

**THE EVALUATION OF URANIUM DISTRIBUTION COEFFICIENTS
IN UNSATURATED MEDIA**

by

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and

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ABSTRACT

The success of the Yucca Mountain Performance Assessment and other similar studies requires the ability to satisfactorily model the adsorption of radionuclides in unsaturated media. The main objectives of this research were to: 1) develop methods to control the pH and saturation level for unsaturated samples., 2) evaluate possible methods to measure sorption for unsaturated, porous media, and 3) perform preliminary studies on the adsorption of uranium for saturated and unsaturated media.

Uniform saturation levels were maintained in the samples by mixing them in a Turbula™ mixer. The vacuum extraction method allowed uranium sorption to be examined for samples with saturation levels above 50%. Isotopic differentiation was found to work in principle, but difficult to perform in practice. This was because the results were very dependent on matching the pH of the pore and flushing solutions. Pretreating and cleaning the sand improved the stability of the pH, but pH drifts with time were not completely eliminated.

Preliminary experiments examined the uranium distribution coefficient as a function of saturation level using both vacuum extraction and isotopic differentiation. No noticeable change was seen for saturation levels between 50 and 100%. Both uranium adsorption and desorption (in response to dilution) were found to occur in significant amounts within one minute. No consistent effect, however, was seen on the isotopic differentiation results when the uranium concentrations in the flushing solution were varied.

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TABLE OF CONTENTS

	<u>Page</u>
Title Page	1
Abstract	2
Acknowledgments	3
Table of Contents	4
List of Figures	7
List of Tables	8
Chapter 1 Introduction	10
1.1 Yucca Mountain Performance Assessment	10
1.2 Experimental Sorption Methods	11
1.3 Objectives of Thesis	12
Chapter 2 Methods and Materials	13
2.1 Materials	13
2.1.1 Reagents	13
2.1.2 Wedron 510 Sand	13
2.1.3 Electrolyte Solution	14
2.2 Analytical Methods	15
2.2.1 Uranium Analysis	15
2.2.1.1 Atomic Emission Spectroscopy	15
2.2.1.2 Neutron Activation and Uranium Fission	16
2.2.2 pH Measurements	20
2.2.2.1 pH Measurement Equipment	20
2.2.2.2 pH Measurement of Unsaturated Sand	20
Chapter 3 Uranium Solubility Modeling	22
3.1 Use of HYDRAQL	22
3.2 Solubility Results	23
Chapter 4 Control of Experimental Parameters	26
4.1 Sand Moisture Content Distribution	26
4.2 pH Control of Unsaturated Samples	28
4.2.1 Sand and Solution Pretreatment	28
4.2.2 Sand Cleaning	29
4.2.3 pH drift	31

TABLE OF CONTENTS (cont.)

	<u>Page</u>
Chapter 5 Batch Sorption Experiments	34
5.1 Losses of Uranium Due to Equipment Sorption	34
5.1.1 Loss of Uranium Due to Sorption to Container Walls	34
5.1.2 Uranium Losses to Other Equipment	35
5.2 Vacuum Extraction	35
5.2.1 Method Description	35
5.2.2 Removal Efficiency	37
5.2.3 Evaporation	38
5.2.4 Temperature Changes	40
5.2.5 Concentration Versus Extraction Time	40
5.3 Isotopic Differentiation	43
5.3.1 Method description	43
5.3.2 Formula Derivation for K_d	43
5.3.3 Sorption Kinetics	47
5.3.3.1 Saturated Samples	47
5.3.3.2 Sorption During Extraction	49
5.3.4 Desorption Kinetics	50
5.3.4.1 Saturated Samples	50
5.3.4.2 Desorption During Flushing	52
5.3.4.3 Implication of Results	53
5.3.5 Effect of Flushing Uranium Concentration and pH	54
5.3.6 Analysis of Sand	56
Chapter 6 Uranium Adsorption Versus Saturation Level	59
Chapter 7 Conclusions	62
Chapter 8 Recommendations for Future Work	64
Chapter 9 References	66
Appendix A: Surface Complexation	69
A.1 Acid-Base Chemistry of Oxides	70
A.2 Surface Charge	71
A.3 Surface Potential and Double Layer Theory	72
A.4 Metal and Ligand Adsorption	72
A.5 References	73

TABLE OF CONTENTS (cont.)

	<u>Page</u>
Appendix B: Uranium Chemistry	74
B.1 Solubility and Complexation	75
B.2 Uranium Adsorption	78
B.3 References	80
Appendix C: Generic Procedures	82
C.1 Saturated Sorption Experiments	83
C.2 Unsaturated Sorption Experiments	84
C.3 Isotopic Differentiation Sorption Experiments	86
C.4 Equipment Cleaning	89
Appendix D: Dye and Additional Moisture Distribution Tests	90
D.1 Dye Tests	91
D.2 Unsaturated Sand Sample Preparation	91
Appendix E: Titration Curve Experiments	93
Appendix F: Pressurized Gas Extraction and Column Displacement	98
F.1 Pressurized Gas Extraction	99
F.2 Column Displacement	99
Appendix G: Miscellaneous Data	101

LIST OF FIGURES

	<u>Page</u>	
Fig. 3.1	Uranium Solubility vs. pH	24
Fig. 3.2	Uranium Speciation at pH = 6.00	25
Fig. 3.3	Uranium Speciation at pH = 8.00	25
Fig. 4.1	pH Drift vs. Time for Closed Batch Samples	31
Fig. 5.1	Equipment Setup for Vacuum Extraction Method	36
Fig. 5.2	Evaporation vs. Extraction Time	39
Fig. 5.3	Temperature Change of Wet Sand During Extraction	41
Fig. 5.4	Isotopic Differentiation Process	44
Fig. 5.5	Uranium Sorption Kinetics	48
Fig. 5.6	Uranium Desorption Kinetics	51
Fig. 6.1	Uranium Sorption vs. Saturation Level for Cleaned Wedron 510 Sand and 0.1 M KCl	61
Fig. B.1	Potential-pH Diagrams for Uranium/Water and Uranium/Groundwater Systems at 25° C	75
Fig. B.2	Distribution of Uranyl-hydroxy and Carbonate Complexes vs. pH for $PCO_2 = 10^{-2}$ atm and $\Sigma U = 10^{-8}$ M at 25° C	76
Fig. B.3	Distribution of Uranyl Complexes vs. pH for Some Typical Ligand Concentrations in Ground Waters	77
Fig. B.4	The Solubility of Uraninite, UO_2 at pH = 8 and 25° C as a Function of Eh and PCO_2	78
Fig. E.1	Potentiometric Titration Curve	96
Fig. E.2	Normalized Titration Curve	97

LIST OF TABLES

	<u>Page</u>
Table 2.1 Uranium Isotope Weight % in U ₃ O ₈	13
Table 2.2 Chemical Analysis of Wedron 510 Sand	14
Table 2.3 Sieve Results for Wedron 510 Sand	14
Table 2.4 Matrix Effects of NaCl and HNO ₃	16
Table 2.5 Fission Product Data	17
Table 2.6 Comparison of Uranium Concentrations Determined by Different Fission Products	20
Table 3.1 HYDRAQL Recipe	22
Table 4.1 Comparison of Fresh and Clean Sand Solution Chemistry	30
Table 4.2 pH Changes with Preparation Time	32
Table 5.1 Container Sorption Losses	34
Table 5.2 Comparison of Removal Rates	37
Table 5.3 Extraction Efficiency for a Constant Sand Mass and Varying Saturation Levels Using a 10 cm dia. Buechner Funnel	38
Table 5.4 Extraction Efficiency for a Constant Saturation Level and Varying Sample Sizes Using a 10 cm dia. Buechner Funnel	38
Table 5.5 Uranium Concentration vs. Extraction Time	42
Table 5.6 Time Dependence of pH and Sorption	48
Table 5.7 Uranium Desorption in Response to Flushing with 0.1 M NaCl Solution at pH = 5.7	52
Table 5.8 Uranium Desorption in Response to Flushing with 0.1 M NaCl Solution at pH = 8.2	53
Table 5.9 Pore Solution Total Uranium Concentration vs. Flushing Solution U Concentration	55
Table 5.10 Uranium Concentration and pH vs. Sample Preparation Order	56
Table 5.11 Comparison of the Calculated Amount of Uranium Sorbed Determined from the Sand and Solution Uranium Concentrations	57
Table 6.1 Uranium Sorption onto Pretreated Wedron 510 Sand vs. Saturation Level I	59
Table 6.2 Uranium Sorption onto Cleaned, Pretreated Wedron 510 Sand vs. Saturation Level II	60
Table B.1 Equilibrium Constants for Uranium at 25° C	76
Table G.1 HYDRAQL Uranium Solubility Data from Figure 3.1	102
Table G.2 Saturation Levels in 50 ml Polystyrene Tubes	103

LIST OF TABLES (cont.)

	<u>Page</u>
Table G.3 Saturation Levels in 50 ml Polystyrene Tubes and Comparison of Estimated and Actual Saturation Levels	103
Table G.4 Saturation Levels in 50 ml Polycarbonate Tubes and Comparison of Estimated and Actual Saturation Levels	104
Table G.5 Desorption Data from Figure 5.6	104
Table G.6 Titration Data for Appendix E	105

CHAPTER 1 INTRODUCTION

1.1 Yucca Mountain Performance Assessment

Yucca Mountain, Nevada is currently being evaluated as a possible site for the nation's high-level radioactive waste repository. Both the Nuclear Regulatory Commission and the Environmental Protection Agency have imposed limitations on radionuclide releases to the environment. In order to satisfy these criteria, the geochemistry of the site must be studied to determine the effectiveness of the natural barriers present which can inhibit radionuclide migration. Sorption is a broad term which encompasses a variety of physical and chemical interactions between the radionuclide and the rock which can retard the transport of the chemical.

Possible sorption mechanisms appropriate to the Yucca Mountain site include (1) ion exchange on minerals such as clays and zeolites; (2) surface complexation reactions on iron and manganese oxides and oxyhydroxides, framework silicates such as quartz and feldspar, and possibly phosphates and carbonates; and (3) precipitation in solid solutions of carbonates, phosphate, or other low temperature minerals [Patera 1990]. A distribution coefficient is used to describe the ratio of the chemical's concentration on the solid to the concentration in solution. The traditional approach to sorption has been the use of a single distribution coefficient (K_d) to represent linear adsorption and desorption processes in order to calculate a retardation factor (R_f). This K_d did not account for any of the other sorption processes and did not account for many of the variations in chemistry and geology in experiments. Surface complexation models attempt to take into account these differences by determining various reaction constants and physical parameter values. In order to determine these values, experiments must be performed to measure the distribution of a chemical between the aqueous and solid phases under a range of mechanistic parameter variations.

1.2 Experimental Sorption Methods

Experimental sorption studies have historically been either batch sorption studies or dynamic column experiments. These experiments were generally performed under saturated conditions and assumed to be applicable for Yucca Mountain, although the site is to be located in the unsaturated zone. The level of hydrologic saturation can affect the ionic strength, pH, and redox potential, which, in turn, can affect sorption. In addition, the presence of the gas phase may affect the amount of wetting occurring on the solid's surface [Turner 1991]. Available data on the chemistry of unsaturated zone waters from Yucca Mountain suggest these waters have higher ionic strengths (total dissolved solid contents) than do waters common to the saturated zone [Meijer 1990].

The sorption experiments which study the effects of variable saturation use unsaturated columns. Eichholz, Petelka, and Whang [1990] and Gaudet *et al* [1977] achieved steady unsaturated flow by applying a controlled suction at the base of a column for a constant flux of solution. While this is a simple method which can be used for various degrees of saturation, it can take a very long time to attain steady-state conditions because normal gravity does not provide a large enough driving force relative to the low hydraulic conductivities that characterize highly unsaturated conditions. Conca and Wright [1991] have used an Unsaturated Flow Apparatus which uses an ultracentrifuge with an ultralow constant flow pump to apply solution for studies of unsaturated soil, gravel and whole rock. This method is, however, very expensive and designed for very low moisture contents.

McWhorter and Nazareth [1983] describe methods to extract pore solution for analysis. The use of suction through a porous membrane is effective only for relatively wet porous media. Pressurized gas can displace the solution through a porous membrane from a somewhat drier medium. For even drier porous media, linear displacement by an invading solution (such as distilled water) can be used to extract the pore solution. If the column is

sufficiently long, the first amount of effluent released should consist of undiluted antecedent pore solution.

1.3 Objectives of Thesis

The success of the Yucca Mountain Performance Assessment and other similar studies requires the ability to satisfactorily model the adsorption of radionuclides in unsaturated media. Experiments need to be performed to either verify that sorption behavior is the same under both saturated and unsaturated conditions or to quantify these differences. These experiments require a relatively simple, fast, and inexpensive method to measure the sorption of chemicals for unsaturated media. The objectives of this study were to:

1. Develop methods to control the saturation level for unsaturated samples.
2. Evaluate possible methods to measure sorption for unsaturated, porous media and determine which of the methods investigated provided the most accurate results.
3. Perform preliminary studies on the adsorption of uranium for saturated and unsaturated media.
4. Although not an original objective, it became necessary to develop methods to control the pH of unsaturated samples.

CHAPTER 2 METHODS AND MATERIALS

2.1 Materials

2.1.1 REAGENTS

General uranium solutions were prepared by diluting a certified ($1000 \pm 0.5\%$ ppm in 2% HNO_3) inductively coupled plasma (ICP) atomic emission spectroscopy uranium standard (PlasmaChem Associates, Inc.). The isotopically enriched uranium solutions were made from certified solid U_3O_8 samples (U. S. DOE New Brunswick Laboratory) which were dissolved in nitric acid. These samples had the isotopic distribution shown below. Analytical reagent grade chemicals were used for pH adjustments and background electrolyte solutions. Deionized water was used for all solutions.

Table 2.1: Uranium Isotope Weight % in U_3O_8

Standard	^{234}U	^{235}U	^{236}U	^{238}U
U-235	0.7735%	90.098%	0.3337%	8.795%
U-238	0.00016	0.01733	<0.00001	99.9823

2.1.2 WEDRON 510 SAND

The solid examined in this experiment was a commercially available quartz sand (Wedron 510, unwashed and unsieved). Wedron sand was used because its hydrologic and sorptive properties have been extensively studied. Siegel *et al* [1993] described mineralogical analysis, bulk composition and surface leaching experiments, and potentiometric surface titrations performed with Wedron 510 sand. The bulk chemistry and mineralogy suggested that the sand was predominately quartz, but surface studies indicated the presence of small amounts of carbonate, kaolinite, and iron oxyhydroxides. Chemical analyses of the bulk chemical samples and surface leachates from an unsieved sample are shown in Table 2.2 while the size analysis obtained by dry sieving is shown in Table 2.3. The sand porosity was 0.38 and the moisture content at saturation

was 0.34 [Siegel *et al* 1992]. Precise density measurements of the sand were complicated by the fact that the sand packed tighter when wetted. The bulk density used for the sand in all calculations was 1.76 g/cm³

Table 2.2: Chemical Analysis of Wedron 510 Sand

ELEMENT	BULK CONCENTRATION	SURFACE CONC.
Li	1.54 µg/g	0.05 µg/g
Na	1.67	<0.20
Mg	24.7	10.92
Al	2820	482
Si	*	5.4
K	2.52	0.51
Ca	55	23
Ti	83.1	2.55
Fe	242	80.0
Ni	0.18	0.14
Br	1.68	* *

*SiO₂ content was ≈ 100%.

**Analysis not reliable due to contamination.

Table 2.3: Sieve Results for Wedron 510 Sand

U.S. Sieve #	Size Fraction	Weight % of Total
50	fr.>295 mm	8.91
70	295 mm>fr.>212 mm	39.55
100	212 mm>fr.>150 mm	27.74
140	150 mm>fr.>106 mm	16.63
200	106 mm>fr.>74 mm	6.42
Pan	74 mm>fr.	0.75

2.1.3 ELECTROLYTE SOLUTION

The electrolytes used in the experiments were NaCl and KCl. The electrolyte concentration used for most of the experiments was 0.1 M, but 0.01 M was used in some of the early experiments. The higher concentration was needed because the low liquid/solid ratio of unsaturated samples required a large amount of acid or base to be

added during titrations which could affect the overall ionic strength of the sample.

Sodium chloride is commonly used in adsorption experiments and was used for the samples which were analyzed with the ICP. Sodium does, however, have a large neutron absorption cross-section, 0.53 b, and is strongly activated. Na-24 has a half-life of 15 hours and decays with 2.75 and 1.37 MeV gamma rays. The higher energy gamma ray produces a large Compton edge which can obscure isotopes with lower energy gamma rays. Potassium chloride was used for the samples which were analyzed with neutron activation because potassium has lower energy gamma rays and is less radioactive after irradiation. Both K-39 (93.08%, 2.1 b) and K-41 (6.91%, 1.5 b) have higher cross-sections than Na-23, but K-40 ($T_{1/2} = 1.28 \times 10^9$ years, 1.46 MeV γ 11%) and K-42 ($T_{1/2} = 12.42$ hours, 1.52 MeV γ 18%) produce gamma rays with lower energies and result in less activity than sodium [U. S. Dept. of Health, Education, and Welfare 1970].

2.2 Analytical Methods

2.2.1 URANIUM ANALYSIS

2.2.1.1 Atomic Emission Spectroscopy

Uranium solution concentrations were determined with a inductively coupled plasma (ICP) atomic emission spectrophotometer (Spectro Analytical Instruments Model FMD-07). A cross-flow nebulizer was used in early experiments, but most of samples were analyzed using an ultrasonic nebulizer which decreased the lower limit of detection to approximately 30 ppb. The concentration of each sample was measured seven times and the relative standard deviation was better than 2.5% over the range of 0.1 to 15 ppm.

The ICP is very sensitive to the amount of NaCl and HNO₃ in the sample and standards. Table 2.4 shows how the readings increased with decreasing NaCl and HNO₃ concentrations. The analyzed

samples consisted of 10 ml of the original sample solution (or diluted to 10 ml with 0.1 M NaCl if 10 ml was not available) and 1 ml of 22% HNO₃.

Table 2.4: Matrix Effects of NaCl and HNO₃

Uranium Conc.	NaCl	HNO ₃ *	Error†
1 ppm	0.091 M	2.0%	0%
1 ppm	0.090	0.1	+4
5 ppm	0.091	2.0	0
5 ppm	0.090	0.1	+10
5 ppm	0.010	0.1	+21
10 ppm	0.091	2.0	0
10 ppm	0.090	0.1	+7
10 ppm	0.020	0.1	+15
Actual Samples	0.091	2.0	N/A

*Does not include the HNO₃ from the diluted U standard (~ 0.02% for 10 ppm)

†Relative to 0.091 M NaCl and 2.0% HNO₃.

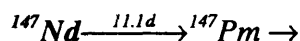
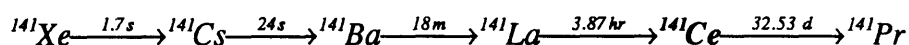
The ICP's data reduction program was not used because detector drift was usually significant enough (>5%) to invalidate the calibration curve within 30 minutes. Instead, the raw readings were printed out and the data analyzed with an Excel spreadsheet program. Upper and lower bounding standards were measured after every four or five samples. The average reading for each standard was taken using the readings immediately before and after the group of samples. The samples' readings were then interpolated between the standards' averages to find the concentration of each sample. While this method was time consuming, it provided the most consistent results.

2.2.1.2 Neutron Activation and Uranium Fission

Exposing natural, stable isotopes to a flux of thermal neutrons often causes the isotopes to become activated. The decay of this radioactive isotope allows the initial concentration of the natural

isotope to be determined. The ^{238}U concentration was determined by observing the decay of the neutron capture product ^{239}U into ^{239}Np .

^{235}U undergoes fission when it is exposed to thermal neutrons. The activity of the resulting fission products and their daughters were used to calculate the initial ^{235}U concentration. The following decay chains were used for determining the ^{235}U concentrations: [Bennett 1966, Walker 1973]



The isotopes whose activities were examined are shown in boldface. These radioisotopes were used because their half-lives were long enough that shorter-lived isotopes could completely decay away, yet still have enough activity to produce a statistically significant peak on the detector. In addition, standards were available for these elements which allowed their absolute full energy peak efficiencies to be determined for the Ge(Li) detector. Because the decay or irradiation time was much longer than the parent's half-life, the decay time of the parent was ignored and the daughter product assumed to be formed directly. Table 2.5 lists isotopic information used in the calculations [U.S. Dept. of Health, Education, and Welfare 1970]:

Table 2.5: Fission Product Data

Fission Product	γ-ray Energy	Half-life	γ-ray Decay %	°Fission Yield	†Isotopic Abundance	†Absorption Cross-section
Ce-143	293 keV	33 hr	46%	6.2 %	11.07%	0.96 b
La-140	487	40.23 hr	40	6.36*	99.91	9.0
La-140	1596	40.23 hr	96	6.36*	99.91	9.0
Nd-147	91	11.1 d	28	2.36	17.19	1.4

° This is the cumulative yield. Assumed to be formed directly.

