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**CHARACTERIZATION OF SURFACE PROCESSES ON
MINERAL SURFACES IN AQUEOUS SOLUTIONS**

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Introduction

Performance assessments by Los Alamos National Laboratory for the DOE's Yucca Mountain Site Characterization Project (YMP) are being done investigating the environmental risk related to long-term disposal of hazardous wastes resulting from the use of radioactive materials that must subsequently be isolated from the environment. The YMP site, located in southwestern Nevada, is intended for the storage of high-level wastes generated by nuclear energy-related activities, including spent fuel and waste from reprocessed fuel rods. The work covered by this contract is necessary for producing a defensible model and dataset, and may be critical for evaluation of repository compliance.

This work, performed by the Environmental Engineering and Science research group at Stanford University, will quantify the adsorption of uranyl on various minerals. The project's principle objective is to provide sorption coefficients for uranyl and other ions of interest to predict radionuclide movements from the repository to accessible environments. This adsorption data is essential for the unambiguous interpretation of field experiments and observations.

In this report, details of the activity and progress made with respect to the study of uranyl adsorption on mineral surfaces is presented and discussed.

Laboratory Program

A set of goals were proposed in the Scope of Work document submitted as part of the January 1993 monthly progress report. The initial work to be performed involved the study of uranyl sorption on quartz and albite. A batch of albite was treated by a preparatory procedure designed to isolate a narrow particle size range. A batch of quartz was also subjected to a preparatory procedure which removed organic carbon and surface impurities. The quartz batch was subsequently used in a series of sorption experiments. The preliminary quartz experiments showed that it was desirable to increase the sensitivity of the radioactive tracer method. Opportunities to do this were explored. We have also prepared a set of preliminary standard procedures (see Appendix) relevant to the sorption experiments.

Preparation of Albite - Albite from Bancroft, Ontario (Wards Natural Science Establishment, Inc., Rochester, NY, USA) was ground in a shatterbox to a fine grain size. The smallest particle fractions ($d < 0.7 \mu\text{m}$) were removed by repeated sedimentation in deionized (MilliQ) water, described in detail later in this section. The specific surface area of the albite sample was determined to be $1.2 \text{ m}^2/\text{g}$ using Kr gas adsorption (BET method). The preparation begins with 60 g of the albite weighed into a 2 L Pyrex beaker. Distilled-deionized CO_2 -free water (obtained from a MilliQ water purification apparatus and boiled for purging dissolved CO_2) was added to the 2000 mL mark on the beaker. A teflon-covered stir bar was placed in the mixture and the beaker was placed on a magnetic stirrer. The beaker was covered by a plexiglass disc lid with a small access

hole. The top was then covered with aluminum foil. The mixture was stirred for 5 minutes at a rate which created a fairly uniform suspension. The beaker was then removed from the stirrer, and the mixture was allowed to stand 4 days. A peristaltic pump fitted with Tygon tubing was set up. A glass tube (approximately 30 cm) was attached to one end of the tubing. The other end was placed in a large bottle. The aluminum foil was lifted up so that the glass tube could be placed through the access hole in the plexiglass disc. The height of the tube opening was adjusted with a clamp at the 300 mL mark on the beaker. The peristaltic pump was then run until the supernatant solution had been removed down to the 300 mL mark. The tube was then removed. The stir bar was then removed with a stir bar retriever, and cleaned under a running stream of distilled water of material attracted to it. The bar was then rinsed with MilliQ water, and wiped dry. It was then returned to the beaker. The process of suspending and settling the albite in solution was then repeated at 3 to 4 day intervals until the supernatant was essentially clear to the 300 mL mark. After the final washing, the supernatant was removed. The albite was then transferred in a slurry to a 65 oz wide-mouth glass bottle with screw top lid using distilled-deionized CO₂-free water. Distilled-deionized CO₂-free water was added to the 2 L mark. A small subsample was withdrawn and dried in an oven at 105°C to determine the solid concentration.

