

DOE-FIU SCIENCE & TECHNOLOGY WORKFORCE DEVELOPMENT PROGRAM

STUDENT SUMMER INTERNSHIP TECHNICAL REPORT-SUMMER 2009

June 8, 2009 to August 14, 2009

The Dissolution of Natural Autunite as a Function of Aqueous Bicarbonate

Principal Investigators:

Melina Idarraga (DOE Fellow Student)
Florida International University

Dr. Dawn Wellman, Mentor
Pacific Northwest National Laboratory

Dr. Yelena Katsenovich, Research Scientist
Applied Research Center

Acknowledgements:

Elsa Cordova

Chris Randall

Florida International University Collaborators:

Leonel Lagos Ph.D., PMP®

Prepared for:

U.S. Department of Energy
Office of Environmental Management
Under Grant No. DE-FG01-05EW07033

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, nor any of its contractors, subcontractors, nor their employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe upon privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any other agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

ABSTRACT

Remediation processes with polyphosphate injection has been practical to sequester uranium in the vadose zone at the Hanford site forming different types of uranium phosphate minerals. Autunite minerals help control the mobility of uranium in groundwater at the Hanford site 300-Area. Autunite minerals are formed as a weathering product of the uraninite (UO_2), and its formation is promoted by the phosphate present in the groundwater. Different factors can affect the kinetic dissolution rate of natural calcium meta-autunite $\text{Ca}[(\text{UO}_2)_2(\text{PO}_4)_2]_2 \cdot 3\text{H}_2\text{O}$ in the environment. Factors such as pH, temperature and different bicarbonate concentrations play an important role in how the autunite mineral contributes to the mobility of uranium back into the environment. In this report, the dissolution rate of autunite will be quantified as a function of different concentrations of aqueous bicarbonate (0.5 – 100 mM), and the effect of different variables, pH (7 – 11) and temperature (23 – 40 °C), will be evaluated in reference to the dissolution rate of calcium (Ca) and phosphorus (P). Single-pass flow-through (SPFT) tests were conducted using each of the bicarbonate buffer solutions and 0.01 M TRIS [*tris (hydroxymethyl) aminomethane*] to simulate the characteristics of natural groundwater. Results for calcium and phosphorus rate of release show that carbonate appears to be the dominant variable for both components of the autunite. Ion exchange, temperature and pH do not show an effect on its rate of release for calcium alone. On the other hand, for phosphorus, the pH and temperature variables demonstrate a direct effect on the rate of release. To really see if the carbonate being present has a potential impact on the calcium, some geochemical modeling should be performed. The research presented here is part of a large effort to quantify the dissolution rate of autunite as a function of aqueous bicarbonate.

TABLE OF CONTENTS

LIST OF FIGURES	v
1. INTRODUCTION	1
2. EXECUTIVE SUMMARY	2
3. RESEARCH DESCRIPTIONS	3
3.1 Single-Pass Flow-Through (SPFT).....	3
3.2 Quantification of Dissolution Rates.....	5
4. RESULTS AND ANALYSIS.....	6
4.1 Calcium Rate of Release:.....	6
4.1.1 Lower Bicarbonate Concentrations.....	6
4.1.2 Higher Bicarbonate Concentrations.....	8
4.2 Phosphorus Rate of Release.....	10
4.2.1 Lower Bicarbonate Concentrations.....	10
4.2.2 Higher Bicarbonate Concentrations.....	12
5. CONCLUSION.....	14
6. REFERENCES	15

LIST OF FIGURES

Figure 1. Hanford Site.....	1
Figure 2. Schematic of SPFT.....	4
Figure 3. Collection of samples.....	5
Figure 4. Ca as a function of 0.5 mM HCO_3^-	6
Figure 5. Ca as a function of 1 mM HCO_3^-	6
Figure 6. Ca as function of 2 mM HCO_3^-	7
Figure 7. Ca as a function of 3 mM HCO_3^-	7
Figure 8. Ca as a function of 25 mM HCO_3^-	8
Figure 9. Ca as a function of 50 mM HCO_3^-	8
Figure 10. Ca as a function of 75 mM HCO_3^-	9
Figure 11. Ca as a function of 100 mM HCO_3^-	9
Figure 12. P as a function of 0.5 mM HCO_3^-	10
Figure 13. P as a function of 1 mM HCO_3^-	10
Figure 14. P as function of 2 mM HCO_3^-	11
Figure 15. P as a function of 3 mM HCO_3^-	11
Figure 16. P as a function of 25 mM HCO_3^-	12
Figure 17. P as a function of 50 mM HCO_3^-	12
Figure 18. P as a function of 75 mM HCO_3^-	13
Figure 19. P as a function of 100 mM HCO_3^-	13