* Ba-140

† Natural isotope which becomes activated

The efficiency of the detector was determined by irradiating samples containing the elements of interest and examining their full energy peaks [Tsoulfanidis 1983].

$$\epsilon = \frac{P_k A_i \lambda}{m a_i N_A e_k \sigma_i \phi (1 - e^{-\lambda t_0}) (e^{-\lambda t_1} - e^{-\lambda t_2})}$$

where:

- ϵ = absolute full energy peak detector efficiency at energy E_k
- P_k = net number of counts under the peak
- A_i = atomic mass of element i
- λ = decay constant of radioisotope produced
- m = mass of the element of interest
- a_i = weight fraction of isotope
- N_A = Avogadro's number
- e_k = probability that a photon of energy E_k is emitted per decay of the isotope
- σ_i = thermal neutron capture cross section
- ϕ = neutron flux: 8×10^{12} ntns/cm²-sec for MIT reactor
- t_0 = irradiation time
- $t_1 - t_2$ = counting time

The initial activity of the fission product was calculated from the decay time.

$$A_i^0 = A_i(\bar{t}) e^{\lambda \bar{t}}$$

where:

- A_i^0 = initial activity of isotope i
- $A_i(t)$ = activity of isotope i at time t
- \bar{t} = average of t_1 and t_2

In the case of ¹⁴⁰La, the initial activity of its parent, ¹⁴⁰Ba was needed.

$$A_i^o = \frac{A_2(\bar{t})(\lambda_2 - \lambda_1)}{\lambda_2(e^{-\lambda_1\bar{t}} - e^{-\lambda_2\bar{t}})}$$

where:

- λ_1 = decay constant of fission product (^{140}Ba)
- λ_2 = decay constant of daughter product (^{140}La)

The previous activities were corrected for any background concentrations of natural isotopes of the fission product in the sand or solution which may have become activated.

$$A_1(\bar{t}) = \frac{A_1^{peak}(\bar{t}) - A_1^{bgd}(\bar{t})}{\varepsilon}$$

where:

$$A_1^{bgd}(\bar{t}) = \frac{ma_i N_A \sigma_i \phi (1 - e^{-\lambda_i t_0}) e^{-\lambda_i \bar{t}}}{A_i}$$

The mass of ^{235}U initially present was then calculated from the initial activities of the fission products and the irradiation time in the reactor.

$$m = \frac{A_i^o A_i}{a_i N_A \sigma_i \phi (1 - e^{-\lambda_i t_0}) y}$$

where:

- y = fission yield

Table 2.6 shows how the uranium concentrations determined by using different fission products varied for three samples.

Table 2.6: Comparison of U Concentrations Determined by Different Fission Products

Isotope	γ Energy	ID3	ID4	ID4a
La-140	1596 keV	1.56	2.15	1.23
La-140	487	1.47	2.02	1.22
Ce-141	145	1.41	1.91	1.15
Nd-147	91	1.59	2.08	1.40
Average		1.51	2.04	1.25
Std. Dev.		5.3%	5.4%	8.5%

2.2.2 pH MEASUREMENTS

2.2.2.1 pH Measurement Equipment

pH measurements were made using glass, combination electrodes, either single (Omega PHE-2114) or double junction (Omega PHE-2214). These electrodes were connected to either an Omega PHB-47 or PHTX-91 pH meter. Calibration was performed using pH 4, 7, and 10 buffers. The measured pH value was assumed to be the $-\log\{H^+\}$.

All pH measurements were made for systems open to the atmosphere. A carbon dioxide selective electrode (Omega ISE-8750) was sometimes used to record the corresponding dissolved carbon dioxide for uranium solutions to ensure that equilibrium with the atmosphere had been attained and thus prevent accidental uranium precipitation.

2.2.2.2 pH Measurement of Unsaturated Sand

pH measurements of unsaturated samples were performed by placing the wet sand into a chromatography column and using a vacuum to extract the solution into a filtering flask. The extracted solution was transferred into a 15 ml centrifuge tube. The filtering flask and the centrifuge tube each contained a few grams of the wet sand which were placed there before the pore solution was extracted. The sand and solution were shaken in the centrifuge tube

for five seconds. The pH of the pore solution was considered to be that of the extracted solution in contact with the wet sand in the 15 ml tube. It was very important to soak all columns, flasks, and funnels in deionized water before use in order to ensure all traces of acid (from the acid bath) were removed.

Because measurement of the pH of unsaturated samples cannot be performed directly with a pH electrode, the pore solution was extracted with a vacuum. The vacuum-extracted pore solution was, however, susceptible to pH changes because it was no longer being buffered by the solid. Measurement of the pH after each step found that these pH changes occurred when the solution was extracted into the filtering flask, when it was placed in the 15 ml tube to have its pH recorded, and while the pH was being recorded. (The solution was transferred into the 15 ml centrifuge tube in order to make the 3 to 6 ml of extracted solution deep enough to accommodate a pH electrode.) A few grams of the wet sand was placed at the bottom of the filtering flask and the 15 ml tube before extraction of the pore solution to reduce these pH changes.

The pH change during extraction was determined by recording the pH of a sand slurry before and after vacuum extraction. The pH of the extracted solution was usually 0.01 or 0.02 pH units lower than the original solution, which is not significant. The extracted solution was even placed on top of the wet sand and extracted again with little or no change to the pH. The pH of the extracted solution would slowly drift, but the wet sand's buffering capability reduced this to less than 0.03 pH units over 10 to 20 minutes.

Soil water extractors often have problems with the CO₂ degassing during extraction and measurement which causes the pH to rise. This occurs because the CO₂ concentration in soil air is often much higher than that found in the atmosphere [Suarez 1986]. The samples in this experiment were brought to equilibrium with the atmosphere and atmospheric air was drawn through the sample during extraction. Because a pH drop and not a pH rise was seen to occur, CO₂ degassing was not observed to be a problem. If anything, the pH drop could be due to CO₂ absorption from the air.

CHAPTER 3 URANIUM SOLUBILITY MODELING

3.1 Use of HYDRAQL

The expected uranium solubility in the experiments was predicted using HYDRAQL.¹ HYDRAQL is a version of the program MINEQL enhanced to incorporate surface complexation models. It begins with an initial guess of the free concentration in solution of the components that define the system being investigated. During subsequent iterations the mathematical solution is improved until the mass balance for each component is satisfied [Papelis, Hayes and Leckie 1988].

HYDRAQL was only used to predict the expected solubility of uranium. The recipe for the system is shown in Table 3.1. Uranium was assumed to be present in the uranyl +VI state as UO_2^{2+} . Bubbling the solutions with air at near neutral pH's should result in any reduced uranium being oxidized. No sand or other solids present as trace components were included in the recipe, nor was any adsorption or ion exchange considered.

The results were used as a tool to prevent uranium precipitation in the stock solutions or during the experiments. All uranium concentrations were kept low enough to provide a safety margin to ensure that any minor changes to pH, uranium

TABLE 3.1: HYDRAQL RECIPE

Species	Concentration (Moles/liter)
Cl ⁻	0.1
CO ₃ ²⁻	open system/10 ^{-4.5} /10 ^{-4.0} /10 ^{-3.5} /10 ^{-3.0}
Na ⁺	0.1
*NO ₃ ⁻	0.0022
†UO ₂ ²⁺	4.2X10 ⁻⁴ /8.4X10 ⁻³

*Due to nitric acid in the ICP standard.

†The excess uranium present would precipitate. The exact initial amount present does have some impact on the overall chemistry when it precipitates, but this was assumed to be minor.

¹ The general chemistry of uranium is described in Appendix B.

concentrations, or carbonate concentration would not lead to precipitation. Typical safety margins were 0.3 pH units and a factor of 3.3 for the uranium concentration.

3.2 Solubility Results

Figure 3.1 shows uranium solubility versus pH for both open and closed systems. The data used to make this graph are listed in Appendix G. The impact of carbonate complexation becomes noticeable above pH 6.5. The low solubility of uranium in closed systems between pH 7.0 and 8.5 (i.e. < 1 ppm) was the main reason that open systems were used in this study. The large difference in solubilities is due to the amount of hydroxyl and carbonate complexation occurring. Figures 3.2 and 3.3 compare the speciation at pH 6 to that of 8. At pH 6, the closed system solubility is 4.3 ppm and uranium exists as hydroxyl complexes and some uranyl ion. The formation of carbonate complexes increases the solubility to 5.0 ppm in an open system. At pH 8, the open system has a uranium solubility of 73 ppm which is over two hundred times greater than the closed system's 0.31 ppm solubility. This is because the uranyl carbonate complexes now comprise 99.71% of the aqueous species. In all the cases, most of the uranium precipitated as $\text{UO}_2(\text{OH})_2$.

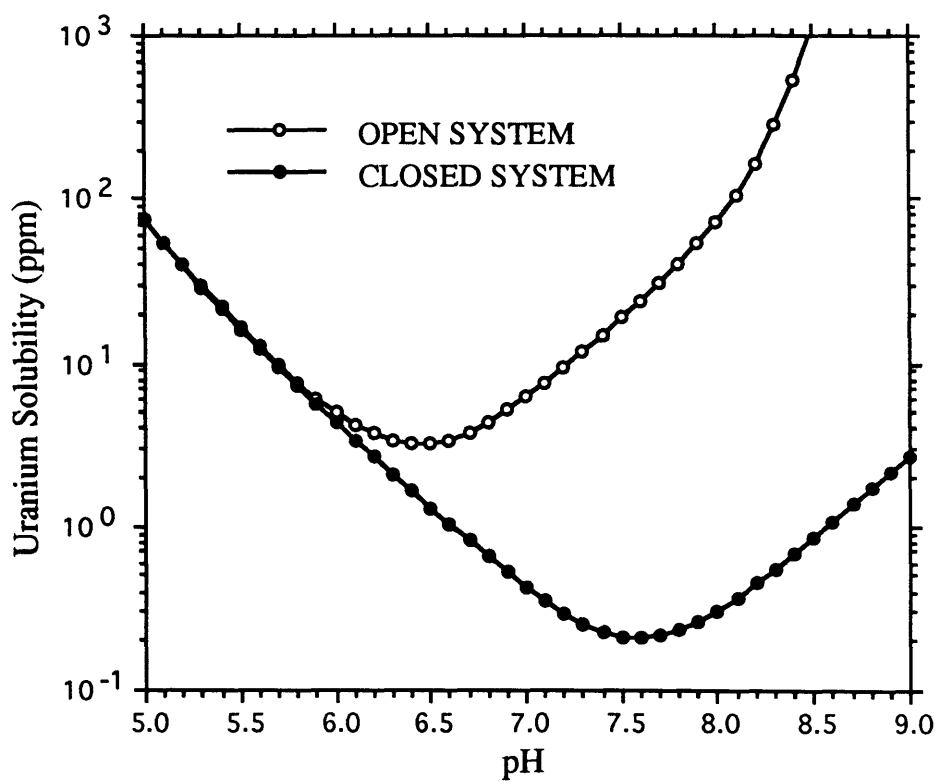


Figure 3.1: Uranium Solubility vs pH
 Open and Closed Systems
 Ionic Strength = 0.1 M

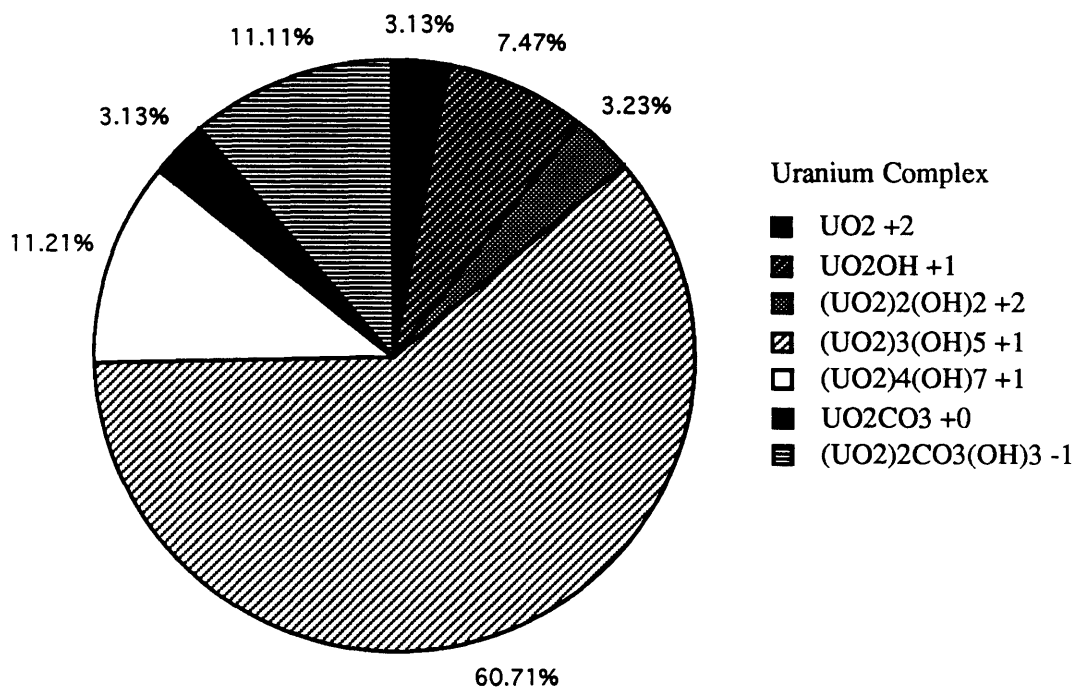


Figure 3.2: Uranium Speciation at pH = 6.00
 Open System, Ionic Strength = 0.1 M
 Uranium Solubility = 5.04 ppm

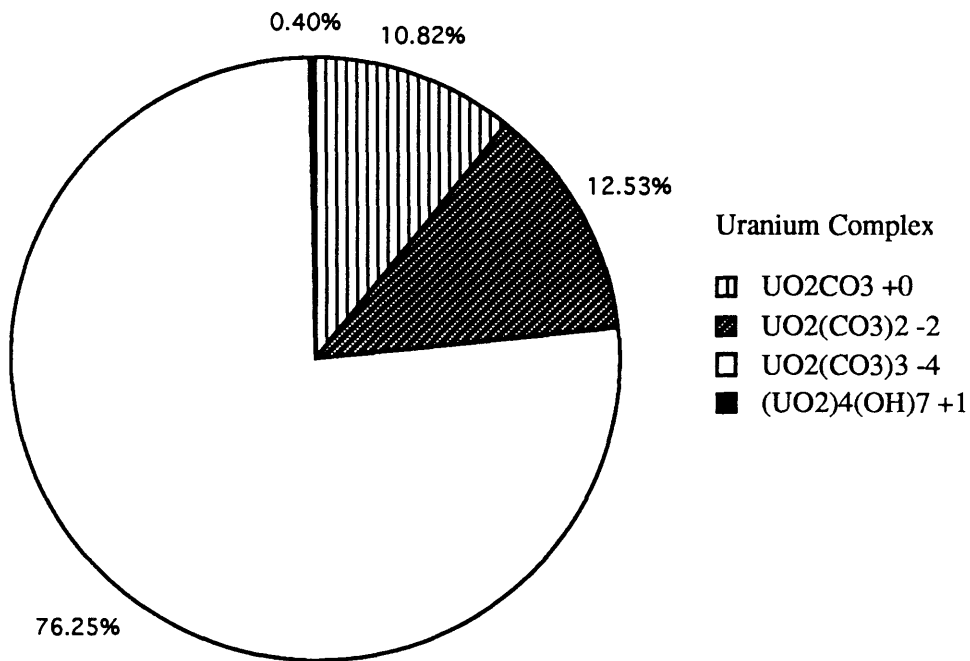


Figure 3.3: Uranium Speciation at pH = 8.00
 Open System, Ionic Strength = 0.1 M
 Uranium Solubility = 72.96 ppm

CHAPTER 4 CONTROL OF EXPERIMENTAL PARAMETERS

4.1 Sand Moisture Content Distribution

Because one of this project's goals was to examine how sorption varied with moisture content, a method had to be developed to achieve and maintain a uniform moisture content throughout the sample. A Turbula™ mixer (Willy A. Bachofen A. G., Basel Turbula™ model T2C) was used because it causes a sample to experience no net force in any direction, averaged over time. It accomplishes this by its unusual motion which combines rotation, translation, and inversion (based on Schatz inversion geometry). According to company literature, this third force subjects the contents of the mixing container to two alternating, rhythmic pulsating motions which have the effect of continuously compressing and thinning out the contents of the container. This alternating acceleration and retardation of particles along changing paths causes the potential energy from the braking phase to pass directly into generation of subsequent acceleration. The surges thus created in the material have a profile of continuously changing energy gradients. Speiser and Tawashi [1964] found that the Turbula™ was able to mix a very small amount (1 part in 850) of a drug in a large bulk of filling material in one direct mixing step. They found that complete homogeneity was attained and remained unchanged by further mixing.

The Turbula's™ unique motion was examined for two purposes:

- 1) as a possible method to cause water introduced at the top of a sand filled tube to become uniformly saturated, and
- 2) as a possible method to maintain uniform moisture contents over several days.

Saturation levels throughout the centrifuge tube were determined by weighing sand samples removed from the tube on an electric balance (Denver XE-100A, precision ± 0.2 mg). Core samples were removed using a 20 ml disposable syringe (with the tip cut off) and then divided into four portions corresponding roughly to the 5 ml increments marked on the syringe. In other experiments, the sand was divided into three to six portions according to the volume

markings on the tube. The saturation level was determined by comparing the mass of the wet sand to the mass of the sand after being dried in an oven.

$$\text{Saturation Level} = \frac{\text{Water Vol.}}{\text{Pore Vol.}} = \frac{(\text{Water Mass})(\text{Sand Density})}{(\text{Sand Mass})(\text{Porosity})(\text{Water Density})}$$

Examinations of the saturation levels in the tubes found that when the water was introduced from the top, there would be a relatively saturated region (usually above 90% saturation) followed by a steep gradient in the saturation level to very low levels (1% or less). Introducing the water approximately every centimeter only resulted in several alternating wet and dry regions.

Although the Turbula™ did not produce a uniform distribution of water in sand, it did maintain the distribution of water in a sample for a long time. Under normal conditions, the pressure head associated with gravity overcomes capillary forces in unsaturated sand and causes the liquid to drain. The Turbula™ negates the effect of gravity, allowing a homogeneous moisture distribution to be maintained. The main obstacle in attaining a nearly uniform moisture distribution in the sand was drainage of the liquid in samples while the tube was being filled. The procedure described in Appendix C minimized these problems. Samples prepared accordingly were found to have saturation levels with relative standard deviations under 6% for absolute saturation levels between 20 and 100%. Typical results of the variability in saturation levels of 6 sections of sand in a 50 ml tube are $31.7 \pm 1.1\%$, $33.7 \pm 1.7\%$, $41.1 \pm 2.7\%$, and $69.1 \pm 1.0\%$. Further results are listed in Appendix G. The precision achieved would allow future experiments to compare the sorption of unsaturated samples whose absolute saturation levels differed by more than 10%. Although a certain amount of both sand and liquid remained in the beaker after packing the wet sand in a tube, the relative change in the system moisture content was found to be less than 0.5%, which was considered negligible.

4.2 pH CONTROL OF UNSATURATED SAMPLES

4.2.1 SAND AND SOLUTION PRETREATMENT

Bringing unsaturated samples to equilibrium with the atmosphere was complicated by the fact that the centrifuge tube was a closed system. Air cannot be bubbled through the sample while in the Turbula™ and the solution would gradually evaporate if left exposed to the air. Thus, unsaturated batch sample titrations require not only the proper amount of base be added for a desired pH, but also that the amount of total carbonate needed to attain equilibrium with atmospheric carbon dioxide be supplied as NaHCO₃, with the remaining alkalinity added as NaOH. Pretreating the sand and solution beforehand was a method investigated to avoid having to determine exactly how much total carbonate is required.

Fresh sand was pretreated by mixing it with a 0.1 M NaCl electrolyte solution and base at ≤ 0.35 solution/solid weight ratio for at least two days. The sample was brought into equilibrium with the atmosphere by bubbling the solution with air until the pH stabilized. This pH was recorded. The mixture was placed into a Buechner funnel and most of the solution was removed from the sand. The pH of the extracted solution was recorded. Several samples of pretreated sand were taken, weighed, dried in an oven and then reweighed in order to determine the residual saturation level. Unsaturated samples were made from the pretreated solution and sand at various saturation levels and mixed in the Turbula™.

The amount of solution remaining in the sand after vacuum extraction varied between 30 and 50% of saturation. The residual saturation tended to increase with the batch size. The percent difference between the estimated (calculated by mass balances) and the actual (determined by weight of wet and dry sand) was usually less than 3%.

Pretreatment produced more consistent pH's than titrating unsaturated samples made with fresh sand. The pH's of the solutions changed only about 0.01 or 0.02 pH units during extraction of the solution from sand slurries (solution/solid ratios ≤ 0.35). The pH's

of the pore solutions of unsaturated samples were measured by extracting their pore solutions after mixing them in the Turbula™. These pH's were lower than the original pH of the sand slurry. This change did not appear to be dependent on the saturation level, but rather on the amount of time the sand and solution were allowed to mix. For example, samples initially at pH 8.45 would have a pH of 8.30 after two days and 8.20 after 8 days. The change in pH in the unsaturated sample with time indicates that slow carbonate dissolution may be occurring. In addition, this drop in pH does lead to disequilibrium with atmospheric CO₂.

