PNNL-23634

Pacific Northwest
NATIONAL LABORATORY

Complete Laboratory Evaluation and Issue a Report on the Impact of Temperature on Uranium Adsorption

September 2014

Gary A. Gill, Li-Jung Kuo, Jordana Wood, Pacific Northwest National Laboratory, Marine Sciences Laboratory, Sequim, WA 98382

And

Chris Janke, Oak Ridge National Laboratory, Oak Ridge, TN

U.S. DEPARTMENT OF
ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information,
P.O. Box 62, Oak Ridge, TN 37831-0062;
ph: (865) 576-8401
fax: (865) 576-5728
email: reports@adonis.osti.gov

Available to the public from the National Technical Information Service
5301 Shawnee Rd., Alexandria, VA 22312
ph: (800) 553-NTIS (6847)
email: orders@ntis.gov <http://www.ntis.gov/about/form.aspx>
Online ordering: http://www.ntis.gov

♲ This document was printed on recycled paper.
(8/2010)

Complete Laboratory Evaluation and Issue a Report on the Impact of Temperature on Uranium Adsorption

Prepared for: U. S. Department of Energy, Office of Nuclear Energy, Fuel Cycle Research and Development Program, Fuel Resources Program

Prepared by: Gary A Gill, Li-Jung Kuo, and Jordana Wood, Pacific Northwest National Laboratory, Marine Sciences Laboratory, Sequim, WA 98382

Chris Janke, Oak Ridge National Laboratory, Oak Ridge, TN

Milestone Number: M2FT-14PN0310021

Work Package Number: FT-14PN031002

Milestone Due Date: 9/20/2014

U. S. DOE-NE Program Manager: Dr. Stephen Kung

Milestone Level: M2

PNNL ERICA Release Number: PNNL-23634

Prepared for
the U.S. Department of Energy
under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory
Richland, Washington 99352

Executive Summary

Time series experiments under controlled laboratory conditions were conducted with three separate formulations of the ORNL amidoxime-based polymeric adsorbent (38H, AF1 and AI8) to assess the impact of adsorption capacity due to temperature. Experiments were conducted by loading the adsorbent into columns and exposing the fibers to filtered ambient seawater at several different temperatures, representative of conditions typically found in the coastal ocean (8-32 °C). Adsorption kinetics and adsorption capacity (µg U/g adsorbent) were assessed using time series determinations of uranium adsorption and one-site ligand saturation modelling.

In all three experiments, a strong, fairly linear, relationship was observed between temperature and adsorption capacity; as the temperature increased, so did the adsorption capacity. However, the three adsorbent formulations showed different temperature responses. For the ORNL 38H, AF160 and AI8 adsorbents, the adsorbent capacity increased 40, 180, and 205 µg U/ g adsorbent/1°C, respectively. These results illustrate quite clearly that warmer waters favor the adsorption capacity performance of the adsorbent, and quite markedly. Simply deploying the AI8 adsorbent in 32 °C seawater, compared to 20 °C seawater, results in a 200 % increase in adsorption capacity (from 2880 to 5800 µg U/g adsorbent) after 35 days of exposure.

Temperature also appears to affect the rate of uranium uptake. Half-saturation times for the three adsorbent materials appear to be longer as the temperature increases. This effect is most pronounced for the AI8 adsorbent, where the half-saturation time increased from 18 days at 8°C to 28 days at 32 °C.

Preliminary assessments predict that shifts in seawater pH of a few 0.1's of a pH unit could impact the adsorption of uranium by as much as 60 percent. A full thermodynamic evaluation of the effect of pH on uranium adsorption is needed to fully evaluate the impact. Such as assessment would also help to provide marine site characteristics for deployment that would lead to optimal uranium adsorption.

Acknowledgments

We thank Jonathan Strivens for support of the seawater exposure system and Jordana Wood for analytical support.

Acronyms and Abbreviations

ICPMS	Inductively Coupled Plasma Mass Spectrometry
ICPOES	Inductively Coupled Plasma Optical Emission Spectrometry
MSL	Marine Sciences Laboratory
ORNL	Oak Ridge National Laboratory
OSLSM	One-Site Ligand Saturation Modelling
PNNL	Pacific Northwest National Laboratory

Contents

Figures

Objective

Assess the impact of temperature on the adsorption capacity of uranium onto amidoxime-based polymeric adsorbents using controlled laboratory conditions.

Background

Two lines of evidence suggest that the adsorption capacity of uranium onto amidoxime-based polymeric adsorbents varies with temperature: (1) Field observations and (2) Thermodynamic studies. Several reports by Japanese scientists have indicated that the adsorption capacity of uranium onto amidoxime-based polymeric adsorbents is positively associated with ambient temperature under field conditions (Shimizu and Tamada, 2004; Tamada et al., 2004; Tamada, 2009). Tian et al. (2012) conducted potentiometric and microcalorimetric measurements of the interaction of glutarimidedioxime with the uranyl ion. Under seawater conditions (uranium concentration = 3.3 ppb, pH = 8.3 and total carbonate = 0.0023 M) the dominate solution form of uranium is the tricarbonate species, $UO_2(CO_3)_3^{4-}$ and glutarimidedioxime is fully protonated. Hence, the overall reaction between uranium in seawater and the glutarimidedioxime ligand can be written:

$$UO_2(CO_3)_3^{4-} + 2H_2A = UO_2(HA)A^- = 3HCO_3^-$$

Where H_2A represents the protonated glutarimidedioxime ligand (Figure 1). Tian et al. (2012) predict this reaction to be endothermic, with an enthalpy of formation of $\Delta H = +16.7$ kJ/mol. This prediction suggests that the reaction should be driven farther to the right (higher adsorption) at higher reaction temperatures.

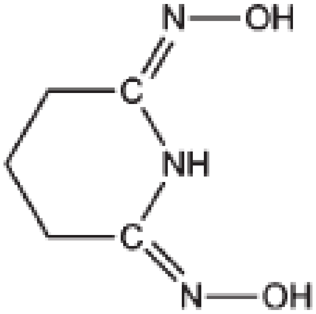

Figure 1. Glutarimidedioxime uranium binding ligand

Experimental Approach

Amidoxime-based polymeric adsorbent fiber materials were packed in columns and exposed to ambient filtered seawater over a range of temperatures spanning typical seawater conditions. Adsorption kinetics and adsorption capacity were assessed using time series determinations of uranium adsorption and one-site ligand saturation modelling.

Ambient Seawater Exposure System

Marine testing is conducted using ambient seawater from Sequim Bay, WA. The MSL has a seawater delivery system that can provide ambient seawater into our “wet laboratory” for scientific investigations. Briefly, ambient seawater is drawn by pump from a depth of 10 m from Sequim Bay through a plastic pipe and is passed through a sand filter to remove large particles. The seawater is then stored in a large volume reservoir tank outside of the laboratory. This seawater is fed into the laboratory facilities via gravity feed through PVC piping.