1. INTRODUCTION

Remediation of uranium contaminated soils is a high priority within the U.S. Department of Energy (DOE). These soils can contaminate the underlying groundwater during the leaching process. Therefore, it is really important to control and monitor the sites contaminated with uranium, such as the Hanford site. The Hanford site (Figure 1) was selected by the U.S. government as the central location for producing plutonium as part of the Manhattan Project during World War II and for research and development activities during the Cold War. The operation of the Hanford site started in 1944 and continued until it was shut down and deactivated in 1989. Today, the remains of high-level nuclear waste introduce a challenging environmental remediation task.

Autunite minerals in the Hanford site 300-Area are formed as a result of phosphate injection utilized to sequester the uranium in subsurface water. Low concentrations of phosphate (10^{-8} M) in groundwater are enough to support the formation of autunite (Reference 1). The mobilization of uranium back into the environment depends on the dissolution kinetics of autunite. Uranyl phosphate minerals are the dominant limiting factor for the solubility of the uranyl cation (UO_2^{+2}).

Previous studies have shown that uranyl phosphate minerals are very stable and have a high insolubility rate. However, these studies are limited to low pH media and to synthetic, instead of natural, autunite. This research focuses on natural autunite, which limits the amount of impurities related to the synthetic autunite, and encompasses a wider range of pH as well as the effect of bicarbonate on the uranium geochemical cycle.

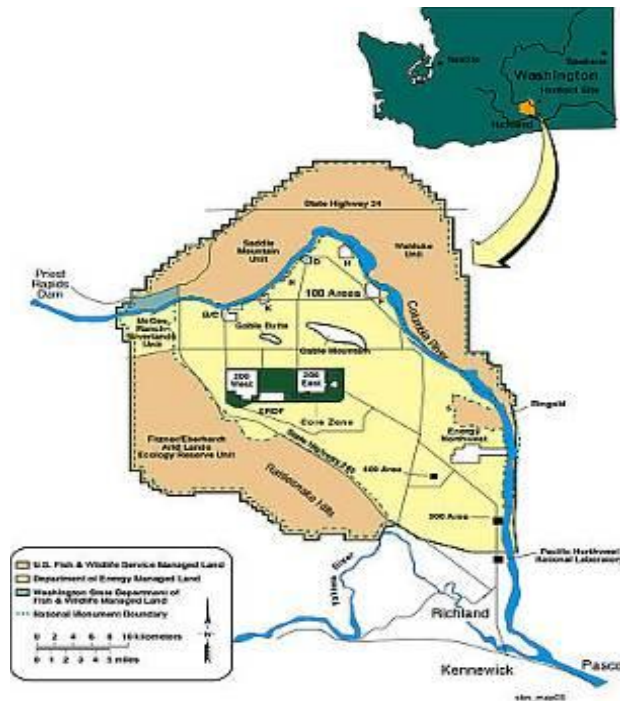


Figure 1. Hanford Site.

2. EXECUTIVE SUMMARY

This research has been supported by the DOE-FIU Science and Technology Workforce Development Initiative Program. During the summer of 2009, a Florida International University (FIU) DOE Fellow (Melina Idarraga) spent 10 weeks doing a summer internship at the Pacific Northwest National Laboratory (PNNL) in the Field Hydrology and Geochemistry group under the supervision and guidance of Dr. Dawn Wellman. This internship was coordinated with PNNL Office of Science and Engineering Education (SEE) and fell under the category of Alternate Sponsored Fellow (ASF). The DOE Fellow's project was initiated in June 8, 2009, and continued through August 14, 2009, with the objective of contributing to FIU's Applied Research Center (ARC) project #2, "Rapid Deployment of Engineered Solutions for Environmental Problems at Hanford," and developing a thesis topic based on the experimental work performed during the internship. During this internship, the student received extensive radiological training before conducting experiments with radiological materials. The purpose of the laboratory work conducted during this internship was to quantify the dissolution rate of autunite as a function of aqueous bicarbonate; this will help to predict the rate of release of uranium back into environment at the Hanford site 300-Area.

