs (i.e., standards) or $5102/5000 = 1.02$ for non-numeric IDs (i.e., samples prepared by diluting to 2% HNO₃). Enter the correct value if the default is inappropriate.
 - b. Load (μ l) — The volume of solution injected into the furnace. 20 μ l is the default value; enter the correct value if needed.
 - c. Exp. — The expansion factor. 10 is the default value; enter the correct value if needed.
3. **Select and average background readings.** See Comment 1 at the bottom of the *data* sheet. Update the formula here to average among the readings taken at the beginning and end of the data set in the absence of any sample. Acceptable readings are those that are self-consistent and do not immediately follow high [Ni] readings. At least three at the beginning and three at the end of the data set should be averaged. The chosen readings should be indicated by setting the font format to underlined (remove any extraneous underlining).
4. **Fit the carryover parameter.** See Comment 2 at the bottom of the *data* sheet. Carryover is fitted by minimizing the *root sum of squares of selected Abs* value, located at the foot of the *Abs (corrected)* column. Mark the selected *Abs (corrected)* values by changing the font format to underline (remove any extraneous underlining). Edit the *root sum of squares of selected Abs* formula to include only those *Abs (corrected)* values from measurements on an empty tube immediately following measurements on the most concentrated standard (the hidden column *I* contains the squares of the values in column *H*). Press the *Calculate Carryover* macro button to invoke the Excel's solver which then finds the *carryover* and *carryover_decay* values that minimizes the *root sum of squares of selected Abs*.
5. **Fit the calibration curve.** Open a new window, switch it to the *calibration* sheet, and arrange the screen so that both windows are visible. Entries in the *Calibration data* area of the *calibration* sheet must be updated to reflect standardization data from the current data set. Fields that require data are:

- a. Run — The second run number of a pair of measurements on a standard.
- b. Wght. — The statistical weight to give a standard, usually between 0 and 1. It may be desirable to set it to some value less than 1 for standards with low [Ni] as the relative precision of these measurements is somewhat lower. Set it to 0 to exclude a standard from the calibration.

Whole rows may be inserted or deleted as required within the *Calibration data* area so long as both the first and last rows remain in their respective positions. In other words, add or remove rows from the middle of the area only. As with the *data* sheet, copy an existing row into newly inserted blank rows.

Select the *Calculate Calibration Curve* macro button to invoke Excel's solver to optimize the curve parameters (*evap_rate*, and *a*, *b*, and *c*). Depending on the speed of the computer and the size of the data set, the solver may time-out before arriving at a satisfactory solution. If this happens, choose *continue*.

The reasonableness of a set of parameters is often readily apparent when the two graphs in the *calibration* sheet are examined. On the *Evaporation* plot, the corrected concentrations should fall along horizontal lines for each standard concentration. On the *Calibration Results* plot, the scatter of the calibration points about the ordinate should be less than ± 0.03 ppb or 0.5%, whichever is larger. Additionally, the parameters should fall within the ranges given in the next section.

Occasionally the solver will converge on unrealistic parameters which probably represent a local rather than global minimum. Assuming that the calibration data are all good, there are two strategies to deal with this. The parameters may be re-initialized with different values before attempting automatic calibration again, or one or more of the parameters may be arbitrarily set to reasonable values, with the solver invoked manually to optimize the remaining parameters.

E.3.4.6 Acceptability Criteria

E.3.4.6.1 Measurements

A measurement is considered acceptable if:

1. No instrumental anomalies were observed,
2. Peak shapes were normal, and
3. The $\pm$ *Range* parameter is less than 0.5% or 0.3 ppb, whichever is greater. (The crossover point is 15 ppb.)

E.3.4.6.2 Calibration parameters

Reasonable values for the calibration parameters are listed below. If the empirically derived parameters deviate from the expected values, then the optimization routine may have found only a local rather than global solution. In such an instance, the input data must be critically reassessed. Some data sets may require certain parameters to be set manually, using values based on previous experience. Typical parameter values are given in Table E.3.

Table E.3. Typical values of calibration parameters

Parameter	Expected value	Comments
Bkg	-0.0010 – 0.0030	Not usually a problem.
carryover	0 – 3%	Not extractable from all data sets. Varies with tube condition. Set manually if necessary.
carryover decay	0.3 – 0.7	Must be < 1. Not extractable from all data sets. Varies with tube condition. Set manually if necessary
evap_rate	0.001 – 0.003	Depends on temperature and humidity.
a	40 – 60	Calibrations for low-Ni data sets (max. standard = 10 ppb) should be < 0 (as negative as -1000).
b	200 – 300	Depends on the sensitivity of the furnace tube. b > 300 is an indication that the tube should be replaced.
c	0 ± 1	Substantial deviation may indicate contamination of standards. Set to zero manually if necessary.

E.3.4.7 Common Difficulties and Failures

The Graphite Furnace Programmer cannot be re-programmed.

The auto-sampler must be “on” in order to re-program the Graphite Furnace Programmer.

Response is poor: 10x absorbance for 50 ppb < 1.8.

Possible causes of poor response include misalignment of the lamp or the furnace tube, use of the wrong slit width, or failure to reduce internal flow to 50 ml/min. Use of uncoated tubes, or grooved and coated tubes without the L'vov platform, or tubes in which the platform had become dislodged, also produces poor response. See the relevant manuals for details on lamp and furnace alignment.

[Ni] in blanks not equal to zero.

This can arise either as a consequence of contamination (of the blank solution, the pipette tip, or the autosampler vial) or because of sublimation of the matrix during the measurement period. In the latter case, the charring step needs to be lengthened to the point that the chart recorder has returned to baseline before the initiation of the measurement step.

E.3.5 Records

The raw data collection form(s) and reduced data (including calibration curves) shall be collected and maintained in the appropriate data package per the draft technical procedure for the sorption experiment being run (e.g., TP-221 or TP-222).

E.3.6 References

Section E.2 of this report, *Batch Sorption Experiments Under Atmospheric and CO₂-free Conditions*.

Section E.7 of this report, *Technical Procedures for Column Studies*.

Perkin-Elmer Operator's manual, *Model 5000 Atomic Absorption Spectrophotometer*.

Perkin-Elmer Operator's manual, *HGA-500 Graphite Furnace*.

Perkin-Elmer *Analytical Methods Using The HGA Graphite Furnace*.

E.3.7 Attachments

Attachment 3. *GFAA Summary — Standards, Samples & Blanks Run as QA Samples*
(analytical precision is calculated from these data)

Attachment 4. *GFAA for Nickel* — A Raw Data Collection Form (2 pages)

Attachment 5. [GFAA_FRM.XLW]data — Sample Data-Reduction Worksheet

Attachment 6. [GFAA_FRM.XLW]calibration — A Calibration Worksheet

Attachment 7. [GFAA_FRM.XLW]macros — Macros Invoked by Buttons on the Data and Calibration Worksheets

E.4 Operating Notes for Flame AAS on the Perkin-Elmer 5000 (using Li as an example)

E.4.1 Purpose

The purpose of this document is describe the specific instrumental settings and procedures used to measure Li concentrations in support of sorption studies at Sandia National Laboratories. Measurements are performed using flame atomic absorption spectroscopy and data is reduced using a Microsoft Excel 4.0 spreadsheet program. A basic familiarity with the AAS and Microsoft Excel 4.0 is assumed.

E.4.2 Definitions

AAS: Atomic Absorption Spectroscopy

Calibration Standards: Test samples containing a known concentration of the element for which the analysis is being performed.

E.4.3 Equipment and Software Resources

This procedure is written for a Perkin-Elmer Atomic Absorption Spectrophotometer, model 5000 equipped with a flame burner assembly. A Microsoft Excel 4.0 spreadsheet program is used for data reduction and fitting of the calibration curve. A 386 class personal computer, or equivalent, can carry out the data reduction with acceptable speed.

E.4.4 Procedures

E.4.4.1 Normal Operating Procedure

1. Install burner assembly (be sure the drain loop has water in it), turn on power to the AA and gas control, and turn on the fuel (replace cylinder when < 75 psig or acetone may damage gas controller) and oxidant.
2. Select the proper lamp, lamp current, high-slit width, and wavelength appropriate for the element of interest. Table E.4 lists instrument setting for Li analysis. Manually re-center the wavelength.
3. Light the burner:
 - a. put the aspirator tube in a beaker of D.I. water.
 - b. push the "gases on" button.
 - c. set the fuel flow rate.
 - d. set the oxidant flow rate.
 - e. push the ignition button.

Table E.4. Instrument settings for lithium

Keyboard control	Setting	Burner control	Setting
Lamp Current	10 mA	Fuel Flow Rate	30
High Slit Width	1.4 nm	Oxidant Flow Rate	50
Wavelength	670.8 nm	Fuel Pressure	12-15 psig
Integration Time	3 s	Oxidant Pressure	50-85 psig
HOLD	On		
AVG	3		

Energy reading should be > 65 (~75)

Sensitivity Check: 1.5 ppm Li solution should give Abs. of 0.2

4. Adjust burner parameters for maximum absorbance. Choose a 0.5 s integration time in CONT, ABS mode. Perform a sensitivity check using a standard of proper concentration and adjust burner position — height (just low enough to avoid occulting the beam) and depth (for maximum absorbance). Adjust the fuel flow and sample flow for maximum absorbance, and record values on data sheet. (Using a graduated cylinder, measure the time to fill it to some predetermined level. This will give the flow rate in ml/s.)
5. Spot-check standards for approximate absorbance range (standards should bracket the sample concentrations; use at least three). If readings exceed 0.8, turn the burner head to reduce sensitivity. Compute the largest usable expansion factor (expanded readings must be less than 10; instrumental noise means that factors larger than 10x yield no additional precision). Choose CONC mode to make use of the expansion factor.
6. Set integration parameters. With the settings suggested in table 1, pushing the READ button initiates a series of three 3 s readings which are then averaged. The averaged value is recorded on the data sheet.
7. Turn on the chart recorder and select sensitivity appropriate to the samples. If the recorder is not recording a real-time signal, see Problem #2, below.
8. Begin data collection. Place the aspirator tube in a sample vial, observe the signal on the chart recorder, and hit READ when the signal is stable (after ~ 5 s). Record the averaged value on the data sheet (attachment 8).

E.4.4.2 Calibration and QA

The largest source of error in flame AAS is due to changes in sensitivity as the flame parameters change (e.g., thermal equilibration, accumulation of deposits on the burner head). Thus a set of calibration standards that bracket the sample concentrations must be run at the start of the session and periodically thereafter. The sample intervals between calibration standards depend on the drift rate, but should probably be no greater than every twenty samples.

As a minimum for quality assurance, run one or more of the standards as an unknown with each group of ≤ 20 samples.

E.4.4.3 Data Reduction

Data reduction is accomplished using an Excel 4.0 spreadsheet. A data set consists of an initial set of readings on the standards, a group of ~ 20 samples, and a final set of readings on the standards. A calibration line for each set of standards readings is found by using Excel's solver routine to fit a quadratic equation to the data. The resulting equation is:

$$[\text{conc.}] = a * (\text{abs})^2 + b * (\text{abs}) + c \quad (\text{E.10})$$

This equation is applied to the i^{th} sample in a group of n samples and linear interpolation is used between the two sets of standards to determine the sample concentration. The calibration curves and standards readings should be plotted to visually check their linearity. Attachments 9 and 10 are a description and a sample Excel 4.0 spreadsheet for reduction of raw data.

E.4.4.4 Problems

1. Burner won't light.
 - a. No gas flow and/or no clicking from electronic ignition. Check all the safety interlocks (drain-bucket float, burner pin, connectors and wiring).
 - b. *Gas flows and ignition glows, but no pilot.* Try several more times. The fuel line probably has not yet been thoroughly flushed with fresh fuel.
 - c. *Pilot lights, but not the burner.* Increase the fuel flow rate. The burner only lights under very fuel rich conditions. Alternatively, try setting the "gases on" button to off, pushing the ignition button, and then hitting the "gases on" button.
2. *Chart recorder won't record continuously*, but instead records only the integrated result as displayed on the control panel. The REC DUP button must have been pressed at some time during the current session. This button is supposed to apply

the current expansion factor to the recorder output. When it does this, the instrument no longer outputs the real-time signal, but instead merely outputs the value of the previous reading until the current one is completed. Turning REC DUP off removes expansion-factor scaling, but does not restore real-time signal output. Re-booting the PE 5000 is the only solution.

3. *Calibration curve is non-linear.* Beer's Law, which states that absorbance is a linear function of concentration, is valid only for absorbances of 0.8 or less. Samples and standards giving higher absorbances must be diluted or the burner head must be set at an angle to reduce the optical path length.

E.4.5 Records

The raw data collection form(s) and reduced data (including calibration curves) shall be collected and maintained in the appropriate data package per the technical procedure for the experiment being run.

E.4.6 References

Section E.2 of this report, *Batch Sorption Experiments Under Atmospheric and CO₂-free Conditions*.

Section E.7 of this report, *Technical Procedures for Column Studies*.

Perkin-Elmer Operator's manual, *Model 5000 Atomic Absorption Spectrophotometer*.

Perkin-Elmer, *Analytical Methods for Atomic Absorption Spectrophotometry*.

E.4.7 Attachments

Attachment 8. AA Raw Data Form

Attachment 9. Description of EXCEL 4.0 Example Li Worksheet

Attachment 10. Sample Excel 4.0 Spreadsheet for Reduction of Raw Li Data

E.5 Br Analysis by Ion-Specific Electrode

E.5.1 Purpose

This document describes the procedures used to measure Br⁻ concentrations in sorption studies at Sandia National Laboratories. The procedure requires concentrations of 20 µg/ml or less; more concentrated samples must be diluted. The limit of detection is ~0.2 µg/ml, and external precision is ~2%. Millivolt readings were collected using a Br⁻-specific electrode coupled to a double junction reference electrode, and concentrations were calculated using the Microsoft Excel 4.0 Solver routine to fit a logarithmic curve to the standard data and assuming a constant drift rate between sets of standards. Prior to using this method, the user should familiarize himself with basic operational techniques, as described in the instruction manuals for the Ion-Specific and Reference Electrodes, and the Ion Analyzer.

E.5.2 Definitions

External Precision: The precision of samples of known concentration in independently-run sample sets.

E.5.3 Equipment And Software Resources

The measurements are performed using an Orion Model 94-35 Bromide Electrode coupled with an Orion 90-02 Double Junction Reference Electrode. An Orion Expandable Ion Analyzer EA-940 meter mounted on an Orion 960 Autochemistry System base is used to collect the data. Microsoft Excel 4.0 is used to fit calibration curves and calculate sample concentrations. An 80386-class personal computer or equivalent can carry out the data reduction with acceptable speed.

E.5.4 Procedures

E.5.4.1 Instrument Setup

Measurements will be taken with an Orion Model 94-35 Br⁻ Ion-Specific Electrode coupled to an Orion 90-02 Double Junction Reference Electrode, and attached to an Orion Ion Analyzer EA940 on an Orion 960 base. Prior to collecting data, the following steps must be performed:

1. Polish the analytical surface of the Br⁻ electrode with an Orion Electrode Polishing strip (Cat. # 94-82-01).
2. If necessary, fill the reference electrode with Orion 90-00-02 filling solution. The electrode should be filled to at least one inch above the level of the liquid to be measured to prevent back-flow.

3. Place the electrodes side by side in the sampling arm of the Orion 960, and place a magnetic stirrer below the arm.
4. Select the proper electrode on the Orion 940 Ion Analyzer and set the parameters to display a millivolt reading (see the operations manual).
5. Check the electrode sensitivity as follows:
 - a. Put 100 ml of deionized water in a beaker. Add a magnetic stirring bar.
 - b. Add 2 ml of Orion Ionic Strength Adjuster (ISA) solution (Cat. # 94-00-11).
 - c. Add 1 ml of 1000 $\mu\text{g/ml}$ Br^- and place on the magnetic stirrer. Turn on the stirrer, and lower the electrodes into the solution. Monitor the mV drift rate until the reading stabilizes (see the Orion 940 operations manual), and record the result on the data sheet (attachment 11).
 - d. Add an additional 10 ml of 1000 $\mu\text{g/ml}$ Br^- to the same beaker, allow the mV reading to restabilize, and record the result.
 - e. The difference between the readings should be 54-60 mV. If it does not fall within this range, then repolish the electrodes and try again.

E.5.4.2 Sample Parameters

Samples and standards should have the same matrix composition; for the sorption studies carried out in support of the caisson experiment, a 0.001 M NaCl solution was used. The millivolt response is logarithmic with respect to concentration, the usable part of the curve falling between 0 and 20 $\mu\text{g/ml}$. Samples which are more concentrated must be diluted; as the most sensitive part of the curve is around 5-10 $\mu\text{g/ml}$, it is recommended that samples be diluted to this range.

In order to properly fit a logarithmic curve to the standard data, at least 4 standards that bracket the sample compositions should be used.

This technique requires that the approximate composition of the samples be known. If this is not so, a preliminary run using 100 or 200 $\mu\text{g/ml}$ standards should be used to determine the necessary dilutions.

E.5.4.3 Data Collection

Each data set consists of three groups; an initial set of standards, a group of unknowns (including at least one standard solution treated as an unknown for a QA check), and a final set of standards. The change in the response curves defined by the initial and final standard sets is used to determine and correct for drift in the electrode response during the run. The drift rate is assumed to be linear; this assumption is less

likely to be true for long runs, so no more than 10 – 12 unknowns should be analyzed in a single group.