Preparation of Quartz - α -Quartz was obtained from Pennsylvania Glass Sand Corp. (Pittsburgh, PA, USA) under the brand name "Min-U-Sil 5". The initial material shows the x-ray diffraction pattern of α -quartz. A cleaning procedure similar to Benjamin (1978) was carried out. The specific surface area was determined to be 6.0 m²/g using Kr adsorption and the standard BET method. Approximately 500 g of quartz was obtained from our solids library. The quartz was roughly divided between three ceramic evaporating dishes, and placed in a muffle furnace at 550°C for 48 hours. The dishes of quartz were then cooled to room temperature in a desiccator. The quartz was then transferred to a plastic jar for storage before refluxing. Refluxing apparatus comprising a hot plate-stirrer, a 6 L erlenmeyer flask and a Graham-type condensor were set up in a perchloric acid digestion fume hood. A ~4 N HCl solution was then prepared by combining 1.8 L of distilled-deionised water and 0.9 L of concentrated HCl in the flask. A stir bar was put in to the flask. The quartz was then added to the HCl while stirring. The condensor was then attached to the flask, and the flask contents were heated to boiling. Refluxing was continued for 4 hours. Heat and stirring were then turned off, and the mixture was allowed to cool and settle overnight. The supernatant solution was removed with a peristaltic pump fitted with Tygon tubing and a glass tube (approximately 30 cm long) attached to the inlet end of the tubing. The outlet was placed in a large bottle to receive the supernatant. As much supernatant was removed as possible, so that the quartz was not significantly disturbed. While shaking, 2 L of distilled-deionised water was added. The flask was capped, and the quartz soaked for 24 hours. After soaking, the supernatant was again removed and replaced with distilled-deionised water. This was repeated 5 times. The supernatant

was removed and replaced with 2.7 L of ~4 N HCl solution. The reflux apparatus was reassembled and boiling was repeated for another 4 hours. Heat and stirring were then turned off, and the mixture was allowed to cool and settle overnight. The soaking procedure was also repeated, and continued until the supernatant pH reached ~4.5. The pH was then adjusted to ~9.5 using dropwise addition of 5 N NaOH. The mixture then stood for 72 hours. The supernatant was removed, and distilled-deionised water was added until pH ~8.7 was reached. The mixture was allowed to stand for 48 hours. The supernatant was removed, and 2.5 L of distilled-deionized CO₂-free water was added. The pH was then adjusted to ~7 with 0.01 N HCl. The mixture was then transferred as a well-mixed suspension to 65 oz wide-mouth glass bottles with screw-top lid. Small subsamples were withdrawn and dried in an oven at 105°C to determine the solid concentrations.

Sorption Experiments - The quartz was subsequently used in uranyl sorption experiments. Experimental conditions include 25°C, 0.1 M ionic strength, 14 g/L colloidal quartz, and 10⁻⁶ M initial uranyl ion concentration. Up to now, experiments with quartz have included calcium or magnesium as competing metal ions.

Three ionic strengths were studied: 0.005 M, 0.010 M and 0.100 M. These ionic strengths were controlled by using a combination of NaCl, CaCl₂ and/or MgCl₂. An initial set of three experiments employed only NaCl. The other sets employed 0.003 M, 0.015 M and 0.033 M CaCl₂ or MgCl₂. The ionic strength was brought to the desired value by supplementing, if needed, with NaCl.

Adsorption edges started at approximately pH 4, and reached a plateau at about pH 7. Adsorption was about 90% of the total uranyl initially added to the solution. Varying ionic strength had little effect on the shape of the adsorption isotherms. At the lowest ionic strength (0.005 M NaCl), the pH edge rises faster than the other ionic strengths investigated, forming the plateau at pH 6 rather than pH 7 (Figure 1). Titrating the solutions above pH 11 provoked a gradual decline in the amount of adsorbed uranyl ion. The titration was significantly extended past pH 11 only for the 0.1 M NaCl experiment because the ionic strength would not be considerably altered by the further addition of base.

The added presence of divalent ions (Ca²⁺ and Mg²⁺) did not appear to affect the adsorption isotherms (Figures 2 and 3); similar pH edges and plateaus were observed with or without these divalent ions. However, the gradual decline in uranyl sorption past pH 11 mentioned earlier was reduced or not observed in the presence of the divalent ions.

Refinement of Radioactive Tracer Method - An effort was made to increase the analytical sensitivity of the radiolabelled-U/liquid scintillation method that is used for quantitating the sorption of uranyl ion. A stock ²³²U solution is purified prior to use in a sorption experiment by eluting an aliquot of the stock solution through an anion exchange resin. We are looking for

Figure 1. Adsorption of uranyl ion onto quartz in the presence of Na^+ and Cl^- .