Adjustment and control of the pH of an unsaturated sample in a closed tube under atmospheric conditions is difficult even if the solid is pure quartz. This adjustment was found to be even more difficult due to carbonate minerals and other trace components that were present in the Wedron 510 sand. Pretreating the sand simplified the surface chemistry by removing some of the soluble trace components from the sand.

4.2.2 SAND CLEANING

Cleaning the sand was examined as a means of removing trace components from the sand before pretreatment. The goal of this was to produce a surface which behaved more like pure quartz and to reduce the pH drop in the unsaturated sample. Fresh sand was placed into a beaker with deionized water and mixed with a Teflon™ stirring bar. The speed of the magnetic stirrer was at the highest level to keep the sand in suspension. Many of the trace components in the sand were dissolved by maintaining it between pH 2.7 and 3.0 until no further additions of acid were required. [Ward 1993] Acid additions were usually required for approximately 12 hours. When the pH stabilized, the sand was rinsed with water to remove the very fine grained material. The wet sand was then placed in a filtered-lined Buechner funnel and rinsed with DI water until the pH of the effluent was above 5.0. The sand was then dried in an oven.

This process should have dissolved most of the carbonate present, but would have had little effect on the iron oxyhydroxides

surface coatings [Ward 1993]. In addition, the Teflon™ stirring bar underwent significant abrasion while mixing the sand. Very small pieces of Teflon remained in the sand after cleaning and rinsing. These pieces tended to float on top of the electrolyte solution during pretreatment and were easily removed by passing the solution through filter paper during pretreatment.

The cleaned sand was much more sensitive to acid and base titrations because much of the buffering capacity had been removed. After acid or base was added to the samples, longer bubblings than normal were needed because the sample would undergo larger pH changes and needed a longer time to reach equilibrium. The samples also underwent larger pH drifts than fresh or pretreated sand because the solution was less buffered.

Table 4.1 compares the pH as well as Na and Fe concentrations of fresh and clean sand samples. These samples consisted of 25 ml of solution and 25 g of Wedron 510 sand.

- 1) clean sand and DI water
- 2) clean sand and 0.1 M KCl
- 3) fresh sand and 0.1 M KCl
- 4) clean sand, 24.5 ml 0.1 M KCl, and 0.5 ml 0.25 M HNO₃
- 5) clean sand, 24.5 ml 0.1 M KCl, and 0.5 ml 0.25 M KOH

Table 4.1: Comparison of Fresh and Clean Sand Solution Chemistry

Sample	pH	Fe	Na
1	5.00	0.08 ppm	0.19 ppm
2	4.94	0.60	1.05
3	7.44	0.01	2.76
4	2.56	4.07	1.22
5	7.44	0.01	1.60

Untitrated samples made with the buffered fresh sand always go to a pH between 7.4 and 7.6 while the clean sand solution go to around pH 5.0. This is closer to the pH_{Zpc} of pure silica, 2.0, than the fresh sand's, but is still quite a bit higher [Schwarzenbach, Gschwend and Imboden 1993].

4.2.3 pH DRIFT

The pH of samples in closed tubes would drift down with time. The pH drifts of several samples are shown in Figure 4.1. The "Saturated: Open" sample was made at a 1:1 solution/solid weight ratio using fresh Wedron 510 sand and was bubbled daily with air. The "Saturated" samples were also made at a 1:1 solution/solid weight ratio using fresh sand. The samples were mixed for one day and bubbled to reach equilibrium with atmospheric carbon dioxide. They were then mixed and the pH recorded at the end. There was no bubbling after the first day. The "Unsaturated: Fresh Sand" samples were pretreated for 6 days. The pH of the sand slurry is shown as day 0. Unsaturated samples were then made from the pretreated sand and solution. The pH was measured after using vacuum extraction to remove the pore solution. In the "Unsaturated: Cleaned Sand" samples, the sand was cleaned by maintaining it between pH 2.8 and 3.0 until no further acid additions were needed. The sand

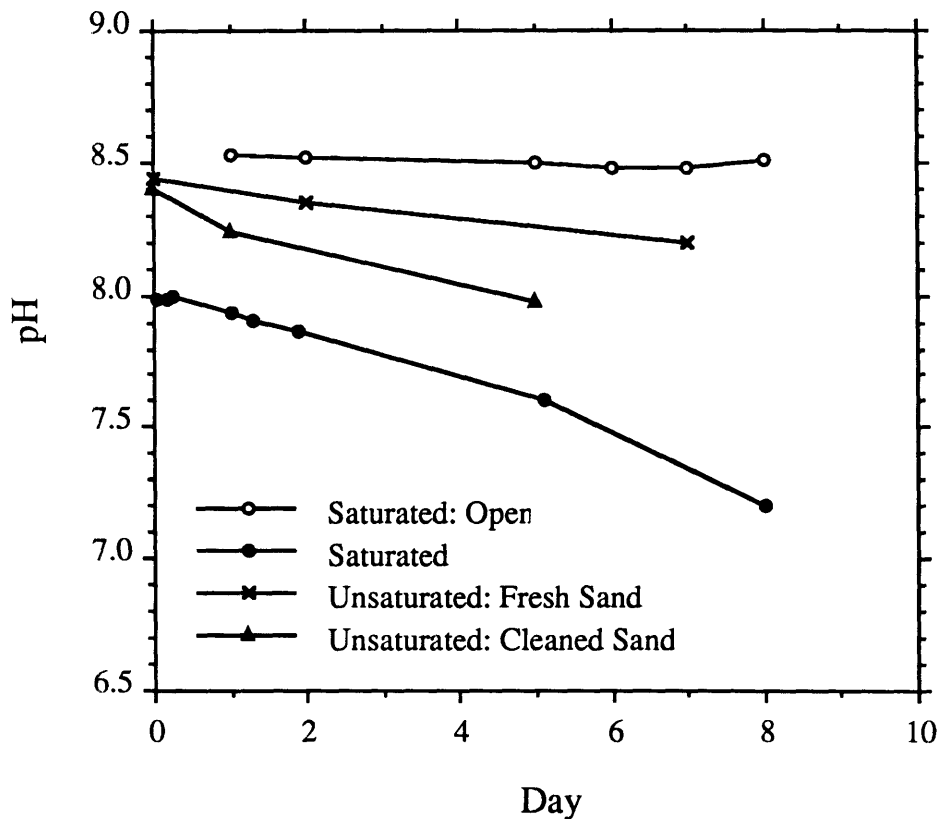


Figure 4.1: pH Drift vs. Time for Closed Batch Samples

was then rinsed with DI water until the pH's stabilized. The sand was pretreated for 4 days before unsaturated samples were made.

The figure shows that the drift usually became noticeable after one day. The pH would continue to drift down daily in tubes kept closed. The pH of samples which were bubbled daily would be lower before being bubbled, but would return to the previous day's approximate pH after being bubbled. For example, in the "Saturated: Open" sample between days 6 and 7, the pH dropped from 8.48 to 8.40 and then subsequently returned to 8.48 after being bubbled. On day 8, it dropped again to 8.43, but then rose to 8.51 after being bubbled.

The pH drift occurred in both saturated and unsaturated samples and occurred whether fresh, pretreated, or cleaned sand was used. Comparing the unsaturated fresh and clean samples, it appears that the effect was more significant in samples with cleaned sand. Saturated samples also showed this effect. Fresh sand samples at a 1:1 ratio had the pH drop from 8.13 to 7.60 over 5 days, while cleaned sand samples had a slightly larger drop from 8.13 to 7.56 over the same time period. The increased drift in the cleaned sand samples was probably due to the smaller buffering capacity it has after the trace components (e.g. carbonates) are dissolved and removed.

The difference in pH between the pretreated sand slurry and the unsaturated sand sample made from it was dependent on the amount of time which elapsed between solution extraction and sample preparation. When preparing unsaturated samples from a large batch of sand, the elapsed time between the first and last sample could be as long as 2 hours. Unsaturated samples were prepared and the elapsed time was recorded. After 1.75 days of mixing in the Turbula™, the pore solutions were removed and their pH's recorded. Table shows how the pH varied.

Table 4.2: pH Changes with Preparation Time

Sample	Elapsed Time	pH
1	15 min.	8.11
2	75	8.18
3	125	8.22

The pH of the extracted solution only changed from 8.46 to 8.45 over the same amount of time. The effect of evaporation on the saturation level over the entire time was only 2%.

The effect on pH was probably due to the residual moisture in the pretreated sand. This water has a high surface area to volume ratio and could undergo much more significant solution-air exchange than the extracted solution in the flask. Because the pH rises with time (and results in a smaller pH drop), it appears that CO₂ is being absorbed from the air. The vacuum extraction method, which sucks air through the sand, could be stripping CO₂ from the remaining pore solution, while not significantly affecting the CO₂ concentrations in the extracted pore solution. Large batches of pretreated sand were split up into smaller sections after this was found out in order to reduce pH variations between the samples.

CHAPTER 5 SORPTION EXPERIMENTS

5.1 Losses of Uranium Due to Equipment Sorption

5.1.1 LOSSES OF URANIUM DUE TO SORPTION TO CONTAINER WALLS

Polypropylene and polycarbonate centrifuge tubes and bottles were used during the early experiments of this project. Parks *et al* [1992] found polycarbonate tubes to be nearly adsorption-free. They found the maximum fraction of U(VI) lost due to adsorption on polycarbonate tubes was 8% or less for their experiments with uranyl solutions at 4.2×10^{-7} M. Tripathi [1983] found less container sorption to systems exposed to atmospheric CO₂, at higher U concentrations, and at higher pH's. These two studies involved samples at high solution volume to container surface area (e.g. 45 ml solution in a 50 ml bottle). Uranium solutions left in polypropylene or polycarbonate containers lost a few percent of the uranium to the container. Other tests did show that the container losses increased with the contact time and also as the solution volume to container surface area ration decreased. See Table 5.1. Because the experiments performed in this project included kinetic studies, samples with varying solution volumes, and unsaturated samples which had low solution volume to container surface area ratios, Teflon™ FEP (fluorinated ethylene propylene) centrifuge tubes were used to simplify calculations because they had negligible sorption losses. A Teflon™ FEP bottle was also used to store the uranium

Table 5.1: Container Sorption Losses

SOLUTION VOLUME	TUBE MATERIAL	TUBE VOLUME	PERCENT LOST
12 ml	Polypropylene	50 ml	8.0%
25	Polypropylene	50	3.7
12	Polycarbonate	50	2.4
25	Polycarbonate	85	3.5
20	Teflon™ FEP	50	<0.5

stock solution after its pH had been raised to between 8 and 9. Losses of uranium to glass were found to be less than 1%.

5.1.2 URANIUM LOSSES TO OTHER EQUIPMENT

Uranium losses to other equipment were estimated by placing uranium solution in contact with the item as it would be in actual use and measuring the final concentration afterwards. Negligible losses were found for pipette tips, syringes, syringe filters (cellulose acetate), and magnetic stirrers. Minor sorption losses were found on the chromatography columns (1.5%) while significant sorption (>10%) was found for filter paper, porcelain Buechner funnels, non-Teflon tubing, and nylon gloves.

Uranium sorption to Buechner funnels and columns during an experiment were determined by acidifying the equipment in order to leach any sorbed uranium. The equipment was weighed before and after being used, dried, and then acidified with 1% HNO₃. This acid was then analyzed for uranium. By performing a material balance for uranium, the total amount sorbed could be found from:

$$\text{Uranium Sorbed} = (\text{Acid Volume})(\text{Acid U Concentration}) - (\text{Solution Remaining})(\text{Solution Final Concentration})$$

The average uranium loss to porcelain Buechner funnels and borosilicate chromatography columns was 11.7% and 1.5%, respectively. Samples with smaller solution volumes had higher percentage losses than drier ones.

5.2 Vacuum Extraction

5.2.1 METHOD DESCRIPTION

This method involved the use of suction to extract the pore solution through a porous membrane. Figure 5.1 shows the equipment setup used for this method. The wet sand was placed into a chromatography column with a Teflon™-coated spatula. A 2-3 cm

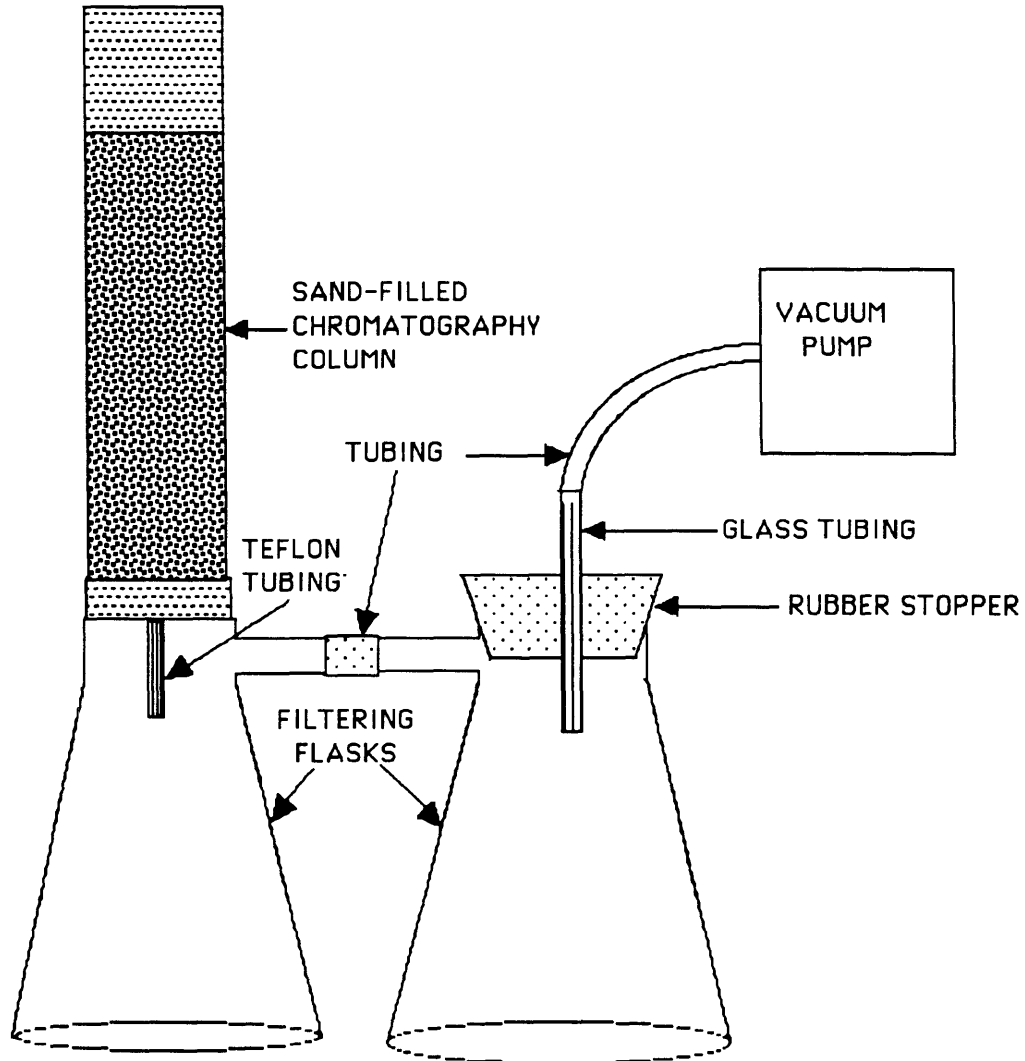


Figure 5.1: Equipment Setup for Vacuum Extraction Method

long piece of Teflon™ tubing was attached to the bottom of the column to allow the extracted pore solution to drip into the flask without being sucked into the attached flask. Vinyl was wrapped around the connection to prevent air leakage. The second flask was used to prevent liquid or sand from being drawn into the vacuum pump. A Danielson model BD-100 vacuum pump was used to provide suction.

5.2.2 REMOVAL EFFICIENCY

The columns were made from borosilicate glass while the column ends were made from polypropylene. They also contained a 20 μm polyethylene disc which provided bed support. The column size was usually 2.5 cm dia. X 10 cm high and had a volume of 49 ml. This size was easy to fill with sand and allowed a large percentage of the pore solution to be removed. Buechner funnels and other sizes of columns were also examined. Buechner funnel bases usually had larger cross-sectional areas which noticeably reduced the strength of the suction and retained larger amounts of solution on their surface. Although reducing the surface area increased the vacuum suction, longer and narrower columns (e.g. 1.5 cm dia. X 30 cm high and 1.0 cm dia. X 50 cm high) had less suction probably because the longer length of sand produced a larger pressure drop. Table 5.2 shows typical extraction rates for various setups. Tables 5.3 and 5.4 show how the extraction efficiency varied with saturation and sample size.

Table 5.2: Comparison of Removal Rates

Sand Mass	Water Volume	Saturation Level	Solution Removed	Equipment	Size
75 g	4.09 ml	28 %	0 %	Chroma Column	2.5 X 10 cm
75	4.09	28	0	Chroma Column*	2.5 X 10 cm
75	5.46	38	3	Buechner Funnel†	10 X 16 cm
75	5.46	38	16	Buechner Funnel†	4.3 X 8.9 cm
75	5.46	38	0	Buechner Funnel°	40 cm, 60 ml
75	5.46	38	25	Chroma Column	2.5 X 10 cm
75	5.46	38	25	Chroma Column	1.5 X 30 cm
75	5.46	38	23	Chroma Column*	2.5 X 10 cm
25	3.41	71	37	Buechner Funnel†	10 X 16 cm
25	3.41	71	47	Buechner Funnel†	4.3 X 8.9 cm
60	8.18	71	73	Chroma Column#	1.0 X 50 cm
75	10.23	71	57	Buechner Funnel†	10 X 16 cm
75	10.23	71	65	Chroma Column	2.5 X 10 cm
75	10.23	71	63	Chroma Column	1.5 X 30 cm

* Pressurized gas used to extract pore solution.

† Funnel lined with filter paper.

° Funnel base was a fritted disc.

Pore solution removed with column displacement method.

Table 5.3: Extraction Efficiency for a Constant Sand Mass and Varying Saturation Levels Using a 10 cm dia Buechner Funnel

Sand Mass	Water Vol	% Saturation	Volume Removed	% Removed	Vol. Remaining
75 g	20.00 ml	138	13.11 ml	66	6.89 ml
75	13.64	94	8.01	59	5.63
75	10.23	71	5.84	57	4.39
75	6.82	47	1.71	25	5.11
75	5.46	38	0.16	3	5.30

Table 5.4: Extraction Efficiency for a Constant Saturation Level and Varying Sample Sizes Using a 10 cm dia Buechner Funnel

Sand Mass	Water Vol	% Saturation	Volume Removed	% Removed	Vol. Remaining
25 g	3.41 ml	71	1.27 ml	37	2.14 ml
50	6.82	71	2.73	40	4.09
75	10.23	71	5.84	57	4.39
100	13.64	71	8.50	62	5.14

The main concerns with this method were: 1) evaporation, 2) temperature changes of the pore solution during extraction, and 3) sorption/desorption of uranium while the solution passed through the column.

5.2.3 EVAPORATION

The amount of evaporation was determined by weighing the flask, column, and the sand and solution they contained after various time periods of vacuum extraction. This allowed the total mass of the pore solution to be determined as a function of time. Figure 5.2 shows the results. Although the total amount of evaporation can be measured, it was not able to be determined whether the evaporation was occurring in the sand or in the extracted solution in the filtering flask. The measured evaporation losses after 20 seconds were 1% for an 80% saturated sample and 1.5% for a 50% saturated one.