The data collection procedure is as follows:

1. Pipette 10 ml of sample into a suitable container. Containers should be acid-washed and rinsed at least 7 times with >18 mega-Ohm deionized water, and must be wide-mouthed to accomodate the two electrodes.
2. Add 0.2 ml of Orion ISA solution to the beaker.
3. Add a teflon-coated magnet, and place on the magnetic stirrer. Turn up the stirring speed until a reasonable agitation rate is achieved. The *same speed* should be used for all standards and samples.
4. Lower the sampling arm until bottoms of both electrodes are submerged in the sample. Make sure that *no air bubbles* are adhering to the analytical surfaces of the electrodes.
5. Monitor the electrode drift rate with the Orion 940 until the desired stability is achieved. The meter gives a ready signal when the drift rate decreases to <1 mV per minute, but a rate of 0.7 mV or less is a better criterion; it is easily achieved by high Br⁻ samples (>1 µg/ml), and yields more consistent data for low concentration samples. This step can take anywhere from tens of seconds to a few minutes, but drift time can be considerably reduced by grouping samples of similar concentration.
6. Once the drift criterion has been met, record the mV reading on the data collection form.
7. Raise the sampling arm and place a waste-water beaker under the electrodes. Rinse the electrodes thoroughly with 0.001 M NaCl and use a clean electrode to wipe the sides of the electrodes dry. Gently wick dry the analytical surfaces on the ends of the electrodes.
8. Repeat the procedure until all samples have been analyzed.
9. Clean, cap, and store the electrodes. If the reference electrode is to be used within a week, it may be stored in its filling solution; otherwise, drain the filling solution and rinse with deionized water (see the Orion 90-01 reference manual for this simple procedure). Do **not** allow the filling solution to crystallize within the electrode.

E.5.4.4 Data Reduction

The raw data is reduced using a Microsoft Excel 4.0 spreadsheet, a sample of which is appended to this document (Attachment 12). A curve of the form:

$$[Conc] = a\left(\frac{x}{c}\right)^b + d \quad (\text{E.11})$$

where x is the potential reading, is fit to each set of standards (Rows 2-5 and 25-28). The variables a,b,c and d (cells J2-J5 and J25-J28) are found using Excel's solver, minimizing the sum of the squares of the residuals (the residuals are shown in column H, and the minimized cells are J6 and J29). These curves are then used to calculate two concentrations for each unknown (columns G and H), which are then weighted according to the run number (columns A and B) to produce a weighted average (column I). Note that the concentrations have been multiplied by the dilution factor, which is in column E (hidden). Each sequence of measurements on unknowns is calibrated separately, using the standards immediately preceding and following the unknowns.

The calculated curves are then plotted with the standard data on the graph (the data used to plot the curves is in columns L and M, not shown), to illustrate the quality of the fit.

The cell contents for the sample worksheet are described in detail in Attachment 13.

E.5.4.5 Acceptability Criteria

Measurements are considered acceptable if :

1. No instrumental anomalies were observed. Data should be discarded if there are sudden changes in the magnitude or rate of electrode response, or in electrode stability.
2. The standard sets do not suggest that unusually large drift has occurred during the course of the run. The higher concentration standards ($\geq 10 \mu\text{g/ml}$) should have virtually no drift ($<0.5 \text{ mV}$).
3. QA samples yield acceptable results -- within ~2% or $0.2 \mu\text{g/ml}$, whichever is greater, of the expected value.

E.5.4.6 Possible Sources of Error

It was noted during the course of a sorption experiment that samples with a pH of 9-10 consistently yielded results a few percent higher than expected. It may be that OH^- interferes slightly with Br^- analysis using the ion-specific electrode. Also, samples which were acidified to 2% nitric acid produced a major change in electrode response; acidified and non-acidified samples and standards should not be run together, as electrode drift will be large and non-linear with respect to time. The nitric acid-induced oxidation of Br^- to $\text{Br}_{2(\text{g})}$ may also be a problem in acidified samples, although this has not been demonstrated.

E.5.5 Records

The raw data collection form(s) and reduced data (including calibration curves) shall be collected and maintained in the appropriate data package per the technical procedure for the sorption experiment being run.

E.5.6 References

Section E.2 of this report, *Batch Sorption Experiments Under Atmospheric and CO₂-free Conditions*.

Section E.7 of this report, *Technical Procedures for Column Studies*.

Orion Research Inc. *Instruction Manual for Model EA 940 Expandable Ionanalyzer*.

Orion Research Inc. *Instruction Manual for Model 94-35 and 94-53 Halide Electrodes*.

Orion Research Inc. *Instruction Sheet for Model 90-02, Double Junction Reference Electrode*.

E.5.7 Attachments

Attachment 11. BR_FORM.XLS—A Data Collection Form (2 pages)

Attachment 12. BR_EX.XLS—A Sample Data Reduction Worksheet

Attachment 13. BREX_DOC.DOC—A Description of EXCEL 4.0 Example Br Worksheet (the cell contents in the sample worksheet)

E.6 Potentiometric Titrations to Determine Surface Charge

E.6.1 Purpose

The goal of this document is to describe the specific instrumental settings and procedures used to measure surface charge as a function of pH in support of sorption studies at Sandia National Laboratories. Measurements are performed using a prototype automated titrator to control the rate of acid or base addition in response to user-selected stability criteria. Titration curves collected in background electrolyte strengths ranging from 0.0005 to 0.1 M, in conjunction with surface area and site density parameters derived from other sources, are used to calculate intrinsic acidity and association constants via the double-extrapolation method for the triple-layer model of surface complexation. The intrinsic constants obtained for the triple layer model are most useful at low ionic strengths (less than 0.1 M).

E.6.2 Definitions

E.6.2.1 Units

C: Coulomb.

l: Liter.

M: Molar (moles/l).

SLPM: Standard liter per minute. A measure of gas flow relating volume to time at standard temperature and pressure (298 K and 1 atm).

S: Siemen. A measure of conductivity, equal to 1 ohm^{-1} .

E.6.3 Equipment And Software Resources

E.6.3.1 Equipment List

Automated Titrator: A prototype/limited production model constructed by George Redden of Stanford University under contract to Sandia National Laboratories. It is described in detail in the following section.

Reactor: a closed container with stirrer whose headspace can be purged with Ar, and with ports for the pH electrode and acid- and base-delivery tubing.

pH Meter: used to monitor the potential of the pH electrode and communicate this information to the titrator computer via an RS232 interface. The software supports only Orion 940 or 720a meters.

pH Combination Electrode: an Orion 8102 is preferred because of its fast response, but others may be used if their response times and filling-solution leakage rates are acceptable.

pH Buffers: Commercially prepared buffers of pH 4, 7, and 10.

Ar Gas Supply: adjustable flow rate 0.1 – 1.5 l/min. Standard purity Ar must be treated to remove trace acidic gases. Treatment is described in the following section.

Normalized Acid and Base: conjugate acids compatible with the background electrolyte (i.e. HCl and NaOH for NaCl), 0.05 – 0.1 N (with normality precision better than $\pm 1\%$).

Conductivity Meter: used to infer ionic strength at the conclusion of a titration. A Hach portable meter (Model 44600 Conductivity/TDS Meter) is recommended; its probe is insensitive to container effects.

Ionic Strength Standards: solutions of 0.001, 0.01, and 0.1 M NaCl (or other background electrolyte).

E.6.3.2 Description of Automated Titrator and Reactor

The automated titrator is a prototype/limited production model built by George Redden of Stanford University under contract to Sandia National Laboratories. It is constructed from commercially available components arranged in a custom rack, and interfaces with an MS-DOS computer via the LPT1 parallel port and an RS-232 serial port. The operating software was also written by George Redden.

E.6.3.2.1 Hardware

The hardware setup is illustrated schematically in Figure E.4. Two 2.5 ml micrometer syringes form the heart of the system. These are actuated by stepper motors under computer control via the printer port and controller/decoders. Standard configuration calls for one syringe to dispense acid, the other base. Each syringe is connected by way of a check valve block to a reagent reservoir and to the reactor. The block contains gravity-operated check valves that allow reagent to flow either from the reservoir into the syringe or from the syringe into the reactor. During filling, the upper (reactor) valve closes while the lower (reservoir) valve opens, whereas during dispensing the upper opens and the lower is closes. This arrangement permits the syringes to be refilled under software control during a titration if more than 2.5 ml reagent is required. To prevent siphoning through the check valves and syringes, the solution level in the reagent bottles must be below the solution level in the reactor.

The syringe tips in the reactor are critical to the performance of the system. Their openings must be extremely narrow (250 – 300 μm) with a gradual taper in order to minimize diffusion of reagent into the reactor. During the course of a titration, only the required syringe tip is to be immersed in the reactor; the other is be partially withdrawn in

Figure E.4. Autotitrator schematic.

order to eliminate diffusion of its reagent as a source of uncertainty. Positioning is performed manually. The tips themselves are teflon capillary tubes that were heated and drawn like glass. Standard capillary tubing has inadequate wall thickness, but the tubing used for Fisher/Oxford 1 – 10 μ l ultramicropipettors works well (standard Eppendorf-style ultramicropipet tips have too large an opening). Because the very small opening constricts reagent flow, the stepper motors must be run at a slow setting to avoid overpressuring the tubing connections.

The pH is monitored by a combination electrode located in the reactor. When analyzing coarse materials that settle rapidly (i.e., sand), the electrode must be shielded from the direct flow to avoid discrepancies induced by the sedimentation potential (Bates, 1973). A 10 ml plastic syringe body may be modified to slip snugly over the electrode body by boring out the nozzle end with a hand reamer. A 2 mm vent hole should be drilled near the top (nozzle end) and the finger grips should be removed. When installed as shown in Figure E.4, the shield should project 2 – 3 mm past the end of the electrode. The electrode is connected to a pH meter that, when polled by the computer, integrates the analog potential reading for ~1 s, converts it to a digital value, and then transmits it to the

computer. An RS-232 serial interface connects the meter and computer. The potential-to-pH conversion is handled either by the operating software or during data reduction.

The reactor must have ports for the pH electrode, syringe tips, a variable-speed paddle-type stirrer, and Ar purge gas, and should be inert with respect to the suspension under study and to pH changes. A 250 ml Nalgene polypropylene jar with a Mason-threaded cap is presently in use. In this narrow jar, 100 ml solution provides sufficient depth for immersion of the pH electrode above the stirrer paddle, and total volumes up to ~200 ml can be accommodated. The relatively thick cap (~2 cm high) can be clamped alone, allowing simple removal of the jar without disturbing any of the instrumentation. As there is no water jacket, the reactor temperature is the same as the ambient laboratory temperature (usually 23 – 25°C at Sandia National Laboratories) to better than $\pm 0.1^\circ\text{C}$.

The headspaces of the reactor and the basic reagent bottle are continuously purged with humidified, deacidified Ar. The Ar subsystem is not pictured in Figure E.4. The total Ar flow is adjustable, at rates of 0.1 – 1.5 l/min as measured by a precision flow gauge immediately downstream of the regulator. Standard purity Ar passes through a cartridge filled with ascarite to remove trace acidic gases (e.g., CO_2), then through a $0.01\ \mu\text{m}$ filter to remove dust from the ascarite, and finally through a bubbler filled with deionized water for humidification and to remove trace basic gases (e.g., NH_3).

E.6.3.2.2 Software — titrate.exe

No formal documentation exists for *titrate.exe*, the operating software, but it is largely self-documenting during operation through use of context-sensitive cues that appear at the bottom of the screen. The software functions as a set of interrelated utilities that perform a variety of tasks:

1. Buret (syringe) control — permits purging, filling, and rate adjustment.
2. pH electrode calibration routines — performs on-line calibration of electrode response. (difficult to use — edit *lastcal.dat* directly before starting *titrate.exe*)
3. pH monitor — records pH at a user-specified interval and integration time. Its operation may be suspended, allowing addition of acid or base via the computer-controlled syringes.
4. pH stat — maintains reactor pH within specified limits by adding a fixed aliquot of acid or base when the limits are exceeded.
5. Titrator — performs automated titrations according to selectable stability criteria. The reagent aliquot volume added is specified as a function of pH.

Only the Titrator functions will be discussed in more detail. Two modes of operation are permitted by the program. In the first, the pH is recorded and an aliquot of reagent is added after a specified time interval. This mode is not optimal because the electrode requires longer to reach equilibrium at near-neutral pH than at high or low pH. In the

second mode, the pH is recorded and an aliquot of reagent is added after the electrode potential has ceased to drift. The stability criteria are adjustable and may vary as a function of pH. Two parameters are used: *n* specifies the number of acceptable readings required, and *Time or potential diff.* specifies the maximum acceptable potential difference between subsequent readings. In either mode, the amount of reagent to be added is specified as a function of pH.

Titration parameters are stored in *.run files. Table E.5 is an annotated version of such a file; the actual file contains only the numbers, without the headers or comments. These files may be edited directly or modified using a built-in facility which is invoked as a titration run is being configured.

E.6.3.2.3 Performance standards

Ideally, the measured pH in the reactor should be stable in the absence of further reagent additions. To verify adequate pH stability, begin by stripping the CO₂ from an aliquot of >10 MOhm water by vigorous stirring while under Ar purge. For this test, neither the syringe tips nor the pH electrode are in the reactor (their ports are plugged). After ~30 minutes, measure the pH — it should be 6.8 – 7.3. A deviation indicates contamination of either the reactor or the Ar gas. If the pH is acceptable, continue to monitor it for another ~30 minutes. Acceptable drift is less than 0.2 pH units in 30 min; greater drift points to trouble with the pH electrode.

Test for excessive diffusion of reagents from the syringe tips by placing the tips in contact with the solution, adding acid to adjust the pH to ~4, raising the acid tip, and then adding base to adjust the pH back to 7 and monitoring the pH for ~30 minutes with the base tip in contact with the solution. Next, add base to raise the pH to ~10, raise the base tip, then add acid and so on. Acceptable drift here depends upon acid and base concentration and must be judged by experience. For 0.05 N reagents and 100 ml solution in the reactor, drift of ~0.4 pH units is typical.

More routinely, stability of the reactor pH may be verified by stripping the CO₂ from an aliquot of electrolyte by Ar purging and vigorous stirring for ~30 minutes, adjusting the pH to neutral (reagent-grade NaCl commonly contains minor acidic contamination that must be neutralized), withdrawing the syringe tips, and monitoring the pH. Acceptable drift is ±0.003 pH/min once steady-state has been reached, usually within 5 min.

Finally, a titration of electrolyte alone should be performed. Compare the resulting curve of pH vs. acid or base with the calculated theoretical curve for CO₂-free conditions and amount of electrolyte used. Agreement at near-neutral pH should be exact within measurement precision; deviations at extreme values are common, due to the limitations of electrode calibration with buffers of 4, 7, and 10. Deviations at near-neutral pH indicate errors in reagent concentrations or continuing contamination (e.g., Ar or filling-solution problems).

Table E.5. Annotated *titrate.exe* parameter file [Global and pH-sensitive parameters are concatenated into a single text file (*.run file type) that lists each *Value* or triplet of *pH*, *vol*, *n*, on separate lines, in the order given below; the *.run file contains no descriptive text, only numbers; there must be one pH triplet for each range enumerated in (a); in part (b), *vol (ml)* is the amount of reagent to add past the previous pH boundary (given under *pH*), and *n* is the required count of acceptable readings before the electrode is considered to be stable]

(a) Global parameters

Parameter	Value	Comment
Unknown	2	Serves no discernible function, but is part of the parameter file.
Buret	2	Dispense reagent from either syringe 1 or 2.
Response directio	1	1 for base addition, -1 for acid addition.
Criteria typ	2	1 for time intervals, 2 for potential intervals (wait for electrode stability).
Time or potentia diff	.15	Interval value in seconds or mV, depending on Criteria Type
Electrode	1	Port to monitor on pH meter.
# of range	8	Number of pH ranges (see (part b of this table)).

(b) pH-sensitive parameters

pH	vol (ml)	n
2	1.1	6
3	.5	6
4	.2	6
5	.1	6
6	.08	6
7	.06	6
8	.06	6
9	.06	6

E.6.3.2.4 Trouble-shooting

If performance standards cannot be achieved, the possibility of acidic or basic contamination from several sources must be considered:

1. Diffusion of reagents from the syringe tips when they are in contact with the suspension but no reagent is being dispensed. During titrations, withdraw from the suspension the syringe tip that is not being used. Use the most dilute acids and bases practicable. Use narrower syringe tips with a more gradual taper.
2. Siphoning of reagent from a syringe tip. Be sure that the reagent bottles are below the level of the reactor, and be sure that the syringe tips are vertical or are angled into the flow.
3. Contamination of Ar purge gas. If standard-purity Ar is not treated, residual CO₂ will cause drift toward lower pH values. Treatments such as passing Ar through a column of solid NaOH pellets (e.g., Ascarite) introduce basic impurities which will cause drift to higher pH values. One role of the water scrubber(s) is to extract residual contaminants from the Ar gas stream without introducing any new contaminants. If the Ar is suspected of causing pH drift, check the pH of the water scrubber(s) — it should be between 6 and 8.5.
4. Contamination of the pH electrode filling solution. If the electrode has been used to monitor very basic or very acidic solutions, its filling solution may become contaminated by diffusion of the sample solution through the ceramic junction, especially if the electrode's vent hole was covered. Recondition the electrode and change the filling solution.
5. Inadequate exclusion of atmospheric CO₂. Check for inadequate sealing; increase the Ar flow rate if the system is reasonably gas-tight.

E.6.4 Procedures

E.6.4.1 Reagent and Sample Requirements

Samples with sparingly soluble components that affect the pH (i.e., carbonate minerals or silica at high pH) produce results that are difficult to interpret and should be avoided. Various pretreatment techniques may remove such components but may leave residues of their own, whose effects must be evaluated.