Figure 2. Adsorption of uranyl ion onto quartz in the presence of Na^+ , Ca^{2+} and Cl^- .

Figure 3. Adsorption of uranyl ion onto quartz in the presence of Na^+ , Mg^{2+} and Cl^- .

opportunities to maximize the efficiency with which $^{232}\text{U(VI)}$ is isolated. The factors under consideration include (1) the anion exchange resin, and (2) the scintillation cocktail.

The resin used up till now is the BioRad AG1X8 100-200 mesh Cl^- form (Richmond, CA). The separation involves the collection of four fractions: an initial acidified solution containing the ^{232}U stock solution, and an elution with concentrated HCl followed by two elutions with 0.1 N HCl . The alpha-beta particle energy spectrum of the fractions (Figure 4) shows a large contribution to total counts from the first two fractions in which ^{228}Th and other daughter products dominate. This might be attributable to the low-grade stock solution that was acquired. The fourth fraction contains the cleaned up ^{232}U which is subsequently used as the radioactive tracer. We have also increased column length and equilibration periods between fraction collection to optimize exchange of uranyl ion. A similar separation was set up using BioRad AGMP1 100-200 mesh Cl^- form, but it proved to have much slower flow rates without significantly improved separation.

We also evaluated our choice of scintillation cocktail. We acquired samples of Ultima Gold, Ultima Gold XR, and Ultima Gold AB from Packard Instruments to compare with the Ecolite (+) currently used (ICN Biomedicals, Irvine, CA). All these cocktails are considered environmentally-safe. In testing the analytical performance of these cocktails, we prepared samples with a range of pH and NaCl concentrations. A preliminary review of the energy spectra indicates that Ecolite (+) performs most consistently (maintains peak shape; limited peak shift), followed closely by Ultima Gold XR, and Ultima Fold AB. However, white precipitate consistently forms when using Ecolite (+) which may hinder the probe geometry in the scintillation vial. Based on manufacturer technical specifications, and the above findings, we intend to employ Ultima Gold XR for a trial period.

Summary

Laboratory work was initiated after a Scope of Work was presented. Batches of quartz and albite were prepared for sorption experiments. A series of experiments investigating the sorption of uranyl ion onto quartz in the presence of Ca^{2+} and Mg^{2+} were begun. Approximately 90% of the uranyl ion was adsorbed at the maximum sorption plateau, with the sorption edge occurring in the range of pH 4 to 7. A steady decline in the quantity of uranyl ion adsorbed was observed after pH 11. The radioactive tracer analytical method is being refined with respect to purification with an anion-exchange resin, and selection of the most suitable scintillation cocktail. Laboratory work will continue with a series of experiments investigating the sorption of uranyl ion on albite.

Reference

Benjamin, M. M. (1978) Effect of competing metals and complexing ligands on trace metal adsorption at the oxide-solution interface, PhD Thesis, Stanford University.

COUNTS IN 60 MINUTES

Figure 4. Spectra of anion exchange fractions from separation of $0.025 \mu\text{Ci } ^{232}\text{U(VI)}$ on BioRad AG1X8 100-200 mesh Cl^- form resin. (50 μL of each fraction mixed with 15 mL scintillation cocktail, except Th2 fraction in which 250 μL of fraction was used).

STANDARD PROCEDURE

Cleanup of ^{232}U by Anion Exchange

Colin Ong

August 23, 1993

Revision No. 0

1.0 APPLICABILITY

This procedure outlines the procedure for separating ^{228}Th daughter product impurity from a ^{232}U stock sample by anion exchange chromatography. This procedure affects uranium sorption experiments in which ^{232}U is used as a radioactive tracer for analytical quantitation by a liquid scintillation analyzer.

1.1 Principle: ^{232}U disintegrates to form ^{228}Th , emitting an α particle over a half-life of 70 years. The chemistry of separating Th(IV) and U(IV) on the basis of anion exchange properties was presented by Kraus et al., (1956) which showed that this separation could be carried out using HCl. Quantitative recovery of Th and U was shown by Berman et al., (1960) by using an anion exchange resin. U was shown to absorb to the resin in a 9.6 M HCl matrix, and elute with 0.1 M HCl.