3. RESEARCH DESCRIPTIONS

Natural calcium meta-autunite, $\text{Ca}[(\text{UO}_2)(\text{PO}_4)]_2 \cdot 3\text{H}_2\text{O}$ (herein designated GHR) was obtained from north-eastern Washington State. The material was characterized using ICP-OES and ICP-MS analyses, X-ray diffraction and scanning electron microscopy to confirm the composition, structure and morphology of the autunite minerals as 98-99% pure autunite with calculated anhydrous structural formula consistent with Ca-autunite: $\text{Ca}[(\text{UO}_2)(\text{PO}_4)]_2$. Electron microprobe analyses further indicated that the autunite mineral contains ~3 waters of hydration per formula unit (p.f.u.). Powdered samples of GHR were prepared to be within -100 to + 200 mesh.

Dissolution rates were determined over the temperature range of 23° to 40°C. A series of solution compositions, all prepared with a de-ionized (DI) water, included 0.5, 1, 2, 3, 25, 50, 75, 100 mM bicarbonate and 0.01 M *tris(hydroxymethyl)aminomethane* (TRIS) buffer, were used to investigate element release from natural autunite minerals over the pH interval of 7 to 11 at 23°C. Concentrated nitric acid (HNO_3) and 5 M lithium hydroxide (LiOH) solutions were used to adjust the solutions to the target pH.

3.1 Single-Pass Flow-Through (SPFT)

The dissolution kinetics of autunite minerals were determined using a single-pass flow-through (SPFT) apparatus over the temperature range of 23° to 40°C and flow rates of 1 and 1.5 L d⁻¹, respectively. The SPFT apparatus, illustrated schematically in Figure 2, consists of a syringe pump (Kloehn model 50300) that transfers solution from an influent reservoir to Teflon reaction vessels. The reactors are *perfluoroalkoxy* (PFA) (Savillex) vessels that consist of a top and bottom piece that, when screwed together, forms a ~40 mL capacity jar. The top half contains ports for ingress and egress of solution. Transport of influent from the reservoir to the reaction vessels and effluent solution to collection vials was accomplished via 1.59 mm Teflon tubing. The reactors were housed in hot plates that were set to the experimental temperature of interest. The temperature of the solution within the reactors was measured with a digital thermocouple (Glas-Col model TC105) accurate to within ±2°C.

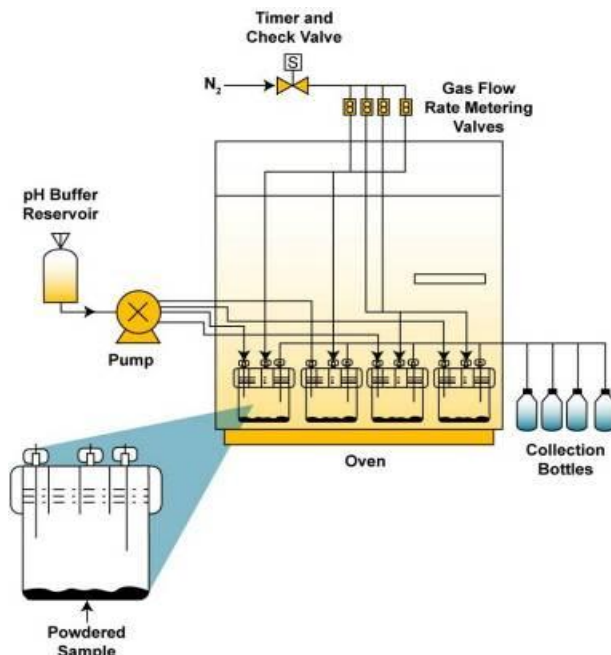


Figure 2. Schematic of SPFT.

Each reactor contained a thin layer of the powdered sample of Ca-autunite on the bottom of the reactor. This configuration prevents fluid from being pumped directly through the sample. Advantages of this configuration are that bubbles formed in the fluid transfer lines do not become entrained in the sample, which could alter the exposed surface area. This setup also minimizes the potential for grains becoming entrained in flow currents, as may be the case for fluid flowing directly through a powdered specimen. Entrainment of particles may result in spuriously faster rates due to collisions with other grains, the reactor walls generating additional surface area, or high energy sites with greater reactivities.

Blank samples were drawn prior to addition of the autunite sample. Effluent solution continuously flowed out of the reactors and was collected in vials next to the hot plates. Figure 3 shows the student collecting samples. Experiments were run until steady state conditions (constant element concentrations over time) prevailed, which was the time necessary to exchange ~12 reactor volumes. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was used to determine the effluent concentrations of calcium (Ca) and phosphorus (P).



Figure 3. Collection of samples by DOE Fellow.