Physically, the sample may consist of particles up to the size of coarse sand, and may be loaded in solution densities of up to 1 g solid per ml electrolyte. For more finely divided samples (e.g., powders), such a density may lead to significant electrochemical effects that should be evaluated for their influences on pH and conductivity measurements.

For titrations using a NaCl electrolyte, NaOH and HCl are used for pH adjustment. NaOH is nonvolatile and is degraded only by absorption of atmospheric CO₂, whereas HCl

is gaseous and is readily lost from solution in significant quantities. 0.05 N NaOH has a shelf life of at least two months whereas HCl may last for only several weeks before concentration losses become significant.

Two intensive parameters are required for successful data reduction: the specific surface area and the density of surface sites.

E.6.4.2 Calibration and Data Collection

E.6.4.2.1 Overview

A data-collection session includes mixing the electrolyte and solid to create a suspension, purging with Ar while stirring vigorously to remove CO₂, calibrating the pH electrode, adjusting the pH to the desired initial value, performing the titration, readjusting the pH to near-neutral, and measuring the conductivity to infer the final ionic strength. The ionic strength may then be increased by addition of salt and the measurement cycle repeated.

E.6.4.2.2 Preparing the suspension

For measurements at very low ionic strength ($<0.002\ M$) use >10 Mohm water, because the inherent leakage of the pH electrode will produce an increase in ionic strength of $\sim 0.0005\ M$ during the titration; otherwise use electrolyte of the desired concentration. Combine the desired mass of solid and volume of electrolyte and allow to equilibrate. If the solid is stored dry, it may be necessary to allow several hours for thorough hydration of the surface. In the absence of quantitative data on equilibration, allow 48 hours. If the sample is stored as an aqueous paste or thick suspension, this step may be omitted.

After equilibration, place the suspension in the reactor and stir vigorously while purging the headspace with Ar. A deep vortex should be present, maximizing the area of the gas:liquid interface. Sparging the suspension with Ar would be slightly more effective, but causes splashing resulting in droplets hanging from the reactor walls and lid which may fall back into the suspension during titration. The CO₂-free pH should be neutral to slightly acidic, and 45 min purging is sufficient.

E.6.4.2.3 pH electrode calibration and leakage rate

Two aspects of the pH electrode require calibration: its filling-solution leakage rate and its electrical response to pH.

For proper function, a small flow of the electrode's internal filling solution must seep through a porous junction usually located near the pH-sensing bulb. For the Orion ROSS 8102 electrode, the filling solution is $3\ M$ KCl and leakage occurs at a rate of $10 - 40\ \mu\text{l/hr}$, an amount that can contribute significantly to the ionic strength of the suspension during the course of a titration. Quantify the leakage rate by immersing the electrode to its normal depth in a known quantity of >10 Mohm water in the reactor. Stir the solution and purge with Ar for at least two hours. Remove the electrode, noting the elapsed time, and

measure the conductivity of the solution to infer the salt concentration (see the section *Conductivity Measurements and Final Ionic Strength*). The leakage volume is inconsequential, so rate of KCl addition is the only important parameter and is calculated as follows:

$$\text{leakage } (\mu\text{mole/min}) = \frac{\text{salt conc. (mmole / ml)}}{\text{elapsed time (min)}} \cdot \text{volume (ml)} \cdot 1000 \left(\frac{\mu\text{mole}}{\text{mmole}} \right) \quad (\text{E.12})$$

Calibration of the pH electrode is performed in the usual manner, using commercially available buffers of pH 4, 7, and 10. The buffers and electrode should be at ambient temperature. Based on the ambient temperature, look up the true pH for each buffer in the supplier's literature. Place the electrode in each buffer until its potential reading, as indicated by the pH meter operating in mV mode, has stabilized to a drift rate of less than ± 0.5 mV/min. The buffers should be stirred or agitated. Because of hysteresis after measuring the pH 10 buffer, the preferred order of operation is 7, 10, 4. Note the potential readings, along with the time, date, temperature, and meter I.D. in the logbook for the electrode. To update the parameters for *titrate.exe*, enter these values in *lastcal.dat* by using a text editor. In *lastcal.dat*, the first five lines correspond to the calibration for electrode #1, the second five for #2. Each line lists the pH followed by an arbitrary number of space and then the potential in mV. Use the existing *lastcal.dat* as a template.

E.6.4.2.4 Titration

Purge the syringes. Twice is sufficient for the acid syringe, but five times is recommended for the base syringe to ensure that all base that may have absorbed CO₂ while residing in the tubing or syringe has been washed out. If reagent concentration is to be changed, remove the pickup tubes from the reagent bottles, purge until all tubing and syringes are as full of air as possible, and then disassemble the syringes and blot dry with kimwipes. Reassemble and purge with the fresh reagents until all air has been expelled; then purge twice more, for a minimum total of at least five purge cycles.

Adjust the suspension pH to the desired starting value. It is preferable to begin at an acidic pH and titrate by adding NaOH rather than beginning at alkaline pH and adding HCl.

Configure *titrate.exe* to perform the titration. This is accomplished by choosing *Titration* from the program's main menu. The program responds by displaying the default parameter file and asks if it should proceed with these parameters. If modifications are required, a negative answer will allow previously stored parameter files to be retrieved from disk and then be modified until they suit the purpose at hand. The sample parameters given in Table E.5 are a suitable starting point for titrations on systems consisting of 100 – 150 ml electrolyte and 10 – 20 m² surface area.

After the run parameters have been established, the program requests some information about the system for the data-file header. The first three lines are for any comments about the titration. Next the user is prompted for the name of the adsorbent

(e.g., acid-washed Wedron 510) and its concentration (enter the mass (g) used). The fourth line requests information about the titrant. Enter its identification and its concentration (normality (N)). The final line requests the nominal ionic strength of the suspension (molarity (M)) and its volume (e.g., 150 ml). Next, if all the header information has been entered correctly, hit <space> to initiate the titration.

The titrator will run unattended during the titration, but because the final ionic strength must be determined immediately after the titration is completed, its progress should be monitored periodically. As soon as the titrator is finished, note the time and then measure the ionic strength as outlined in the next section.

E.6.4.2.5 Conductivity measurements and final ionic strength

Ionic strength is determined by using a conductivity meter to compare the conductivity of the reactor suspension with that of reference solutions. For this use, the meter does not require calibration for absolute conductivity. Instead, the conductivities of two standards, one above and one below that of the reactor, allow the conductivity of the reactor to be found by linear interpolation. Algebraically,

$$I_{\text{sample}} = I_{\text{Std.1}} + \kappa_{\text{sample}} \cdot \frac{I_{\text{Std.2}} - I_{\text{Std.1}}}{\kappa_{\text{Std.2}} - \kappa_{\text{Std.1}}} \quad (\text{E.13})$$

where I is the ionic strength and κ is the measured conductivity. Response appears to be linear over at least three orders of magnitude (0.001 – 0.1 M).

Measurements are performed with a Hach Conductivity/TDS meter (model 44600). This battery-powered instrument is equipped with a probe that is insensitive to proximity effects of the container walls (unavoidable when measurements must be performed on small volumes of sample). The instrument should be warmed up for at least five minutes before making measurements. To make a measurement, the probe is immersed and shaken or tapped to expel all trapped air, completely filling it with the solution to be measured. Repeat until a high, consistent reading is obtained. Rinse and dry the probe thoroughly between solutions.

Conductivity is also a function of pH, with that portion of the measurement attributable to $[\text{H}^+]$ or $[\text{OH}^-]$ becoming significant for $I < 0.005$ M. An empirical pH correction is found by assuming that the effect of pH is independent of ionic strength and may be subtracted out. For titrations terminated at pH 9, the contribution of the increased OH^- concentration relative to neutral conditions is $\sim 6 \mu\text{S/cm}$. This was determined by measuring the conductivity of an air-saturated 0.001 M NaCl standard (pH 6.5, $P_{\text{CO}_2} = 10^{-3.5}$ atm), adding NaOH to adjust the pH to 9, and remeasuring the conductivity without permitting equilibration with atmospheric CO_2 . The conductivity change from 129.1 to 135.4 $\mu\text{S/cm}$ was substantially larger than the value of $\sim 1.3 \mu\text{S/cm}$ expected from the addition of NaOH.

Carbonate species are not an important contributor to conductivity for solutions in equilibrium with air at $\text{pH} < 7$ — the conductivity of >10 Mohm water in equilibrium with air is only $\sim 1 \mu\text{S}/\text{cm}$. Thus its contribution to the total conductivity of the standards is neglected.

E.6.4.2.6 Notebook information

For each titration run, the information listed in Table E.6 should be recorded in the laboratory notebook.

E.6.4.3 Data Reduction

Initial data reduction is partially automated by a post-processor (*filter.exe*) and a set of spreadsheet macros. The data file produced by *titrate.exe* (Table E.7a) consists of a header with lines for comments (three), time, date, sorbent, sorbent mass, reagent, reagent concentration, ionic strength, electrolyte volume, pH buffers, and buffer potentials. The data block begins after three lines containing only the three characters "-" and contains unlabeled columns for reagent volume, electrode potential and time.

The raw data is processed by *filter.exe* to produce the text file shown in Table E.7b. The electrode calibration data are fit by least-squares to a quadratic expression, permitting calculation of pH values from potentials, and time readings are converted from seconds to minutes. Reagent volumes are converted to μeq .

The filtered data are imported into a spreadsheet program (e.g., Excel) and manipulated by a series of macros to produce the spreadsheet shown in Table E.8 and the graphs in Figure E.5. Any obvious irregularities in the experimental data will be apparent in the graphs. The example data are free from such irregularities: pH vs. $\mu\text{eq}/\text{g}$ is a smooth curve, and stabilization time vs. $\mu\text{eq}/\text{g}$ shows a hump centered on pH 7, typical of pH measurements at low ionic strength.

E.6.4.3.1 Corrections and adjustments

Several corrections to the experimental data are calculated at each step of the titration: total electrolyte volume, and ionic strength. Total electrolyte volume is merely the sum of the initial volume of electrolyte and the reagent added at the current (n th) step and each preceding step and is denoted V_n^{Ti} . The volume of reagent added is usually small, but can become significant at low or high pH when titrating with a relatively dilute reagent.

Ionic strength changes during the course of a run for two reasons. At low ionic strength, leakage of filling solution from the pH electrode causes ionic strength to continually increase. At high ionic strength, the titrating reagent (which is salt-free) will dilute the electrolyte. Other factors, such as dissolution of a soluble component of the sorbent, are neglected. Because of this, samples cannot be meaningfully titrated under conditions where they exhibit significant solubility (e.g., quartz at $\text{pH} > 9$ or goethite at $\text{pH} < 4$).

Table E.6. Information to be recorded in the laboratory notebook

Parameter	Sample value	Comments
Solid I.D. and mass	100 g acid-washed Wedron 510	
Electrolyte I.D. and vol.	100 ml 0.01 M NaCl	
Ar flow rate	0.4 SLPM _{air}	Flow gauge is calibrated for air, not Ar. Ar has a specific gravity of 1.4 relative to air.
Stirrer setting	2.3	
Titration reagent	0.05001 M NaOH (DBW 9/16/93)	
Datafile I.D.	30827c	Use the last digit of the year, followed by the month and day. For multiple datafiles on the same date, add a letter (a, b, c, . . .).
Parameter File I.D.	30820b	The parameter file may be named after the first datafile it was used with.
Temperature	23.5°C	
Start time	17:35	Could be used along with elapsed time to calculate the finish time.
Finish time	18:00	Important for calculating electrode leakage correction
Neutralizing reagent (if used)	0.15 ml 0.4737 M HCl	Both volume and concentration are important for calculating corrections to ionic strength
Final pH	7.4	pH at which conductivity measurements will be made.
Time electrode removed from reactor	18:10	Important for calculating electrode leakage correction. May be the same as Finish time.
Conductivity		
K _{reactor}	1.257 mS/cm	The final ionic strength is calculated by linear interpolation.
K _{Std. 1}	1.153 mS/cm - 0.01 M NaCl	
K _{Std. 2}	10.31 mS/cm - 0.1 M NaCl	

Table E.7. Sample titration output file (character strings are surrounded by quotes)

(a) Raw	(b) Filtered for importing into a spreadsheet				
<pre> "" "" "" "11:40:11" "09-17-1993" "acid-washed Wedron 510" 150 "NaOH" .05797 .0005 150 4 7.01 10.02 -888 -888 167.1 -3.3 -182.5 -888 -888 "_" "_" "_" 0 146.525 68 .1 126.975 348 .2 94.875 747 .28 61.5 1477 .36 15.125 2127 .42 -22.5 2678 .48 -58.75 3118 .54 -86.60001 3508 .6 -103.675 3978 </pre>	<pre> Titration "" "" "" "11:40:11" "09-17-1993" "acid-washed Wedron 510" 150 "NaOH" .05797 .0005 150 4 7.01 10.02 -888 -888 167.1 -3.3 -182.5 -888 -888 "a*1E6" "b*1E2" "c" "pH=a*mV^2+b*mV+c" -2.4805 -1.7258 6.9531 "_" "_" "_" "µeq" "pH" "vol" "mV" "min" 0.000 4.371 0.000 146.525 1.133 -5.797 4.722 0.100 126.975 5.800 -11.594 5.293 0.200 94.875 12.450 -16.232 5.882 0.280 61.500 24.617 -20.869 6.691 0.360 15.125 35.450 -24.347 7.340 0.420 -22.500 44.633 -27.826 7.958 0.480 -58.750 51.967 -31.304 8.429 0.540 -86.600 58.467 -34.782 8.716 0.600 -103.675 66.300 </pre>				

Table E.8. Spreadsheet produced from filtered data (Table E.7b) by data-reduction macros

Titration							
Titration of acid-washed Wedron 510, i = 0.005 M							
11:40:11							
9/17/93							
acid-washed Wedron 510							
150							
NaOH							
0.05797							
0.0005							
150							
4	7.01	10.02	-888	-888			
167.1	-3.3	-182.5	-888	-888			
a*1E6	b*1E2	c	pH=a*mV^2+b*mV+c				
-2.4805	-1.7258	6.9531					
-							
-							
-							
	<u>µeq</u>	<u>µeq/g</u>	<u>pH</u>	<u>vol</u>	<u>mV</u>	<u>min</u>	<u>del min</u>
	0	0	4.371	0	146.525	1.133	1.133
	-5.797	-0.03865	4.722	0.1	126.975	5.8	4.667
	-11.594	-0.07729	5.293	0.2	94.875	12.45	6.65
	-16.232	-0.10821	5.882	0.28	61.5	24.617	12.167
	-20.869	-0.13913	6.691	0.36	15.125	35.45	10.833
	-24.347	-0.16231	7.34	0.42	-22.5	44.633	9.183
	-27.826	-0.18551	7.958	0.48	-58.75	51.967	7.334
	-31.304	-0.20869	8.429	0.54	-86.6	58.467	6.5
	-34.782	-0.23188	8.716	0.6	-103.675	66.3	7.833

Figure E.5. Titration curve and stabilization-time plot obtained from a single run [filtered data (Table E.7b) is manipulated automatically with a series of spreadsheet macros to produce these graphs].

To calculate the two corrections, total ionic strength is taken to be the sum of effects of the conjugate ion of the reagent, pH (i.e., H^+ and OH^-), the leakage of the electrode, and the salt present initially. Algebraically,

$$I^{Ttl} = I^{rgnt} + I^{pH} + I^{elctrd} + I^{salt} . \quad (E.14)$$

Each of the component ionic strengths may be calculated from the experimental data and the defining equation for ionic strength:

$$I = \frac{1}{2} \sum_i m_i z_i^2 , \quad (E.15)$$

where m_i is the concentration (moles/l, M) and z_i is the charge of an ion in the electrolyte. All of the ionic components considered here are univalent, so $z_i = 1$ for all ions i , and will not be explicitly included in the following discussion.

A titration run consists of a total of k steps, where the n th step is an intermediate step. Thus X_n is a quantity or measurement at the n th step, and ΣX_n is the cumulative amount added up to and including the n th step.

The contribution of the conjugate ion of the reagent (e.g., Cl^- for HCl or Na^+ for NaOH) is calculated from the amount of reagent added (Q_n^{rgnt}) and the total solution volume (V_n^{Ttl}) by:

$$I_n^{rgnt} (M) = \frac{1}{2} \cdot \frac{\sum_{j=1}^n Q_j^{rgnt} (\mu\text{mole})}{V_n^{Ttl} (ml)} \cdot 0.001 \left(\frac{\text{mole} \cdot ml}{\mu\text{mole} \cdot l} \right) . \quad (E.16)$$

The contribution of H^+ and OH^- to the total ionic strength is found directly from Eq. E.15, the dissociation constant for water (K_w) and the definition of pH:

$$I_n^{pH} (M) = \frac{1}{2} (10^{-pH_n} + 10^{pH_n - K_w}) . \quad (E.17)$$

The contribution of electrode leakage is given by the product of time elapsed to the n th step (et_n) and a constant leak rate (dQ^{elctrd}/dt):

$$I_n^{elctrd} (M) = et_n (\text{min}) \cdot \frac{dQ^{elctrd}}{dt} \left(\frac{\mu\text{mole}}{\text{min}} \right) \cdot \frac{1}{V_n^{Ttl} (ml)} \cdot 0.001 \left(\frac{\text{mole} \cdot ml}{\mu\text{mole} \cdot l} \right) . \quad (E.18)$$

The factor of 1/2 does not appear because both the anion and the cation contribute to the ionic strength.