A depiction of the manifold system used for seawater exposure of adsorbent materials is given in Figure 2. Seawater from the large outside tank is fed sequentially through 5 µm and then 1 µm cellulose filters and then collected in a 180 L fiberglass reservoir tank referred to as a “head tank”. Seawater in the head tank can be heated to the desired temperature. Temperature controlled seawater is drawn from the head tank with a pump (non-metallic pump head), passed through a 0.45 µm polyethersulfone membrane cartridge filter (Memtrex MP, GE Power and Water), and into a 12-24-port PVC manifold. Pressure in the manifold is controlled with a gate valve at the outlet of the manifold. The experimental setup currently has five separate manifolds, each with 12-24 ports, linked to three separate head tanks, permitting simultaneous testing of 110 adsorbent materials.

Adsorbent materials for seawater exposure are packed into columns or cartridges and are held in place by a combination of glass wool and/or glass beads. Packed columns/cartridges are mounted in one of the port positions on the seawater manifold (See Figures 2 and 3). Flow-rates are measured at the outlet of each column/cartridge using a DigiFlow turbine flowmeter system attached to an automated 8 or 36 channel recording system built on National Instruments software. Initial studies in FY 2012 were conducted using a series of peristaltic pumps to deliver water from the head tank to cartridges stacked in series containing absorbent.

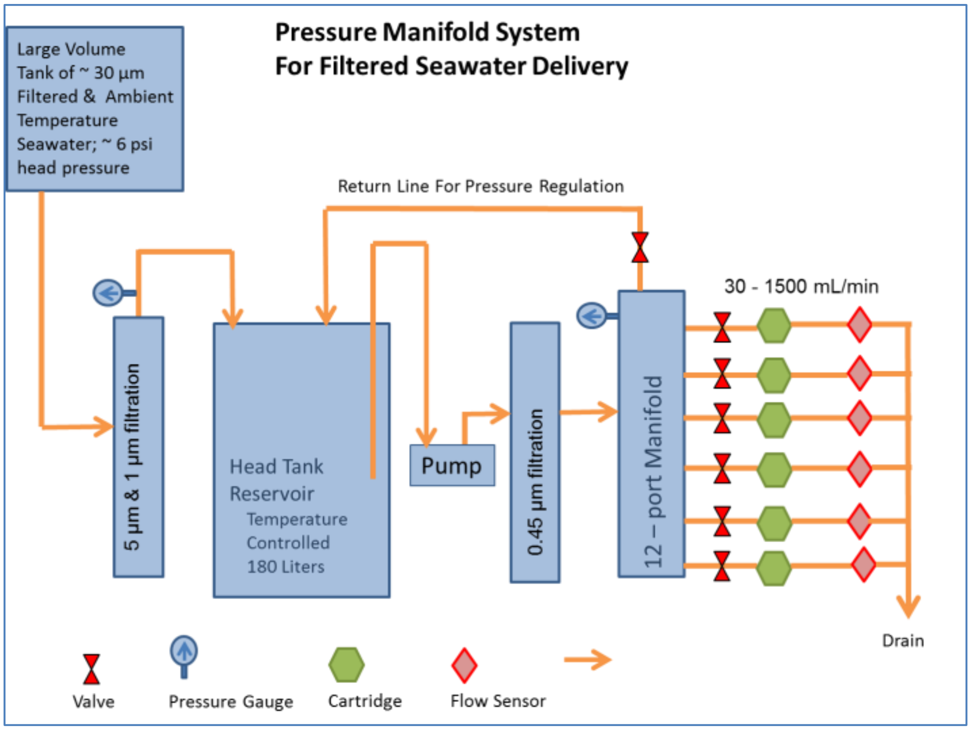

Figure 2. Layout and Components of Seawater Manifold System for Exposing Uranium Adsorbents to Ambient Seawater

Figure 3. Seawater manifold and PNNL style columns containing uranium adsorbent material.

One-Site Ligand Saturation Modelling

The binding of the uranyl ion to the amidoxime-based polymeric adsorbent was evaluated using a one-site ligand saturation model, which was parameterized using SigmaPlot©. The best fit line representing the time series adsorption of uranium is given by:

$$u = \frac{\beta_{\max} t}{K_d + t}$$

Where *u* is uranium capacity (µg U/g adsorbent), t is exposure time (days), $\beta_{\max}$ is the adsorption capacity at saturation (µg U/g adsorbent), and K_d is the half-saturation time (days).

Experimental Procedures

Temperature Control

Three independent seawater exposure manifolds were used for each experiment, each set to a different temperature, nominally 8 or 10 °C, 20 °C, and 30 or 32 °C. Temperatures of 20 and 30/32 °C were achieved using the normal seawater exposure systems. Controlled heating was achieved using an immersion heater installed in the head tanks feeding the manifolds. The 8/10°C temperature required cooling of the feed seawater using a constant temperature bath. A tee was placed in the ambient temperature seawater line after it had passed through the 5 and 1 µm filtration cartridges and before it reached the head tank reservoir. A peristaltic pump was used to draw seawater from the filtered and ambient temperature feed line and force this seawater through a 0.45 µm filter cartridge and then through a coil of polyethylene tubing immersed in a constant temperature bath. The seawater exiting the constant temperature bath was fed directly to an 8-port manifold that would hold the columns for the low temperature exposure. The temperature of the seawater exiting the test columns was monitored and recorded every 5 minutes using an Omega model HH804U handheld meter equipped with a long lead and non-metallic temperature probe. Data recording and storage was achieved by attaching the meter to a laptop computer.

Preparation of Adsorbent Columns for Testing

Amidoxime-based polymeric adsorbent materials were prepared by Chris Janke of Oak Ridge National Laboratory (ORNL). PNNL received three separate formulations of the ORNL adsorbent material for temperature testing. They are referred to as 38H, AF1 and AI8 formulations. Adsorbent material was shipped dry to PNNL and they were conditioned as described below immediately before packing into columns. The conditioning procedure consisted of soaking the fibers in a 2.5% (~0.44 M) potassium hydroxide solution at 80°C for 3 hours. 1 mL of the KOH solution was used per mg of adsorbent material. Immediately upon 3 hours of conditioning, the adsorbent was rinsed with several volumes of deionized water. A nominal mass of 60 mg of dry fiber adsorbent was used to pack individual columns (time points) in the experiments. The conditioned fiber was poured into a column and held in place with glass wool. Glass beads were used to fill the remainder of the void volume in the columns. In select columns, a “disk” of the Japanese woven adsorbent was placed on the exit side of the column to serve as a quality control check.

Water Quality Measurements

Salinity and pH measurements were conducted daily on each of the three manifolds. Salinity was determined using a handheld YSI salinometer. pH measurements were made with a standard pH meter and probe that was calibrated weekly using NIST traceable buffers.

Determination of Uranium and Trace Elements

Determination of Uranium and Trace Elements on Adsorbent materials

Adsorbent materials exposed to seawater were washed with deionized water to remove salts and dried on a class-100 clean-air bench. The dried fibers (50-100 mg) were weighed and then digested with 10 mLs of a high-purity (Optima, Fisher Scientific) 50% aqua regia acid mixture (3:1; hydrochloric acid: nitric) for 3 hours at 85°C on a hot block. Analysis of uranium and other trace elements is conducted using either a Perkin-Elmer 4300 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) or a Thermo Scientific ICapQ Inductively Coupled Plasma Mass Spectrometer (ICP-MS). Quantification with both instruments is based on standard calibration curves.