3.2 Quantification of Dissolution Rates

Dissolution rates obtained from the SPFT tests are based on steady-state concentrations of elements released from the solid phase to the effluent solution. The rates are normalized to the element mass fraction present in the autunite composition by the following formula:

$$r_{i,j} = \frac{C_{i,j} - \bar{C}_{i,b} q_j}{f_i S_j} \quad (1)$$

Where: $r_{i,j}$ = normalized release rate based on element i at the j^{th} sampling, $\text{g m}^{-2} \text{d}^{-1}$

$C_{i,j}$ = concentration of the element of interest, i , in the effluent at the j^{th} sampling, g L^{-1}

$\bar{C}_{i,b}$ = average background concentration of the element i in the influent, g L^{-1}

q_j = flow rate at the j^{th} sampling, L d^{-1}

f_i = mass fraction of the element in the sample, dimensionless

S_j = surface area of the powdered specimen at the j^{th} sampling, m^2

In cases where the analyte is below background count, the background concentration of the element is set at the value of the lower limit of quantification (LOQ) and the calculated dissolution rate is, therefore, the maximum dissolution rate. The LOQ of any element is defined as the lowest concentration calibration standard that can be determined reproducibly during an analytical run within 10% error. Flow rates were determined gravimetrically at each sampling interval. The value of f_i is calculated from the chemical composition of the solid phase.

4. RESULTS AND ANALYSIS

The liquid concentrations for calcium and phosphorus were determined by inductively-coupled plasma-optical emission spectroscopy (ICP-OES) in [$\mu\text{g L}^{-1}$], these results were processed and the rate of release of each element was obtained in [$\text{mol m}^{-2} \text{s}^{-1}$]. The quantification of this dissolution rate was explained in detail under the research description section. The graphs below show the rate of release of Ca and P as a function of different bicarbonate concentrations.

4.1 Calcium Rate of Release

4.1.1 Lower Bicarbonate Concentrations

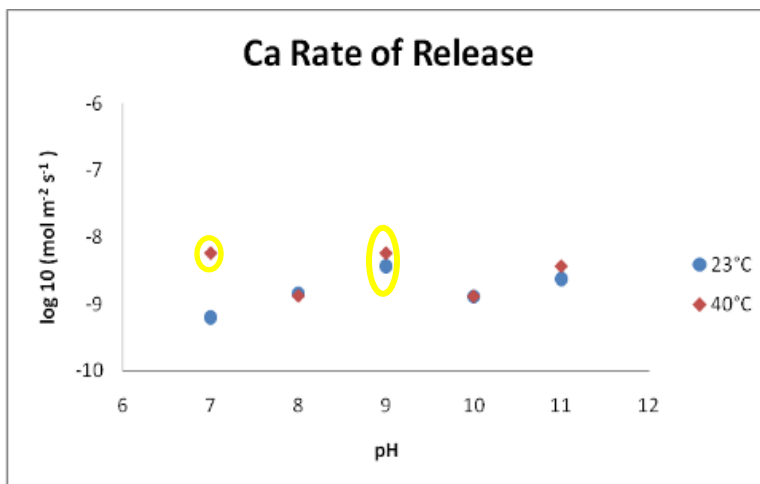


Figure 4. Ca as a function of 0.5 mM HCO_3^- .

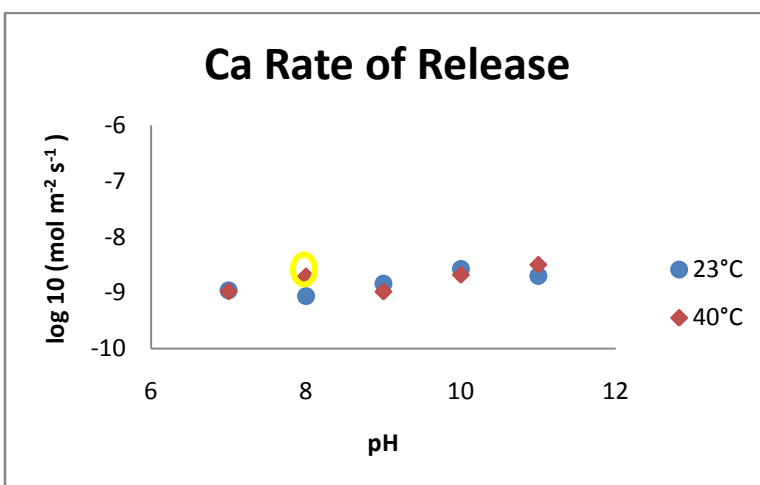


Figure 5. Ca as a function of 1 mM HCO_3^- .