The contribution of salt initially present is given by

$$I_n^{salt} (M) = \frac{Q^{salt} (\text{mmole})}{V_n^{Ttl} (ml)} \cdot 1 \left(\frac{\text{mole} \cdot ml}{\text{mmole} \cdot l} \right) , \quad (E.19)$$

and again the factor of 1/2 does not appear for the same reason. The quantity of salt present initially, Q^{salt} , is inferred from measurement of the final ionic strength, $I_{\text{final}}^{\text{Til}}$, by subtracting the other contributions. Without explicitly indicating units,

$$Q^{\text{salt}} = I_{\text{final}}^{\text{salt}} \cdot V_{\text{final}}^{\text{Til}} = \left(I_{\text{final}}^{\text{Til}} - (I_{\text{final}}^{\text{rgnt}} + I_{\text{final}}^{\text{pH}} + I_{\text{final}}^{\text{elctrd}}) \right) \cdot V_{\text{final}}^{\text{Til}} . \quad (\text{E.20})$$

These corrections are easily made by pasting the filtered data into a spreadsheet template. They are critical for measurements at low ionic strength, where the ionic strength may increase by 50% over the course of the titration, and volume may increase by 10% if dilute reagents are used.

E.6.4.3.2 Calculation of surface charge

The surface charge, σ , is calculated from charge balance considerations for the electrolyte. For strong acid and base titrating reagents (e.g., HCl and NaOH here), the relevant charge balance equation is

$$\text{Na}^+ + \text{H}^+ + \text{-SOH}_2^+ = \text{Cl}^- + \text{OH}^- + \text{-SO}^- , \quad (\text{E.21})$$

where -SOH_2^+ and -SO^- are protonated and dissociated surface species, respectively. H^+ is assumed to be the potential-determining ion; surface complexation of the background electrolyte ions (e.g., Na^+ and Cl^- here) is assumed to be negligible for purposes of charge balance. In any case, the dominant electrolyte-surface reaction may be Na^+ exchange for H^+ , a reaction that leaves the magnitude of the surface charge unaffected. Additionally, any effect the container has on pH is also assumed to be negligible (an assumption easily tested by experiment).

Several terms are combined for computational convenience. Neglecting Na^+ and Cl^- from the background electrolyte, let $C_{\text{acid}} = [\text{Cl}^-] - [\text{Na}^+]$, the difference between added acid and base. Define σ , the surface charge, as $\sigma = [\text{-SOH}_2^+] - [\text{-SO}^-]$. Finally, neglecting the difference between concentrations, let $[\text{H}^+] - [\text{OH}^-] = 10^{-\text{pH}} - 10^{\text{pH}-K_w}$. Equation E.21 may now be written as

$$s = C_{\text{acid}} - 10^{-\text{pH}} + 10^{\text{pH}-K_w} . \quad (\text{E.22})$$

Charge density in units of concentration must now be converted to $\mu\text{C}/\text{cm}^2$ in order to be of use in electrical double layer calculations of association constants. The specific surface area, S_a (m^2/g), of the sorbent is required and may be obtained from the literature or by methods outside the scope of this document. Recasting C_{acid} in terms of the experimental quantities Q_{acid} (the molar quantity of acid added) and V (the electrolyte volume), Eq. E.21 can be rewritten:

$$\sigma \left(\frac{\mu\text{C}}{\text{cm}^2} \right) = \left(\frac{Q_{\text{acid}} (\mu\text{mole})}{V (\text{ml})} \cdot 0.001 \left(\frac{\text{mole} \cdot \text{ml}}{\mu\text{mole} \cdot \text{l}} \right) - 10^{-\text{pH}} \left(\frac{\text{mole}}{\text{l}} \right) + 10^{\text{pH} - K_w} \left(\frac{\text{mole}}{\text{l}} \right) \right) \cdot \frac{V (\text{ml})}{M (\text{g}) \cdot S_a (\text{m}^2/\text{g})} \cdot 0.001 \left(\frac{\text{l}}{\text{ml}} \right) \cdot F \left(\frac{\text{C}}{\text{mole}} \right) \cdot 100 \left(\frac{\mu\text{C} \cdot \text{m}^2}{\text{C} \cdot \text{cm}^2} \right). \quad (\text{E.23})$$

Now the surface charge density, σ , may be calculated for each step of a titration run, permitting construction of plots of surface charge vs. pH.

E.6.4.3.3 Correcting surface charge for uncertainties in added acid

Surfaces for which the potential determining ion is H^+ yield curves of surface charge vs. pH that possess an inflection point at zero net surface charge. The pH condition at this point-of-zero charge is denoted the pH_{PZC} . For practical purposes, the pH_{PZC} is independent of ionic strength. This property suggests that the pH_{PZC} could be determined by locating the inflection point, or by locating the point of intersection of a family of curves at various ionic strengths. This approach is possible for pH_{PZC} 's near neutral, but at extreme pH values the uncertainty in the surface charge becomes large because it is found by difference between two large numbers, the pH and the amount of acid added (or the pOH and the amount of base added). Additionally, it is often difficult to determine precisely the amount of acid or base added to reach the initial pH at the start of the titration, and the sorbent itself often contains an unquantified level of acid or base contamination as a residue from various pretreatments.

For surfaces with low pH_{PZC} 's, such as quartz, it is more effective to determine the pH_{PZC} by some other method (e.g., electrophoretic mobility) and then adjust the measured titration curves to pass (or extrapolate) through the pH_{PZC} by adding an offset to each curve. Algebraically, an adjustable parameter Q_{offset} is added to the quantity of acid Q_{acid} in Eq. 0 to give a new acid quantity Q_{acid}^* to be used in its place:

$$Q_{\text{acid}}^* = Q_{\text{acid}} + Q_{\text{offset}} \quad (\text{E.24})$$

Choosing the proper value for Q_{offset} for each curve in a family is best done by spreadsheet with a live graph similar to Figure E.6 to provide instant feedback as Q_{offset} is varied for each curve. In semi-log space, Q_{offset} is optimal when the curvature has been minimized for each curve. The resulting family of lines should all have the same slope and show an even spacing as a function of ionic strength. In linear space, each line should extrapolate through the pH_{PZC} . Data that deviate from linearity on the semi-log plot or that do not extrapolate through the pH_{PZC} should be excluded from further consideration. Such deviations are symptomatic of problems with stability of the solution pH due to acidic or basic contamination (see section 5.2.3), or arise at low pH for materials with low pH_{PZC} due to error-propagation when the difference is taken between two large numbers.

Curve-fitting thus depends only on choosing the proper Q_{offset} to produce a straight line in semi-log space (log surface charge vs. pH). Deviating data points at low pH are excluded because of probable systematic errors and the increasing uncertainty discussed

Figure E.6. Semi-log surface charge vs. pH for acid-washed Min-U-Sil quartz at various ionic strengths [each curve has been linearized by choosing an appropriate Q_{offset} ; points below pH ~ 4.75 should be excluded from further consideration because of probable systematic errors implied by the erratic trends. The curve for 0.0004 – 0.0006 M is slightly concave downward at pH 6 because ionic strength increased during the titration from low to high pH; all curves steepen slightly at high pH, a consequence of the breakdown of the approximation $\alpha/(1 - \alpha) \approx \alpha$ as the surface becomes more highly charged (see Eq. 7 for Q_{a2} in Attachment 14).

previously. Internal consistency of the data set is verified by consistent displacements toward higher surface charge with increasing ionic strength, and by the projection of each titration through the pH_{PZC} on a linear plot of surface charge versus pH.

E.6.4.4 Double-Extrapolation Plots for Surface-Complexation Parameters

The purpose of potentiometric titrations on quartz is to provide two input values for the triple-layer model of surface complexation — the intrinsic equilibrium constant for proton loss by the surface (K_{a2}), and the stability constant for complexation of the background-electrolyte cation (K_{Na}). An overview of the triple-layer model as it applies to quartz is provided in Attachment 14. The present section is concerned solely with the mechanics of the double-extrapolation procedure for $\text{p}K_{a2}$ and $\text{p}K_{\text{Na}}$. Precision of the extrapolation for $\text{p}K_{a2}$ is probably better than ± 0.2 units, controlled mainly by the data at low I . For $\text{p}K_{\text{Na}}$, precision is probably only ± 0.4 for data with maximum $I = 0.1$ M.

The double-extrapolation method provides a means of extrapolating from real experimental conditions to a hypothetical condition of zero net surface charge and zero ionic strength. In the hypothetical state, electrostatic terms and activity coefficients become unity, permitting calculations of equilibrium constants from measured concentrations. Two extrapolations are required. Each titration curve is first extrapolated to zero net surface charge, and then the resulting array of points is extrapolated to zero ionic strength.

The extrapolation is performed graphically on a plot of the apparent equilibrium constant, Q , versus a linear combination of α_- , the fraction of deprotonated sites, and the ionic strength, I . Because the pH_{ZPC} for quartz is low ($\text{pH} \sim 2$), only development of negative charge (deprotonation) needs to be considered for titrations over the pH range 4 – 9. The surface charge, σ , divided by the site density, N_s , yields α_- according to

$$\alpha_- = \frac{-\sigma(\mu\text{C}/\text{cm}^2)}{N_s(\text{sites}/\text{nm}^2)} \cdot 0.06239 \left(\frac{\text{sites} \cdot \text{cm}^2}{\mu\text{C} \cdot \text{nm}^2} \right) \quad (\text{E.25})$$

(see Eq. 5 in Attachment 14). The apparent equilibrium constant, Q , is calculated from measurable quantities by neglecting electrostatic terms. Thus, for K_{a2} and K_{Na} , the respective expressions for Q_{a2} and Q_{Na} are

$$\text{p}Q_{a2} = \text{pH} - \log \frac{\alpha_-}{1 - \alpha_-} \quad , \quad \text{and} \quad \text{p}Q_{Na} = \text{pH} - \log \frac{\alpha_-}{1 - \alpha_-} + \log[\text{Na}^+] \quad (\text{E.26})$$

(see Eqs. 6 and 11 in Attachment 14).

The double-extrapolation technique was first applied to potentiometric titration data by James et al. (1978). An example is provided in Figure E.7. To find $\text{p}K_{a2}$, plot $\text{p}Q_{a2}$ vs. $\alpha_- + c_1\sqrt{I}$, where c_1 is an adjustable parameter used to maximize dispersion ($c_1 = 0.05$ in Figure E.7). The intractable electrostatic term in $\text{p}K_{a2}$ is zero when $\alpha_- = I = 0$, so $\text{p}K_{a2} = \text{p}Q_{a2}$ here. Data from individual titration runs are plotted and extrapolated to $\alpha_- = 0$ (an x coordinate of $c_1\sqrt{I}$); a semi-log plot (Figure E.7a) is used because of its greater precision at small x values. These points are transferred to a linear plot (Figure E.7b), and then connected and extrapolated to $I = 0$, giving an estimate of $\text{p}K_{a2}$. The data most critical to an accurate determination of $\text{p}K_{a2}$ are those acquired at the lowest ionic strength, but, problematically, the ionic strengths of these data are the most uncertain, so these data must be interpreted with care.

A second estimate may be obtained by extrapolating to $I = 0$ first along contours of constant α_- , connecting these points, and then extrapolating to $\alpha_- = 0$. As may be seen in Figure E.7b, for quartz this requires extrapolating around a bend, with little control near the y intercept, and thus does little to constrain the estimated value of $\text{p}K_{a2}$.

A similar approach may be used to find $\text{p}K_{Na}$. Here, $\text{p}Q_{Na}$ is plotted vs. $(\alpha_- + c_1\sqrt{I})$, and contour lines are double-extrapolated to $\alpha_- = 0$ and $I = 1 \text{ M}$ (thus, $\log I = 0$). A modified double-extrapolation plot (Figure E.8) is more commonly used, substituting $\text{p}Q_{a2}$ for $\text{p}Q_{Na}$ to

Figure E.7. Double-extrapolation plot for K_{a2} on acid-washed Min-U-Sil (open symbols represent extrapolated points): (a) semi-log extrapolation to find intersection with ticks at $\alpha_- = 0$ for each ionic strength and (b) linear plot to find $\text{p}Q_{a2}$ $I = 0$, $\alpha_- = 0$.

Figure E.8. Double-extrapolation for K_{Na} on acid-washed Min-U-Sil (open symbols represent extrapolated points; points for $\alpha_- = 0$ are from Figure E.7a, and do not fall exactly on a smooth curve here).

provide greater dispersion of the data. This substitution is legitimate because at $\alpha_- = 0$, $I = 1$ M both the electrostatic term and $\log [Na]$ equal zero in the expression for pK_{Na} , giving $pK_{Na} = pQ_{Na} = pQ_{a2}$. This also permits the use here of the precisely extrapolated pQ_{a2} values from Figure E.7b for the extrapolation to $\alpha_- = 0$.

E.6.5 Records

The raw data collection form(s) and reduced data (including calibration curves) shall be collected and maintained in the appropriate data package per the technical procedure for the sorption experiment being run.

E.6.6 References Cited

- Bates, R. G., 1973: *Determination of pH*, John Wiley & Sons, Inc., New York, NY, 479 pp.
- Davis, J. A., R. O. James, and J. O. Leckie, 1978: "Surface Ionization and Complexation at the Oxide-Water Interface, 1. Computation of Electrical Double Layer Properties in Simple Electrolytes," *Journal of Colloid and Interface Science*, **63** (3), 480-499.

James, R. O., J. A. Davis, and J. O. Leckie, 1978: "Computer Simulation of the Conductometric and Potentiometric Titration of the Surface Groups of Ionizable Latexes," *Journal of Colloid and Interface Science*, **65** (2), 331-344.

Yates, D. E., S. Levine, and T. W. Healy, 1974: "Site Binding Model of the Electrical Double Layer at the Oxide-Water Interface," *Journal of the Chemical Society of London Faraday Transactions*, **70**, 1807-1818.

E.6.7 Attachments

Attachment 14. Triple-Layer Model of Surface Charge for Quartz (3 pages)

E.7 Technical Procedures for Soil Column Studies

E.7.1 Purpose

The purposes of the column studies described in this procedure are to:

1. Characterize the parameters - porosity, bulk density and hydraulic conductivity - of saturated and unsaturated soils and other unconsolidated porous materials.
2. Characterize transport properties of tracers through saturated and unsaturated soils and other unconsolidated porous material under different flow and chemistry conditions. The primary transport properties of interest are dispersivity and retardation factor. The primary factors which affect the transport properties are interstitial velocity, mineralogy and solution composition.
3. The overall objective of column studies is to give indication of the validity of various transport models that either assume adsorption equilibria or use chemical kinetics to determine fluid concentrations. For example, if it is found that the equilibrium model is valid in certain ranges of flows and pH's, then predictions can be made for those ranges using batch equilibrium data.

E.7.2 Definitions

Bottom Plate: A metallic or non-metallic plate used at the bottom of soil columns in order to allow for the flow of water without the flow of air.

Feed Line: Pump tubing that feeds tracer or electrolyte solution from the reservoir to the column

Hanging Column: A column in which suction is provided at the bottom using a tube filled with liquid. The amount of suction provided is equivalent to the vertical length of the filled tube. For example, 50 cm of water in the tube would apply 50 cm of suction at the bottom of the column. One atmosphere is 34 feet or 1036 cm of water.

O-Ring: A gasket material formed in a ring to provide sealing of two surfaces upon compression.

Peristaltic Pump: A type of fluid pump which operates by squeezing elastic tubing.

Pinch Valve: A plastic valve which operates by compression or release of the elastic tubing inserted through the valve.

Steady State: A condition in which parameters such as saturation and liquid flow rate are constant.

Saturated: A condition of the soil matrix in which the saturation is essentially 1; that is, all of the pores are filled with liquid.

Saturation: The amount of water contained in a soil matrix determined as the volume of water divided by the volume of the pores.

Saturation Curve: The relationship between the saturation of a soil matrix and the amount of suction applied to the matrix water. The curve consists of the draining portion and the filling section which are not identical.

Tensiometer: An element of a soil column used for determining the tension or suction applied to water in a soil matrix. The principle used is the measurement of the vacuum created when water is withdrawn from a tube initially filled with water.

Tracer: Any of a number of soluble species used to indicate the flow of water through a soil matrix. A tracer may or may not interact with the soil. Some commonly used tracers are Br^- , Li^+ , I^- , and tritium.

Unsaturated: A condition of the soil matrix in which the saturation is less than 1.

E.7.3 Equipment and Software Resources

The experiments are carried out in commercially available Plexiglas columns fitted with tensiometer ports. A peristaltic pump is required to saturate and maintain flow through the column, and an automatic fraction collector is needed to collect the column effluent. A pH meter is necessary if the pH is to be monitored during the experiment, and a calibrated balance is also needed to determine weights of feed and effluent samples. No specific software is necessary to perform this experiment.

E.7.4 Procedures

Some preliminary steps are required before running the saturated or unsaturated experiments. These are described in section E.7.4.1. Some of the steps for the saturated and unsaturated column procedures are the same. The steps of the two operating modes are summarized in the Table E.9 and are described in detail in sections E.7.4.2 and E.7.4.3. The procedure for determining the saturation curve, that is, saturation as a function of suction, is described in section E.7.4.4.

E.7.4.1 Preliminary Steps

The preliminary steps for either the saturated or unsaturated column experiments are scale calibration check, pump calibration and determination of average weight of fraction collector test tubes.

E.7.4.1.1 Calibration of the feed scale

To check the calibration of the feed scale, weigh a 1000 ml graduated cylinder empty, with 500 ml and with 1000 ml of water in it. If the scale does not read the correct weights for the volumes, recalibrate the scale according to the instructions manual for the scale.