Determination of Uranium in Seawater

Determination of uranium in natural seawater samples is conducted using ICP-MS and the method of standard addition calibrations. Addition calibration is a variant of the standard additions method and is often used when all samples have a similar matrix. Instrumental calibration curves were prepared in Sequim Bay seawater that was diluted 20-fold with high purity deionized water and then spiked at 4 different concentration levels: 0.1, 0.2, 0.3, and 0.4 µg/L, along with a 2% nitric acid blank in diluted seawater. The seawater samples were then analyzed at 20-fold dilution with high purity deionized (DI) water and then quantified using the matrix matched additions calibration curve. The standard reference material CASS-5 (Nearshore seawater reference material for trace metals) available from the National Research Council Canada, which is certified for uranium (3.18 ± 0.10 µg/L), was also analyzed at a 20-fold dilution every 10 samples to verify the analytical results. The uranium recovery for the analysis of CASS-5 ranged from 93-99% (n=9). Duplicate analyses and matrix spikes were conducted with each batch of samples. The relative percent difference for duplicates ranged from 1-5%, and the recovery of matrix spikes ranged from 93-109% (n=11).

Preparation of ORNL Adsorbent Materials

The ORNL adsorbent materials including 38H, AF160 and AI8 are all amidoxime-based, high-surface area polyethylene adsorbent fibers that were prepared by the radiation-induced graft polymerization method as illustrated in Figure 4, for the ORNL Adsorbent 38H (Tamada, 2009). This method involves four processing steps: electron beam irradiation of high surface area polyethylene fibers; co-grafting polymerizable monomers containing nitrile groups and hydrophilic groups to form grafted side chains throughout the fiber; conversion of nitrile groups to amidoxime groups; and alkaline conditioning of the grafted fibers.

Prior to irradiation, the polyethylene fibers were placed inside a plastic bag and sealed under nitrogen. The bag was then put inside an insulated container and placed on top of dry ice and irradiated to a dose of 200 kGy using 4.9 MeV electrons and 1 mA current from an electron beam machine. After irradiation, the fibers were immersed in a flask containing a previously de-gassed solution of acrylonitrile and methacrylic acid in dimethylsulfoxide (ORNL Adsorbent 38H) and placed in an oven at 65 °C for about 18 hours. After the grafting reaction was complete, the fibers were drained from the solution and washed with dimethylformamide (DMF) to remove any monomers or co-polymer by-products. The fibers were then washed with methanol to remove the DMF and dried at 50 °C under vacuum for 72 hours. The ORNL Adsorbents AF160 and AI8 were prepared in a similar fashion to the ORNL Adsorbent 38H except that the methacrylic acid monomer was replaced by a different hydrophilic monomer. The irradiated and grafted polyethylene fibers were placed in a flask containing 10 weight % hydroxylamine hydrochloride in 50/50 (w/w) water/methanol at 80 °C for 72 hours. The fibers were then washed with deionized water followed by a methanol rinse and allowed to dry at 50 °C under vacuum for 72 hours. After the amidoximation reaction the polyethylene fibers were added to a flask containing 2.5 weight % KOH and heated for 3 hours at 80 °C then washed with deionized water until the pH was neutral.

Results

Three separate experiments were conducted using three separate amidoxime-based absorbent materials provided by Chris Janke of Oak Ridge National Laboratory. The results obtained for the individual experiments are presented below.

Experiment 1 –ORNL Adsorbent 38H

A summary of the time series measurements of uranium adsorption on the ORNL 38H adsorbent at three different temperatures is shown in Figure 5. Details associated with the one-site ligand saturation modelling of the experimental data are given in Table 1. The temperature record for the experiment is shown in Figure 6. Overall statistics for the temperature record are given in Table 2. The time series pH measurements for the three experiments is shown in Figure 7.

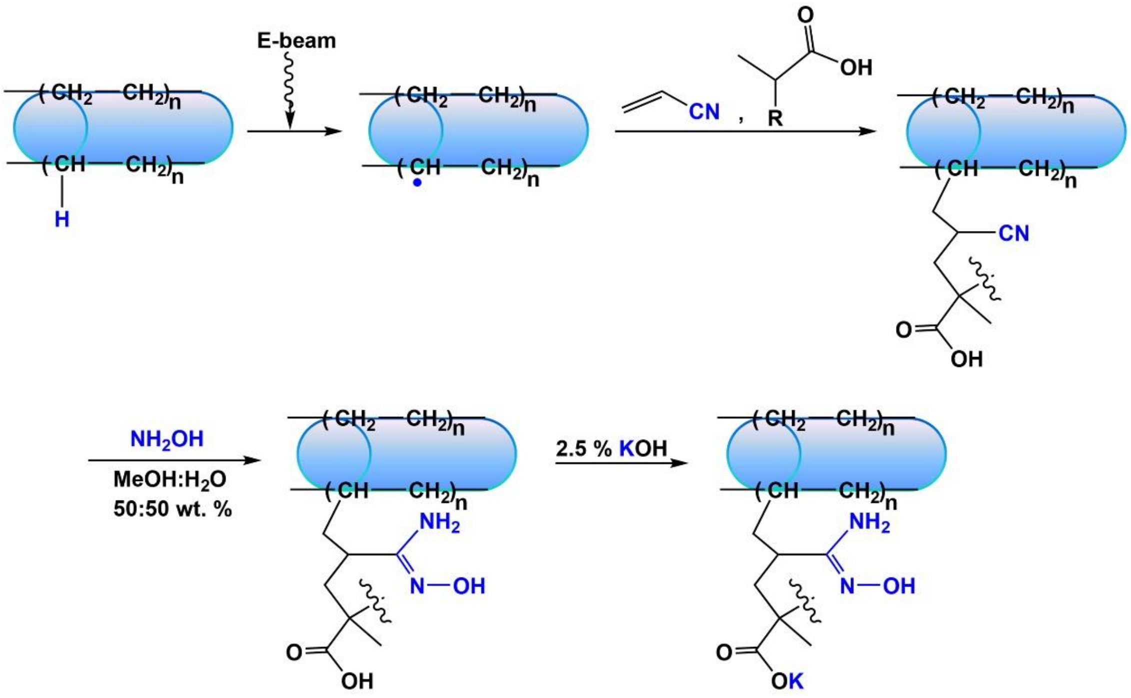

Figure 4. Reaction Scheme for Preparation of the ORNL Adsorbent 38H.