2.0 DEFINITIONS

Ion exchange ~ a chromatographic procedure in which molecules are separated according to charge.

Liquid scintillation analysis ~ an analytical technique in which radioactivity in the form of nuclear decay emissions is detected and quantified with the use of scintillator molecules which convert kinetic energy into photons.

3.0 RESPONSIBLE STAFF

All members of the project staff may perform this procedure after proper training.

3.1 Training required: Safety training for using Environmental Engineering & Science laboratories is needed, and is provided by individual research groups. Approval from Health Physics is needed for handling radioactive chemicals, and is attained by attending the Radiation Protection course provided by the Environmental Safety Facility at Stanford University.

3.2 Other training: Quality assurance (QA) training is required of project staff performing work for Los Alamos Contract No. 9-X62-X6146-1 concerning the Yucca Mountain Project.

4.0 PROCEDURES

Any deviations from these stated procedures will be documented in the laboratory databook. All reusable items coming in contact with the radioisotope should be labelled with radioactive warning labels (yellow tape). All reagents (except ^{232}U stock solution which is kept in own tray) should be transferred before fraction collection to smaller containers and kept in the tray. Room temperature is desirable though not critical in this procedure. Pipetters selected for YMP are used, and have been calibrated within past one year.

4.1 Preparing an area for separation of radioisotopes: Use a shallow plastic tray for secondary containment. Line the inside of the tray with adsorbent paper. Clearly mark the tray with radioactive warning labels indicating the use of ^{232}U .

4.2 Packing a column with anion exchange resin: Secure a Polyprep column (BioRad, Richmond, CA) above tray in upright position with a clamp and stand. Weigh out approximately 2 g (± 0.02 g) of AG1-X8 100 - 200 mesh anion exchange resin (BioRad) into a 50 mL Pyrex beaker. Slurry the resin with 10 mL of MilliQ H_2O (distilled-deionized water). Pour the slurry into the column. Transfer remaining resin by washing beaker with a stream of MilliQ H_2O . Dislodge any trapped air bubbles by tapping side of column. Cap the column and allow resin to settle. See BioRad Catalog Number 140-9997, "Guide to Ion Exchange" for further information.

4.3 Fraction collection: Snap off tip from column and drain solution into a waste collection bottle. Pass through 5 mL concentrated HCl in 0.5 mL portions (conditioning the resin with Cl^-), and collect outflow in waste collection bottle. In a 20 mL plastic scintillation vial, combine 50 μL ^{232}U stock solution (equivalent to 0.025 μCi activity) with 2 mL concentrated HCl . Pour ^{232}U solution into column, and collect fraction in a 10 mL glass vial labelled "Th1". Wash column with 2 mL concentrated HCl in 0.5 mL portions, and collect fraction in a 10 mL glass vial labelled "Th2". Begin elution of ^{232}U by adding 2 mL 0.1 M HCl (0.5 mL portions) to column, and collect fraction in a 10 mL glass vial labelled "U1". Remaining ^{232}U is eluted with 2 mL 0.1 M HCl (0.5 mL portions), and the fraction is collected in a 10 mL glass vial labelled "U2". Wash resin by adding another 2 mL of 0.1 M HCl . Cap column tip when there is about 2 mm of solution head remaining above the resin. Replace cover on column.

4.4 Analysis for anion exchange separation: Combine 10 μL of each fraction (Th1, Th2, U1, U2) with 15 mL of scintillation cocktail in a scintillation vial. Analyze on liquid scintillation counter (Packard TR2500/AB, Meriden, CT), and compare emission spectra. See Packard Publication No. 169-3052 Rev. G, "Liquid Scintillation Analysis, Science and Technology".

5.0 REFERENCES

Berman, S. S., McKinney, L. E. and Bednas, M. E. (1960) "The separation of carrier-free ^{234}Th (UX₁) from Uranium by anion-exchange", *Talanta*, 4, pp. 153-157.

Kraus, K. A., Moore, G. E. and Nelson, F. (1956) "Anion-exchange studies. XXI. Th(IV) and U(IV) in hydrochloric acid. Separation of Thorium, Protactinium and Uranium", *J. Amer. Chem. Soc.*, 78, pp. 2692-2695.