Table E.9. Summary of saturated and unsaturated column procedures

Saturated column	Unsaturated column
1. Assemble column under water.	1. Assemble column under water.
2. Fill column with sand.	2. Prepare tensiometers.
3. Fill column with background solution.	3. Fill column with sand.
4. Feed pulse of tracer into column.	4. Fill column with background solution to drive out air pockets.
5. Flush out tracer with background solution.	5. Attain steady-state for unsaturated flow by adjusting suction/drainage.
	6. Feed pulse of tracer into column.
	7. Flush out tracer with background solution.

E.7.4.1.2 Calibration of the peristaltic pump

To calibrate a peristaltic pump using the smaller feed tubing to be used for the tracer and flushing of tracer with electrolyte, place the smaller feed tubing into the pump head and secure the tubing using the tabs attached to the tube. Secure the tubing holder and turn on the pump. Place the suction end of the tubing into a beaker of water. (The tubing may have to be extended using a fitting and another section of tubing in order to reach into the beaker.) If water is not drawn out of the beaker, gradually tighten the tubing holder using the screw on the holder until the water is drawn up to the pump and through the feed tubing. Stop the pump. Weight the beaker.

Guess at the pump setting required for the desired feed rate. Turn on the pump with the speed set at the guessed setting. Weigh the beaker again after 10 minutes. Calculate the flow rate. Repeat the procedure until enough data is collected for a calibration curve in the range of the desired pumping speed.

E.7.4.1.3 Determination of average weight of fraction collector test tubes

To determine the average weight of the fraction collector test tubes, weigh ten empty tubes with the caps on. Take the average and use it as the tare for determining sample weights. The samples from the fraction collector will be removed from the fraction collector, capped and then weighed.

E.7.4.2 Saturated Column Experiments

The steps required for running a saturated column test are detailed below. Enter all data on the Saturated Column Setup Form (Attachment 15).

E.7.4.2.1 Assembly of the column under water

Figure E.9 shows the various parts of a column. Most commercially purchased columns are fitted with a bottom porous plate which allows for the flow of liquid without drawing air. It is essential that the pores of the plate and the space between the porous plate and the bottom of the column be filled with water to exclude trapped air bubbles and ensure nearly equal distribution of suction and flow over the cross section of the column. If the porous plate is metallic, place it in boiling water to force out air from the pores. If the porous plate is a hydrophilic non-metallic material, bubbles will be ejected as the porous plate is wetted. The bottom of the column should be provided with a fitting that allows connection to plastic or rubber tubing. Assemble the column under water (in a bucket or

Figure E.9. Diagram of column parts.

container). The volume in the tubing should be filled with water. After assembly, remove the column from the bucket and dry the outside and inside surfaces in preparation for filling with soil.

E.7.4.2.2 Filling the column with soil and measuring bulk density

Measure the dimensions of the soil-filled portion of the column and calculate the volume ($[\pi (\text{diameter}^2)/4] \times \text{length}$). The bulk density is the weight of the sand in the column divide by the volume of the filled height of column. Two methods are used for filling the column. The first method produces a nearly homogenous sand bed whereas the second method produces a micro-layered soil bed. These are detailed in methods A and B below.

E.7.4.2.2.1 Filling the column to produce a nearly homogenous bed

Add the soil to the column through a funnel and two other Plexiglas tubes of the same height and diameter as shown in Figure E.10. Place a screen between adjacent columns to break up the stream of soil during its fall and thus mix the particles of different sizes. Below the second screen, the stream of dry soil becomes spray-like. This is an indication that sufficient mixing is occurring.

Figure E.10. Column filling equipment.

E.7.4.2.2.2 Filling the column to produce a microlayered bed

Weigh a beaker of dry soil. Add the soil from the beaker in about 20 g portions into the column. After every 100 g of soil is added, pack the column lightly with a flat object such as the back end of a hammer. When the column is fully packed, weigh the beaker again. The difference in weights is the weight of soil in the column. Because as the soil settles after landing, smaller particles tend to separate from larger particles, thus forming micro-layers.

E.7.4.2.3 Filling the column with solution and measuring porosity

In order to minimize entrapment of air bubbles, the column is filled from the bottom up. The bottom of the column between the porous plate and the bottom plate should already be filled with water using the procedure in Section E.7.4.2.1. Fill the inlet and discharge lines of the pump with background solution (see Figure E.11). Connect the tubing running from the bottom of the column, which is also filled with water and closed with a pinch valve, to the discharge line of the feed pump. Weigh the feed beaker. Open the pinch valve and turn on the pump at a rate of about 10 ml/min. Place the cover, with exit tubing attached, over the top of the column. Secure the cover with bolts. Open the pinch valve on the exit of the column to allow air to exit when solution is pumped into the column. Full saturation is detectable when the solution begins to exit the top of the column. The pore volume is the difference in feed solution weight before and after filling minus the volume between the porous plate and the column top and any associated tubing volume. The porosity of the soil-filled column is equal to the pore volume of liquid divided

Figure E.11 Experimental set-up for saturated column test.

by the total volume of the column. The volume in the line from the top of the column to a fraction collector may also be estimated at this time by continuing the pumping until the line is filled.

E.7.4.2.4 Running a pulse of tracer through a saturated column

Figure E.11 shows the experimental setup for a saturated column run. The components of the set-up are (1) a syringe or peristaltic pump, (2) a column, (3) a fraction collector and (4) associated tubing and valves. After the column has been filled with background electrolyte solution in Step 3, the column is ready for the introduction of tracer. If the soil pH does not remain stable when solution is run through it, a buffered electrolyte solution may be used to obtain the desired pH.

For most runs through a column, the flow rate will be significantly lower than that used to fill the column initially, so that a reduction in speed alone for a peristaltic pump may not produce steady flow at the lower flow rate. If necessary, change the pump tubing to a smaller size, as described below, before pumping tracer solution into the column. Reset the pump for the desired flowrate using the smaller size tubing before the column is filled with electrolyte solution.

E.7.4.2.4.1 Changing the pump tubing (feed line)

Turn off the pump. Close the pinch valve on the bottom tube of the column. Disconnect the feed line from the bottom tube and the barb fitting. Remove the feed tube from the pump and replace it with the smaller tube for addition of tracer. Place the suction end of the small tube in the beaker of tracer and the discharge end into a waste beaker. Set the pump to the maximum speed and turn on the pump to flush the feed line with tracer solution. After 2 or 3 tubing volumes of tracer have gone through the line, turn off the pump and adjust the setting to the previously calibrated setting for the run. Connect the feed line to the bottom line of the column, using the barb fitting; be careful to avoid air bubbles in the line. If air bubbles are present, use a syringe to fill the gap(s) with electrolyte and then make the barb connection.

E.7.4.2.4.2 Connecting the column to the fraction collector

Connect the top of the column to the automatic fraction collector using tubing. Install the automatic control valve, provided with the fraction collector, in the line leading to the fraction collector. This valve should be open whenever the pump is pumping and solution is flowing through the column. The valve should be normally open when the fraction collector power is on. When the fraction collector is changing test tubes, it sends a signal to shut off the valve. Calculate the volume in the line from the top of the column to the fraction collector from the diameter of the tubing and the length of the line if not previously determined by filling with electrolyte solution (This volume, as well as the volume in the bottom line and top and bottom porous plates, must be accounted for in the calculations of pore volumes in pulse breakthrough calculations, especially for determinations of retardation factors for conservative or nearly conservative tracers).

E.7.4.2.4.3 Run the pulse

Set the fraction collector to operate on a timed cycle. Set the sample time to that required to fill 3/4 of the sampling tube at the desired flow rate.

Weigh the tracer beaker before pumping the required volume into the column. The volume of the pulses used are usually about 25 to 30% of the pore volume. However, larger pulses can be run as well. The amount of tracer fed into the column is determined from the difference in weight of the tracer beaker before and after addition and the solution density.

E.7.4.2.5 Flush the tracer pulse through the column

After pumping the tracer pulse into the column, turn the pump off. Shut off the pinch valve on the bottom line of the column and disconnect the feed line at the barb connection (See Figure E.11). Either replace the feed line with a new tube or quickly flush the line with 2 or 3 volumes of electrolyte solution. Turn off the pump. Reconnect the feed line to the bottom line of the column, making sure there are no air bubbles, and set the pump to the desired speed for the run. Open the pinch valve and start the pump to continue the run. Record the start time and the weight of the feed flask.

The fraction collector is inside of a box to minimize sample volume reduction by evaporation. If the sample tube is left outside of the box, the estimated amount of evaporation is about 0.2 ml/day. Determine the total volume of electrolyte run through the column by adding the weights of the filled sample tubes minus the weight of the tubes. Instead of weighing all of the tubes individually, use an average of 10 empty tube weights as the tare. Check the sum of the solution in the tubes by weighing the feed electrolyte flask before and after the run.

E.7.4.3 Unsaturated Column Experiments

The steps required for operating an unsaturated column test follow (refer also to Figure E.12): Enter all data on the Unsaturated Column Setup Form (Attachment 16).

E.7.4.3.1 Assemble the column under water

Use the same procedure as Step 1 for the saturated column.

E.7.4.3.2 Install the tensiometers

Install the tensiometers in the two side ports using the threaded fittings with teflon tape. Fill the tensiometers by placing the column horizontally and injecting electrolyte solution through the septum using a syringe, thus filling all of the tensiometer with solution without leaving air pockets. The electrolyte solution remains in the tensiometer because of its surface tension in the pores of the porous plug. Use a paper towel to remove any excess solution that is forced out of the porous plug by the syringe. In order to improve contact between the porous plug and the sand bed, place a small piece of hydrophilic

Figure E.12. Experimental set-up for unsaturated column test

material, such as paper towel, over each of the porous plugs. The moisture from the plugs is sufficient to cause the paper to adhere to the side of the column.

E.7.4.3.3 Fill the column with sand and measure the bulk density

Fill the column with sand and measure the bulk density just as in steps E.7.4.2.2.1 or E.7.4.2.2.2 of the saturated column procedure. Some of the solution from the tensiometer may be drawn into the sand due to the small sand particles causing stronger capillary pull than the porous plug material. This will cause a small error in the measurement of porosity.

E.7.4.3.4 Fill the column with background solution

Fill the column with solution from the bottom in order to drive out air which otherwise might be trapped in the column and hinder the flow of water. Use Step E.7.4.2.3 of the saturated column procedure, but with one exception: the column top is left open and full saturation is determined visually when the soil at the top of the open column is seen to be wetted. Turn off the pump. Be careful to prevent the formation of horizontal cracks in a micro-layered column; cracks can occur if solution pumping is continued after the column

is saturated since the soil is not pressed down with the top of the column. With a homogeneous bed, the particles are interlocked so that cracks are not likely to develop. Determine the pore volume from the solution density and the difference in feed solution weight before and after filling the column. The porosity is equal to the pore volume divided by the total volume of the filled portion of the column (sand plus water).

E.7.4.3.5 Attaining steady-state flow

It is important to attain steady state flow through the column before addition of tracer. Otherwise, the progression of the pulse through the bed would be attributed to both dispersion and changes in pore velocity, and it would be impossible to distinguish between the two effects. After the column has been filled with solution, place the cover on the top of the column. Leave a gap between the cover and the column edge by placing washers over the bolts that bolt the cover to the top of the column. Shut off the pinch valve at the bottom of the column and disconnect the feed line at the barb connection (see Figure E.12). Attach a known length of tubing to the bottom tube at the barb connection. The length of hanging tube (in cm), which is numerically equal to the applied suction (cm suction) required for the desired saturation, can be estimated from the saturation curve for the sand. The procedure for obtaining the saturation curve is given in Section E.7.4.4. Since the suction required for a hanging column for the desired saturation was developed under non-flowing conditions, it is expected that for the desired flow, the required suction will be somewhat greater. Drain the column from the bottom into a beaker of known weight by opening the pinch valve.

E.7.4.3.6 Calculate saturation at various stages of draining the column

From the amount of solution drained, estimate the average saturation of the column at a given time from mass balance and knowledge of the porosity. The average saturation is

$$\theta = (pv - (m / \rho + tv)) / pv \quad (E.27)$$

where pv is the pore volume, tv is the volume in the hanging tube, m is the mass of solution drained into the beaker and ρ is solution density.

E.7.4.3.7 Attain steady-state flow at the desired saturation

Drain the column until the desired average saturation is obtained. Start the pump and feed electrolyte solution to the top of the column at a flow rate corresponding to the desired pore velocity for the experiment. This is done by using the appropriate size feed tubing and pumping the solution at the previously calibrated setting. Every 15 minutes record the tensiometer readings near the top and near the bottom of the column as well as the weights of the drainage beaker and the electrolyte feed container. When the tensiometer readings are nearly equal, assume that steady state has been attained. Determine the saturation of the column at this point by reading the draining portion of a previously determined saturation curve and check by a mass balance calculation. Stop the

pump. Weigh the electrolyte feed container. Close the pinch valve at the bottom of the column.

E.7.4.3.8 Adding a pulse of tracer into an unsaturated column

Connect the drainage tube to the control valve on the fraction collector. Adjust the height of the fraction collector so that the suction applied to the column, which is the height difference from the bottom of the column to the test tube, is the same as that used to obtain steady-state flow. The volume in the line from the bottom of the drainage line to the fraction collector can be estimated from the diameter of the fraction collector tubing and the length of the line. This volume as well as the volume in the bottom porous plates, must be accounted for in the calculations of pore volumes in pulse breakthrough calculations, especially for determinations of retardation factors for conservative or nearly conservative tracers.

E.7.4.3.9 Adjust settings on the fraction collector

Set the fraction collector to operate on a timed cycle. Set the sample time to that required to fill 3/4 of the sampling tube at the desired flow rate. Place the fraction collector inside of a box to minimize sample volume reduction by evaporation. If the tube is left outside of the box, the estimated amount of evaporation is about 0.2 ml/day. Determine the total volume of electrolyte run through the column by adding the weights of the 3/4 filled sample tubes. Check by weighing the electrolyte container before and after the run.

E.7.4.3.10 Inject tracer pulse into column

Remove the feed line from the electrolyte solution. Place the feed line into the tracer solution and quickly flush the feed line with 2 to 3 volumes of tracer, sending the discharge to a waste beaker. Place the tracer container on a scale and record the tracer container weight. Connect the feed line to the top of the column. Turn on the pump; simultaneously open the pinch valve at the bottom of the column and turn on the fraction collector. When enough tracer has been pumped into the column, about 25 to 30% of the pore volume, turn off the pump. Simultaneously close the pinch valve at the bottom of the column. Record the weight of the tracer container.

E.7.4.3.11 Flush the tracer pulse through the column

Remove the feed line from the tracer solution container and from the top of the column. Install a new pump line or flush the old line quickly (with the pump at maximum speed) with 2 or 3 volumes of electrolyte. Reconnect the feed line to the top line of the column. Place the electrolyte container on the scale and place the feed line into the electrolyte solution. Record the weight of the electrolyte container. Start the pump and simultaneously open the pinch valve at the bottom of the column. Run as many pore volumes of electrolyte through the column as required to obtain breakthrough of the tracer pulse.

E.7.4.4 Obtaining a Saturation Curve for the Soil

E.7.4.4.1 Determination of size of soil sample to use

Figure E.13 shows the apparatus for determining saturation curves. Actual saturation in soil may vary significantly with height along the soil bed for long beds. Therefore, the smaller the sample, the better the data. However, for very small samples, not enough space is available for insertion of a tensiometer port. Because of these limitations, and the fact that standard columns come with tensiometer ports at a height of 5 cm, a 10 cm sand bed is chosen.

E.7.4.4.2 Prepare for data entry

The operating steps for determining the saturation curve are listed below. Enter all data on the Column Saturation Curve Setup Form (Attachment 17).

Figure E.13. Experimental set-up for determining saturation curves.

E.7.4.4.3 Saturate the soil sample

Saturate the soil column with by pumping electrolyte solution into the bottom of the column using a set-up similar to that shown in Figure E.11. Determine the amount of solution required for saturation by the difference in weight of the electrolyte feed container. Shut off the pinch valve at the bottom of the column.

E.7.4.4.4 Fill the burette and the line from the burette to the column with electrolyte solution

Add electrolyte solution to the burette. Open the burette stopcock to fill the volume below the stopcock. Close the stopcock. Leave enough electrolyte in the burette to allow for a reading.

Connect tubing from the bottom of the column to the bottom of the burette; if there is air in the tubing below the pinch valve, add electrolyte with a syringe to displace the air before connecting. The tubing connecting the bottom of the column and the bottom of the burette should be long enough to make a U so that the liquid level in the burette is even with the top of the soil bed, and also to allow for enough freedom to lower the burette about 70 cm. Connect the top of the column to the top of the burette with tubing to allow for displacement of air as the saturation changes later in the experiment.

E.7.4.4.5 determine the drainage curve

With the level of solution in the burette even with the top of the soil bed, open the pinch valve and the stopcock. Lower the burette in increments of about 5 cm. After each increment, allow 1 hour for draining of the column. At 1/2 hour and 1 hour, record the solution level in the burette. The reading on the burette minus the initial reading is the amount of solution drained from the soil bed. The difference between the solution level and the level of the porous plate at the bottom of the column is numerically equal to the amount of suction applied; calculate these values for the 1/2 and 1 hour periods. If there is not a significant difference between the 1/2 hour and 1 hour readings, it is assumed that the system has reached equilibrium. If there is a significant difference, then allow another hour for equilibration. In the region where saturation changes quickly with suction, use smaller increments.