In order to determine the impact of evaporation on the extracted pore solution's uranium concentration, identically

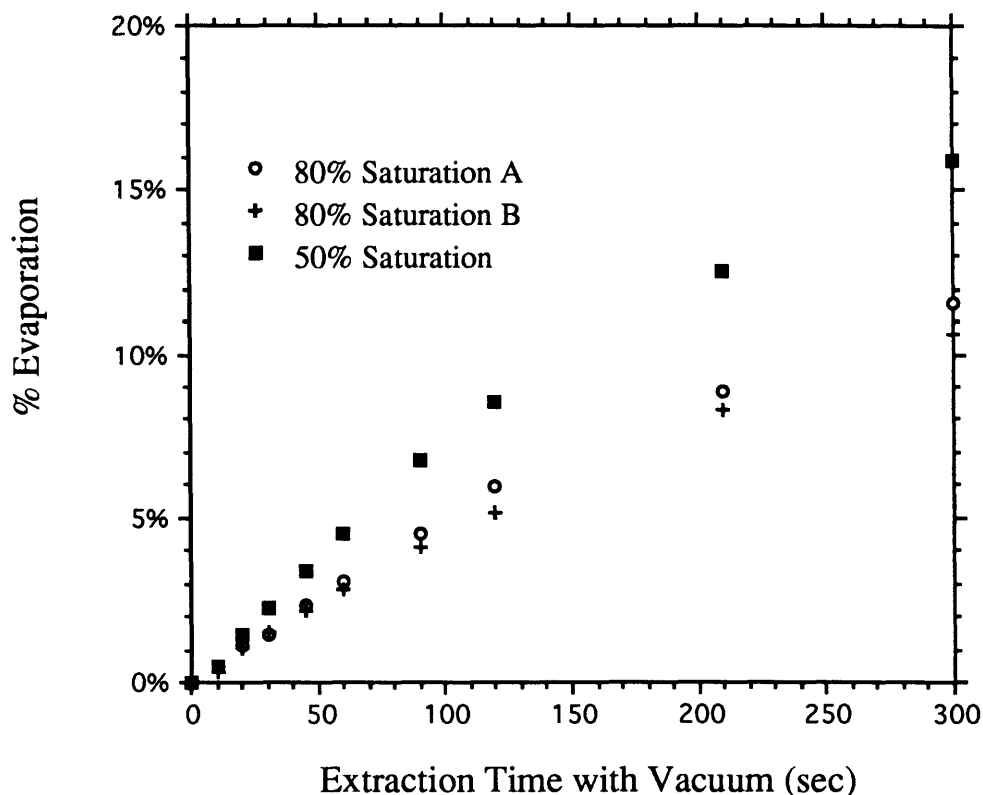


Figure 5.2: Evaporation vs Extraction Time

prepared unsaturated samples underwent different vacuum extraction periods and had their final uranium concentrations compared. For 90% saturated samples, the sample undergoing a 2 minute extraction had a uranium sorption 3.3% higher than the one with a 30 second extraction (90.1 vs. 87.2%). When the experiment was repeated with a slightly drier samples (70% saturated), a sample undergoing a 5 minute extraction had a uranium sorption 1.9% lower (84.4 vs. 86.0%) than a 30 second extraction sample. In both cases, the effect of evaporation on the uranium sorption results was relatively small and statistically, probably not differentiable. For the twenty second extraction times used in the experiments, evaporation should be negligible.

5.2.4 TEMPERATURE CHANGES

The temperature of the sand decreases during vacuum extraction of the pore solution. This is due to evaporative cooling and/or adiabatic expansion. Temperature probes inserted into the sand during extraction found temperature drops as large as 12.8° C. This could affect the results because of the temperature dependence of changes equilibrium constants for hydrolysis, complexation, and adsorption. Figure 5.3 shows how the temperature changed with time. Maest *et al* [1985] examined uranium sorption onto clays for 25°, 50°, and 75° C and found that uranium adsorption increased with increasing temperature. The effect of relatively small temperature drops on the sorption results was examined by having the vacuum suck air through a column containing ice (wrapped to reduce water leakage) before passing through the sand. This did not significantly affect the results. The twenty second extraction periods used in the experiments should result in the temperature decreasing only 1 or 2 ° C, which is negligible.

5.2.5 CONCENTRATION VERSUS EXTRACTION TIME

The uranium concentration in the pore solution was examined as a function of withdrawal time to determine if the concentration varied. Unsaturated samples were prepared according to the procedure in Appendix D except that the pore solution was removed in four sections. The removed pore solution sections were each diluted to 10 ml with 0.1 M NaCl and acidified. The concentrations were then compared to a similar sample which had its pore solution removed all at once. The results are shown in Table 5.5.

In all three samples, there was a continuous increase in the U concentration with extraction time. Sample A had the most significant variation in U concentration, ranging between 0.97 and 1.45 ppm. Although the relative standard deviation of the concentration was over 17%, the effect of this on the estimated percent of U sorbed was much smaller, it only varied between 86.1

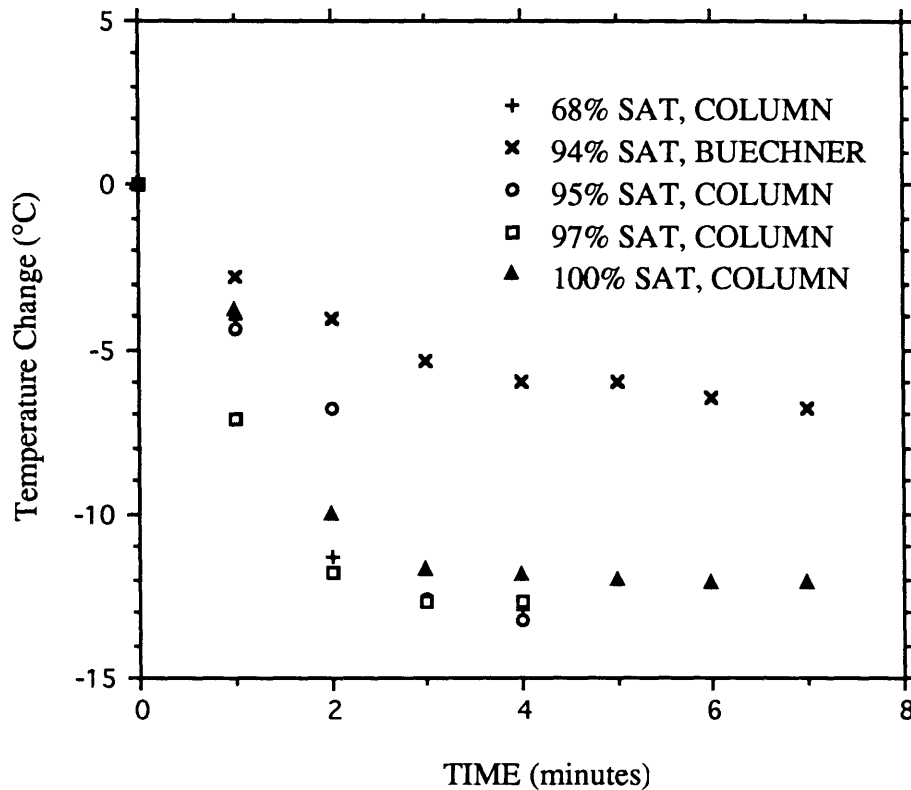


Figure 5.3: Temperature Change of Wet Sand During Extraction

and 80.4%. Samples removed from the longer column were not much different from those removed from shorter columns.

The increasing concentration with extraction time is postulated to be due to the fact that the last portion of the solution removed also underwent the most evaporation. Increasing evaporation would increase the U concentration. Other possible explanations for this observation could be that:

- a) the first amounts of pore solution removed had larger sorption losses to the column's filter and other equipment, or
- b) that the solution drained out of the smallest pores last which may have had a different chemistry or surface area.

The small volumes of some of the samples and their larger dilutions could also be a systematic source of error. It is unlikely the variations were due to non-uniform initial U concentrations in the pore solutions because the variations were not random, but showed a consistent trend in all the samples.

Table 5.5: Uranium Concentration vs. Extraction Time

Sample A: 84% Saturated, Total Pore Solution Volume = 10.3 ml

pH = 8.11, Initial U Conc. = 7.4 ppm

Sample	Volume Removed	U Concentration	% Sorbed	% Difference vs. Control
Control	5.50 ml	1.33 ppm	81.8	
1	2.75	0.97	86.9	6.2
2	2.00	1.21	83.7	2.3
3	1.00	1.43	80.6	-1.5
4	0.90	1.45	80.4	-1.7
average		1.27±0.22	82.9±3.1	1.3

Sample B: 101% Saturated, Total Pore Solution Volume = 12.8 ml

pH = 8.26, Initial U Conc. = 7.5 ppm

Sample	Volume Removed	U Concentration	% Sorbed	% Difference vs. Control
Control	7.50 ml	2.06 ppm	72.7	
1	1.50	2.03	72.9	0.3
2	2.00	2.35	68.7	-5.5
3	2.00	2.51	66.4	-8.7
4	2.25	2.55	66.0	-9.2
average		2.36±0.24	68.5±3.2	-5.8

Sample C: 100% Saturated, Total Pore Solution Volume = 12.6 ml

pH = 8.26, Initial U Conc. = 7.6 ppm

Sample	Volume Removed	U Concentration	% Sorbed	% Difference vs. Control
Control	7.50 ml	2.06 ppm	72.7	
1	2.00	2.24	70.4	-3.1
2	2.00	2.43	67.9	-6.6
3	2.00	2.42	68.0	-6.5
4	1.50	2.65	65.0	-10.6
average		2.44±0.17	67.8±2.2	-6.7

Note: Samples A and B used a 2.5 cm dia. X 10 cm high column while C used a 1.5 cm dia. X 30 cm high one.

Differences between the control sample's concentration and the average of the periodic samples was likely due to variations between similar samples, because it was not consistently higher or lower.

5.3 Isotopic Differentiation

5.3.1 METHOD DESCRIPTION

The isotopic differentiation method takes advantage of the fact that different isotopes of the same element chemically behave the same, but can be distinguished from one another. As shown in figure 5.4, solid/water systems were equilibrated with enriched ^{235}U solutions and were then flushed with enriched ^{238}U solutions. The relative concentration of ^{238}U in the flushing solution to the equilibrated ^{235}U concentration in the pore solution must be adjusted to prevent sorption or desorption during flushing. The concentration of ^{235}U in the extracted solution will then be determined by neutron activation.

A more detailed description of the procedure is found in Appendix C.

5.3.2 FORMULA DERIVATION FOR K_d

The calculation of the distribution coefficient K_d in the isotopic differentiation method requires a material balance to be performed for the uranium and solution. Flushing the sand column dilutes the uranium concentration and changes the solution volumes. The following section describes the derivation of formulas which were used to calculate K_d 's from either the sand's or the effluent solution's ^{235}U concentration.

It was assumed that the uranium concentration in the flushing solution was greater than the pore solution's concentration. This should prevent the ^{235}U adsorbed to the sand from desorbing during flushing. It was also assumed that isotopic exchange was minimal during flushing because the higher uranium concentration in the flushing solution should cause the forward sorption reaction to be much larger than the reverse desorption reaction. In addition, the flushing solution volume was assumed to be large enough so that all of the pore solution was flushed out of the sand.

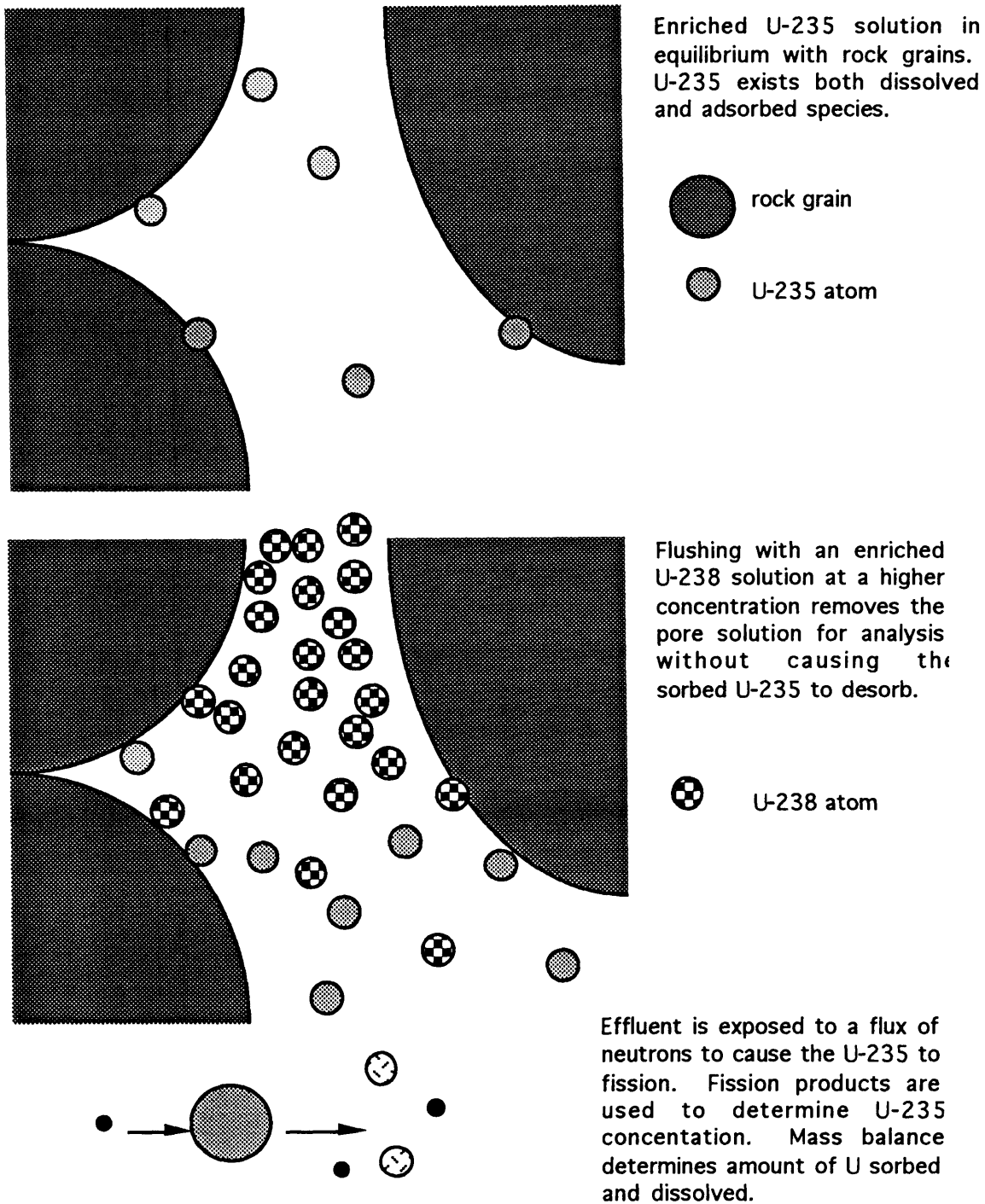


Figure 5.4: Isotopic Differentiation Process

Part A. Determination of K_d from Sand U-235 Concentration

The total amount of uranium in the system is equal to the volume of the pore solution, V_o (ml), and the ^{235}U concentration in the original solution, C_o ($\mu\text{g/ml}$). When equilibrium has been reached, the uranium is partitioned between the solution, now at a concentration of C_{sol} ($\mu\text{g/ml}$), and the solid, which has a mass M_s (g) at a concentration of f_{sand} ($\mu\text{g/g}$).

$$C_{sol}V_o + f_{sand}M_s = C_oV_o \quad (1)$$

The distribution coefficient can be rearranged as:

$$K_d = \frac{f_{sand}}{C_{sol}} \Rightarrow C_{sol} = \frac{f_{sand}}{K_d} \quad (2)$$

After the pore solution has been flushed out, all of the ^{235}U is now in the effluent, which has a volume V_c (ml) at a concentration C_f ($\mu\text{g/ml}$). The effluent volume is equal to the pore solution volume plus the flushing solution volume minus the amount of solution remaining in the sand at the end.

$$C_fV_c + f_{sand}M_s = C_oV_o \quad (3)$$

C_f can be determined from the ratio of the original pore solution volume to the effluent volume:

$$C_f = \frac{C_{sol}V_o}{V_c} = \frac{f_{sand}V_o}{V_cK_d} \quad (4)$$

Equation 4 is substituted into equation 3 and rearranged to determine the distribution coefficient.

$$\frac{f_{sand}V_o}{K_d} + f_{sand}M_s = C_oV_o \quad (5)$$

$$f_{sand}V_o = K_d(C_oV_o - M_Sf_{sand}) \quad (6)$$

$$K_d = \frac{f_{sand}V_o}{C_oV_o - M_Sf_{sand}} \quad (7)$$

Part B. Determination of K_d from the U-235 Concentration in the Effluent

This derivation is similar Part A. It starts with equation 3.

$$C_fV_c + f_{sand}M_S = C_oV_o \quad (3)$$

The sand ^{235}U concentration is defined in terms of the solution volumes and the distribution coefficient.

$$K_d = \frac{f_{sand}}{C_{sol}} \Rightarrow f_{sand} = K_dC_{sol} \quad (8)$$

$$C_{sol} = \frac{C_fV_c}{V_o} \therefore f_{sand} = \frac{K_dC_fV_c}{V_o} \quad (9)$$

Equation 9 is substituted into equation 3, which is rearranged to find the distribution coefficient.

$$C_fV_c + \frac{K_dC_fV_cM_S}{V_o} = C_oV_o \quad (10)$$

$$K_d \left[\frac{C_fV_cM_S}{V_o} \right] = C_oV_o - C_fV_c \quad (11)$$

$$K_d = \frac{V_o(C_oV_o - C_fV_c)}{C_fV_cM_S} \quad (12)$$

5.3.3 SORPTION KINETICS

The kinetics of uranium sorption and desorption were examined to determine the magnitude of any sorption or desorption occurring during the flushing stage of isotopic differentiation.

5.3.3.1 Saturated Samples

Uranium sorption versus time was examined for a sample containing a relatively high solution/solid ratio. Samples containing 19.95 ml of 0.1 M NaCl, 0.05 ml of 0.25 M NaHCO₃, and 25 g fresh sand were mixed on a hematology mixer for a day and brought to equilibrium with the atmosphere by bubbling the solution with air. The average pH was 7.94 ± 0.04 . Five milliliters of a 50 ppm U solution at pH 8.2 were then added to make the initial U concentration 10 ppm. The solutions were then shaken by hand for 15 seconds and placed on a hematology mixer for time periods varying between one minute and several days. Near the end of each measurement period, 10 ml of solution were removed for analysis and the final pH value was recorded. This pH was 8.00 ± 0.02 . A more detailed description of the procedure is found in Appendix C.

Figure 5.5 shows the amount of uranium sorbed versus time for a saturated sample. The sorption kinetics graph shows that much of the uranium had been sorbed within one minute. Longer sorption experiments were run, but the pH of the samples would start to drift significantly after a day as shown in Table 5.6. None of the samples were bubbled during this time period and this might have resulted in samples not being in equilibrium with the atmosphere. The amount of time to reach equilibrium could not be determined because of the pH drop. This is because increases in sorption with time cannot be differentiated from those due to changes in uranium's distribution coefficient. At the lower pH's the samples drifted to, uranium's distribution coefficient is expected to increase due to the reduction in non-sorbing carbonate complexes.

Most of the uranium sorption was seen to occur within the first hour. For the samples with pH ≈ 8 , uranium appears to have

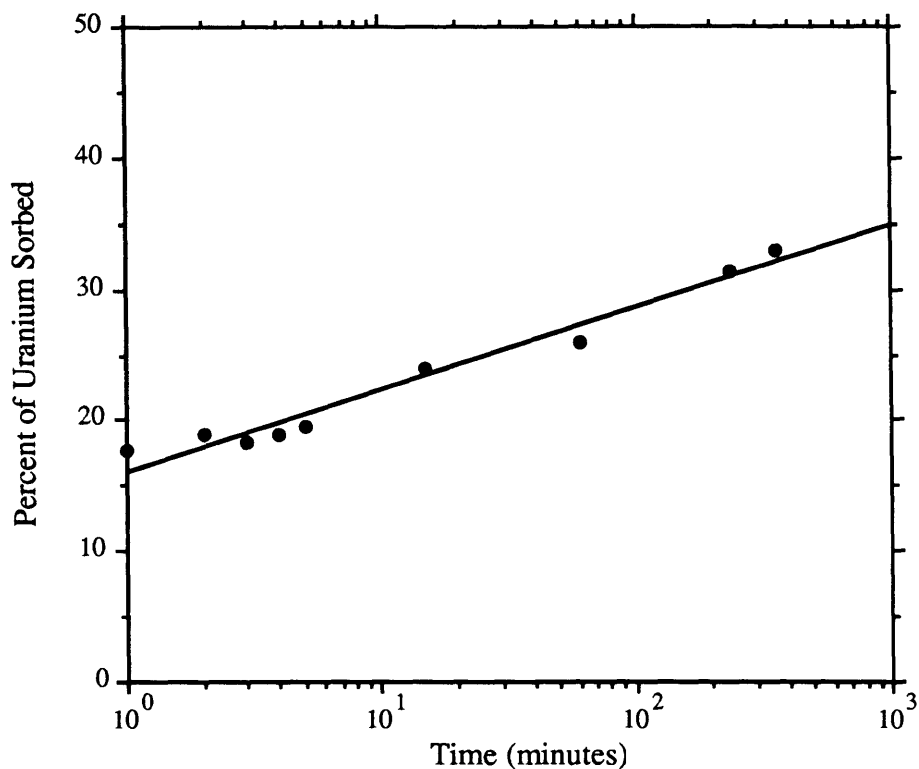


Figure 5.5: Uranium Sorption Kinetics
 Initial U Concentration: 10 ppm
 25 g sand, 25 ml 0.1 M NaCl
 pH=8.00 Open System

Table 5.6: Time Dependence of pH and Sorption

Time Mixed	Final pH	Percent of U Sorbed
1 min.	7.97	18
2	8.03	19
3	7.99	18
4	7.98	19
5	7.98	20
15	7.99	24
1.0 hour	7.99	26
3.8	7.99	31
5.8	8.00	33
1.0 day	7.94	38
1.3	7.91	38
1.9	7.87	43
5.1	7.60	46
8.0	7.20	62

reached equilibrium within two days. This is similar to the results found by other investigators. Nakayama [1991] found that most of the neptunium sorption for biotite and goethite occurred within the first 30 minutes with equilibrium occurring within two to five hours for biotite and 2 days or more for goethite. Tripathi [1983] found that it took five hours for uranium to reach equilibrium with goethite for 0.1 M ionic strength. The slow approach to equilibrium is usually assumed to reflect the diffusion of sorbate species into the sorbent matrix and the slow alteration of sorbent properties.