STANDARD PROCEDURE

 ^{232}U Isotope Dilution and Preparation of Radioactive-Labelled $\text{UO}_2(\text{NO}_3)_2$

Colin Ong

September 27, 1993

Revision No. 0

1.0 APPLICABILITY

This procedure describes the method and materials for preparing a radioactive-labelled solution of $\text{UO}_2(\text{NO}_3)_2$, by ^{232}U isotope dilution. This procedure affects uranium sorption experiments in which ^{232}U is used as a radioactive tracer for analytical quantitation by a liquid scintillation analyzer. This procedure follows the standard procedure *Stanford-SEEP-JOL-001*.

1.1 Principle: ^{232}U disintegrates to form ^{228}Th , emitting an α particle over a half-life of 70 years. This phenomenon is detectable using the liquid scintillation analysis instrument method. By doping a $\text{UO}_2(\text{NO}_3)_2$ solution with a minute quantity of radioactive ^{232}U , UO_2^{2+} can be quantitatively determined in the sorption experiments. This assumes that the radioactively-labelled UO_2^{2+} reacts in proportion to its presence relative to non-labelled UO_2^{2+} .

2.0 DEFINITIONS

Isotope Dilution ~ an analytical procedure whereby an isotope is exchanged to form radioactively-labelled compounds in order to enable detection of an analyte by detection of a radioactive phenomenon.

Liquid scintillation analysis ~ an analytical technique in which radioactivity in the form of nuclear decay emissions is detected and quantified with the use of scintillator molecules which convert kinetic energy into photons.

3.0 RESPONSIBLE STAFF

All members of the project staff may perform this procedure after proper training.

3.1 Training required: Safety training for using Environmental Engineering & Science laboratories is needed, and is provided by individual research groups. Approval from Health Physics is needed for handling radioactive chemicals, and is attained by attending the Radiation Protection course provided by the Environmental Safety Facility at Stanford University.

3.2 Other training: Quality assurance (QA) training is required of project staff performing work for Los Alamos Contract No. 9-X62-X6146-1 concerning the Yucca Mountain Project.

4.0 PROCEDURES

Any deviations from these stated procedures will be documented in the laboratory databook. All reusable items coming in contact with the radioisotope should be labelled with radioactive warning labels (yellow tape). All reagents should be transferred before the dilution step to smaller containers and kept in the tray. Room temperature is desirable though not critical in this procedure. Pipetters selected for YMP are used, and have been calibrated within past one year. The procedure checklist (Attachment I) may be used as a guideline in performing this procedure. The quantities enumerated in this procedure results in a 10^{-4} M U solution.

4.1 Preparing an area for handling of radioisotopes: Use a shallow plastic tray for secondary containment. Line the inside of the tray with adsorbent paper. Clearly mark the tray with radioactive warning labels indicating the use of ^{232}U . No special preparation is required around the balance benchtop area. Reagents must be transported with secondary containment taken into consideration.

4.2 Isotope Dilution: Label a 30 mL plastic scintillation vial with radioactivity warning label. Include prep date. This vial is used for storing the radioactive-labelled compound. Weigh 6.762 g of MQ H_2O into the vial. Next, pipette in 238 μL of 1000 ppm uranyl nitrate (Banco Uranium Reference Standard). Acidify solution with 1 mL 0.1 M HCl. Dope the solution with 2 mL of ^{232}U obtained from the U2 fraction collected from the anion exchange process. Using the above portions, 10 mL of 10^{-4} M U solution is made.

4.3 Methods Calculation:

$$\begin{aligned} [\text{U}] \text{ in Stock Uranyl Nitrate} &= 1000 \text{ ppm (mole weight} = 238.028) \\ &= 0.004201 \text{ M} \end{aligned}$$

$$\therefore 238 \mu\text{L of this solution contains } 1.0 \times 10^{-6} \text{ moles U}$$

Thus, dilution of the U standard reference solution aliquot to a final volume of 10 mL will result in a prepared solution of 1.0×10^{-4} M U concentration.

STANDARD PROCEDURE

Batch Sorption of UO_2^{2+} on Solids

Colin Ong

September 29, 1993

Revision No. 0

1.0 APPLICABILITY

This procedure describes the method and materials performing a batch sorption experiment involving uranyl ion and a solid. This procedure affects uranium sorption experiments in which ^{232}U is used as a radioactive tracer for analytical quantitation by a liquid scintillation analyzer. Preparation of some materials employed in this procedure are described in standard procedures *Stanford-SEEP-JOL-001* and *Stanford-SEEP-JOL-002*.