E.7.4.4.6 Determination of suction and saturation for plotting the draining curve

At each stage in the lowering of the burette in the draining process, the amount of suction is numerically equal to the distance from the bottom of the sand sample to the solution level in the burette. At the start of the experiment when the solution level in the burette was the same as the top of the sand sample, the reading on the burette is V_0 . As the burette is lowered, with the stopcock open, solution is drained from the sand into the burette, causing the burette reading to increase to V . The volume drained from the column is thus $V - V_0$. If the pore volume is p_v , then the saturation, defined as the fraction of the pore volume actually filled with solution, is

$$\theta = (V - V_0)/pv \quad (\text{E.28})$$

E.7.4.4.7 Determine the filling curve

When the saturation no longer changes significantly with increase in suction, start to determine the filling half of the saturation curve by raising the burette at about 5 cm increments. As in the draining process, use discretion in determining the increment for the region where the saturation changes quickly. Suction and saturation are determined for the filling curve in the same way as for the draining curve. Figure E.14 shows an example of a saturation curve, indicating the draining and filling portions.

E.7.5 Records

The following records shall be collected and maintained in a data package for the column experiments:

1. The Saturated or Unsaturated Column Setup Form and Column Saturation Curve Setup Form (if used). See attached forms.
2. Raw data produced by the analysis of the samples using Graphite Furnace Atomic Absorption Spectroscopy, Flame Atomic Absorption Spectroscopy, or Ion Specific Electrode analysis. Refer to the appropriate Draft Technical Procedures when performing the analyses (e.g., Sections E.3, E.4, and E.5).

Figure E.14. Saturation curve.

3. All worksheets and graphs generated during the reduction of the raw analysis data and
4. Any plots, memos, correspondence, etc. concerning the column experiment, or any deviations from the technical procedures used during the course of the experiment

E.7.6 References

Section E.5 of this report, *Br⁻ Analysis by Ion-Specific Electrode*.

Section E.4 of this report, *Operating Notes for Flame AAS on the Perkin-Elmer 5000 (using Li as an example)*.

Section E.3 of this report, *Ni Analysis by Graphite-Furnace AAS*.

Section E.1 of this report, *Procedure for pH Measurement Under Atmospheric and CO₂-free Conditions*.

Section E.8 of this report, *Procedure for Washing Glassware for Reactive Tracer Studies*.

E.7.7 Attachments

Attachment 15. Saturated Column Setup Form

Attachment 16. Unsaturated Column Setup Form

Attachment 17. Column Saturation Curve Setup Form

E.8 Procedure for Washing Glassware for Reactive Tracer Studies

E.8.1 Purpose

The purpose of this document is describe procedures to wash glassware so as to minimize possible contamination in subsequent batch or column experiments.

E.8.2 Definitions

Nanopure Water: Water having a electrical resistance greater then 18 Mohms.

Alconox, Pez, or RB35: Detergent specifically for washing glassware.

E.8.3 Equipment And Software Resources

Equipment needed:

1. Sink with de-ionized and Nanopure water.
2. Suitable container for the nitric acid bath (15 liter minimum capacity, unbreakable material with a cover).

No software is required for the performance of this TP.

E.8.4 Procedures

E.8.4.1 Prior to Washing

1. Remove any writing on glassware with Ethanol and a paper towel.
2. Place paper towel in an appropriate container for disposal as hazardous waste.
3. Place emptied/rinsed glassware in a detergent bath (Alconox, Pez, or RB35) until glassware is to be washed. Do not allow bath to evaporate.

E.8.4.2 Washing Procedure

1. Empty the wash solution in the bath and replace with fresh detergent solution. Place glassware in bath.
2. Clean glassware using a scrub brush, removing all traces of any chemical residue stuck on the glassware. Use a scrubbing pad for extreme cases of chemical residue build-up.
3. Rinse thoroughly with tap water to remove all traces of detergent.

4. Rinse seven times with De-ionized water.
5. Place in a 10% Nitric Acid bath for one to two hours (after two hours the acid may be absorbed onto the poly-ethylene bottles).
6. Rinse glassware no less than seven times with Nanopure De-ionized water.
7. Let air dry in an area where no contamination is possible. If in a hurry, place glassware into a drying oven at approximately 50-60°C until dry. Do not leave plasticware in the oven too long because it may eventually melt.
8. Return clean/dry labware to cabinets labeled "Acid-Washed Labware" in lab B-59.
9. Items not placed in cabinet should be sealed with parafilm to indicate "acid-washed" status.

E.8.4.3 Acid Bath Replacement

The acid bath should be emptied, the container cleaned, and the solution replaced when one or all of the following has occurred:

1. The volume of acid has decreased due to evaporation and drag-out to the point where the glassware can no longer be completely submerged. Replenishment may be an option if the remaining criteria are not met.
2. There is sufficient contamination, determined by testing of the bath for Ni, Li, and Br. Assuming detection limits of 0.3 µg/l, 0.035 mg/l, and 0.2 mg/l for Ni, Li, and Br analysis respectively, and a dilution factor of 100 from bath to analysis, the maximum bath contamination levels are 30 µg/l, 3.5 mg/l, and 20 mg/l for Ni, Li, and Br respectively. These contamination levels should be checked every fortnight or month depending on usage.
3. There is substantial sedimentation in the bath.
4. It has been six months since the last replacement.

E.8.5 Records

There are no record keeping requirements for this procedure.

Attachment 1:

Specific Conditions for Adsorption Experiments With Wedron 510 Sand in Support of Caisson Transport Experiments

The experimental procedure described here has been used to measure adsorption of Ni, Li, and Br by Wedron 510 sand in contact with 0.001 M NaCl. The adsorption data obtained will be used in modeling transport of these elements through Wedron sand in the Sandia-Los Alamos caisson experiments.

The batch experiments were carried out using a sand/electrolyte ratio of 1:1 — 20 g sand and 20 ml 0.001 M NaCl. Samples were run in triplicate over the pH range from 5 to 10, with 2 electrolyte and 2 sand blanks each at pHs of 5, 7, and 10. Two spike samples were also collected, to determine the actual amount of spike added to the samples. In all, 41 samples comprised each sample set:

3 samples each at pHs of 5, 6, 6.5, 7, 7.5, 8, 8.5, 9, 10	=	27
2 electrolyte and 2 sand blanks each at pHs of 5, 7, 10	=	12
2 samples of the spike	=	<u>2</u>
Total		41

Each sample uses 20 g sand; an entire sample set uses 660 g sand; care should be taken that enough homogeneous material is available before starting the procedure.

Titration curves for the 20 g sand/20 ml 0.001 M NaCl system under both CO₂-free and atmospheric conditions are given in Figure 1. These can be used to estimate the amount of 50 mM acid or base that must be added to each sample to achieve the target pH.

When calculating the percent adsorption and K_d for each sample, the blank levels for the element of interest in the Wedron sand must be considered. For Ni, the exchangeable Ni in the sand is ~35ng/g (see Appendix B of this report). For Li and Br, blanks are below the detection limits of the methods used to analyze for these elements (see Sections E.4 and E.5 of this report).

Figure 1. Titration curves for 20 g Wedron sand: 20 ml 0.001 M NaCl.

Attachment 2: Batch Adsorption Setup Form

page__of__

[illegible]

Attachment 3: GFAA Summary — Standards, Samples, and Blanks Run as QA Samples (analytical precision is calculated from these data)

GFAA Summary — Standards, Samples & Blanks run as QA Samples

I.D.	Conc. (ppb)	Internal Precision	Meas. - Nominal
<i>Blank (DBW, 8/31/92, 0.01 M NaCl)</i>			
	-0.21 ± 0.10 ppb		-0.21
	0.16 ± 0.12 ppb		0.16
	0.05 ± 0.05 ppb		0.05
	0.06 ± 0.05 ppb		0.06
	0.16 ± 0.02 ppb		0.16
	0.22 ± 0.39 ppb		0.22
	0.24 ± 0.18 ppb		0.24
	0.32 ± 0.10 ppb		0.32
	0.59 ± 0.24 ppb		0.59
	0.32 ± 0.11 ppb		0.32
avg ± 1s	0.19 ± 0.21 ppb		
<i>2 ppb standard (DBW, 8/31/92, 0.01 M NaCl)</i>			
	2.24 ± 0.09 ppb		0.24
	2.09 ± 0.07 ppb		0.09
	2.19 ± 0.15 ppb		0.19
	2.14 ± 0.02 ppb		0.14
	1.79 ± 0.21 ppb		-0.21
	1.95 ± 0.11 ppb		-0.05
avg ± 1s	2.07 ± 0.17 ppb		
<i>5 ppb standard (DBW, 8/31/92, 0.01 M NaCl)</i>			
	5.14 ± 0.13 ppb		0.14
	5.42 ± 0.16 ppb		0.42
	4.93 ± 0.06 ppb		-0.07
avg ± 1s	5.16 ± 0.25 ppb		
<i>10 ppb standard (DBW, 8/31/92, 0.01 M NaCl)</i>			
	9.97 ± 0.08 ppb		-0.03
	10.14 ± 0.26 ppb		0.14
	10.16 ± 0.08 ppb		0.16
	9.96 ± 0.14 ppb		-0.04
	9.77 ± 0.21 ppb		-0.23
	9.97 ± 0.02 ppb		-0.03
avg ± 1s	10.00 ± 0.14 ppb		
<i>20 ppb standard (DBW, 8/31/92, 0.01 M NaCl)</i>			
	20.18 ± 0.52 ppb		0.18
	20.04 ± 0.58 ppb		0.04
	20.22 ± 0.43 ppb		0.22
	19.90 ± 0.23 ppb		-0.10
	20.27 ± 0.16 ppb		0.27
	20.39 ± 0.17 ppb		0.39
	20.10 ± 0.03 ppb		0.10
avg ± 1s	20.16 ± 0.16 ppb

1. Scatter appears to be constant over the range 0 – 20 ppb. The weighted average of the standard deviations is 0.18 ppb.
2. The samples near 40 ppb are unusually scattered compared to the others. These data, however, are the only ones that are entirely independent of the calibration curves. The other data all are from standards also used to construct the calibration curves, although those data were not part of the calibration curves.
Neglect the 40 ppb samples, it appears that the observed scatter is about 1% of the measured value for samples > 20 ppb.

Conclusion

The 1-standard-deviation external precision appears to be ±0.2 ppb for samples < 20 ppb or 1% for samples greater than 20 ppb. The 2-s.d. limits shown above are merely these limits doubled.

GFAA Summary – Standards, Samples & Blanks run as QA Samples

I.D.	Conc. (ppb)	Internal Precision	Meas. - Nominal
------	----------------	-----------------------	--------------------

50 ppb standard (DBW, 8/31/92, 0.01 M NaCl)

	50.07 ± 0.20 ppb	0.07
	50.08 ± 0.02 ppb	0.08
	50.10 ± 0.35 ppb	0.10
	49.12 ± 0.09 ppb	-0.88
	50.62 ± 0.15 ppb	0.62
	50.13 ± 0.09 ppb	0.13
	50.02 ± 0.18 ppb	0.02
avg ± 1s	50.02 ± 0.45 ppb	

100 ppb standard (DBW, 8/31/92, 0.01 M NaCl)

	100.77 ± 0.25 ppb	0.77
	97.76 ± 0.02 ppb	-2.24
	101.33 ± 0.12 ppb	1.33
avg ± 1s	99.95 ± 1.92 ppb	

2BIM3-0 from 2nd Ceramic Sampling Cup Breakthrough Experiment

	40.18 ± 0.16 ppb	1.43
	39.13 ± 0.24 ppb	0.38
	39.37 ± 0.11 ppb	0.62
	37.27 ± 0.05 ppb	-1.48
	37.88 ± 0.07 ppb	-0.87
	38.66 ± 0.35 ppb	-0.09
avg ± 1s	38.75 ± 1.05 ppb	

4.90 ppb std. (CSC, 11/16/92, 0.001 M NaCl)

	4.45 ± 0.11 ppb	-0.45
	4.50 ± 0.08 ppb	-0.40
	4.48 ± 0.01 ppb	-0.42
avg ± 1s	4.48 ± 0.03 ppb	

20 ppb standard (CSC, 11/16/92, 0.001 M NaCl)

	19.92 ± 0.08 ppb	-0.08
	20.14 ± 0.23 ppb	0.14
	20.08 ± 0.25 ppb	0.08
avg ± 1s	20.05 ± 0.11 ppb	

50 ppb standard (CSC, 11/16/92, 0.001 M NaCl)

	50.24 ± 0.34 ppb	0.24
	50.73 ± 0.16 ppb	0.73
	50.43 ± 0.01 ppb	0.43
	49.52 ± 0.12 ppb	-0.48
avg ± 1s	50.23 ± 0.51 ppb	

Attachment 4: GFAA for Nickel — A Raw Data Collection Form (2 pages)

GFAA for Ni

Operator: _____

Date: _____

Page 1 of ____

Be sure to note any variations from the standard settings given below!

AAS Settings:		Lamp (Element, #): <u>Ni</u>		Integration time (s): <u>5</u>	
		Current (ma): <u>25</u>		Conc. or Abs?: <u>Conc</u>	
		Lambda (nm): <u>232.0</u>		Peak Area or Ht.?: <u>Area</u>	
		Slit (nm): <u>L 0.2</u>		Energy: _____	
Graphite Furnace Programmer:				Optical Pyrometer: _____	

	Step #	Temp. (°C)	Ramp (s)	Hold (s)	Record	Read (s)	Interrupt Flow
drying	1	110	1	15			
dehydrating	2	250	25	0			
charring	3	1400	10	4	10		
measuring	4	2600	0	6	yes	1	yes
purging	5	2700	1	4	yes		
baseline	6	110	1	9	yes	4	

Run #	Sample ID	Readings:		Sample – Baseline	Exp. factor	Comments
		Sample	Baseline			
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
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16						
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21						
22						
23						
24						
25						
26						
27						

[illegible]

Date:

Page ____ of ____

Run
#

**Sample
ID**

Readings:
Sample

Baseline

**Sample –
Baseline**

Exp. factor	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100

Comments

Attachment 5: [GFAA_FRM.XLW]data — Sample Data-Reduction Worksheet

GFAA-Ni: GFAA_FRM Brief sample description...

#	I.D.	Dil. Ratio	Load (µl)	Sample— Baseline	Exp.	Raw Abs	Abs (corrected)	Conc.	Avg. ± 1 S.E. (ppb)	Comments
1				-0.022	10	<u>-0.002</u>				
2				-0.024	10	<u>-0.002</u>				
3				-0.032	10	<u>-0.003</u>				
4				-0.035	10	<u>-0.004</u>	-0.0006			
5	50	1.00	20	2.338	10	0.234	0.2367	49.9		
6	50	1.00	20	2.373	10	0.237	0.2368	49.9	49.90 ± 0.02	
7	100	1.00	20	4.513	10	0.451	0.4492	110.6		
8	100	1.00	20	4.612	10	0.461	0.4552	112.3	111.47 ± 0.62	
9				0.070	10	0.007	<u>-0.0006</u>			
10				0.004	10	0.000	<u>-0.0015</u>			
11				-0.010	10	-0.001	<u>0.0003</u>			
12	10	1.00	20	0.533	10	0.053	0.0561	10.0		
13	10	1.00	20	0.523	10	0.052	0.0544	9.6	9.81 ± 0.12	
14	41-6	1.02	20	3.738	10	0.374	0.3755	88.4		
15	41-6	1.02	20	3.835	10	0.384	0.3805	89.7	89.06 ± 0.47	
16	41-7	1.02	20	3.461	10	0.346	0.3408	77.9		
17	41-7	1.02	20	3.514	10	0.351	0.3455	79.1	78.49 ± 0.43	
18	41-8	1.02	20	6.324	10	0.632	0.6266	173.1		
19	41-8	1.02	20	6.424	10	0.642	0.6327	175.1	174.13 ± 0.71	
20				0.108	10	0.011	-0.0010			
21	41-8	1.02	20	3.495	10	0.350	0.3457	78.6		
22	41-8	1.02	20	3.520	10	0.352	0.3477	79.0	78.80 ± 0.15	
23	41-8	1.02	20	3.548	10	0.355	0.3502	79.6	79.30 ± 0.20	
24	100	1.00	20	4.701	10	0.470	0.4643	111.9		
25	100	1.00	20	4.778	10	0.478	0.4704	113.7	112.81 ± 0.61	
26				0.096	10	0.010	<u>0.0013</u>			
27				0.022	10	0.002	<u>0.0001</u>			
28				-0.003	10	0.000	<u>0.0009</u>			
29	41-9	1.02	20	1.488	10	0.149	0.1516	29.1		
30	41-9	1.02	20	1.505	10	0.151	0.1512	28.9	29.00 ± 0.05	
31	41-10	1.02	20	1.637	10	0.164	0.1634	31.5		
32	41-10	1.02	20	1.628	10	0.163	0.1618	31.1	31.33 ± 0.14	
33	50	1.00	20	2.494	10	0.249	0.2483	50.2		
34	50	1.00	20	2.515	10	0.252	0.2491	50.3	50.27 ± 0.04	
35	10	1.00	20	0.610	10	0.061	0.0580	9.9		
36	10	1.00	20	0.582	10	0.058	0.0576	9.8	9.86 ± 0.03	
37	5	1.00	20	0.306	10	0.031	0.0314	5.2		
38	5	1.00	20	0.300	10	0.030	0.0318	5.3	5.24 ± 0.02	
39	0	1.00	20	0.063	10	0.006	0.0083	1.3		
40	0	1.00	20	0.043	10	0.004	0.0067	1.1	1.21 ± 0.09	
41	50	1.00	20	2.468	10	0.247	0.2494	49.8		
42	50	1.00	20	2.519	10	0.252	0.2512	50.1	49.94 ± 0.12	
43	41-10	1.02	20	1.534	10	0.153	0.1509	28.2		
44	41-10	1.02	20	1.728	10	0.173	0.1709	32.4	30.33 ± 1.49	
45	41-10	1.02	20	1.604	10	0.160	0.1589	29.8	31.12 ± 0.93	

GFAA-Ni: GFAA_FRM Brief sample description...