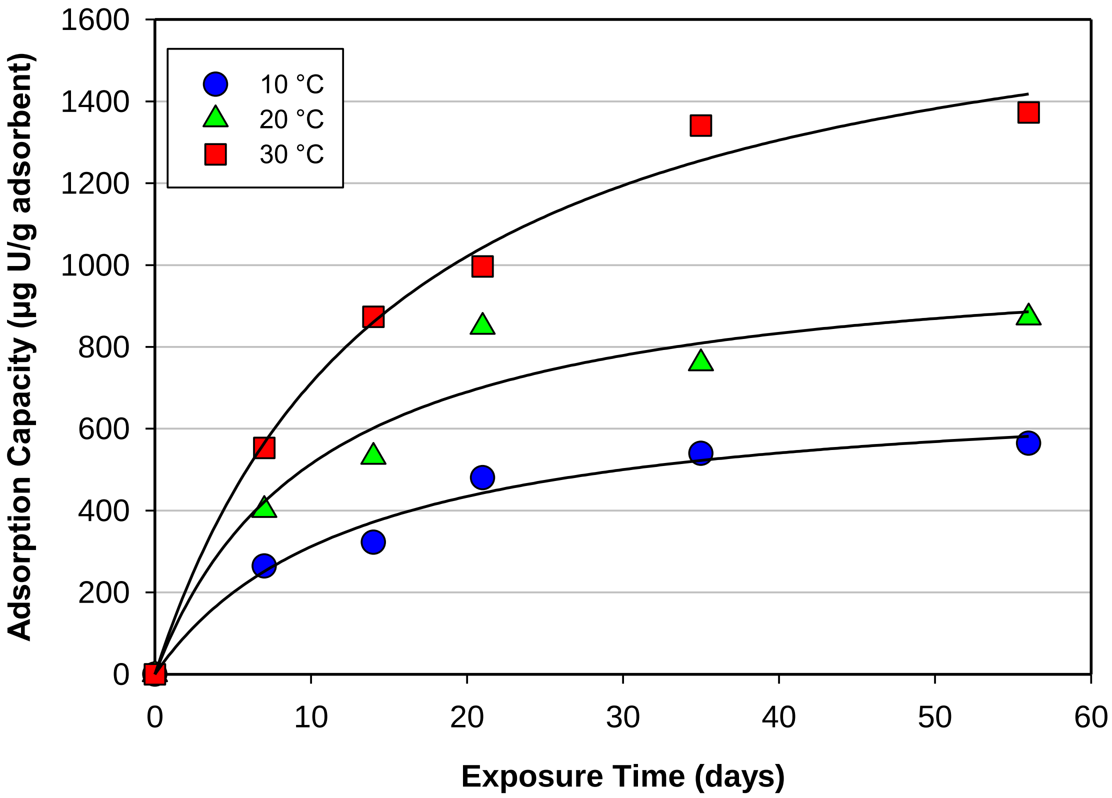

Figure 5. Time series measurements of uranium adsorption capacity with the ORNL 38H adsorbent at three different temperatures. Lines drawn through the data points were generated with an one-site ligand saturation model. All data are normalized to a salinity of 35.

Table 1. One-site ligand saturation modelling of time series measurements from experiment 1

Temperature	Half-Saturation Time (days)	56 Day Adsorption Capacity (µg U/g adsorbent)	Saturation Capacity (µg U/ g adsorbent)
10	12.9 ± 3.3	564	716 ± 63
20	10.5 ± 4.5	872	1050 ± 140
30	15.4	1370	1810 ± 110

Table 2. Temperature Statistics for Experiment 1

	10 °C	20 °C	30 °C
Average	10.1	20.1	30.6
STD	0.26	0.96	0.83
CV	2.6%	4.8%	2.7%

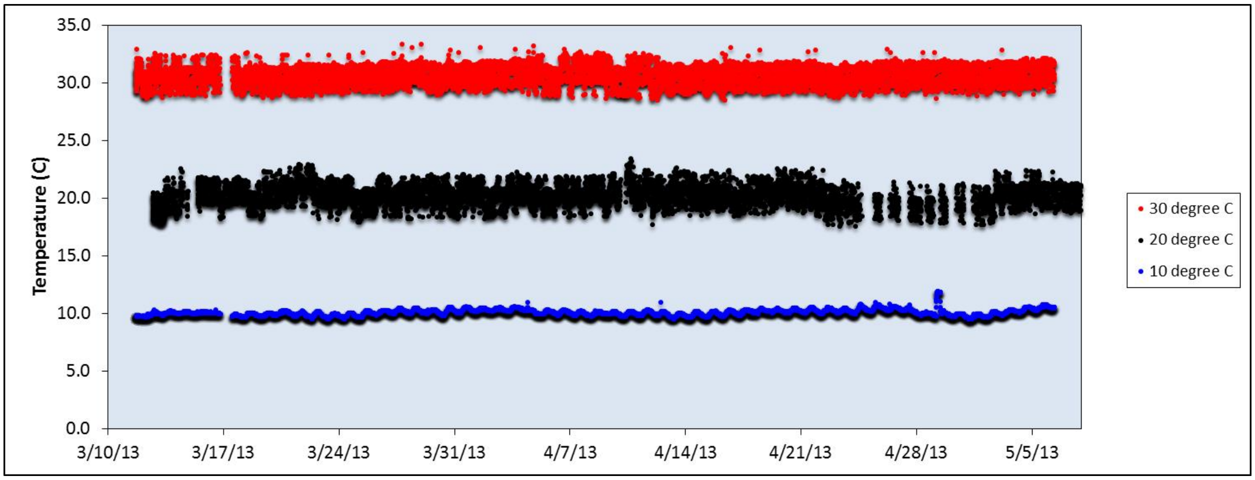

Figure 6. Temperature record for experiment 1.

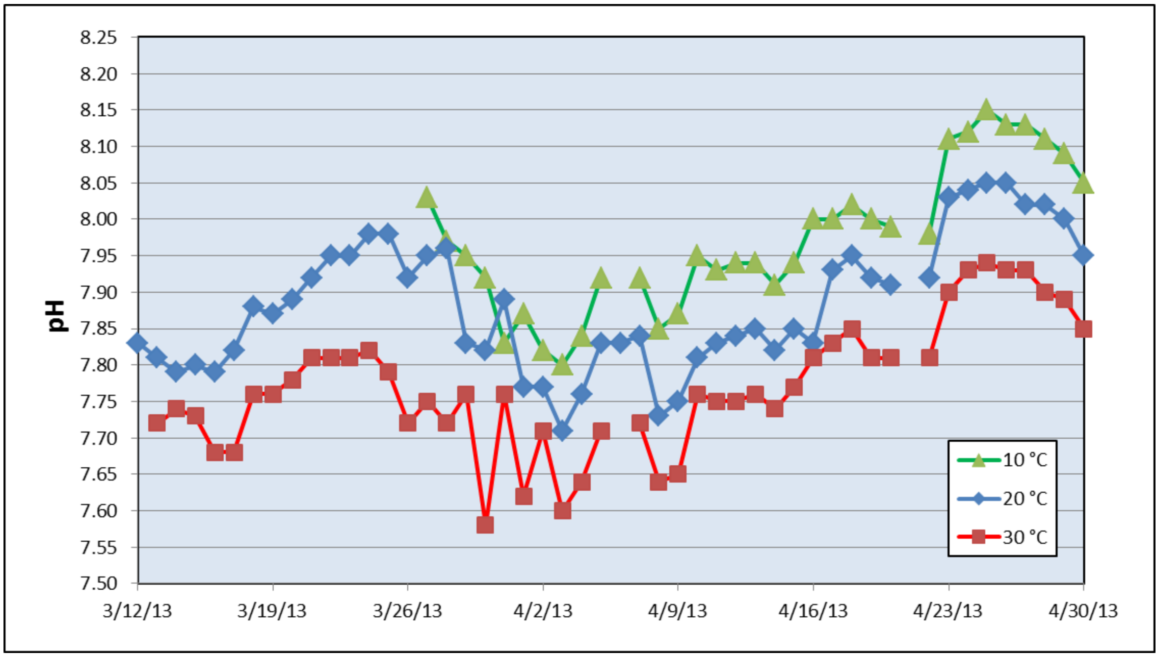

Figure 7. pH in the three temperature systems for Experiment 1. Average pH's for the 10, 20 and 30 °C experiments were 7.97 ± 0.10, 7.88 ± 0.09, and 7.77 ± 0.09, respectively.