1.1 Principle: Solids containing surface hydroxyl groups may form surface complexes with cations such as UO_2^{2+} . Since the coordination of the cations involves exchange with a proton, the binding of the UO_2^{2+} is pH dependent, and this results in a narrow interval of 1 to 2 pH units in which the sorption of the UO_2^{2+} rises approximately from zero to 100% sorption (see Stumm, 1992, pp. 13-24, for detailed discussion). The shape of the sorption isotherm is of main interest to this experiment. In addition, the coordination of the surface sites becomes competitive when other cations are present, and affects the pH range in which sorption occurs. Differences in the sorption isotherm that occur due to competitive processes are also of primary interest. Surface sorption sites can also be modified with the use of ligands such as EDTA which affects the sorption isotherm because of the formation of ternary surface complexes (see Schindler, 1990).

2.0 DEFINITIONS

Batch sorption ~ an experimental technique in which reagents are continuously agitated to maintain system homogeneity. In this case, it applies to a stirred system in which solids are continuously suspended and exposed to a uniform solution composition.

Liquid scintillation analysis ~ an analytical technique in which radioactivity in the form of nuclear decay emissions is detected and quantified with the use of scintillator molecules which convert kinetic energy into photons.

3.0 RESPONSIBLE STAFF

All members of the project staff may perform this procedure after proper training.

3.1 Training required: Safety training for using Environmental Engineering & Science laboratories is needed, and is provided by individual research groups. Approval from Health

Physics is needed for handling radioactive chemicals, and is attained by attending the Radiation Protection course provided by the Environmental Safety Facility at Stanford University. Familiarization with pH measurement procedure (e.g. calibration with buffers) and equipment is also necessary.

3.2 Other training: Quality assurance (QA) training is required of project staff performing work for Los Alamos Contract No. 9-X62-X6146-1 concerning the Yucca Mountain Project.

4.0 PROCEDURES

Any deviations from these stated procedures will be documented in the laboratory databook. All reusable items coming in contact with the radioisotope should be labelled with radioactive warning labels (yellow tape). All non-preparatory reagents should be transferred before the sorption step to smaller containers and kept in the temperature-regulated experimental chamber. The sorption and equilibration step should be carried out at 25°C. Pipetters selected for YMP are used, and have been calibrated within past one year. In instances where precise pipetter volume deliveries are desired, the pipetter should be calibrated at the desired volume setting recently before use. The procedure checklists (Attachment III and IV) may be used as a guideline in performing this procedure.

4.1 Preparation of materials: Standardized HCl and NaOH solutions are required. A supply of CO₂-free MQ H₂O (boil MQ H₂O for 20 minutes; cool and store under Ar) is also needed for preparation of the reactor vessel solution and dilution of reagents. At least 4.5 mL of a 10⁻⁴ M U solution should be available, prepared according to the standard procedure *Stanford-SEEP-JOL-002*.

The rest of this section describes the experimental setup and does not have to be repeated on successive uses of this standard procedure. The experiment area may be regulated by means of whole-room temperature control or with the use of a heating element attached to a proportional temperature controller. The experiment requires a container large enough to hold the reactor vessel and sub-sample containers which acts as secondary containment. Room to place the pipetter is also desirable. Mark the container with radioactive warning label. Arrange the container on a magnetic stirrer so that the reactor vessel is conveniently located inside the secondary container. Arrange the pH meter and electrode stand so that the electrode can reach the reactor vessel. Connect a Tygon tube from the Ar supply to the container. The gas should first pass through a gas washing bottle containing MQ H₂O for humidification, then another containing glass beads serving as a liquid trap, before reaching the container.

4.2 Preparation of reactor vessel solution: The reactor vessel is a 500 mL polycarbonate jar (Nalgene Cat. No. 2119-0500). The jar should be cleaned by soaking for 4 hours in 1 N HCl, followed by rinsing with MQ water. Purge a 500 mL volumetric flask (F1) with Ar (time will vary

depending on flow rate). Fill the flask with approximately 500 mL of CO₂-free MQ H₂O. Purge a 500 mL volumetric flask (F2) with Ar. Weigh into F2 the desired amounts of solid phase reagents. Add 400 g CO₂-free MQ H₂O from F1, and allow reagents to dissolve. Stir up contents of solid suspension on a magnetic stirrer, and add 50 mL of the suspension to the reagent solution in F2. Purge the headspace of flask, F2, with Ar. Equilibrate the reaction vessel solution.