5.3.3.2 Sorption During Extraction

As the pore solution was being removed, the solution in the upper portion of the column passed through the sand below it. The uranium in the solution could possibly sorb onto this sand as it passed by.

Identical unsaturated samples were prepared as described in Appendix C. The pore solutions were removed using both 2.5 cm dia. X 10 cm high and 1.5 cm dia. X 30 cm high columns. The samples were at 102% saturation, pH 8.22, and had an initial uranium concentration of 6.20 ppm. The amount of uranium sorbed were 67.6% and 68.2%. This indicated that having the pore solution pass through 3 times as much sand did not affect the results.

This issue was also examined by removing pore solutions from unsaturated samples with a vacuum and then placing the solution back on top of the sand in the column. The pore solution was removed again with a vacuum. The uranium concentration in the reextracted pore solution was compared to samples in which the pore solution was removed only once. The samples were at 91% saturation, pH 8.21, and had an initial uranium concentration of 9.55 ppm. The amount of uranium sorbed for the control was 77.9% while it was 75.0% and 76.5% for the samples whose pore solutions were removed twice. This slight decrease in the apparent amount of uranium sorbed is probably due to evaporation. The solutions which were extracted twice would undergo more evaporation which would

increase uranium concentrations and reduce the estimated amount of uranium sorbed to the sand.

5.3.4 DESORPTION KINETICS

5.3.4.1 Saturated Samples

Uranium desorption in response to an increase in the solution/solid ratio was also examined. Samples containing 11.96 ml of 0.1 M NaCl, 0.04 ml 0.1 M NaHCO₃, and 15 g of fresh quartz sand were mixed for a day and brought to equilibrium with the air by bubbling the solution with air. Three milliliters of a 50 ppm uranium solution at pH 8.2 were added. The solutions were mixed for 24 hours and brought to equilibrium with the atmosphere. The pH's of the solutions were recorded and 10 ml of the solutions were then removed for determination of the equilibrated uranium concentrations. The 5 ml remaining in the sand was then diluted to 30 ml. The diluting solution was an electrolyte solution which had been pretreated with sand for 48 hours and had the same pH as the sorption samples. The diluted samples were mixed for various time periods before being sampled again and the pH recorded. The average pH was 7.89 ± 0.03 before dilution and 7.90 ± 0.03 after dilution.

In a separate experiment, the amount of uranium which had desorbed was determined by performing mass balances for uranium at various stages of the experiment. These mass balances are shown in Appendix G. Figure 5.6 shows how the amount of uranium desorbed from the sand varied with time. Because of uncertainties in the time to reach equilibrium noted in the previous paragraph, there is the possibility that the samples were not fully at equilibrium when dilution occurred which would affect the desorption results.

While not as fast as sorption, noticeable desorption had occurred within one minute. Nakayama [1991] and Tripathi [1983] examined the reversibility of neptunium and uranium sorption in response to a change in pH. Both found the reactions to be reversible

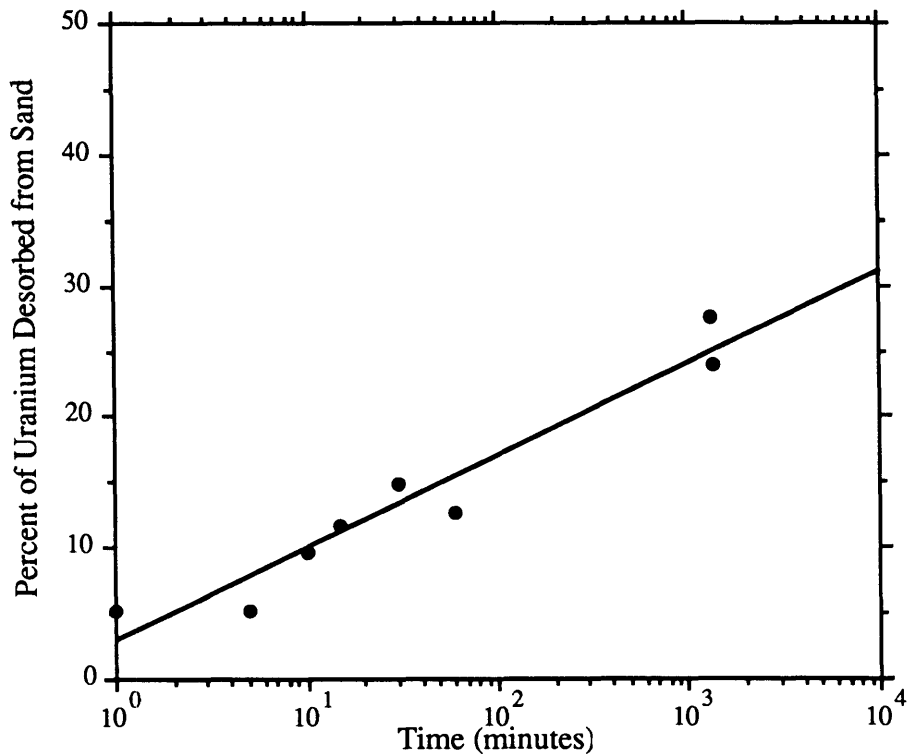


Figure 5.6: Uranium Desorption Kinetics

Initial system consisted of 15 g silica sand and 15 ml 0.1 M NaCl at 10 ppm U. 10 ml removed after 24 hr and 25 ml of 0.1 M NaCl added. pH remained constant at 7.90 under open conditions.

and that the percent sorbed would return to the previous value when the initial pH was restored. Newman *et al* [1991] studied the desorption of lithium in response to dilution with Yucca Mountain groundwater to lithium-treated tuff. They found the desorption kinetics to be slower than the sorption kinetics, which agrees with this project's findings. One possible reason given for this was that during sorption there was a relatively large metal mass in solution which produced a "large driving force" that enhanced adsorption kinetics. During desorption, the smaller amount of metal adsorbed produced a smaller driving force back into solution, resulting in a slower rate of transfer.

5.3.4.1 Desorption During Flushing

The amount and rate of desorption of uranium from unsaturated sand as a result of flushing was also examined. Unsaturated samples were prepared according to the procedure in Appendix C. After the pore solution of the samples were removed, ten ml of electrolyte solution containing no uranium were then added to the top of the column. The pore solution was extracted again. This was repeated five times. The flushing solutions were either 0.1 M NaCl solutions which were in equilibrium with the atmosphere (pH 5.7) or which had been pretreated with the sand (pH 8.2). The total amount of flushing solution was approximately equal to four pore volumes. Mass balances were performed for uranium to determine how much uranium was sorbed to the sand, in the extracted solution, or in the pore solution to determine whether any desorption was occurring. Tables 5.7 and 5.8 shows the amount of desorption from the sand with repeated 10 ml flushings.

**Table 5.7: Uranium Desorption in Response to Flushing with
0.1 M NaCl Solution at pH 5.7
118% Saturated, pH = 8.2
Total Initial U = 12.8 ml*10.16 ppm = 130.05 μ g**

Number of Flushes	Effluent U Conc.	U in Effluent (μ g)	U in Pore Solution (μ g)	U in Sand (μ g)	Amount of U Desorbed
Pore Soln.	3.68 ppm	31.28	16.99	82.95	0.0%
1	1.86	49.88	0	80.17	3.4
2	0.25	52.38	0	77.67	6.4
3	0.079	53.17	0	76.88	7.3
4	0.048	53.65	0	76.40	7.9
5	0.043	54.08	0	75.97	8.4

Uranium desorption from the sand in response to flushing was seen in both samples, but was much greater for the higher pH sample. For this sample, almost half of the uranium desorbed from the sand. The higher pH flushing solution would contain a larger amount of uncomplexed carbonate ions which could easily complex with the uranium and sorb less. Previous experience has shown that

**Table 5.8: Uranium Desorption in Response to Flushing with
0.1 M NaCl Solution at pH 8.2
91% Saturated, pH = 8.2
Total Initial U = 11.31 ml*9.55 ppm = 108.01 μ g**

Number of Flushes	Effluent U Conc.	U in Effluent (μ g)	U in Pore Solution (μ g)	U in Sand (μ g)	Amount of U Desorbed
Pore Soln.	2.48 ppm	16.12	11.93	79.96	0.0%
1	2.32	39.32	0	68.69	14.1
2	1.18	51.12	0	56.89	28.9
3	0.65	57.62	0	50.39	37.0
4	0.42	61.82	0	46.19	42.2
5	0.31	64.92	0	43.09	46.1

the pH of the first flushing solution was probably raised to 7 or so as it passed through the sand. At these pH's, uranium's solubility is lower, but its distribution coefficient is often higher because of the increase in hydroxyl complexes. This is probably why the amount of desorption was smaller. In both cases, uranium desorption can occur fairly fast, because the elapsed time between flushing solution addition and extraction was approximately 45 seconds.

5.3.4.3 Implications of Results

The kinetics experiments were performed to assess the impacts of kinetics on the feasibility of using isotopic differentiation. The proper choice of the ^{238}U concentration in the flushing solution relative to the equilibrated ^{235}U concentration in the pore solution could influence the sorption results. Relatively fast sorption implies that if a higher concentration of the ^{238}U was used in the flushing solution, it could cause uranium in the pore solution to be adsorbed during mixing and flushing. As the flushing solution mixes with the pore solution, sorbing uranium would not discriminate between the ^{235}U , which was previously at equilibrium, and the new ^{238}U atoms. Thus, the lower extracted ^{235}U concentration would produce a distribution coefficient which was too large. Relatively fast desorption implies that if the flushing solution had a lower uranium concentration, ^{235}U atoms previously sorbed could desorb,

resulting in a distribution coefficient which was too low. The actual results described in Section 5.3.5, however, indicated that kinetics did not significantly affect the results.

5.3.5 EFFECT OF FLUSHING SOLUTION URANIUM CONCENTRATION AND pH

Experiments were conducted to determine the effect of the flushing solution uranium concentration on the results. Unsaturated samples, containing cleaned Wedron 510 sand at 100% saturation and 8.0 ppm uranium (91% ^{235}U , 9% ^{238}U), were mixed in the Turbula for 2.75 days. The pore solutions were then flushed out with 36 ml of enriched ^{238}U (99.98%) solution. The flushing solution volume was approximately three times the pore solution volume. The flushing solution was added in 9 ml increments which were removed with a vacuum. Vacuums were used to reduce the mixing time of the pore and flushing solutions in the sand. This mixing time ranged between 20 and 45 seconds. The estimated equilibrated uranium concentration of the pore solution was between 1.5 to 2.5 ppm uranium. Because previous experiments (see sections 5.3.3 and 5.3.4) had indicated that both sorption and desorption occurred fairly quickly, the uranium concentration of the flushing solution was varied between 0.03 ppm and 50 ppm. The effluent solution (containing the pore solution and some of the flushing solution) was mixed to achieve a uniform concentration. Ten ml of this was then filtered, placed in an acid-washed bag, and dried in an oven. The dried samples were sealed and irradiated in the reactor for 1.1 hours. Blanks of the pretreated electrolyte and uranium solutions were also irradiated in order to determine background concentration levels of La, Ce and Nd. Appendix C describes the procedure in more detail.

A control sample had its pore solution removed with vacuum extraction. Its uranium concentration was then determined with the ICP and compared to the isotopic differentiation samples.

Table 5.9 shows the calculated equilibrated pore solution uranium concentrations ($^{235}\text{U} + ^{238}\text{U}$) and pH's for various flushing

solutions. There was no identifiable trend in the pore solution concentration with the flushing solution's uranium concentration. Despite earlier concerns described in 5.3.4.3, no evidence of uranium sorption or desorption occurring during mixing of the pore and flushing solution was noticeable.

Table 5.9: Pore Solution Total Uranium Concentration vs. Flushing Solution Uranium Concentration

Flushing Soln. ²³⁸ U Conc.	Pore Soln. °U Conc.	Flushing Soln. pH†	Effluent pH*	% of Flush Soln. U Sorbed
0.03 ppm	1.36 ppm	7.85	8.11	0
3.00	2.98	8.11	8.23	47%
15.00	1.51	8.10	8.02	36
50.00	2.04	8.05	8.12	49

°²³⁵U + ²³⁸U at equilibrium with the sand.

†This is the pH of the flushing solution before it was used.

*This is the pH of the mixed pore and flushing solution that was removed.

The pH of the pore and flushing solutions appeared to significantly affect the results. The pH of the pore solution was found to vary with the order that the samples were made. This was described in section 4.2.3. As shown in Table 5.10, those made later generally had higher pH's and contained significantly higher amounts of ²³⁵U.

The amount of uranium sorbed from the flushing solution during flushing was found by comparing the concentration of ²³⁸U in the extracted solution (corrected for dilution with the pore solution) and the initial concentration. As shown in Table 5.9, it appeared that between 35 and 50% of the ²³⁸U in the flushing solution was sorbed while it passed through the column. This indicated that although the uranium in the flushing solution was quickly sorbed, the mixing time of the pore and flushing solutions was short enough that it apparently did not affect the uranium concentration in the equilibrated pore solution.

Table 5.10: Uranium Concentration and pH vs. Sample Preparation Order

Order Made	Effluent pH	Total U Conc.
1	N/A	†0.96 ppm
2	*8.10	N/A
3	8.02	1.51
4	8.12	2.04
5	°8.11	°1.36
6	8.23	2.98

†This sample was not flushed. Analyzed on the ICP.

*This was the pH of just the pore solution. It was not flushed.

°This pH would have been higher except that its flushing solution pH was 7.85 instead of the normal 8.10. The lower pH probably caused some of the dissolved uranium to sorb while flushing.

5.3.6 ANALYSIS OF SAND

During a sorption experiment, the uranium can be dissolved or sorbed to the sand grains, suspended particles or colloids. All of the previous experiments have examined the uranium concentration in the solution after it has been passed through a filter. This solution contains uranium which is dissolved or sorbed to colloids. It was assumed that the remaining uranium was sorbed to the sand. The uranium concentration on the sand was examined to determine whether this was a valid assumption.

The uranium concentration on the sand was determined by removing approximately 2 g of wet sand. The sand was weighed, dried in an oven, and reweighed to determine the sand's mass and the amount of uranium solution present. The dried sand was acidified with 5 ml of HNO₃ and mixed for 30 minutes to leach the uranium off the sand. Four ml of the solution was then removed and filtered with a 0.20 μm cellulose acetate syringe filter.

The uranium concentration for five sand samples were analyzed. Samples 1, 4 and 5 were removed before the pore solution was flushed or removed with a vacuum, while samples 2 and 3 were removed from the top of the column after flushing with 36 ml of 50 or 3 ppm ²³⁸U solution, respectively. The first three samples were

acidified with 0.005 M HNO₃ and analyzed with neutron activation. The last 2 samples, which were from a different experiment, were acidified with 22% HNO₃ and analyzed on the ICP.

Table 5.11: Comparison of the Calculated Amount of Uranium Sorbed Determined from the Sand and Solution Uranium Concentrations

(Initial uranium conc. = 8.04 ppm, pH ≈ 8.2)

Sample	Saturation Level	²³⁵ U Sand Conc.	²³⁸ U Sand Conc.	% U Sorbed (from sand)	% U Sorbed (from soln.)
1	103%	*1.13 ppm	0.19 ppm	78%	75%
2	103	2.36	*5.11	164	75
3	103	1.76	*0.35	123	63

(Initial uranium conc. = 11.37 ppm, pH ≈ 8.2)

Sample	Saturation Level	Sand U Concentration	% U Sorbed (from sand)	% U Sorbed (from soln.)
4	68%	*1.17 ppm	78%	72%
5	86	*1.12	59	53

*These concentrations were corrected for the amount of uranium which dried on the sand from the residual solution. This solution was assumed to be all pore solution for 1, 4, and 5 and all flushing solution for 2 and 3.

Comparisons of the calculated amount of uranium sorbed determined from the sand and solution uranium concentrations for the three samples removed before flushing or vacuum extraction (samples 1, 4, and 5) show that the two values were in good agreement, although the sand value was always a little higher. From samples 2 and 3, it was seen that the amount of ²³⁵U (i.e. uranium from the pore solution) sorbed onto the sand increased dramatically after flushing. In fact, more ²³⁵U was found than what would be expected if all the ²³⁵U in the pore solution sorbed or precipitated evenly onto the sand. Precipitation did not appear to have occurred because the uranium concentrations were sufficiently below the solubility limit. Another possibility was that much of the uranium in the pore solution could have sorbed while mixing with the flushing solution before being extracted. Evidence of sorption

occurring during this mixing was seen by the increase in the ^{238}U sand concentration. Increased sorption was plausible for the second sample because the flushing solution's uranium concentration was much higher than the pore solution's (50 vs. 2 ppm), but not for the last sand sample because the pore and flushing solutions had approximately the same uranium concentration. The final reason for the high ^{235}U concentrations could be heterogeneous concentrations of uranium on the sand.

Samples 2 and 3 showed an increase in the ^{238}U concentration after flushing. This suggests that some of the uranium in the flushing solution was being sorbed during flushing. Comparing the sand ^{238}U values to that predicted from the solution data (see Table 5.9), the sand values showed much lower ^{238}U concentrations than expected: 5.11 seen vs. 14 ppm expected for 2, 0.35 vs. 0.77 ppm for 3. The reason for the unexpected increase in ^{235}U sorption and decrease in ^{238}U sorption will be investigated in the future.

CHAPTER 6 URANIUM ADSORPTION VERSUS SATURATION LEVEL

Preliminary experiments were performed which examined uranium sorption versus saturation level. These were done with both vacuum extraction and isotopic differentiation.

The first experiment examined uranium sorption to pretreated (but not cleaned) sand in a 0.1 M NaCl matrix. The pH was approximately 8.25. The samples were mixed in the Turbula™ for 1 day and the pore solutions were removed with vacuum extraction. The results are shown in Table 6.1. With the exception of the first sample, the K_d's were nearly constant. Low saturation samples like the first one were susceptible to errors because the volume of the extracted solution was small, 2.2 ml, and it was harder to achieve a uniform U concentration in the pore solution. In the drier samples, a very small amount of highly concentrated uranium solution must be mixed with a much larger volume of slightly wet sand.

Table 6.1: Uranium Sorption onto Pretreated Wedron 510 Sand vs. Saturation Level I

Saturation Level	Initial U Conc.	Final U Conc.	% of U Sorbed	K _d (ml/g)
55%	9.46 ppm	1.63 ppm	83%	0.51
73	9.58	2.64	72	0.37
89	9.67	3.16	67	0.36
118	10.16	3.95	61	0.36

The second experiment examined the sorption of sand to pretreated, cleaned Wedron 510 sand in a 0.1 M KCl matrix. Three samples were run for three different saturation levels. For each saturation level, isotopic differentiation was used for two of the samples and vacuum extraction for the third. The samples were mixed for three days. The flushing solution had a concentration of 2.3 ppm and a pH of 8.2. The flushing volume was 36 ml. This procedure is described in more detail in Appendix C. The results are shown in Table 6.2.

**Table 6.2: Uranium Sorption onto Cleaned, Pretreated
Wedron 510 Sand vs. Saturation Level II**

Saturation Level	pH of †Effluent	Initial U Conc.	Final U Conc.	% of U Sorbed	Kd (ml/g)
49%	8.24	10.46 ppm	2.50 ppm	76.1%	0.30
* 49	N/A	10.54	1.45	86.2	0.59
49	8.21	10.50	3.28	68.8	0.21
68	8.31	11.26	3.44	69.4	0.30
* 68	8.19	11.40	3.19	71.9	0.34
67	8.22	11.44	4.79	58.1	0.18
87	8.34	11.22	4.52	59.7	0.25
* 86	8.17	11.36	5.40	53.0	0.19
85	8.39	11.47	4.25	62.9	0.28

†This is the pH of the pore solution for the vacuum extraction method and the pH of the extracted pore and flushing solutions for the isotopic differentiation method.

*This sample's pore solution was removed with vacuum extraction and analyzed on the ICP.

The major issue in this experiment was the range of pH's seen, 8.17 to 8.39. This wide range was especially surprising because the samples were prepared in three batches to reduce pH changes during preparation (see Section 4.2.3). The pH's shown in Table 6.2 for the isotopic differentiation were the effluent's and not the pore solutions. Since almost all of the effluent pH's were above the flushing solution's 8.2, the pore solution appeared to have been at a higher pH, such as 8.3 or 8.4. In this case, the more saturated samples would have had a higher pH because they were less diluted with the flushing solution than less saturated samples. The pH's recorded by vacuum extraction, 8.19 and 8.17, were similar to that found in similar experiments, but were lower than that found in the effluent solution. It appeared that either vacuum extraction or flushing was altering the pH.