Experiment 2 –ORNL Adsorbent AF160

A summary of the time series measurements of uranium adsorption on the ORNL AF160 adsorbent at two different temperatures is shown in Figure 8. Details associated with the one-site ligand saturation modelling of the experimental data are given in Table 3. The temperature record for the experiment is shown in Figure 9. The time series pH measurements for the three experiments is shown in Figure 10.

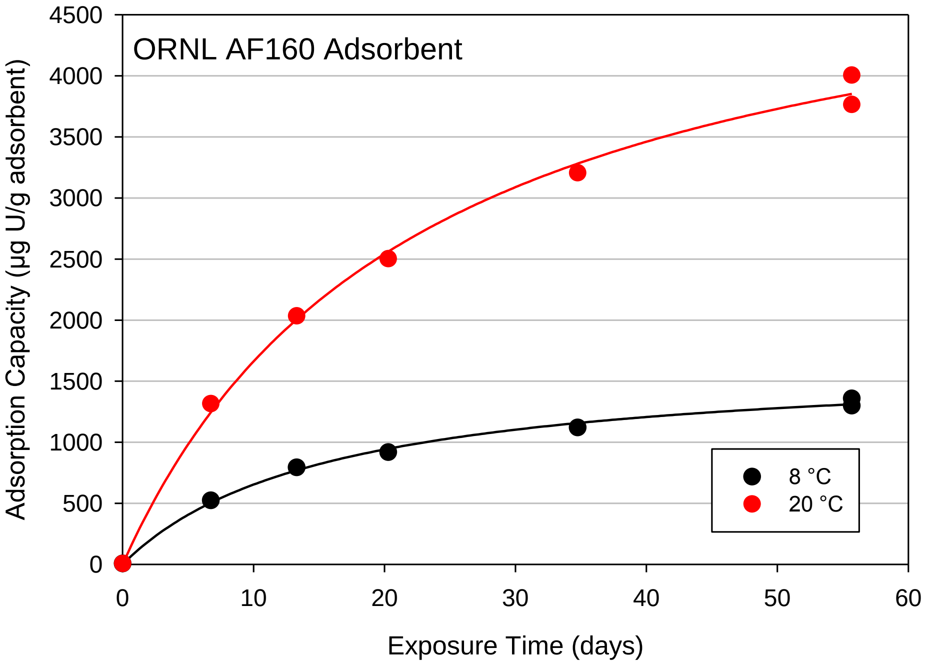

Figure 8. Time series measurements of uranium adsorption capacity with the ORNL AF160 adsorbent at two different temperatures. Lines drawn through the data points were generated with a one-site ligand saturation model.

Table 3. One-site ligand saturation modelling of time series measurements from experiment 2 with ORNL adsorbent AF160. All data are normalized to a salinity of 35 psu.

Temperature	Half-Saturation Time (days)	56 Day Adsorption Capacity (µg U/g adsorbent)	Saturation Capacity (µg U/ g adsorbent)
8	15.7 ± 1.6	1360	1680 ± 57
20	22.6 ± 2.3	4000	5420 ± 220

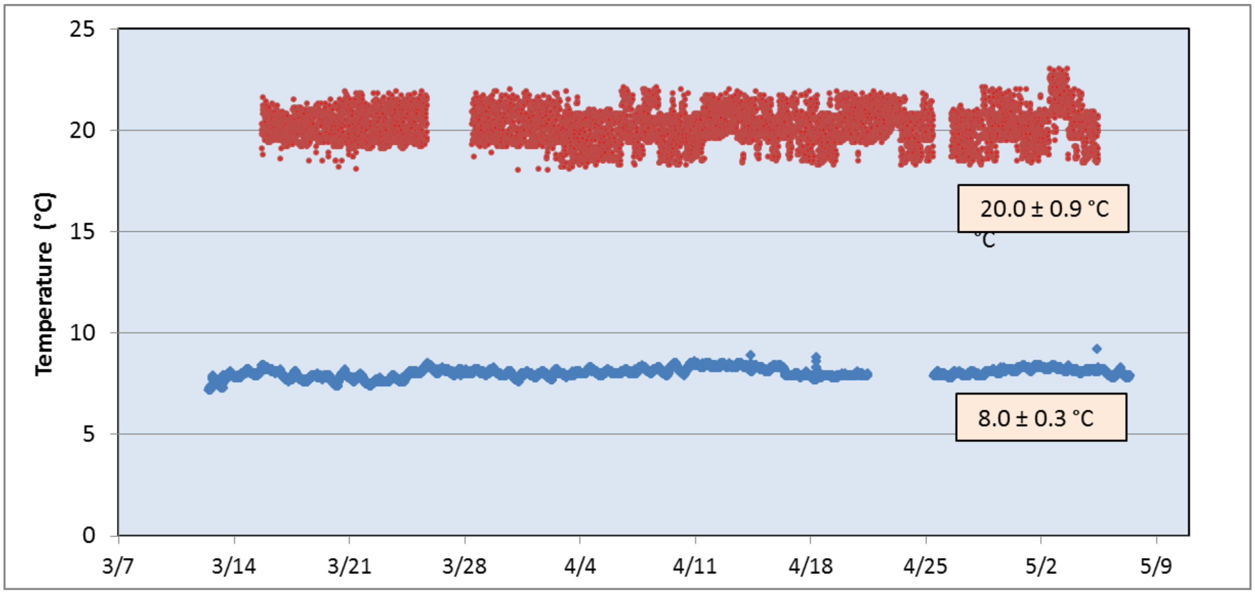

Figure 9. Temperature Record for Experiment 2.