4.3 Sorption: Purge the secondary containment with Ar. Place reaction vessel in secondary container. Pour the solution from F2 into the reactor vessel. Blanket the reactor vessel solution for 10 minutes with Ar while stirring.

Calibrate the pH meter and electrode using the pH 4 and 10 buffers. Note the expiration dates and lot numbers of the buffers.

Measure and record the pH of the sorption solution. If the pH is not at the desired starting point, adjust with HCl or NaOH, and let the solution stand 15 minutes.

Extract 8 mL of the solution (serves as a blank) using a pipetter, and store in a 15 mL polycarbonate centrifuge tube. Using a calibrated pipetter, add 4.5 mL of the 10⁻⁴ M U solution, and allow the batch solution to stir for 5 minutes. Measure and record the pH. Extract another 8 mL sample into a centrifuge tube. Immediately acidify this sample with 200 µL concentrated HCl. This sample serves as the UTOT sample.

Extract a 15 mL sample into a 30 mL polycarbonate jar. Using a calibrated pipetter, add NaOH (0.1 M or 1.0 M) to titrate the batch solution to the desired pH. Record the stable pH reading. Extract another 15 mL sample into a 30 mL polycarbonate jar. Repeat titration with NaOH and sampling for the desired pH range.

Place all samples in 30 mL polycarbonate jars in a shaker set at 200 rpm for 24 hours.

4.4 Phase separation: Remove the jars from the shaker and transport them to the secondary container. Purge the secondary containment with Ar. Under an Ar blanket, measure and record the pH of the shaken samples, and transfer with a pipetter 8 mL from each jar to 15 mL centrifuge tubes. Centrifuge all centrifuge tubes (includes blank and UTOT) at 2000 rpm for 20 minutes.

4.5 Liquid scintillation analysis: Extract using a pipetter 3 mL from each centrifuge tube into a 30 mL plastic scintillation vial. Dispense 15 mL of scintillation cocktail into each vial, and shake to mix well. Rack the samples in the Varistte™ cassettes with the blank in the first slot, the UTOT in the second slot, and the remaining slots holding the titration samples. Insert the appropriate protocol flag. Analyze on liquid scintillation counter (Packard TR2500/AB, Meriden, CT). See Packard Publication No. 169-3052 Rev. G, "Liquid Scintillation Analysis, Science and Technology". General guideline counting conditions include: 60 minutes count time, CPM data mode and count region from 200 to 2000 keV. The accuracy, sensitivity and precision of the analysis may be attenuated by adjusting the aforementioned and other counting conditions

(luminescence correction, e.g.). Also, the analysis may be accelerated by use of custom shortcuts (background subtract and % reference features, e.g.) and macros.

4.6 Construction of the adsorption isotherm: The adsorption data is represented in a scatterplot with %U adsorbed on the vertical axis, and pH on the horizontal axis. The %U adsorbed value is calculated with the formula:

$$\%U_{\text{adsorbed}} = \left(1 - \frac{\text{cpm}_{\text{sample}}}{\text{cpm}_{U_{\text{TOT}}}} \right) * 100$$

The function of this formula can be incorporated into the counting protocol with the use of macros. The isotherm may be crudely constructed by joining adjacent data points.

4.6 Cleaning of containers: Empty all contents in sink. Flush sink with running water. Place scintillation vials in original carton marked with isotope used, and call Health Physics for pick-up. All polycarbonate containers should be acid washed and rinsed in MQ H₂O for subsequent use. Additionally, the centrifuge tubes should be placed in a sonicator for 1 hour, then rinsed again with MQ H₂O.

5.0 REFERENCES

Schindler, P. W. Co-adsorption of metal ions and organic ligands: Formation of ternary surface complexes. In *Mineral-Water Interface Geochemistry*; Hochella, M. F. Jr., White, A. F., Eds.; Reviews in Mineralogy, Vol. 23, Mineralogical Society of America: Washington, DC, 1990; pp. 281- 307.

Stumm, W. *Chemistry of the solid-water interface*. John Wiley and Sons: New York, 1992.