Figure 6.1 shows the K_d vs. the saturation level using the data from Table 6.2 and 5.9. The data were divided into three pH groups because of the range in sample pH's. The lower pH samples were expected to have higher K_d 's because as the pH decreases, sorbing hydroxyl complexes increase and non-sorbing carbonate complexes

decrease (see Figure B.2). No noticeable trend with saturation level was evident. This agreed with what was seen with the data in Table 6.1.

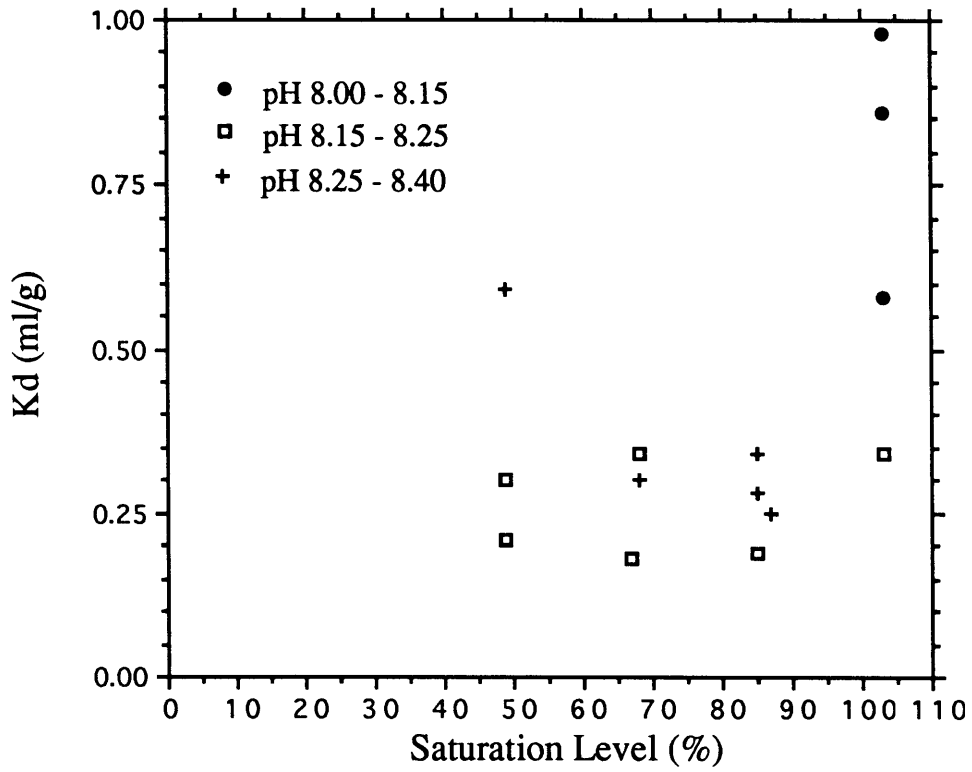


Figure 6.1 Uranium Kd vs. Saturation Level for Cleaned Wedron 510 Sand and 0.1 M KCl

CHAPTER 7 CONCLUSIONS

A number of issues related to the development of test methods for measuring K_d 's in unsaturated soil have been resolved.

Uniform saturation levels can be maintained throughout an experiment using a Turbula™ mixer with enough accuracy so that variations in sorption results due to changing saturation levels can be examined.

Pretreatment and cleaning of the sand produced more consistent pH's for unsaturated samples than a single step titration of fresh sand. The pH drift with time in batch samples still needs to be eliminated. Stronger cleaning processes, such as cleaning the sand with boiling HCl, could remove trace components not currently removed and produce a material which behaves more like pure quartz. Extensive cleaning and pretreatment of the solid could, however, interfere with the goal of evaluating the sensitivity of sorptions to variations in saturation as part of site-characterization studies by altering the surface chemistry.

The vacuum extraction method allowed uranium sorption to be examined for samples with saturation levels above 50%. Twenty seconds was usually enough time to remove most of the pore solution which can be extracted. Using this short of an extraction time, evaporation would be less than 1.5% and the temperature drop only 1 or 2° C. Experimental difficulties in the examination of sorption in soils below 50% saturation limited this method for three reasons:

- (1) During pretreatment, the residual saturation level in the sand was between 25 and 35%. Thus, the amount of spiked uranium solution needed was very small and difficult to ensure that there was a uniform uranium concentration throughout the pore solution.
- (2) The amount of pore solution removed by a vacuum becomes smaller (less than one ml), and
- (3) The smaller amounts of pore solution undergo relatively larger solution losses due to evaporation.

Isotopic differentiation appeared to work in principle, but was difficult to perform in practice. This was because the results were very dependent on matching the pH of the pore and flushing solutions which was complicated by the pH drifting in the samples with time. In addition, the estimated pH of the pore solution based on the extracted and flushing solutions' pH's did not agree with the pH measured with vacuum extraction. Although the kinetics of uranium adsorption and desorption were found to be fast, pH was the more critical parameter. This was because uranium's distribution coefficient is very sensitive to pH.

Preliminary experiments examining uranium distribution coefficients as a function of saturation level using both vacuum extraction and isotopic differentiation found generally constant values for saturation levels between 50 and 100%. Both uranium adsorption and desorption (in response to dilution) were found to occur in significant amounts within one minute. No consistent effect, however, was seen on the isotopic differentiation results when the uranium concentrations in the flushing solution were varied.

CHAPTER 8: RECOMMENDATIONS FOR FUTURE WORK

The isotopic differentiation method still requires additional work before any firm conclusions can be drawn. The most important task is to be able to achieve relatively consistent and predictable pH's between samples. Once the pH can be held constant, any effects of the uranium concentration in the flushing solution on the results could be more clearly observed. In addition, the dependence of distribution coefficients on the saturation level, if any, could be examined with more certainty.

No matter which method is used, the pH, final uranium concentration, and carbonate concentration need to be known for each sample. All three of these must be known to adequately define a uranium/electrolyte/sand system. Unfortunately, these parameters cannot be measured *in situ* or during the course of the experiment with current practice. In addition, the small pore solution volumes does not allow more than one parameter to be measured in a single sample. This forces one to assume the parameters are consistent between samples. Using larger samples (e.g. 250 ml) would provide enough pore solution so that it could be divided up into three portions, allowing all three parameters to be measured for one sample. This remedy would not allow the pH of isotopic differentiated samples to be determined though. The use of fluorometric indicators is currently being investigated to see if the pH of an unsaturated sample can be measured *in situ* without affecting uranium adsorption [Helman 1992].

Other issues that need to be investigated are listed below.

- (1) Since much of the uranium exists in the form of carbonate complexes, the carbonate concentration in the pore solution and any possible changes to it during flushing need to be determined.
- 2) How much of the uranium sorbs to the sand when the sand initially comes in contact with the uranium solution in the beaker should be examined. This sorption could affect the uniformity of the uranium concentration in the tube and the extracted pore solution.

- 3) A procedure also needs to be developed which can produce uniform uranium distributions for samples with saturation levels under 50%.

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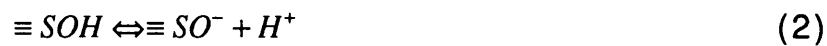
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APPENDIX A: ADSORPTION

This appendix briefly explains the chemistry of the solid-water interface and how it relates to adsorption. The following is summarized from Stumm [1992] and Schwarzenbach, Gschwend and Imboden [1993].

A.1 Acid-Base Chemistry of Oxides

Oxides and oxyhydroxides, such as quartz, are covered with surface hydroxyl groups in the presence of water. These surface groups are represented by a generalized hydrolyzed species $\equiv SOH$ and undergo proton exchange reactions with the solution like dissolved acids:



Acid-base equilibrium constants can describe the uptake and release of protons:

$$K_{a1} = \frac{[\equiv SOH][H^+]}{[\equiv SOH_2^+]} \tag{3}$$

$$K_{a2} = \frac{[\equiv SO^-][H^+]}{[\equiv SOH]} \tag{4}$$

These equilibrium constants describe both the intrinsic reactivity of the O-H bond and the electrostatic free energy of moving H^+ to and from a charged surface.

$$K_{a1} = K_{a1}^{int} e^{\frac{F\psi}{RT}} \tag{5}$$

$$K_{a2} = K_{a2}^{int} e^{\frac{F\psi}{RT}} \tag{6}$$

where

F = Faraday constant (C/mol)

ψ = surface potential relative to the bulk solution (V)

R = molar gas constant (J/mol-K)

T = absolute temperature (K)

A.2 Surface Charge

The surface of the solid develops an electrical charge from:

- 1) chemical reactions at the surface,
- 2) lattice imperfections at the solid surface, and
- 3) adsorption of a hydrophobic species or surfactant ion.

This study was mostly concerned with surface chemical reactions.

During titration of an oxide in an electrolyte with acid or base (C_a and C_b = concentration of each, respectively), we find that:

$$C_a - C_b + [OH^-] - [H^+] = [\equiv SOH_2^+] - [\equiv SO^-] \quad (7)$$

If the concentrations of the surface species are expressed in terms of mol/kg (indicated as "{}"), the surface charge σ (C/m²) can be calculated:

$$\sigma = \frac{(\{ \equiv SOH_2^+ \} - \{ \equiv SO^- \}) * F}{s} \quad (8)$$

where s is the specific surface area (m²/kg). When these two surface species are present in equal concentrations, the surface has zero net charge and is referred to as the pH of the zero point of charge, pH_{zpc} :

$$[\equiv SOH_2^+] = [\equiv SO^-] \quad (9)$$

This pH is not affected by the concentration of the inert electrolyte and is related to the intrinsic equilibrium constants:

$$pH_{zpc} = 0.5[pK_{a1}^{int} + pK_{a2}^{int}] \quad (10)$$

For SiO₂, the pH_{zpc} is 2.0.

A.3 Surface Potential and the Double Layer Theory

The Guoy-Chapman Theory describes the distribution of free charges near a surface. An electrical double layer is assumed in which one layer exists as a fixed or surface charge attached top the solid surface and the other is distributed diffusively in the liquid and contact. The theory relates the surface charge density to the potential at the surface ψ :

$$\sigma = \frac{(8RTc\epsilon\epsilon_0)^{\frac{1}{2}}}{10^3} \sinh\left(\frac{z\Psi F}{2RT}\right) \quad (11)$$

where

ϵ = dielectric constant of water

ϵ_0 = permittivity of free space (C/V-m)

c = molar electrolyte concentration (M)

z = ionic charge

The double layer thickness K^{-1} (m) is defined by:

$$K = \left(\frac{2F^2 I 10^3}{\epsilon\epsilon_0 RT}\right)^{\frac{1}{2}} \quad (12)$$

where I is the ionic strength.

As the pH increases, ψ becomes less and less positive as reaction 1 proceeds to the right and more and more negative as reaction 2 continues to the right. The overall effect is to make it harder to move H^+ away from an oxide surface as the solution pH increases. This effect is reflected in the exponential terms in 5 and 6.

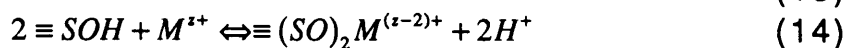
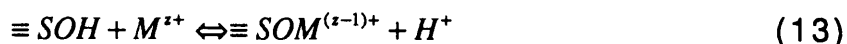
A.4 Metal and Ligand Adsorption

According to Dzombak and Morel [1990], surface complexation models have the following characteristics:

- 1) Sorption takes place at specific surface coordination sites;
- 2) Sorption reactions can be described by mass law equations;

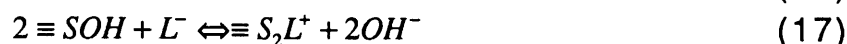
- 3) Surface charge results from the sorption reaction itself; and
 4) The effect of surface charge on sorption can be taken into account by applying a correction factor derived from the electric double layer theory to the mass law constants for surface reaction.

Metal ions form surface complexes with hydrous oxides by coordinating the metal ion with the oxygen donor atoms and releasing protons from the surface. Examples of metal binding reactions include:



The metal ion competes with H⁺ or other metal ions for sites. Metal adsorption is very pH dependent and usually rises from zero to almost 100% over only 1-2 pH units.

During ligand adsorption, the surface hydroxy is exchanged for a different ligand. Typical ligand exchange reactions include:



The ligand competes with OH⁻ and other ligand ions for the Lewis acid of the hydrous oxide central ion. Ligand exchange is also very dependent on pH and is favored by lower pH values.

A.5 References

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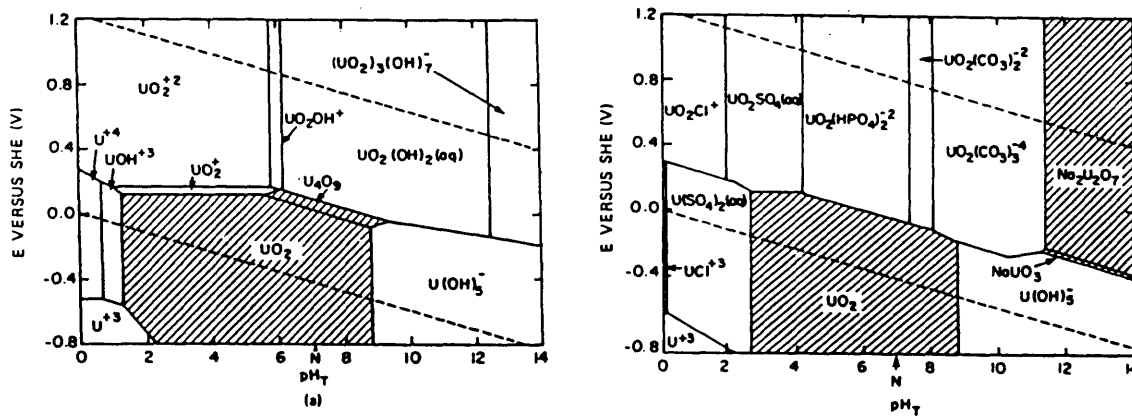
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APPENDIX B: URANIUM CHEMISTRY

B.1 Solubility and Complexation

Uranium may occur in aqueous solutions as trivalent U^{3+} , the tetravalent uranous ion U^{4+} , pentavalent $U(V)O_2^+$, or the hexavalent uranyl ion $U(VI)O_2^{2+}$. Only the uranous and uranyl ions are of practical importance because the other two are unstable [Benedict *et al* 1981]. Figures B.1 shows the Eh-pH diagram for water and typical groundwater systems at 25° C [Paquette and Lemire 1981]. Uranium can also undergo photochemical reduction from U(VI) to U(V) when exposed to ultra-violet and/or visible light. The light will excite the species which will react with most reductants [Bell 1983]. Adsorbed U(VI) can be reduced to U(IV) by mobile reductants such as H_2S or CH_4 or by the sorbent itself if it is organic matter. If reduction does not follow adsorption, U(VI) can be desorbed by increasing the alkalinity at constant pH or raising the pH [Langmuir 1978].



Uranium solubility is a function of both pH and Eh. It is dominantly transported in the oxidized U(VI) state and generally considered insoluble in the reduced U(IV) state [Turner 1991]. Uranite, UO_2 - $\text{UO}_{2.25}$, $\alpha\text{-U}_3\text{O}_8$, schoepite, $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}(\text{c})$, and sometimes coffinite are the stable uranium oxides and hydroxides in water at 25°C [Langmuir 1978].

Uranium in natural waters is usually complexed, not only with carbonate, but also with hydroxide, phosphate, fluoride, sulfate, organics and perhaps silicate. These complexes greatly increase the solubility of uranium minerals and the mobility of uranium in surface and ground waters. Figure B.2 shows the distribution of uranyl-hydroxy and carbonate complexes versus pH [Langmuir 1978]. Table B.1 shows the equilibrium constants for hydrolysis and complexation reactions at 25° C applicable to this study [Lemire and

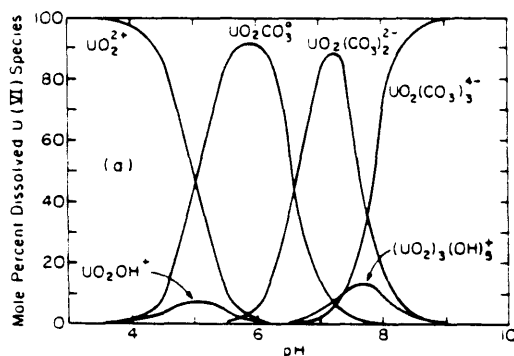


Figure B.2: Distribution of Uranyl-hydroxy and Carbonate Complexes vs. pH for $\text{P}\text{CO}_2 = 10^{-2}$ atm and $\Sigma\text{U} = 10^{-8}$ M, at 25°C.

TABLE B.1: EQUILIBRIUM CONSTANTS FOR URANIUM AT 25° C

<u>Reaction</u>	<u>Log K</u>
$\text{UO}_2^{2+} + \text{H}_2\text{O} = \text{UO}_2(\text{OH})^+ + \text{H}^+$	- 5.8 ± 0.4
$2\text{UO}_2^{2+} + 2\text{H}_2\text{O} = (\text{UO}_2)_2(\text{OH})_2^{2+} + 2\text{H}^+$	- 5.6 ± 0.4
$3\text{UO}_2^{2+} + 5\text{H}_2\text{O} = (\text{UO}_2)_3(\text{OH})_5^+ + 5\text{H}^+$	-15.6 ± 0.4
$3\text{UO}_2^{2+} + 7\text{H}_2\text{O} = (\text{UO}_2)_3(\text{OH})_7^- + 7\text{H}^+$	-31 ± 4
$\text{UO}_2^{2+} + 2\text{H}_2\text{O} = \text{UO}_2(\text{OH})_2(\text{aq}) + 2\text{H}^+$	-12 ± 1
$\text{UO}_2^{2+} + \text{CO}_3^{2-} = \text{UO}_2(\text{CO}_3)(\text{aq})$	-10.1 ± 0.4
$\text{UO}_2^{2+} + 2\text{CO}_3^{2-} = \text{UO}_2(\text{CO}_3)_2^{2-}$	-17.1 ± 0.4
$\text{UO}_2^{2+} + 3\text{CO}_3^{2-} = \text{UO}_2(\text{CO}_3)_3^{4-}$	-21.4 ± 0.4
$\text{UO}_2^{2+} + \text{Cl}^- = \text{UO}_2\text{Cl}^+$	- 2 ± 1

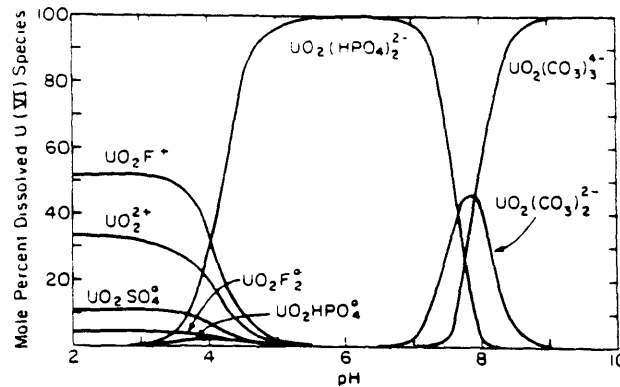


Figure B.3: Distribution of Uranyl Complexes vs. pH for Some Typical Ligand Concentrations in Groundwaters of the Wind River Formation at 25° C. $P_{CO_2} = 10^{-2.5}$ atm, $\Sigma F = 0.3$ ppm, $\Sigma Cl = 10$ ppm, $\Sigma SO_4 = 100$ ppm, $\Sigma PO_4 = 0.1$ ppm, $\Sigma SiO_2 = 30$ ppm

Tremaine 1980]. Figure B.3 shows the comparative importance of the various uranyl complexes in groundwater [Langmuir 1978].

Uranous (IV) fluoride complexes predominate below pH 3-4 and the highly stable phosphate and carbonate complexes in normal pH ranges. Figure B.4 shows that a rise in P_{CO_2} from the atmospheric value of $10^{-3.5}$ atm to a groundwater value of 10^{-2} atm increases the solubility of UO_2 by more than 1000 times for Eh values above -0.05 V [Langmuir 1978]. At lower Eh, the extreme insolubility of uraninite and coffinite at normal groundwater pH makes uranium practically immobile. However, for each unit increase in pH in the low Eh range, the concentration of U in solution increases by an order of magnitude. This is because of the increasing stability of U(VI) hydroxide and U(VI) carbonate complexes at higher pH [Langmuir 1978]. At high Eh, the effect on U concentration in solution of changing pH at constant Eh is even greater. This occurs because U(VI) becomes dominant over U(IV) as Eh increases and U(VI) forms very stable carbonate complexes. Thus, uranium solubilities which are approximately 10^{-3} ppm under reducing environments can

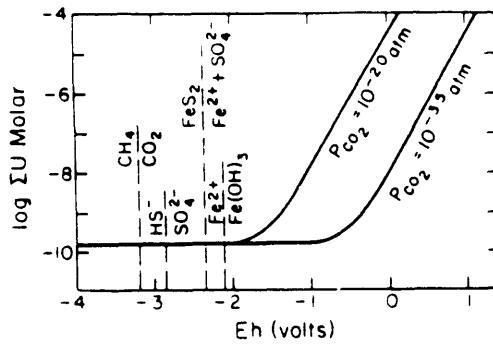


Figure B.4: The Solubility of Uraninite, $\text{UO}_2(\text{c})$, at $\text{pH} = 8$ and 25°C as a Function of Eh and PCO_2 . Also Shown Are the Eh Values for Some Important Redox Reactions Computed Assuming: $\text{CH}_4 = \text{CO}_2$, $\text{SO}_4^{2-} = \text{HS}^-$, $\text{Fe}^{2+} = 10^{-4} \text{ M}$ and $\text{SO}_4^{2-} = 10^{-3} \text{ M}$.

reach hundreds of ppm under oxidizing conditions [Deutsch and Serne 1984]. In addition, all oxidation states of uranium and plutonium can form very strong complexes with both naturally occurring humic and fulvic acids, but these tend to strongly sorb to clays.