#	I.D.	Dil.	Load	Sample- Ratio	Exp. (µl) Baseline	Raw Abs	Abs (corrected)	Conc.	Avg. ± 1 S.E. (ppb)	Comments
46	41-10	1.02	20	1.673	10	0.167	0.1662	31.3	30.55 ± 0.53	
47	41-10	1.02	20	1.712	10	0.171	0.1700	32.1	31.69 ± 0.27	
48	41-10	1.02	20	1.727	10	0.173	0.1714	32.3	32.20 ± 0.09	
49	41-11	1.02	20	0.089	10	0.009	0.0076	1.2		
50	41-11	1.02	20	0.082	10	0.008	0.0092	1.5	1.35 ± 0.09	
51	41-11	1.02	20	0.092	10	0.009	0.0113	1.8	1.66 ± 0.12	
52	41-B1	1.02	20	0.025	10	0.003	0.0051	0.8		
53	41-B1	1.02	20	0.025	10	0.003	0.0052	0.8	0.83 ± 0.00	
54	41-B2	1.02	20	0.018	10	0.002	0.0046	0.7		
55	41-B2	1.02	20	0.024	10	0.002	0.0052	0.8	0.78 ± 0.04	
56	41-B3	1.02	20	-0.005	10	-0.001	0.0023	0.4		
57	41-B3	1.02	20	-0.017	10	-0.002	0.0011	0.2	0.27 ± 0.07	
58				-0.026	10	<u>-0.003</u>	0.0003			
59				-0.031	10	<u>-0.003</u>	-0.0002			
60	0	1.00	20	0.052	10	0.005	0.0081	1.3	1.26	
61	0	1.00	20	0.042	10	0.004	0.0070	1.1	1.17 ± 0.06	
62	5	1.00	20	0.291	10	0.029	0.0318	5.1		
63	5	1.00	20	0.297	10	0.030	0.0321	5.1	5.08 ± 0.01	
64	10	1.00	20	0.569	10	0.057	0.0591	9.6		
65	10	1.00	20	0.592	10	0.059	0.0609	9.9	9.75 ± 0.11	
66	50	1.00	20	2.583	10	0.258	0.2598	50.1		
67	50	1.00	20	2.615	10	0.262	0.2601	50.0	50.05 ± 0.01	
68	100	1.00	20	5.040	10	0.504	0.5012	114.7		
69	100	1.00	20	5.065	10	0.507	0.4995	114.0	114.33 ± 0.24	
70	50	1.00	20	2.693	10	0.269	0.2606	49.9		
71	50	1.00	20	2.667	10	0.267	0.2606	49.8	49.87 ± 0.03	
72				0.036	10	0.004	<u>-0.0009</u>			
73				0.007	10	0.001	<u>0.0008</u>			
74				-0.003	10	0.000	<u>0.0016</u>			
75				-0.006	10	-0.001	0.0022			

Comments on background correction: 0.0030 – root sum of squares of selected Abs

1. Background (raw absorbances with a completely purged empty tube; underlined):

-0.0028

2. Carryover from previous readings is considered to be:

carryover: n-1 1.42% carryover_decay: 0.48

n-2 0.69%

n-3 0.33%

These values minimize the root sum of squares of selected absorbances, which are underlined.

3. Calibration parameters from calibration worksheet:

a 172.1 c 0.00
b 172.2 evap 1.9E-03

4. General comments on samples or standards...

Attachment 6: [GFAA_FRM.XLW]calibration — A Calibration Worksheet

<i>Calibration Worksheet – GFAA FRM</i>							<i>Calibration results</i>																																																																															
<i>Calibration data</i>							a	b	c																																																																													
<table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th>Run</th> <th>Std. Conc.</th> <th>Wght</th> <th>Abs</th> <th>Raw Conc.</th> <th>Conc.</th> <th>Diff.² *wt.</th> </tr> </thead> <tbody> <tr><td>6</td><td>50</td><td>1.00</td><td>0.237</td><td>50.42</td><td>49.90</td><td>0.010</td></tr> <tr><td>13</td><td>10</td><td>1.00</td><td>0.055</td><td>10.04</td><td>9.81</td><td>0.038</td></tr> <tr><td>34</td><td>50</td><td>1.00</td><td>0.249</td><td>53.48</td><td>50.27</td><td>0.072</td></tr> <tr><td>36</td><td>10</td><td>1.00</td><td>0.058</td><td>10.53</td><td>9.86</td><td>0.019</td></tr> <tr><td>38</td><td>5</td><td>1.00</td><td>0.032</td><td>5.61</td><td>5.24</td><td>0.055</td></tr> <tr><td>63</td><td>5</td><td>1.00</td><td>0.032</td><td>5.68</td><td>5.08</td><td>0.006</td></tr> <tr><td>65</td><td>10</td><td>1.00</td><td>0.060</td><td>10.95</td><td>9.75</td><td>0.060</td></tr> <tr><td>67</td><td>50</td><td>1.00</td><td>0.260</td><td>56.39</td><td>50.05</td><td>0.003</td></tr> <tr><td>71</td><td>50</td><td>1.00</td><td>0.261</td><td>56.56</td><td>49.87</td><td>0.018</td></tr> <tr><td colspan="7" style="text-align: right;">sum: 0.280</td></tr> </tbody> </table>							Run	Std. Conc.	Wght	Abs	Raw Conc.	Conc.	Diff. ² *wt.	6	50	1.00	0.237	50.42	49.90	0.010	13	10	1.00	0.055	10.04	9.81	0.038	34	50	1.00	0.249	53.48	50.27	0.072	36	10	1.00	0.058	10.53	9.86	0.019	38	5	1.00	0.032	5.61	5.24	0.055	63	5	1.00	0.032	5.68	5.08	0.006	65	10	1.00	0.060	10.95	9.75	0.060	67	50	1.00	0.260	56.39	50.05	0.003	71	50	1.00	0.261	56.56	49.87	0.018	sum: 0.280							172.1	172.2	0.000
Run	Std. Conc.	Wght	Abs	Raw Conc.	Conc.	Diff. ² *wt.																																																																																
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sum: 0.280																																																																																						
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<div style="border: 1px solid black; padding: 5px; display: inline-block;">Calculate Calibration Curve</div>																																																																																						
<div style="border: 1px solid black; padding: 5px; display: inline-block;">Print</div>																																																																																						
<i>Comments</i> 1. Constants a, b & c are from the quadratic equation: $\text{RawConc} = a \cdot \text{abs}^2 + b \cdot \text{abs} + c.$ 2. Evap is the average concentration drift per run weighted by both the measured concentration and the weighting factor. The final concentration is calculated by: $\text{Conc.} = \text{RawConc} / (1 + \text{run} \cdot \text{evap})$ 3. All constants are calculated using the solver feature of Excel to minimize the sum of the squares of the differences between the given and calculated concentrations.																																																																																						
Evaporation 																																																																																						
Calibration Results: Measured vs. Nominal Concentration 																																																																																						
<i>Assumptions</i> 1. The drift rate is a linear function of run number and concentration. (It is probably due to evaporation from the autosamp vials.) For the evap_rate, the weight of each standard is the product of its concentration and weighting factor. 2. The shape of the calibration curve is constant (it is not a function of run number) and is well-approximated by a parabolic curve. For the parameters a, b, and c, the weight of each standard is proportional to its weighting factor.																																																																																						

Attachment 7:
[GFAA_FRM.XLW]macros—Macros Invoked by Buttons on the
Data and Calibration Worksheets

Calc_cal_curve

```
=CALCULATION(3)
=CALCULATE.NOW()
=SOLVER.OPTIONS(1000,1000,0.0005,FALSE,FALSE,1,1,1,0.05,FALSE)
=ECHO(FALSE)
=SOLVER.OK(!sum,2,0,(!a,!b,!_c,!evap))
=SOLVER.SOLVE()
=CALCULATION(1)
=RETURN()
```

Calc_carryover

```
=CALCULATION(3)
=CALCULATE.NOW()
=SOLVER.OPTIONS(1000,1000,0.1,FALSE,FALSE,1,1,1,0.05,FALSE)
=ECHO(FALSE)
=SOLVER.OK(!sum_of_errors,2,0,(!carryover,!carryover_decay))
=SOLVER.SOLVE()
=CALCULATION(1)
=RETURN()
```

Print

```
=CALCULATE.NOW()
=PRINT()
=RETURN()
```

Attachment 8: AA Raw Data Form

Flame AA Raw Data

Operator: _____ Date: _____ Page 1 of _____

Element: _____ Experiment Title: _____

Settings: Lamp (Element, Position): _____
 Lamp Current (ma): _____
 Wavelength (nm): _____
 High Slit Width (nm): _____
 Energy: _____

Reading Time: _____
 Readings Averaged: _____
 Sample Flow Rate (ml/min): _____

Gases:
 Oxidant: _____ Pressure (approx.) _____ Flow (approx.): _____
 Fuel: _____ Pressure (approx.) _____ Flow (approx.): _____

Run #	Sample ID	Reading (average)	Exp. Factor	Comments
1				
2				
3				
4				
5				
6				
7				
8				
9				
10				
11				
12				
13				
14				
15				
16				
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29				
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31				
32				
33				
34				

Attachment 9: Description of EXCEL 4.0 Example Li Worksheet

The raw Li AAS data is reduced using an EXCEL 4.0 worksheet. Attachment 3 is an example of one such worksheet; sets of standards are run before and after each sample set and fit to separate quadratic curves, the formula of which is given in cells I3 and J3. The concentration of each sample is interpolated from each curve; these two values are then weighted according to the order of the sample in the sample set, and summed to produce a weighted average concentration.

The worksheet can be divided into two parts; those rows dealing with the standards (4-8 and 29-33), and those which deal with the unknowns (15-20).

For the standards:

Column B:

Rows 4-8 and 29-33:
Standards used, in text format.

Column C :

Rows 4-8 and 29-33:
Standards used, in numerical format.

Column D:

Rows 4-8 and 29-33:
Expansion factor for each standard.

Column E:

Rows 4-8 and 29-33:
Recorded absorbance reading for each standard.

Column F (hidden):

Rows 4-8 and 29-33:
Actual absorbance reading (Abs. Rgd. multiplied by the expansion factor).

Column G:

Rows 4-8
Calculated concentrations of the first standard set, using best-fit curve parameters generated by EXCEL Solver. For Row n:

$$G_n = \$J\$4 * F_n^2 + \$J\$5 * F_n + \$J\$6$$

Rows 28-33
Calculated concentrations of the second standard set, using best-fit curve parameters generated by EXCEL Solver. For Row n:

$$G_n = \$J\$29 * F_n^2 + \$J\$30 * F_n + \$J\$31$$

Column H:

Rows 4-8 and 29-33

Squares of the residuals. For Row n:

$$H_n = (G_n - D_n)^2$$

Cells J7 and J32

Square root of the sum of the residuals squared. This is the cell that is minimized using EXCEL Solver to find the best-fit curve for the standard sets.

$$J7 = \text{SUM}(H4:H8)^{0.5}$$

$$J32 = \text{SUM}(H29:H33)^{0.5}$$

Rows 29-33

Squares of the residuals. For Row n:

$$H_n = (G_n - C_n)^2$$

Column I

Rows 4-6 and 29-31

Labels for the best-fit curve parameters.

Column J

Rows 4-8 and 29-33

Numerical values for the best fit curve parameters for standard sets 1 and 2. These are the cells which are allowed to vary while using EXCEL Solver to find the best fit curve for the initial standard sets.

For the unknowns:

Column A

Rows 15-20

Integer value representing the order of the sample in the sample set, starting the numbering with 0.

Column B

Rows 15-20

Weighting of the initial standard set relative to the final in determining the concentration in the sample. For Row n:

$$B_n = 1 - (A_n / \$A\$20)$$

Column C

Rows 15-20

Sample designations.

Column D

Rows 15-20

Expansion factor for samples.

Column E

Rows 15-20

Recorded absorbance reading for each sample.

Column F (hidden)

Rows 15-20

Actual sample absorbance reading (Abs. Rgd. multiplied by the expansion factor).

Column G

Rows 15-20

Calculated concentration for each sample using the standard curve derived from the first standard set. For Row n:

$$G_n = \$J\$4 * F_n^2 + \$J\$5 * F_n + \$J\$6$$

Column H

Rows 15-20

Calculated concentration for each sample using the standard curve derived from the second standard set. For Row n:

$$G_n = \$J\$29 * F_n^2 + \$J\$30 * F_n + \$J\$31$$

Column I

Rows 15-20

Weighted average concentration. For Row n:

$$I_n = G_n * B_n + H_n * (1 - B_n)$$

Attachment 10:

Sample Excel 4.0 Spreadsheet for Reduction of Raw Li Data

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
1	Standard Set 1															
2		1st	Std.	Exp.	Abs.	Actual	Calc	Coefficients								
3		Std	Conc	factor	Rdg.	Abs.	Conc	Residuals	for ax^2+bx+c							
4		Blank	0.0	10	0	0.000	0.014	1.93E-04	a= 0.177							
5		0.1 ppm	0.1	10	0.136	0.014	0.105	2.81E-05	b= 6.720							
6		0.5 ppm	0.5	10	0.667	0.067	0.463	1.38E-03	c= 0.014							
7		1.0 ppm	1.0	10	1.489	0.149	1.018	3.38E-04	rms= 0.044							
8		5.0 ppm	5.0	10	7.28	0.728	5.000	2.11E-07								
9																
10																
11																
12																
13	Run	Wght.		Exp.	Abs.	Actual	Conc.	Conc.	Conc.							
14	#	1st stds	Sample	factor	Rdg.	Abs.	1st stds	2nd stds	(ppm)							
15	0	1.00	5LiBr-10	10	0.015	0.002	0.024	0.024	0.024							
16	1	0.80	5LiBr-13	10	0.012	0.001	0.022	0.022	0.022							
17	2	0.60	5LiBr-15	10	0.074	0.007	0.064	0.058	0.062							
18	3	0.40	5LiBr-17	10	8.108	0.811	5.578	5.818	5.722							
19	4	0.20	5LiBr-16	10	2.369	0.237	1.616	1.482	1.509							
20	5	0.00	5LiBr-14	10	0.012	0.001	0.022	0.022	0.022							
21																
22																
23																
24																
25																
26	Standard Set 2															
27		2nd	Std	Exp.	Abs.	Actual	Calc	Coefficients								
28		Std	Conc.	factor	Rdg.	Abs.	Conc	Residuals	for ax^2+bx+c							
29		Blank	0.0	10	0.001	0.000	0.016	2.58E-04	a= 1.684							
30		0.1 ppm	0.1	10	0.149	0.015	0.102	4.66E-06	b= 5.791							
31		0.5 ppm	0.5	10	0.756	0.076	0.463	1.37E-03	c= 0.015							
32		1.0 ppm	1.0	10	1.654	0.165	1.019	3.79E-04	rms= 0.045							
33		5.0 ppm	5.0	10	7.128	0.713	4.999	3.99E-07

Attachment 11: BR_FORM.XLS -- A Data Collection Form (2 pages)

Bromide analysis using Ion-specific electrode Date: _____ Page 1 of ____
Operator: _____ Experiment title: _____

Br electrode sensitivity check

100 ml H ₂ O +2 ml ISA adjuster	mV reading
+ 1ml 1000 ppm Br:	
+ 10 ml additional 1000 ppm Br:	
Difference (should be 45-60 mV):	

Run #	Sample ID	Dilution	mV reading	Comments:
1				
2				
3				
4				
5				
6				
7				
8				
9				
10				
11				
12				
13				
14				
15				
16				
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40				
41				

Attachment 12:
BR_EX.XLS -- A Sample Data Reduction Worksheet

Operator: _____

Date: _____

Page ____ of ____

[illegible]

Attachment 13: Description of EXCEL 4.0 Example Br Worksheet

The raw Br ion-specific electrode data is reduced using an EXCEL 4.0 worksheet. Attachment 2 is an example of one such worksheet; sets of standards are run before and after each sample set and fit to separate exponential curves, the formula of which is given in cell J1. The concentration of each sample is interpolated from each curve; these two values are then weighted according to the order of the sample in the sample set, and summed to produce a weighted average concentration.

The worksheet can be divided into two parts; those rows dealing with the standards (1-7 and 25-32), and those which deal with the unknowns (10-23).

For the standards:

Column C:

Rows 4-7 and 28-31
Standards used, in text format.

Column D (hidden):

Rows 4-7 and 28-31
Standards used, in numerical format.

Column E:

Rows 4-7 and 28-31
Dilution factor for each standard.

Column F:

Rows 4-7 and 28-31
Recorded millivolt reading for each standard.

Column G:

Rows 4-7
Calculated concentrations of the first standard set, using best-fit curve parameters generated by EXCEL Solver. For Row n:

$$G_n = J\$4 * (F_n / J\$6)^{J\$5} + J\$7$$

Rows 28-31

Calculated concentrations of the second standard set, using best-fit curve parameters generated by EXCEL Solver. For Row n:

$$G_n = J\$28 * (F_n / J\$30)^{J\$29} + J\$31$$

Column H:

Rows 4-7

Squares of the residuals. For Row n:

$$H_n = (G_n - D_n)^2$$

Row 8

Square root of the sum of the residuals squared. This is the cell that is minimized using EXCEL Solver to find the best-fit curve for the first standard set.

$$H_8 = \text{SUM}(H_4:H_7)^{0.5}$$

Rows 28-31

Squares of the residuals. For Row n:

$$H_n = (G_n - D_n)^2$$

Row 32

Square root of the sum of the residuals squared. This is the cell that is minimized using EXCEL Solver to find the best-fit curve for the second standard set.

$$H_{32} = \text{SUM}(H_{28}:H_{31})^{0.5}$$

Column I

Rows 4-7 and 28-31

Labels for the best-fit curve parameters.