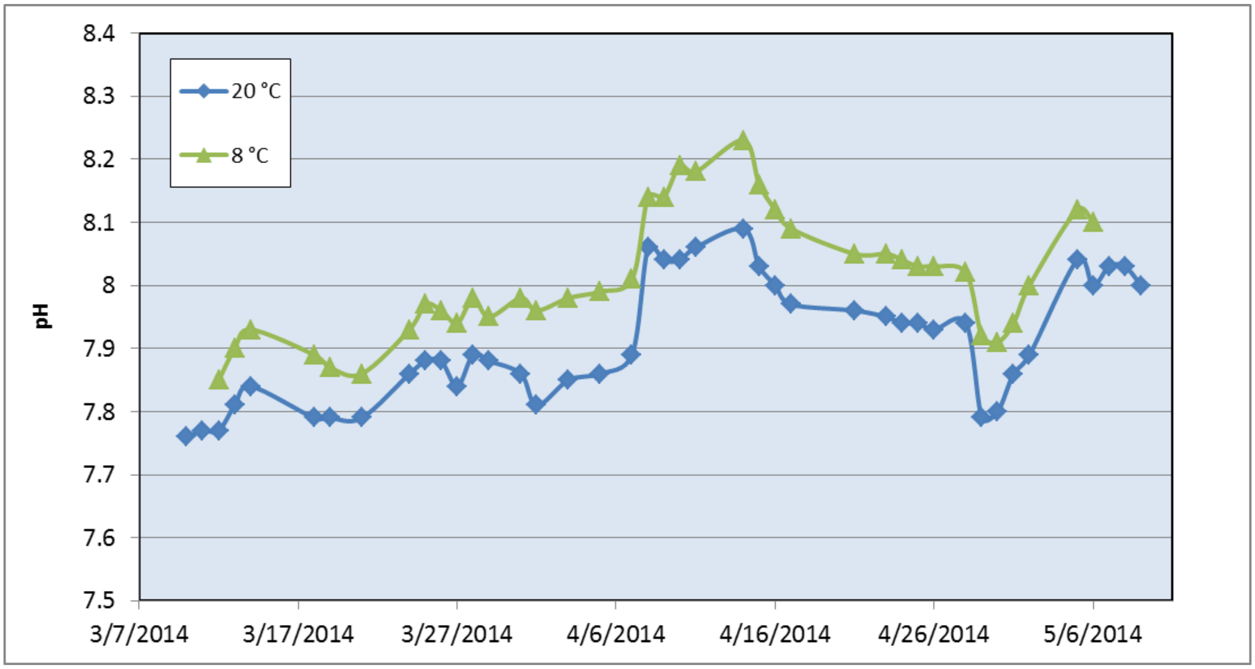

Figure 10. pH Record for Experiment 2

Experiment 3 – ORNL AI8 Adsorbent

A summary of the time series measurements of uranium adsorption on the ORNL AI8 adsorbent at three temperatures (nominally 8, 20 and 32 °C) is shown in Figure 11. Details associated with the one-site ligand saturation modelling of the experimental data are given in Table 4. The temperature record for the experiment is shown in Figure 12. The time series pH measurements for the three temperatures are given in Figure 13. The experimental design for this experiment differs slightly from the previous experiments in that a special head tank was employed for the 8°C exposure to permit sparging of the water for CO_2 (g) equilibration. This change was made because the test temperature was markedly different than the feed water temperature. Because CO_2 (g) saturation is a function of temperature, CO_2 (g) equilibration was deemed appropriate to adjust the pH.

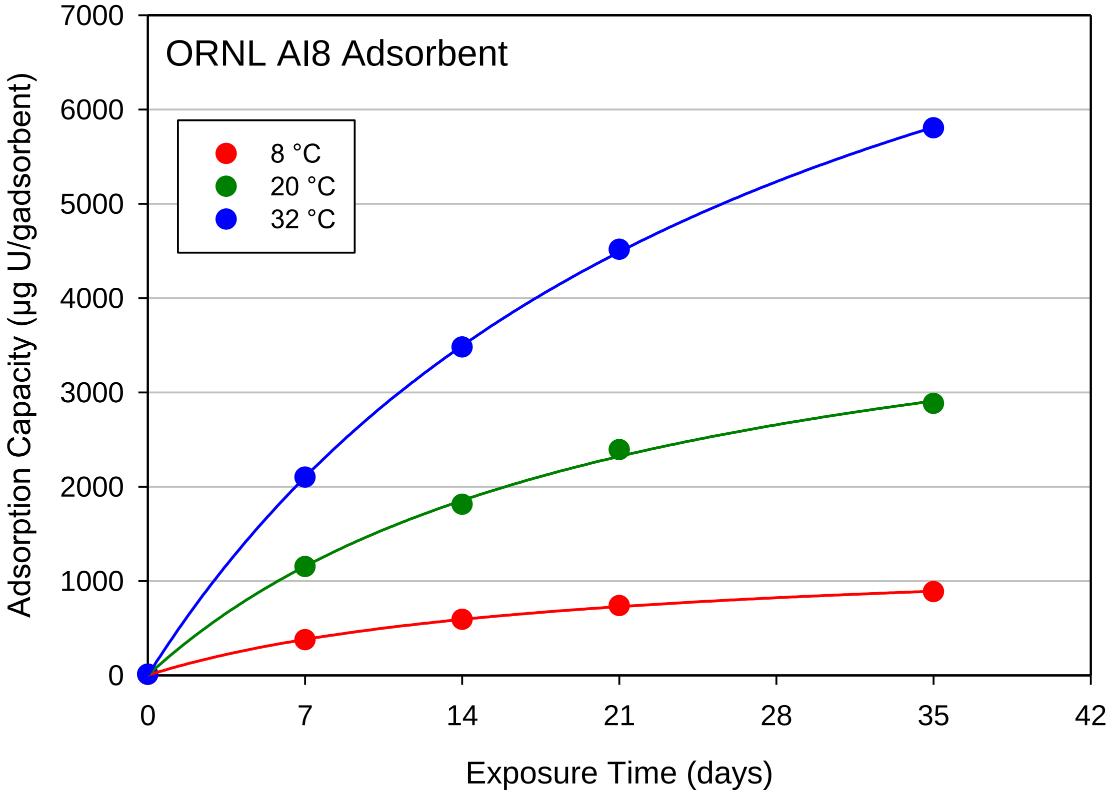

Figure 11. Time series measurements of adsorbent capacity for three different temperatures with the ORNL adsorbent AI8. Lines drawn through the data points were generated with a one-site ligand saturation model.

Table 4. One-site ligand saturation modelling of time series measurements from experiment 3 with ORNL adsorbent AI8. All data are normalized to a salinity of 35 psu.

	Half-Saturation Time (days)	35 Day Adsorption Capacity* (µg U/g adsorbent)	Saturation Capacity* (µg U/ g adsorbent)
8	17.9 ± 0.9	874	1340 ± 32
20	21.3 ± 2.2	2850	4680 ± 236
32	27.7 ± 0.6	5730	10400 ± 120