B.2 Uranium Adsorption

Uranium adsorption has been studied for both pure minerals and whole rock samples. The relative sorption abilities of various minerals for uranium is shown below [Ticknor *et al* 1991]:

Hematite \approx Kaolinite \approx Goethite \approx Muscovite \approx Chlorite $>$ Illite
 $>$ Calcite $>$ Gypsum $>$ Quartz $>$ Epidote

In 0.01 M NaCl, all of these minerals show K_d 's greater than 100 ml/g over a pH range from 6.5 to 8.0 while uranium sorption on whole rock tuff samples in J-13 water is in the range of 0 - 30 ml/g. Uranium adsorption is very sensitive to pH, but relatively insensitive to ionic strength [Meijer 1990b]. Uranium sorption by most minerals exhibits a sharp increase as a function of pH at a pronounced sorption edge usually between pH 2 to 6. The dominant

adsorbed uranyl complexes is uncertain, but $\text{UO}_2(\text{OH})^+$, $\text{UO}_2(\text{OH})_2$, $\text{UO}_2(\text{OH})_3^-$ and $(\text{UO}_2)_3(\text{CO}_3)_5^{+2}$ have all been proposed [Turner 1991].

Hydroxyl complexes are strongly adsorbed, while uranyl carbonates, sulfate, and probably fluoride complexes inhibit adsorption (the latter two only under acidic conditions) [Wanty *et al* 1991, Langmuir 1978]. Tripathi [1983] found that up to pH 7, the adsorption behavior of U(VI) was almost the same for carbonate-free and carbonate-bearing systems. Uranium adsorption was very high when $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ was the predominant aqueous species, but there was a sharp decrease in adsorption when $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ were dominant.

Both Hsi and Langmuir [1985] and Park and Leckie [1992] studied the effect of competing cations on uranium adsorption and did not find any effect by the presence of Ca^{2+} or Mg^{2+} in solution. For minerals, such as clays or zeolites where ion exchange is expected to be the dominant sorption mechanism, Tsunashima *et al* [1981] and Vochten *et al* [1990] found that uranium was selected preferentially relative to monovalent cations, while divalent cations significantly reduced uranium sorption.

Uranium and plutonium exhibit maximum sorption to colloids near pH 6 and lower sorption at higher and lower pH values. At high pH, low sorption occurs because both colloid and dominant species are negatively charged. A similar process occurs at low pH, when both are positively charged. If, however, at an intermediate pH, the dominant actinide species change from negative to positive while the colloid zeta potential is still negative, maximum sorption would be expected [Shade *et al* 1984]. Thus, the pH range of minimum solubility of U(VI) minerals is pH 5 to 8.5, which is also the pH range of maximal uranyl sorption on most important colloidal materials [Paquette and Lemire 1981].

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APPENDIX C: STANDARD PROCEDURES

Procedures are described for performing saturated and unsaturated sorption experiments. These procedures incorporate the procedures used for saturated sample titrations, preparing unsaturated samples for moisture distribution experiments, and sand pretreatment.

I. Saturated Sorption Experiments

Part A: pH Adjustment and Sand Pretreatment

1. Place the Wedron 510 sand and 80% of the 0.1 M NaCl electrolyte solution into a 50 ml Teflon™ Oak Ridge centrifuge tube.
2. Add the base or acid as 0.25 M NaHCO₃ or HNO₃.
3. Shake the tube by hand for one minute.
4. Connect a fused crystalline alumina gas diffusing stone to an aquarium pump with tubing and an in-line air filter.
5. Wrap the stone with a narrow piece of a laboratory wiper. Place a 5 ml disposable pipette tip over the wrapped stone to minimize the air leakage.
6. Suspend the pipette tip in the free-standing solution of the sample in such a way as to avoid splashing the solution out of the tube. Bubble the solution for 10 minutes.
7. Mix the samples for 24 hours on a hematology mixer.
8. Bubble the solution until the pH stabilizes. Another 10 minutes is usually sufficient. Samples with high solution volumes or large pH adjustments often require longer bubblings. For samples with low solution/solid ratios, mix the sample several times by hand during the bubbling.
9. Record the final pH.

Part B: Uranium Sorption

10. Add the remaining 20% of the solution volume as 50 ppm uranium solution in a 0.1 M NaCl matrix.

11. Mix the sample on a hematology mixer for the desired amount of time. Bubble the solution with air daily. Record the mixing time and pH.
12. Remove 10 ml of the solution with a pipette.
13. Pass the solution through a 0.45 mm cellulose acetate filter attached to a plastic 20 ml syringe, into a 15 ml polypropylene centrifuge tube containing 1 ml of 22% HNO₃.
14. Measure the final U concentrations with inductively coupled plasma atomic emission spectroscopy.

II. Unsaturated Sorption Experiments

Part A: Pretreatment Procedure for Unsaturated Samples

1. Using data from saturated sample titrations, determine how much acid or base is needed for a desired amount of sand and solution. The amount of solid used should be at least 20% more than actually required because some of the sand is spilled or left behind in containers.
2. Prepare the samples as described in Procedure I, Part A. Instead of pretreating each sample in its own tube, combine all of the samples in one experiment in one 500 ml polyethylene bottle.
3. When the pH stabilizes, place a filter into a Buechner funnel, which is connected to a vacuum.
4. Remove most of the solution from the sand into a filtering flask.

Part B: Preparation of Unsaturated Samples

5. Place the electrolyte solution in a glass beaker. Add the concentrated uranium solution to the beaker to reach the desired uranium concentration and gently mix the solutions together by hand.
6. Add the pretreated (and still moist) sand into the beaker slowly to avoid splashing. Record the amount of pretreated sand added. The sample size usually consisted of approximately 65 g sand

and between 6 and 13 ml of solution at an initial uranium concentration of 10 ppm.

7. Take several samples of the pretreated sand while filling the beaker. Record its weight when wet and later after it has been dried in an oven. Determine the residual saturation level in the sand.
8. Mix the solution and solid together with a Teflon™ spatula until the moisture content is visually uniform.
9. Carefully pack the wet sand into a centrifuge tube. Mix the sand in the beaker frequently during packing. Shake the tube periodically to enable the wet sand to settle.
10. When the tube is full, mix it in the Turbula™ for 10 minutes to let the sand settle.
11. Add sand, if needed, to completely fill the tube. Weigh the sand filled tube.
12. Seal the tube's lid with electrical tape and place the tube back in the Turbula™.
13. Place the sample tubes inside a larger container which is then placed inside the Turbula™ and usually mixed for 2 days at 42 rpm.

Part C: Vacuum Extraction of the Pore Solution

14. The setup of the vacuum extraction method is as follows. A 2.5 cm dia. and 10 cm high borosilicate chromatography column is placed on top of a 125 ml filtering flask. The interface of these two items is sealed with vinyl to prevent air leakage. A 2-3 cm long piece of Teflon™ tubing is attached to the bottom of the column to allow the extracted pore solution to drip into the flask without being carried along with the air. The filtering flask is connected to another filtering flask with tubing to prevent water being sucked into the vacuum. A glass tube is placed through a rubber stopper on top of the second flask. This tube is connected to the vacuum pump.
15. Take the tube out of the Turbula™ and empty the sand into the column using a Teflon™ coated spatula.

16. Run the vacuum to remove the pore solution. Twenty seconds usually removes most of the pore solution which can be extracted.
17. Remove the pore solution from the filtering flask with a pipette. Record the amount removed.
18. Pass the solution through a 0.45 μm cellulose acetate filter attached to a plastic 20 ml syringe, into a 15 ml polypropylene centrifuge tube containing 1 ml of 22% HNO_3 .
19. Dilute the sample to 11 ml with 0.1 M NaCl if needed.
20. In each batch, prepare a few extra samples in the same manner. (At least one pH sample for every 3 sorption samples.) Remove their pore solutions and record their pH as described in Section 2.2.2.2 in the main text.

III. Isotopic Differentiation Sorption Experiments

Part A: Preparation of Uranium Solutions

1. Place a Teflon™ magnetic stirring bar in a volumetric flask and a glass funnel on top.
2. Weigh a cleaned glass dish on a balance.
3. Carefully place the powdered U_3O_8 on the dish with a Teflon™-coated spatula. Record the mass.
4. Pour the uranium powder into the flask. Rinse the dish with nitric acid to remove any remaining powder.
5. Partially fill the flask with deionized water and nitric acid.
6. Using a magnetic stirrer equipped with a heater, begin to mix and heat the solution. Do not boil.
7. The uranium will start to dissolve when the water becomes very warm. Add nitric acid and DI water as needed.
8. When all of the uranium has dissolved, allow the water to cool down to room temperature before filling up the volumetric flask. Add extra water to compensate for the bar's volume.
9. Use this solution to make the stock solution used in the experiments.

10. To make the stock solution, add enough KCl to a another volumetric flask to reach the desired ionic strength.
11. Pipette the required amount of concentrated uranium solution into the flask and fill the rest with DI water.
12. Raise the pH of the solution to approximately 5 with KOH.
13. Start to bubble the solution. Do not use an airstone. Use a small glass tube attached to the hose. Do not let the solution come in contact with the hose.
14. Add KHCO_3 to reach the desired pH. Make sure the solution is at equilibrium with atmospheric CO_2 by bubbling the solution until the pH stabilizes.
15. Store the uranium solution in a Teflon bottle.

Part B: Preparation of Unsaturated Samples

16. Pretreat cleaned Wedron 510 sand and 0.1 M KCl electrolyte solution as described in Part A of Procedure II.
17. Prepare the unsaturated samples as described in Procedure II, Part B with the following modifications:
 - a) Use the enriched ^{235}U solution. The initial concentration of 100 ppm was diluted to approximately 10 ppm with pretreated electrolyte solution.
 - b) Record the mass of the centrifuge tube when it is empty and after it has been filled.

Part C: Flushing the Pore Solution

18. The flushing solution is highly enriched ^{238}U in a 0.1 M KCl matrix. The pH should match as close as possible the expected pH of the sample. The U concentration was varied, but often the expected final equilibrated U concentration of the pore solution was used.
19. Record the mass of an empty filtering flask (with a Teflon magnetic stirring bar in it). Record the mass of a column.
20. The setup is the same as that used in the vacuum extraction method.

21. Empty the sand into the column using a Teflon-coated spatula.
22. Record the weights of the empty centrifuge tube and sand-filled column. Avoid spilling the sand while weighing the sand.
23. Add 9 ml of the flushing solution to the top of the column. Turn on the vacuum for 20 seconds to remove the pore solution.
24. Repeat step 23 three more times.
25. In the filtering flask, mix the extracted solution with the stirring bar for 20 seconds.
26. Remove 22 ml of solution and pass it through a 0.20 μm cellulose acetate filter (attached to a plastic 20 ml syringe) into a beaker.
27. Record the weight of the sand-filled column and the filtering flask containing the extracted solution.
28. Place 10 ml of the filtered solution inside a plastic bag. This bag should have been acid-washed with 15% HNO_3 on the inside and outside and heat-sealed at the bottom.
29. Place another 10 ml of the filtered solution into a 15 ml polypropylene centrifuge tube containing 1 ml of 22% HNO_3 . This sample is a backup.
30. Record the pH of the remaining unfiltered solution in the filtering flask.
31. With the solution-filled bag standing upright in a small beaker, dry the sample at approximately 75° C in an oven.
32. Heat-seal the other end of the bag. Place this bag inside of another bag and heat-seal the outer bag. Write the sample identification with a permanent marker on the outer bag.
33. Irradiate the sample in the reactor for approximately 1 hour. Let the shorter-lived radioisotopes decay for a week before analyzing the sample.
34. Measure the activity with a Ge(Li) detector.

Part D: Sand Analysis

35. Record the weight of a small glass dish.
36. Place the sand sample in the dish and record the weight.
37. Dry the sample in an oven overnight. Record the weight.

38. For a 2 g sand sample, add 5 ml of 22% HNO₃. Mix the sand and acid.
39. After 30 minutes, remove 4 ml of the acid, filter it, and place it in an acid-washed plastic bag.
40. Follow steps 32 - 34 in Part C.

IV. Equipment Cleaning

All centrifuge tubes and other equipment were washed with 1% HNO₃ to leach any previously sorbed uranium. The tubes were then filled with deionized water for 48+ hours, which was changed at least twice, to remove any HNO₃ remaining in the plastic which could later affect the sample's pH.

A Note About Sample Bubblings

Because the experiments were conducted under open conditions, the solutions were usually bubbled with air. Large volumes of electrolyte solution were bubbled with a fused crystalline alumina gas diffusing stone. Sorption samples were bubbled for 10 minutes with air using a 5 ml polypropylene pipette tip placed over a gas diffusing stone which was connected to an aquarium pump. This method was used because, although it took longer to reach equilibrium, it resulted in smaller solution losses during bubbling (0.05 ml versus 0.21 ml) and less cross-contamination of solutions between samples. For a typical sample which underwent the following: bubbled twice with a pipette tip, pH measured, U stock solution added, bubbled once more, and solution removed; approximately 0.23 ml of solution was lost. This corresponded to 0.9% for a sample containing 25 ml and would result in a 0.7% increase in the actual uranium concentration of the overall sample (based on 20 ml 0.1 M NaCl and 5 ml U stock solution). Because this is less than 1%, reported values in this study were not corrected for these effects.

**APPENDIX D: DYE AND ADDITIONAL MOISTURE DISTRIBUTION
EXPERIMENTS**

D.1 Dye Tests

Fluorescent dye (Rhodamine WTS, 556 nm) was added to 50 ml sand-filled centrifuge tubes to observe the transport of liquids through the sand while being mixed in the Turbula™. The dye was introduced at the top of the tube or in intervals throughout the tube. The amount of dye used corresponded to saturation levels between 20% and 80%.

It was observed that mixing the sample in the Turbula actually slowed down the transport of the dye compared to a sample standing upright. This is because the Turbula's motion did not give the liquid any pressure head, whereas the standing sample was subjected to gravity. The dye would flow down the tube as long as it could nearly saturate the sand or until trapped air beneath the front prevented further downward transport. This probably occurred because the sand's capillary suction prevented the dye in samples, which were below 50% saturation, from completely draining to the bottom of the tube after standing upright for two weeks. The front of dye usually tapered off very quickly, although occasional fingers of dye would snake erratically around the tube. Changing the Turbula's speed of rotation from 20 to 90 rpm had no noticeable effect on the results.

D.2 Unsaturated Sand Sample Preparation

Technique was the single most important factor in preparing unsaturated samples. It was found that it was better to place the dry sand in the beaker first and then the solution. This way any drainage of the liquid was to the drier bottom portion. It was harder to mix the sand and water uniformly when the reverse was used because the bottom tended to be wetter. The beaker must be constantly mixed while filling the tube to prevent the water from draining to the bottom of the beaker. The amount of time the tube is upright must also be minimized to reduce drainage. Mixing about 25% more of the sand and solution than actually needed also produced better moisture distributions. Drainage was much more

significant in wetter samples because the sand's hydraulic conductivity increases with saturation level.

Wedron 510 sand always packed tighter when it became wet. It also settled considerably while being mixed in the Turbula™. This would cause voids, sometimes quite large, to appear in the tube over time. Weighing the tube before and after this occurred showed that this did not result from any water leakage. In tubes which had curved ends, spheres of sand would form and roll around in the voids. The voids usually did not occur in samples with saturation levels below 60% because they did not compact as much. Packing too much sand in the tubes, though, would force some of the liquid out or cause the tube's lid to unscrew during mixing. Usually, the wet sand was mixed in the Turbula™ briefly to settle the sand and then refilled to the top.

APPENDIX E: TITRATION CURVE EXPERIMENTS

The control of pH in batch sorption tests usually involves the use of a titration curve which shows the solution pH as a function of the amount of acid or base added to an electrolyte solution for a given concentration of a suspended solid. The chemistry of unsaturated systems, however, is complicated by the presence of the gas phase and because the solid volume is several times greater than the solution volume. In addition, the solution must be exposed to air to reach equilibrium with the atmosphere without undergoing significant evaporation losses to the relatively small amount of solution present.

Because a wide variety of liquid/solid ratios were used in the experiments, the possibility of producing a titration curve which could estimate the pH of a mixture as a function of solution volume, solid mass, and alkalinity added was attempted. During titration of a solid in an inert electrolyte solution under open conditions, the following empirical equation was assumed valid:

$$C_b - C_a + Alksand = \{OH^-\} - \{H^+\} + \{HCO_3^-\} + 2\{CO_3^{2-}\} \quad (1)$$

where C_a and C_b are the concentration of acid or base added per liter. The carbonate and bicarbonate activities were calculated from the solution pH and atmospheric CO_2 concentration. *Alksand* is a wide encompassing term that includes changes to the overall alkalinity of the system due to charged surface functional groups and the precipitation and dissolution of the solids present. *Alksand* is assumed in this study to be a function of pH and the amount of solid mass present (although it is recognized that this term involves a variety of processes that may be dependent on solubility limits, total sand mass, available surface area, time, or the concentrations of other species present). If the above equation is rearranged, *Alksand* can be found from the amount of base or acid added and the final pH:

$$Alksand = C_a - C_b + \{OH^-\} - \{H^+\} + \{HCO_3^-\} + 2\{CO_3^{2-}\} \quad (2)$$

When the concentration of the aqueous species is multiplied by the solution volume the total number of moles of alkalinity contributed by the sand is estimated. This result is divided by the sand mass to determine how the alkalinity of the system due to the sand varies with pH on a normalized sand mass basis. This function, referred to as Δ , has dimensions of moles/gram and is defined as:

$$\Delta = \frac{Alksand * Vsol}{Msand} = \frac{(C_a - C_b + \{OH^-\} - \{H^+\} + \{HCO_3^-\} + 2\{CO_3^{2-}\}) * Vsol}{Msand} \quad (3)$$

where M_{sand} is the sand's mass in grams.

The procedure for titrating saturated samples is described in Procedure I, Part A of Appendix C. For unsaturated sample titrations, electrolyte solution and base were mixed until the sand's moisture level was visually uniform. The sand was then placed into a centrifuge tube and mixed in the Turbula™ mixer. Vacuum extraction was used to remove the pore solution for pH measurement.

In performing titrations, much of the base added for high liquid/solid samples at higher pH's was used to increase the bicarbonate and carbonate concentrations in the solution as additional CO_2 was absorbed from the air, while for unsaturated samples much of the base added was used to overcome the buffering action of the solid phase. Base additions for saturated samples were performed with $NaHCO_3$ because it has the advantage of adding approximately one carbonate ion for every unit of alkalinity added and thus greatly speeds up the time to reach equilibrium with the atmosphere. After titrations were complete, excess CO_2 was driven off by bubbling air through the sample until the pH stabilized. Electrolyte loss during bubbling was approximately 0.05 ml for a 10 minute bubbling.

Over 150 titrations were performed on saturated samples with different liquid/solid ratios. These results are tabulated in Table G.6 of Appendix G. Figure E.1 shows the titration curve for samples containing 25 g Wedron 510 sand and 25 ml 0.1 M NaCl.