Column J

Rows 4-7

Numerical values for the best fit curve parameters for standard set 1. These are the cells which are allowed to vary while using EXCEL Solver to find the best fit curve for the initial standard set.

Rows 28-31

Numerical values for the best fit curve parameters for standard set 2. These are the cells which are allowed to vary while using EXCEL Solver to find the best fit curve for the final standard set.

For the unknowns:

Column A

Rows 12-23

Integer value representing the order of the sample in the sample set, starting the numbering with 0.

Column B

Rows 12-23

Weighting of the initial standard set relative to the final in determining the concentration in the sample. For Row n:

$$B_n = 1 - (A_n / \$A\$23)$$

Column C

Rows 12-23
Sample designations.

Column D (hidden)

Rows 12-23
Empty.

Column E

Rows 12-23
Dilution factor for each sample.

Column F

Rows 12-23
Recorded millivolt reading for each sample.

Column G

Rows 12-23
Calculated concentration for each sample using the standard curve derived from the initial standard set. For Row n:

$$G_n = E_n * \$J\$4 * (F_n / \$J\$6)^{\$J\$5} + \$J\$7$$

Column H

Rows 12-23
Calculated concentration for each sample using the standard curve derived from the final standard set. For Row n:

$$G_n = E_n * \$J\$28 * (F_n / \$J\$30)^{\$J\$29} + \$J\$31$$

Column I

Rows 12-23
Weighted average concentration. For Row n:

$$I_n = G_n * B_n + H_n * (1 - B_n)$$

Other information:

The data points for the best fit curves shown on the graph are in columns K-M (not shown).

Column K

Contains mV values for the best-fit curves. In this example, values ranged from 61 to 148, and using a step size of 3 produced a smooth curve when graphed.

Column L

Calculated calibration curve using the best-fit parameters for standard

set 1. For Row n:

$$Ln = \$J\$4 * (Kn / \$J\$6)^{\$J\$5} + \$J\$7$$

Column M

Calculated calibration curve using the best-fit parameters for standard
set 2. For Row n:

$$Mn = \$J\$28 * (Kn / \$J\$30)^{\$J\$29} + \$J\$31$$

Attachment 14: Triple-Layer Model of Surface Charge for Quartz

Potentiometric titrations measure the adsorption or release of protons by the surfaces present in the reactor. The actual reactions by which protons are exchanged have been modeled extensively in the literature; the triple-layer model of surface-complexation theory is adopted here, as outlined by Yates et al. (1974) and Davis et al. (1978). This model assumes that the surfaces are insoluble and are composed of partially coordinated O^{2-} atoms that behave amphoterically, existing as $-O^-$, $-OH$, or $-OH_2^+$, depending upon solution conditions. Effects of ionic strength are incorporated through the formation of weak ion-pair-like complexes with charged surface sites.

Because quartz has such a low pH_{PZC} , only surface-charge development by proton loss will be considered. This is described by

where K_{a2} is the intrinsic equilibrium constant for this reaction, $-SO$ represents an oxygen at the surface, and $[H_s^+]$ is the H^+ activity at the surface. $[H_s^+]$ differs from the proton activity in the bulk solution because of the electrostatic attraction between the negatively charged surface and the positively charged protons. Protons are assumed to bind exactly at the surface (at zero distance), and the surface-solution interface is assumed to resemble a parallel-plate capacitor, so the proton activity at the surface is related to the measurable bulk proton activity by

$$[H_s^+] = [H^+] \cdot e^{\left(\frac{-e\psi_0}{kT}\right)} , \quad (2)$$

where e is the charge on an electron, ψ_0 is the mean potential at the surface, k is Boltzmann's constant, and T is the absolute temperature.

The degree of ionization of the surface is described by α_- . At low ionic strength, where the proportion of surface sites occupied by electrolyte cations is negligible, one may write

$$\alpha_- = \frac{[-SO^-]}{\sum [-SOX^{\pm n}]} , \text{ and } 1 - \alpha_- = \frac{[-SOH]}{\sum [-SOX^{\pm n}]} , \quad (3)$$

where $\sum [SOX^{\pm n}]$ is the total concentration of surface sites.

The surface charge concentration, σ , may be found by applying the principle of mass balance to the system, along with measurement of pH. Letting $C_{acid} + C_{base}$ denote the net concentration of acid and base added to the system, and neglecting the difference between activities and concentrations,

$$\sigma = C_{acid} + C_{base} - [H^+] + [OH^-] . \quad (4)$$

Now, α_- may be calculated directly from the experimentally measurable surface charge, σ :

$$\alpha_- = \frac{-\sigma}{N_s} \quad (5)$$

Substituting α_- into the expression for K_{a2} {eqn. 6.1} gives

$$K_{a2} = \frac{\alpha_- \cdot [H^+]}{1 - \alpha_-} \cdot e^{\left(\frac{-e\psi_0}{kT}\right)} \quad , \text{ or } \quad pK_{a2} = pH - \log \frac{\alpha_-}{1 - \alpha_-} + \frac{e\psi_0}{2.3kT} \quad (6)$$

Operationally, it is useful to define an apparent equilibrium constant, Q_{a2} , for surface ionization based only on observable quantities:

$$Q_{a2} = \frac{[-SO^-][H^+]}{[-SOH]} = \frac{\alpha_- \cdot [H^+]}{1 - \alpha_-} \quad \text{or} \quad pQ_{a2} = pH - \log \frac{\alpha_-}{1 - \alpha_-} \quad (7)$$

Note that Eqs. 6 and 7 differ only by the electrostatic term, which is itself a function of the degree of surface ionization. At zero net surface charge ($\alpha_- = 0$, $\psi_0 = 0$), the electrostatic term equals zero, so that $pK_{a2} = pQ_{a2}$. Recall also that the expression for α_- (Eq. 3) is strictly valid only when ionic strength equals zero. Extrapolation to these conditions from real titration data is covered in the next section.

The electrolyte-cation-association equilibrium constant, K_{Na} , is described in similar terms. Here, the reaction is assumed to be ion exchange, with Na^+ replacing H^+ at the surface:

A crucial difference lies in the closeness of approach of the two cations, however. Protons are assumed to form complexes at zero distance from the surface, whereas Na^+ can only approach the surface at some distance β because of steric hindrances from its waters of hydration. The Na^+ activity at β relative to the bulk solution is given by

$$[Na_s^+] = [Na^+] \cdot e^{\left(\frac{-e\psi_\beta}{kT}\right)} \quad (9)$$

At high Na^+ concentrations (~ 1 M), essentially all ionized surface sites are complexed with Na^+ . Thus the degree of ionization, α_- , becomes (at zero net surface charge)

$$\alpha_- = \frac{[-SO^-Na^+]}{\sum [-SOX^{\pm x}]} \quad , \text{ and } \quad -\alpha_- = \frac{[-SOH]}{\sum [-SOX^{\pm x}]} \quad (10)$$

Strictly, this is true only at zero net surface charge, where any sites not occupied by Na^+ will be occupied by H^+ . The concentrations of other surface species (e.g., $-\text{SOH}_2$, $-\text{SO}^-$) are negligible in comparison.

Substituting Eqs. 6.2, 6.8, and 6.9 into 6.7 yields

$$K_{\text{Na}} = \frac{\alpha_- \cdot [\text{H}^+]}{1 - \alpha_- \cdot [\text{Na}^+]} \cdot e^{\left(\frac{e\psi_\beta - e\psi_0}{kT}\right)}, \text{ or } pK_{a2} = \text{pH} - \log \frac{\alpha_-}{1 - \alpha_-} + \log[\text{Na}^+] + \frac{e\psi_\beta - e\psi_0}{2.3 kT} \quad (11)$$

An apparent stability constant, Q_{Na} , is defined for operational convenience based solely on observable quantities:

$$Q_{\text{Na}} = \frac{[-\text{SO}^-\text{Na}^+][\text{H}^+]}{[-\text{SOH}][\text{Na}^+]} = \frac{\alpha_- \cdot [\text{H}^+]}{(1 - \alpha_-) \cdot [\text{Na}^+]}, \text{ or } pQ_{\text{Na}} = \text{pH} - \log \frac{\alpha_-}{1 - \alpha_-} + \log[\text{Na}^+] \quad (12)$$

Again, Eqs. 6.10 and 6.11 differ only by the electrostatic term, so that at zero net surface charge ($\alpha_- = 0$, $\psi_0 = 0$), the electrostatic term equals zero, and that $pK_{\text{Na}} = pQ_{\text{Na}}$. Recall also that the expression for α_- (Eq. 3) is strictly valid only at zero net surface charge. Extrapolation to this condition from real titration data is covered in the next section.

References Cited

- Davis, J. A., R. O. James, and J. O. Leckie, 1978: "Surface Ionization and Complexation at the Oxide-Water Interface, 1. Computation of Electrical Double Layer Properties in Simple Electrolytes," *Journal of Colloid and Interface Science*, **63**, (3), 480-499.
- Yates, D. E., S. Levine, and T. W. Healy, 1974: "Site Binding Model of the Electrical Double Layer at the Oxide-Water Interface," *Journal of the Chemical Society of London Faraday Transactions*, **70**, 1807-1818.

Attachment 15: Saturated Column Setup Form

[illegible]

Attachment 16: Unsaturated Column Setup Form

[illegible]

Attachment 17: Column Saturation Curve Setup Form

[illegible]

Appendix F

Adsorption of Ni, Li, and Br by Synthetic Materials Used in the Caisson Tests

D. B. Ward, W. C. Cheng, M. D. Siegel, and C. R. Bryan

F-2

F.1 Adsorption on Plastics Containers

Ni adsorption on several plastics [low-density polyethylene (LDPE), polypropylene (PP), polyallomar (PA), and polycarbonate (PC)] has been investigated as a function of pH in three studies. In the first study, which simulated static storage of raw samples, two samples of effluent from a Wedron 510 sand column containing initial concentrations of 1.0 and 4.6 ng/ml Ni ($1.7 \cdot 10^{-8}$ and $7.8 \cdot 10^{-8}$ M) were spiked with 5 or 50 ng/ml Ni, and aliquots were equilibrated for two days in LDPE bottles (both new and acid-washed). Some concentration-dependent adsorption occurred, amounting to 7% and 3% at final Ni concentrations of 5 – 10 ng/ml ($8.5 - 17 \cdot 10^{-8}$ M) and 45 – 50 ng/ml ($7.7 - 8.5 \cdot 10^{-7}$ M), respectively.

In the second study, which was designed to maximize the effect of any adsorption phenomena, small aliquots of 0.01 M NaCl containing either 5 or 50 ng/ml Ni were equilibrated in large containers for nine days with continuous agitation. Container materials included PP, PA, and PC, and solution pH was adjusted to cover the range 5–9. The results are illustrated in Figure F.1. No adsorption was evident for PP and PA containers at pH < 6 or for PC containers at pH < 5. Adsorption increased steadily with increasing pH from ~10% at pH 7 to > 80% at pH 9.5. At pH > 9, only the samples spiked with 5 ng/ml Ni provided adsorption data; the 50 ng/ml samples exceeded the solubility of $\text{Ni}(\text{OH})_2$ at these pHs.

The third study used the same PC and PA containers used in the adsorption experiments, and the same electrolyte volume (20 ml), concentration (0.001M NaCl), and equilibration time (3 days). Samples from pH 4 to 10 were spiked with 5 or 100 ng/ml Ni, allowed to equilibrate, and then filtered and sampled. The results were similar for both tube types, and agreed those of the previous study; adsorption was negligible below pH 6, about 10% at pH 7, and then increased dramatically to >80% at pH 9.5 to 10.

Desorption was investigated in both studies by acidifying the equilibrated samples to 1% HNO_3 , re-equilibrating for five days with continuous agitation, and then comparing the final with the initial Ni concentrations. Adsorption appears to be fully reversible for samples originally at pH 8 or less before acidification (Figure F.1). At higher original pH values, the data are equivocal; some irreversible adsorption may occur.

A long-term storage experiment involving acidified samples was also carried out. Samples of 0.01 M NaCl were spiked with 0, 5, or 50 ng/ml Ni, acidified to 1% HNO_3 , and placed in LDPE bottles for storage. The solutions were sampled periodically, over a period of 108 days. Sample variation was somewhat larger than expected, but was non-systematic, suggesting that adsorption onto container walls was not significant.

Although each of the plastics becomes a significant adsorber of Ni under neutral and alkaline conditions, the surface area of the centrifuge tubes used in the adsorption experiments ($\sim 0.009 \text{ m}^2$) is negligible relative to that of the sand used ($\sim 2.4 \text{ m}^2$), so the tubes are unlikely to have a measurable effect on K_{ds} determined using this method. All of the plastics are suitable for use as geochemical sampling vessels for acidified solutions. Acidification need not be immediate, as Ni is readily stripped from the vessel walls by 1% HNO_3 .

Figure F.1 Stability of aqueous Ni in polypropylene, polyallomar, and polycarbonate containers

F.2 Adsorption of Li, Ni, and Br by Ceramic and Hollow Fiber Samplers

The uptake of tracers by the hollow-fiber dialysis tubing and high-flow ceramic samplers was evaluated. Dialysis tubing has been used in previous Los Alamos caisson experiments. Because of concerns that the tubing will collapse under high extraction suctions, the ceramic cups were also considered for this experiment. Batch adsorption tests were carried out using approximately 3 g of tubing and 30 ml 0.01 M NaCl solution, containing 50 ng/ml Ni, 10 µg/ml Li, and 1 µg/ml Br. Samples were agitated for 1 day. The equilibrium pH was 5.8 and adsorption of the tracers was negligible.

Adsorption of Ni, Br, and Li onto Soil Moisture B1M3 ceramic samplers was measured in batch and flow-through experiments. Batch experiments were carried out on a ceramic sampler that had been ground to <200 mms, and pre-equilibrated for 18 hours in 0.01 M NaCl electrolyte in 40 ml PC centrifuge tubes. No attempt was made to control the pH; using a solution:solid ratio of 9 ml/g, the equilibrium pH was 8.3. Sufficient tracer solutions were added together to the centrifuge tubes to yield initial concentrations of 50 ng/ml ($8.5 \cdot 10^{-7}$ M) Ni, 10 mg/ml ($1.4 \cdot 10^{-3}$ M) Li, and 1 mg/ml Br, respectively. The centrifuge tubes were agitated on hematology mixers for 2 days, and the centrifuged (11,000 rpm for 10 minutes). The supernatant was collected and analyzed for the tracers

as described in Appendix E. The K_d 's measured for Ni, Br and Li were 61, -6, and -4 ml/g respectively. The negative K_d 's may indicate leaching of tracers from the ceramic samplers.

Three flow-through experiments were carried out under atmospheric conditions in which 0.01 M NaCl solutions with nominal concentrations of 50 ng/ml Ni ($8.5 \cdot 10^{-7}$ M), 1 mg/ml Li ($1.4 \cdot 10^{-4}$ M) and 7.3 mg/ml Br ($9.1 \cdot 10^{-5}$ M) were drawn through a B1M3 ceramic sampler at 0.35 ml/min. In the first and second experiments, attempts were made to buffer the pH at near neutral and alkaline values with sodium borate buffer, using 10 and 4 mg/ml B solutions, respectively; in the third experiment, the pH was controlled by atmospheric CO_2 and the properties of the ceramic sampler. The pH in the first experiment stayed constant at 8.8; in the second and third experiments, it decreased from 7.6 to 7.3 and 7.2 to 6.5, respectively, as atmospheric CO_2 diffused into the solutions.

Breakthrough curves for Li and Br from the first experiment are shown in Figure F.2. For both elements, breakthrough (defined at $C/C_0 = 100\%$) was achieved after 50 ml of solution had been eluted. The final concentrations were from 5 to 10% higher than that of the feed solution. This may be due to evaporation during the time required for analysis; alternatively, tracer elements may be leaching from the ceramic cup.

Figure F.2. Li and Br breakthrough curves for flow through B1M3 ceramic sampler

Ni breakthrough curves for pH 6.5 and 7.4 from the second and third experiments are shown in Figure F.3. In each case, breakthrough ($C/C_0 = 100\%$) was not reached until approximately 1000 ml of solution had passed through the ceramic sampler. The concentration of Ni in the feed reservoir was measured at the end of the experiment and found to be 40 ng/ml rather than the expected value of 50 ng/ml. The reason for this discrepancy is unknown but may be experimental error or adsorption of Ni by the glass reservoir vessel.

The results of the batch and flow-through tracer tests indicate that the B1M3 ceramic cups would not be suitable solution samplers for Ni tracer studies. Ni adsorption by the

electrodialysis tubing is negligible, therefore this material will be used to study Ni migration in the caisson. The batch and flow-through experiments indicate that Br and Li are not adsorbed by the ceramic cups; however, there is some evidence that these elements may be leached from this material. Solutions obtained with the ceramic cups will be analysed for Br and Li; but additional samples will be collected with the dialysis tubing and analysed for these tracers.

Figure F.3. Ni breakthrough curves for flow through B1M3 ceramic sampler

YUCCA MOUNTAIN SITE CHARACTERIZATION PROJECT

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