***Normalized to a salinity of 35 psu**

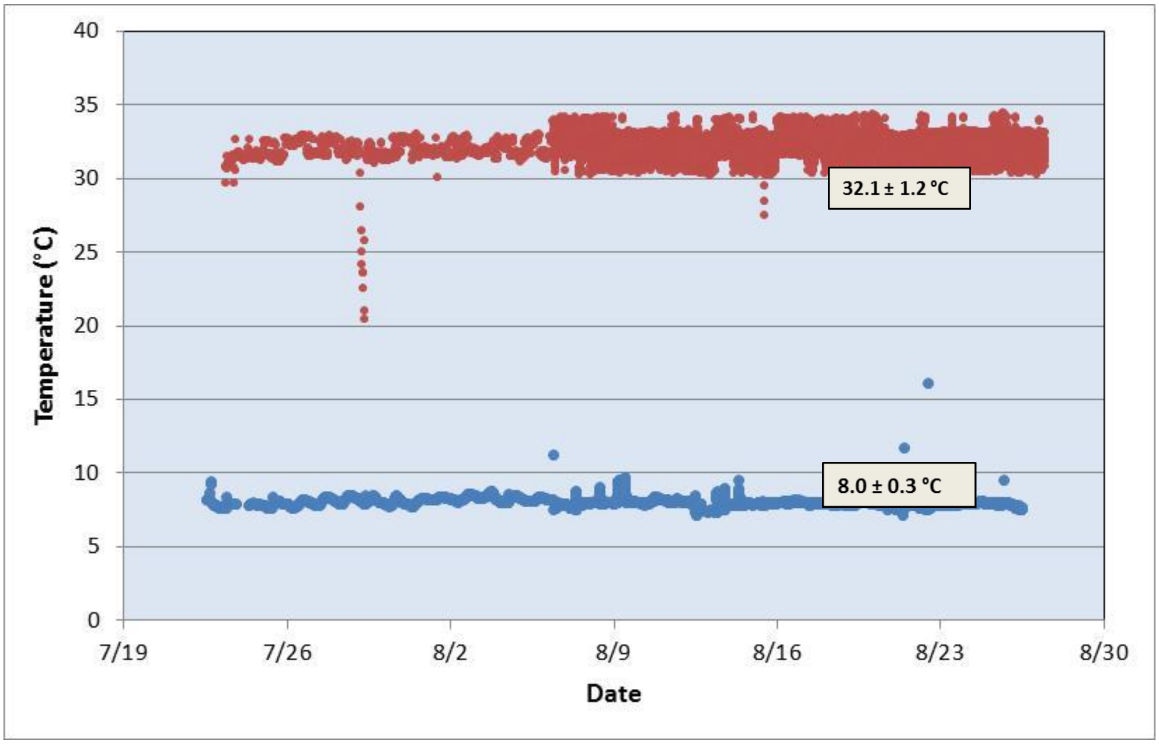

Figure 12. Temperature Record for Temperature Experiment 3.

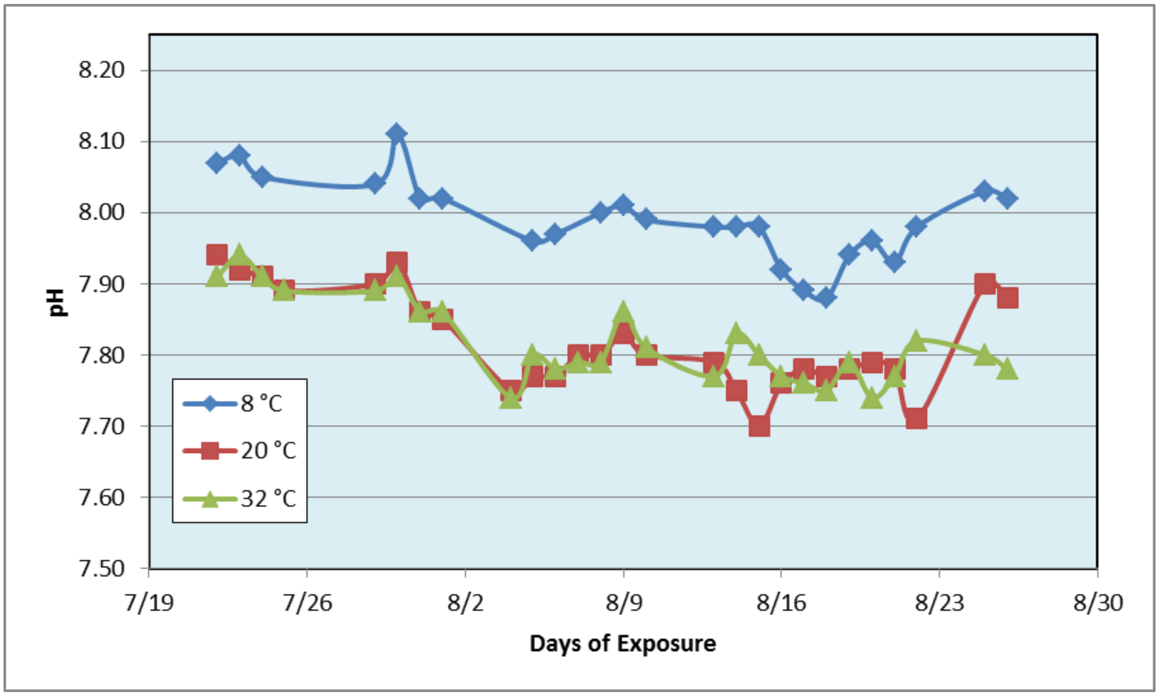

Figure 13. pH Record for Temperature Experiment 3.

Discussion

Effect of Temperature on Adsorption Capacity

A summary of the effects of temperature dependence on adsorption capacity for experiments 1-3 is shown in Figure 14. In all cases, there is a strong relationship between the increase in adsorption capacity as temperature increases, permitting the prediction of adsorption capacity, for a given adsorbent, at any temperature. For experiment 1, with the ORNL 38H adsorbent, the adsorbent capacity increased 40 µg U/g adsorbent/1°C. Correspondingly, in experiment 2, the ORNL AF160 adsorbent increased 180 µg U/ g adsorbent/1°C. Experiment 3, with the ORNL adsorbent AI8, had the highest increase in capacity with increasing temperature - 205 µg U/ g adsorbent/1°C. This is a very clear and dramatic increase in adsorption capacity as a function of increasing temperature.

The particular batch of ORNL 38H adsorbent used for experiment 1 did not have a very high adsorbent capacity compared to previous assessments of the adsorbent. Typically, the 38H adsorbent had a capacity of around 3260 µg U/g adsorbent after 56 days of exposure at 20 °C. The reason for the low capacity is unknown, but since all the test material was from a common batch, the temperature effects are still deemed significant.

Effect of pH on Adsorption Capacity

The effect of pH on adsorption capacity can be seen by using an equilibrium expression that has a proton explicit in the reaction expression. Tian et al (2012) give the following equilibrium expression:

$$UO_2^{2+} + 2A^{2-} + H^+ = UO_2(HA)A^-$$

This reaction has an equilibrium constant of Log β = 36.8 at 25 °C and 0.5 ionic strength. Written in this form, it is clear that if the pH of the solution decreases, the $[H^+]$ will increase, and the overall reaction will be driven farther to the right (Le Chatelier's principle). The major question here is whether the adsorption effects observed at different temperatures could be the result of the small differences observed in pH between the experimental temperatures (see Figures 6, 9, and 12).

A first-order assessment of pH effects can be made by manipulating the equilibrium expression to evaluate how the uranium equilibrium shifts between solution and adsorbed forms with changes in pH. The equilibrium expression for the above reaction is:

$$\text{Log } \beta = [UO_2(HA)A^-] / [UO_2^{2+}]\,[A^{2-}]^2\,[H^+]$$

Rearranging this expression to put the uranium species on one side of the expression gives the ratio of the adsorbed to unabsorbed uranium:

$$[UO_2(HA)A^-] / [UO_2^{2+}] = \text{Log } \beta/[A^{2-}]^2\,[H^+]$$

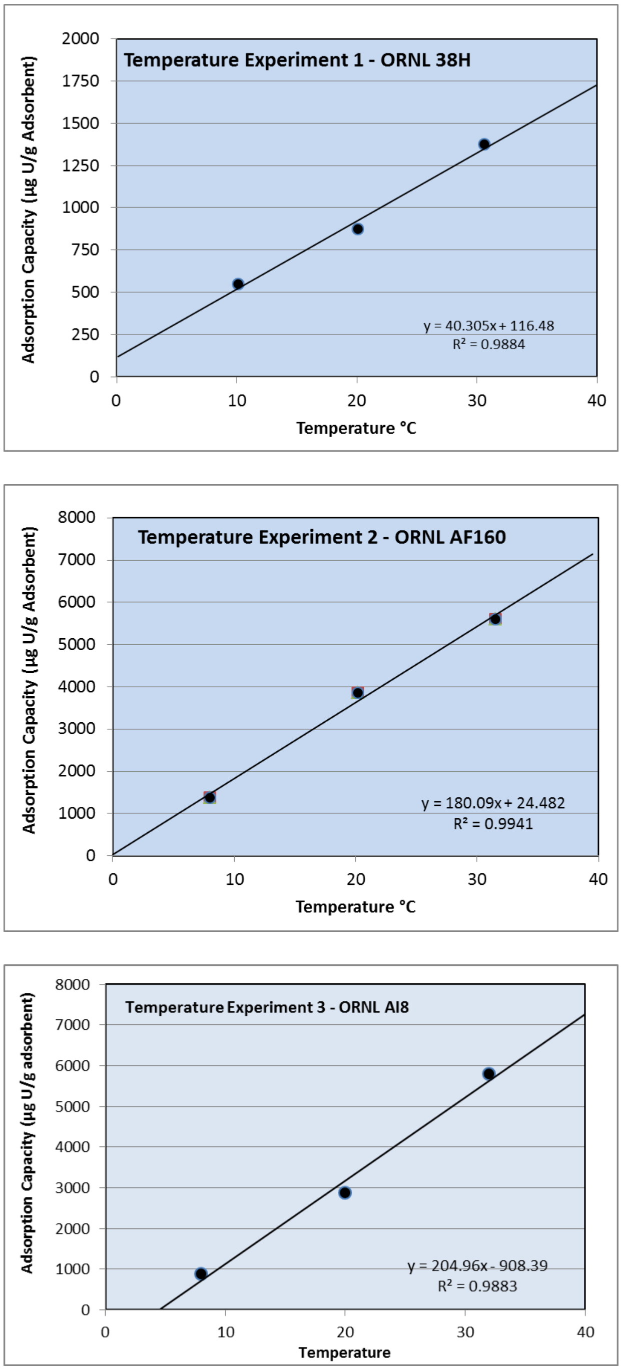

Figure 14. Temperature dependence on adsorption capacity for experiments 1-3. For experiments 1 and 2, the data points represent the adsorption capacity after 56 days of exposure. The data points for experiment 3 represent the adsorption capacity after 35 days of exposure. The 32 degree point capacity for experiment 2 was taken from a separate biofouling experiment run concurrently with the temperature experiment. All data were normalized to a salinity of 35 psu.

Rearranging this expression to put the uranium species on one side of the expression gives the ratio of the adsorbed to unabsorbed uranium:

$$[UO_2(HA)A^-] / [UO_2^{2+}] = \text{Log } \beta/[A^{2-}]^2 [H^+]$$

For a given experiment, the concentration of the binding ligand on the adsorbent is fixed (A_T = constant). Hence, the only parameter which can affect the ratio of uranium in solution to the uranium adsorbed is the pH. The change in pH observed between the temperature experiments is on the order of 0.2 pH units. For a typical seawater case, a change pH from 8.0 to 8.2 would correspond to a change in $[H^+]$ from 1×10^{-8} M to 6.3×10^{-9} M or approximately a 59 % change ($1 \times 10^{-8}/6.3 \times 10^{-9} = 1.59$).

For experiment 1, the % difference between the adsorption capacities at 56 days for the 10 and 20 °C and between 20 and 30 °C is approximately 60%. The % difference in adsorption capacities at 56 days between the 10 and 30 °C experiments was approximately 250%. Hence, it is possible the changes in pH played a role, but they cannot account for the more significant adsorption changes observed between the 10 and 30 °C experiments. Similarly, for experiment 2, the % difference between the adsorption capacities at 56 days for the 8 and 20 °C experiments was approximately 290%, far greater than the 60% change predicted due to pH alone. It is important to emphasize that this assessment is crude and that a full thermodynamic evaluation with all solution speciation and reactions involved in the chemistry of uranium adsorption is warranted to verify this preliminary prediction.

Saturation Kinetics

All three temperature experiments suggest that the rate of adsorbent saturation is effected by temperature, the warmer the water, the slower the saturation kinetics (see Table 5). The one value that does not fit the trend well is the 20 °C value for the 38H adsorbent. However, notice that the standard deviation on determination is larger than the other determinations. Hence, the trend may still be one of increasing half saturation time with temperature. An alternative explanation is that the half-saturation times are a function of adsorption capacity. As adsorption capacity increases, the half-saturation times increase proportionally.

Table 5. Effect of temperature on adsorbent kinetics for three adsorbent materials. Values in the table represent the half-saturation time in days

Adsorbent	8 °C	20 °C	32 °C
38H	12.9 ± 3.3	10.5 ± 4.5	15.4
AF1	15.7 ± 1.6	22.6 ± 2.3	
AI8	17.7 ± 1.0	21.3 ± 2.2	27.7 ± 0.6

Conclusion

Three independent time series tests with natural filtered seawater, with three different formulations of amidoxime-based polymeric adsorbent, all showed a significant increase in the adsorption capacity of uranium as temperature increased. Moreover, the increase in adsorption capacity for a given adsorbent material appears to be fairly linear within typical surface seawater temperature ranges (8-32 °C). For the AF1 adsorbent, an increase of approximately 180 µg U/ g adsorbent/1°C is predicted. The AI8 adsorbent had an even higher temperature effect, 205 µg U/ g adsorbent/1°C. This substantial temperature effect will have marked effect on adsorption capacity and hence economics of the technology. Clearly, the warmer the seawater, the more uranium will be captured for a given mass of adsorbent.

Temperature also appears to affect the rate of uranium uptake. Half-saturation times for the three adsorbent materials appear to be longer as the temperature increases. This effect is most pronounced for experiment 3, where the half-saturation time increased from 18 days at 8°C to 28 days at 32 °C.

Preliminary assessments predict that shifts in seawater pH of a few 0.1's of a pH unit could impact the adsorption of uranium by as much as 60 percent. A full thermodynamic evaluation of the effect of pH on uranium adsorption is needed to fully evaluate the impact. Such as assessment would also help to provide marine site characteristics for deployment that would lead to optimal uranium adsorption.

References

Shimizu, T. and M. Tamada, Practical scale system for uranium recovery from seawater using braid type adsorbent, Proceedings of Civil Engineering in the Ocean, 20, (2004) 617-622.

Tamada, M. (2009). Technology of uranium recovery from seawater. Journal of *Japan Institute of Energy*, **88**: 249-253.

Tamada, M., N. Seko and F. Yoshii (2004). Application of radiation-graft material for metal adsorbent and crosslinked natural polymer for healthcare product. *Radiation Physics and Chemistry*, **71**: 221–225

Tian, Guoxin, Simon J. Teat, Zhiyong Zhang and Linfeng Rao (2012). Sequestering uranium from seawater: binding strength and modes of uranyl complexes with glutarimidedioxime. *Dalton. Trans*., **41**: 11579.