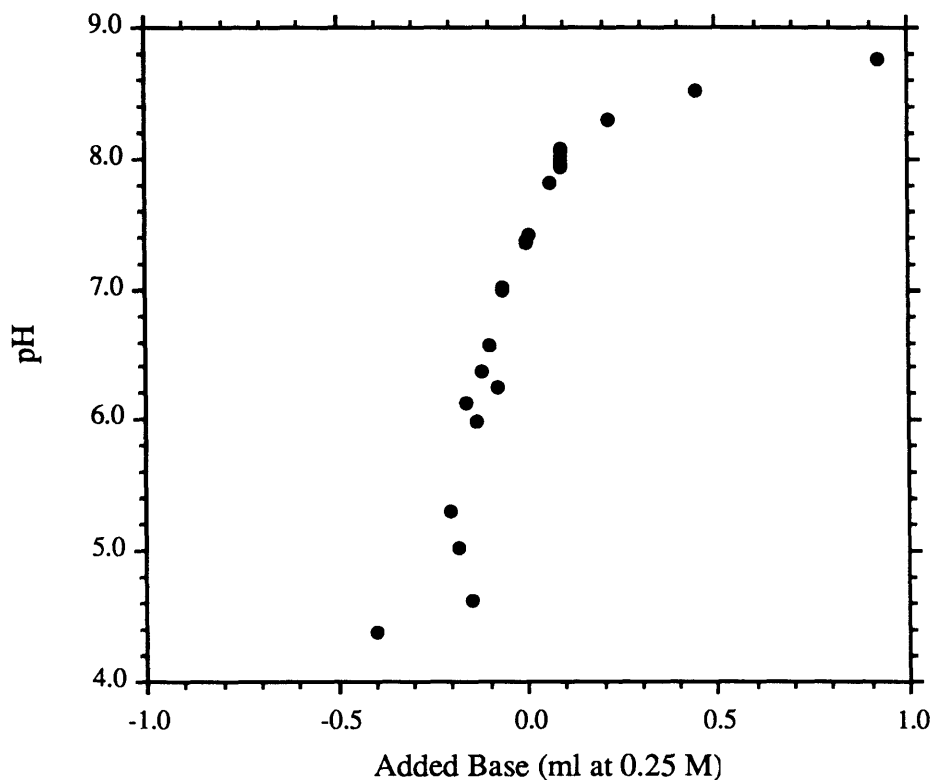


Figure E.1: Potentiometric Titration of 25 g of Fresh Wedron 510 Sand and 25 ml of 0.1 M NaCl Electrolyte Under Open Conditions

Although the empirical approach was a simplification of a rather complicated system, it produced a reasonable curve using the titration data from samples involving a variety of liquid/solid ratios as shown in Figure E.2. This curve was used to estimate the amount of acid or base needed to reach a specific pH based on the amount of electrolyte solution and sand present. This has worked well for saturated samples.

Unsaturated sample titrations were not satisfactory. The closed tube and the inability to bubble the pore solutions prevented the solutions from reaching equilibrium with atmospheric CO_2 . Attempts to achieve a pseudo-open system by adding the required amount of carbonate to the tube were not successful. This is because determination of what portion of the base to add to unsaturated samples as NaHCO_3 and as NaOH was very difficult because of uncertainties on whether the solution was truly in

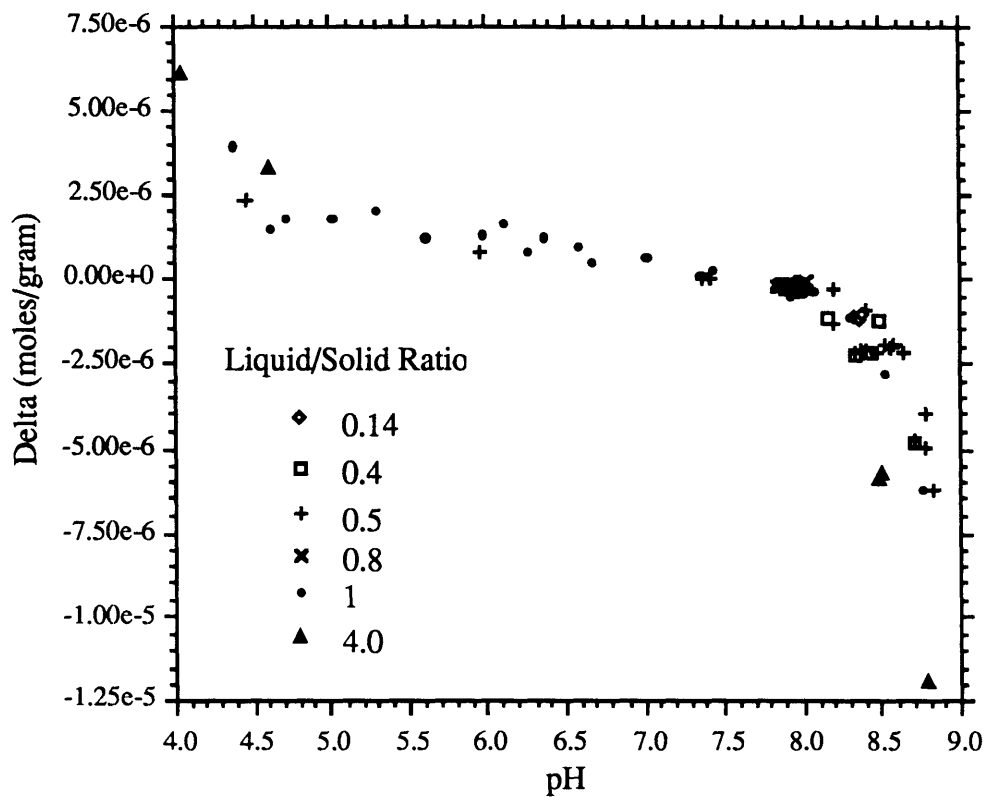


Figure E.2: Normalized Titration Curve for Fresh Wedron 510 Quartz Sand and 0.1 M NaCl at Equilibrium with Atmospheric Carbon Dioxide

equilibrium with atmospheric CO_2 at the measure pH. The determination of the proper portions was also complicated by the presence of carbonates in the sand. Furthermore, the pH of the samples drifted with time which would lead to disequilibrium with atmospheric CO_2 . Whereas pH drifts in samples open to the atmosphere (i.e. bubbled) are relatively minor, those in closed tubes (e.g. unsaturated samples) undergo significant pH drift.

**APPENDIX F: PRESSURIZED GAS EXTRACTION AND COLUMN
DISPLACEMENT**

Pressurized gas extraction and column displacement were both briefly examined as possible methods of performing unsaturated sorption experiments, but were found unsatisfactory.

F.1 Pressurized Gas Extraction

The setup for pressurized gas extraction was very similar to that of vacuum extraction. Instead of using a vacuum, pressurized nitrogen gas was used to displace the pore solution through a porous membrane at the bottom of a column. The column was capped on top and connected to a nitrogen gas cylinder and pressure regulator. Pressures up to 15 psig were used during extraction.

The removal efficiency of the pore solution with pressurized nitrogen gas was very similar to that achieved with a vacuum. The high air flow through the tube suspended more water drops in it which were blown out of the filtering flask. The high air flow rate also caused the temperature drop in the tube to be more significant than vacuum extraction's. Furthermore, the high pressure occasionally blew the lid off of the column which scattered radioactive sand over the lab. The most significant problem with pressurized nitrogen was, however, that it caused the pH to rise considerably. This happened because the lack of CO₂ in the nitrogen gas drove off some of the dissolved carbon dioxide from the solution.

F.2 Column Displacement

In the column displacement method, an invading solution was used to displace the pore solution. As the invading solution displaced the pore solution, the pore solution was compressed until 100% saturation was reached and it was forced out. Longer and narrower columns increased the height of the pore solution column and allowed more of it to be removed without being diluted. Dye was used as the invading solution to visibly determine when breakthrough begins.

This method was not successful for 2.5 cm dia. X 10 cm high and 1.5 cm dia. X 30 cm high columns because the effluent showed

traces of the dye very quickly. The 1.0 cm dia. X 50 cm high column was long enough to allow much of the pore solution to be removed before the dye was seen. This narrow of a column was difficult to pack. This lead to variations in the sand's packing and caused the extraction times to range between 20 and 75 minutes for samples at the same saturation level. The two main problems with this method were 1) extraction times were long relative to uranium sorption/desorption times, and 2) variations in sorption with saturation could be lost because the saturation level is raised to 100% during displacement.

APPENDIX G: MISCELLANEOUS DATA

**Table G.1: HYDRAQL Uranium Solubility Data
from Figure3.1**

pH	Open System	Closed System
5.00	76.25 ppm	76.040 ppm
5.10	54.67	54.444
5.20	39.73	39.488
5.30	29.26	28.995
5.40	21.83	21.535
5.50	16.50	16.162
5.60	12.62	12.243
5.70	9.79	9.350
5.80	7.70	7.190
5.90	6.16	5.562
6.00	5.04	4.325
6.10	4.24	3.377
6.20	3.69	2.647
6.30	3.35	2.080
6.40	3.20	1.640
6.50	3.22	1.297
6.60	3.41	1.028
6.70	3.78	0.818
6.80	4.35	0.653
6.90	5.15	0.525
7.00	6.22	0.426
7.10	7.63	0.351
7.20	9.46	0.294
7.30	11.82	0.253
7.40	14.87	0.226
7.50	18.81	0.211
7.60	23.96	0.207
7.70	30.76	0.214
7.80	40.01	0.233
7.90	53.13	0.264
8.00	72.96	0.309
8.10	105.74	0.371
8.20	165.74	0.452
8.30	283.30	0.558
8.40	535.70	0.693
8.50	1086.70	0.865
8.60	2160.00	1.084
8.70	N/A	1.360
8.80	N/A	1.708
8.90	N/A	2.147
9.00	N/A	2.701

The following three tables contain data discussed in Section 4.1.

Table G.2: Saturation Levels in 50 ml Polystyrene Tubes

Location	5 ml water/50 ml sand	10 ml water/50 ml sand
50 -	30.87%	69.46%
40-50	32.77	68.91
30-40	33.38	69.64
20-30	34.71	69.41
10-20	34.81	67.83
0-10	35.64	69.17
average	33.70	69.07
std. dev.	1.73	0.66
std. dev. %	5.13	0.95

note: Sand and water were mixed in a beaker.

Table G.3: Saturation Levels in 50 ml Polystyrene Tubes and Comparison of Estimated and Actual Saturation Levels

Location	Tube 1	Tube 2
50 -	88.81%	96.17%
40-50	89.47	89.45
30-40	84.23	83.64
20-30	82.66	83.69
10-20	79.96	82.62
0-10	80.43	83.95
average	85.02	84.85
std. dev.	4.71	3.66
estimated sat %	89.97	89.36
% dif: est vs. act	-5.82%	-5.31%

Table G.4: Saturation Levels in 50 ml Polycarbonate Tubes and Comparison of Estimated and Actual Saturation Levels

Location	A	B	C	D
Top 1/4	50.62%	53.11%	86.15%	92.34%
Upper Mid 1/4	53.24	50.94	84.90	86.47
Lower Mid 1/4	55.23	54.42	85.46	89.01
Bottom 1/4	58.53	57.49	84.70	89.19
average	54.41	53.99	85.30	89.25
std. dev. %	6.13	5.07	0.76	2.69
estimated sat %	55.43	55.13	85.95	109.68
%dif: est vs. avg.	-1.88%	-2.11%	-0.75%	1.68%

Note: For the previous 2 tables, sand and water were pretreated. Water was removed from the sand with a vacuum and later added to the wet sand. Material balances were used to estimate the saturation level.

Table G.5: Desorption Data from Figure 5.6

Sample	Desorption Time	Initial U Soln Conc	Equilibrated U Soln Conc	% of U Sorbed onto Sand	Equilibrated Sand U Conc
A	1 min	10.12 ppm	4.763 ppm	52.93 %	5.36 ppm
B	5 min	10.12	5.292	47.71	4.83
C	10 min	10.12	4.498	55.55	5.62
D	15 min	10.12	4.895	51.64	5.23
E	30 min	10.12	5.027	50.33	5.09
F	60 min	10.12	5.299	47.64	4.82
G	22.10 hr	10.12	4.731	53.25	5.39
H	22.35 hr	10.12	4.805	52.52	5.32

Sample	Diluted Solution Uranium Conc	Final Solution Uranium Conc	Final Sand Uranium Conc	% of U Desorbed from Sand
A	0.794 ppm	0.934 ppm	5.08 ppm	5.21 %
B	0.882	1.011	4.57	5.32
C	0.750	1.018	5.09	9.55
D	0.816	1.123	4.61	11.74
E	0.838	1.218	4.33	14.93
F	0.883	1.190	4.21	12.73
G	0.789	1.527	3.91	27.41
H	0.801	1.435	4.05	23.84

Table G.6: Titration Data for Appendix E

Solid (g)	Total Liquid (ml)	0.25 M Base (ml)	Soln/Solid Ratio	Ionic Strength (M)	pH	Delta (mole/g)
10.00	40.10	-0.23	4.01	0.099	4.06	6.10E-06
25.00	25.00	-0.40	1.00	0.098	4.39	3.96E-06
25.00	22.26	-0.37	0.89	0.098	4.39	3.70E-06
50.00	25.30	-0.46	0.51	0.098	4.46	2.32E-06
10.00	40.00	-0.13	4.00	0.100	4.61	3.35E-06
25.00	25.00	-0.15	1.00	0.099	4.62	1.48E-06
20.00	20.35	-0.14	1.02	0.099	4.71	1.77E-06
25.00	24.55	-0.18	0.98	0.099	5.02	1.81E-06
25.00	25.00	-0.20	1.00	0.099	5.30	2.01E-06
20.00	20.25	-0.10	1.01	0.099	5.60	1.25E-06
50.00	25.00	-0.16	0.50	0.099	5.95	8.03E-07
25.00	25.08	-0.13	1.00	0.099	5.98	1.31E-06
25.00	25.00	-0.16	1.00	0.099	6.12	1.61E-06
25.00	25.03	-0.08	1.00	0.100	6.25	8.09E-07
25.00	24.61	-0.12	0.98	0.099	6.36	1.21E-06
25.00	25.00	-0.10	1.00	0.100	6.58	1.02E-06
20.00	20.10	-0.04	1.01	0.100	6.68	5.24E-07
25.00	24.85	-0.06	0.99	0.100	7.00	6.50E-07
25.00	25.01	-0.06	1.00	0.100	7.02	6.53E-07
75.00	10.00	0.00	0.13	0.100	7.19	1.04E-08
25.00	25.00	0.00	1.00	0.100	7.36	1.15E-07
25.00	25.00	0.00	1.00	0.100	7.37	1.18E-07
25.00	25.00	0.00	1.00	0.100	7.38	1.21E-07
40.00	20.00	0.00	0.50	0.100	7.38	6.04E-08
40.00	20.00	0.00	0.50	0.100	7.41	6.47E-08
25.00	24.96	0.01	1.00	0.100	7.42	2.32E-07
75.00	14.00	0.00	0.19	0.100	7.53	3.19E-08
75.00	14.00	0.00	0.19	0.100	7.60	3.75E-08
7.50	16.00	0.03	2.13	0.100	7.78	-3.51E-07
25.00	25.00	0.06	1.00	0.100	7.82	-2.66E-07
25.00	20.00	0.05	0.80	0.100	7.84	-2.20E-07
15.00	15.00	0.03	1.00	0.100	7.85	-7.53E-08
15.00	15.00	0.03	1.00	0.100	7.86	-6.69E-08
25.00	20.00	0.05	0.80	0.100	7.86	-2.07E-07
25.00	20.00	0.05	0.80	0.100	7.86	-2.07E-07
15.00	15.00	0.03	1.00	0.100	7.87	-5.83E-08
25.00	20.00	0.05	0.80	0.101	7.87	-2.00E-07
25.00	20.00	0.05	0.80	0.101	7.87	-2.00E-07
25.00	19.58	0.05	0.78	0.101	7.87	-2.06E-07
25.00	20.00	0.05	0.80	0.101	7.89	-1.86E-07
25.00	20.00	0.05	0.80	0.101	7.89	-1.86E-07
25.00	20.00	0.05	0.80	0.101	7.89	-1.86E-07
25.00	19.72	0.05	0.79	0.101	7.89	-1.90E-07
15.00	15.00	0.03	1.00	0.100	7.90	-3.13E-08
7.50	16.00	0.03	2.13	0.100	7.90	-1.42E-07
25.00	20.00	0.05	0.80	0.101	7.90	-1.78E-07
25.00	20.00	0.05	0.80	0.101	7.90	-1.78E-07
25.00	20.00	0.05	0.80	0.101	7.90	-1.78E-07

Solid (g)	Total Liquid (ml)	0.25 M Base (ml)	Soln/Solid Ratio	Ionic Strength (M)	pH	Delta (mole/g)
25.00	20.00	0.05	0.80	0.101	7.90	-1.82E-07
40.00	16.00	0.07	0.40	0.101	7.90	-2.77E-07
15.00	15.00	0.03	1.00	0.100	7.91	-2.18E-08
25.00	20.00	0.05	0.80	0.101	7.91	-1.71E-07
25.00	20.00	0.05	0.80	0.101	7.91	-1.71E-07
25.00	19.68	0.05	0.79	0.101	7.91	-1.76E-07
15.00	15.00	0.03	1.00	0.100	7.92	-1.22E-08
15.00	15.00	0.03	1.00	0.100	7.92	-1.22E-08
75.00	14.00	0.06	0.19	0.101	7.93	-1.20E-07
25.00	20.00	0.05	0.80	0.101	7.93	-1.55E-07
25.00	20.00	0.05	0.80	0.101	7.94	-1.47E-07
25.00	25.00	0.09	1.00	0.101	7.94	-4.99E-07
25.00	24.66	0.09	0.99	0.101	7.94	-5.05E-07
25.00	20.00	0.05	0.80	0.101	7.95	-1.39E-07
25.00	20.00	0.05	0.80	0.101	7.96	-1.30E-07
25.00	20.00	0.05	0.80	0.101	7.96	-1.30E-07
25.00	19.63	0.05	0.79	0.101	7.96	-1.37E-07
25.00	25.00	0.09	1.00	0.101	7.96	-4.78E-07
25.00	24.47	0.09	0.98	0.101	7.96	-4.88E-07
15.00	15.00	0.03	1.00	0.100	7.97	3.97E-08
25.00	25.00	0.09	1.00	0.101	7.97	-4.67E-07
25.00	24.46	0.09	0.98	0.101	7.97	-4.77E-07
40.00	20.00	0.07	0.50	0.101	8.00	-1.84E-07
25.00	25.00	0.09	1.00	0.101	8.00	-4.33E-07
25.00	24.63	0.09	0.99	0.101	8.00	-4.40E-07
25.00	20.00	0.05	0.80	0.101	8.02	-7.49E-08
25.00	25.00	0.09	1.00	0.101	8.02	-4.09E-07
25.00	25.00	0.09	1.00	0.101	8.05	-3.70E-07
25.00	25.00	0.09	1.00	0.101	8.05	-3.70E-07
25.00	25.00	0.09	1.00	0.101	8.07	-3.43E-07
40.00	16.00	0.24	0.40	0.102	8.16	-1.21E-06
40.00	20.00	0.28	0.50	0.102	8.19	-1.32E-06
40.00	20.00	0.11	0.50	0.101	8.20	-2.52E-07
25.00	25.00	0.22	1.00	0.102	8.30	-1.18E-06
75.00	14.00	0.29	0.19	0.103	8.31	-7.71E-07
40.00	19.00	0.43	0.48	0.103	8.33	-2.17E-06
40.00	16.00	0.43	0.40	0.104	8.33	-2.25E-06
40.00	19.80	0.43	0.50	0.103	8.37	-2.09E-06
75.00	10.00	0.21	0.13	0.103	8.40	-5.28E-07
40.00	20.00	0.25	0.50	0.102	8.40	-9.16E-07
40.00	20.00	0.43	0.50	0.103	8.41	-2.04E-06
40.00	16.00	0.43	0.40	0.104	8.43	-2.13E-06
65.00	9.32	0.19	0.14	0.103	8.46	-5.17E-07
40.00	20.00	0.47	0.50	0.104	8.48	-2.13E-06
65.00	9.32	0.19	0.14	0.103	8.50	-4.96E-07
309.00	105.17	2.24	0.34	0.104	8.50	-1.25E-06
10.00	40.00	0.50	4.00	0.102	8.50	-5.95E-06
10.00	40.00	0.50	4.00	0.102	8.51	-5.79E-06
40.00	20.00	0.44	0.50	0.104	8.52	-1.88E-06
25.00	22.53	0.43	0.90	0.103	8.52	-2.75E-06

Solid (g)	Total Liquid (ml)	0.25 M Base (ml)	Soln/Solid Ratio	Ionic Strength (M)	pH	Delta (mole/g)
25.00	25.00	0.45	1.00	0.103	8.52	-2.78E-06
10.00	40.00	0.62	4.00	0.103	8.55	-8.23E-06
40.00	20.00	0.47	0.50	0.104	8.57	-1.94E-06
40.00	20.00	0.47	0.50	0.104	8.58	-1.92E-06
40.00	17.36	0.50	0.43	0.105	8.64	-2.13E-06
40.00	20.00	0.53	0.50	0.105	8.64	-2.17E-06
40.00	20.00	0.97	0.50	0.107	8.70	-4.71E-06
40.00	16.00	0.93	0.40	0.109	8.70	-4.76E-06
10.00	40.50	1.12	4.05	0.105	8.72	-1.68E-05
10.00	40.00	1.00	4.00	0.105	8.74	-1.34E-05
25.00	22.47	0.87	0.90	0.106	8.75	-6.02E-06
25.00	25.00	0.92	1.00	0.106	8.75	-6.22E-06
50.00	25.00	1.11	0.50	0.107	8.77	-3.98E-06
40.00	17.45	0.98	0.44	0.109	8.78	-4.73E-06
40.00	20.00	1.05	0.50	0.108	8.78	-4.96E-06
10.00	40.00	1.00	4.00	0.105	8.79	-1.19E-05
75.00	14.00	0.62	0.19	0.107	8.80	-1.44E-06
50.00	25.50	1.61	0.51	0.110	8.82	-6.25E-06
75.00	14.00	1.24	0.19	0.113	8.88	-3.37E-06