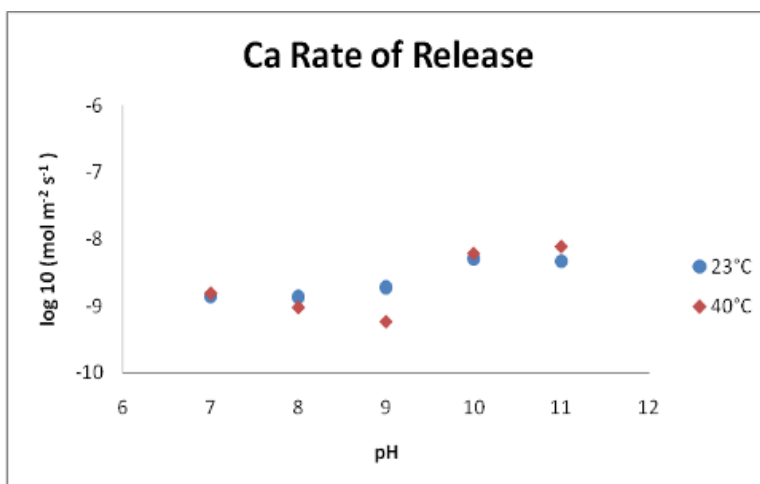


Figure 6. Ca as function of 2 mM HCO_3^- .

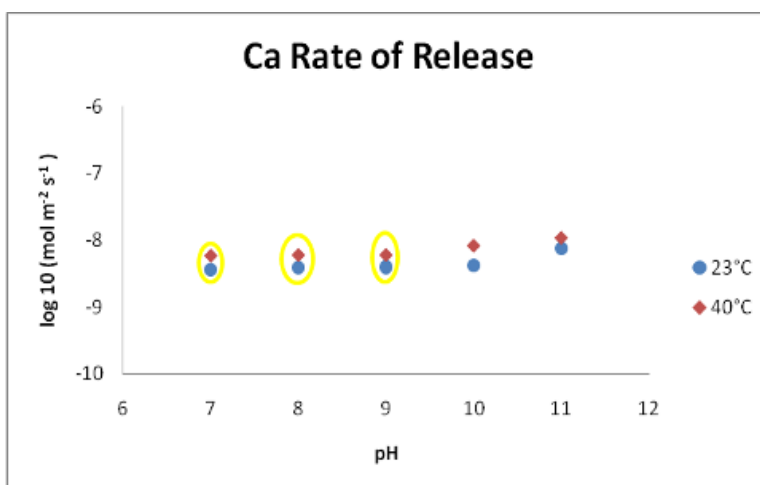


Figure 7. Ca as a function of 3 mM HCO_3^- .

The four graphs shown in Figures 4 through 7 correspond to the set of the four lower bicarbonate concentrations and are more consistent with what was expected, which was a fairly flat rate of release with respect to the different variables. There is a little bit of deviation observed from that at the higher concentrations graphs shown below (Figures 8 to 11), but it is still pretty flat. The deviation might just be analytical error.

4.1.2 Higher Bicarbonate Concentrations

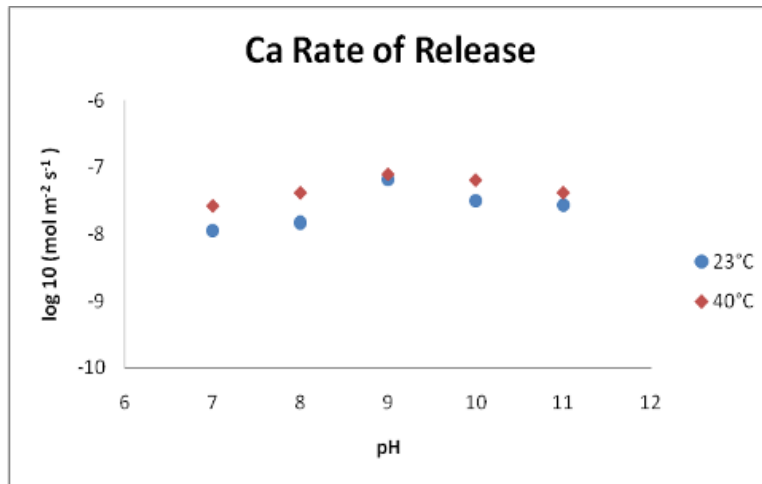


Figure 8. Ca as a function of 25 mM HCO₃⁻.

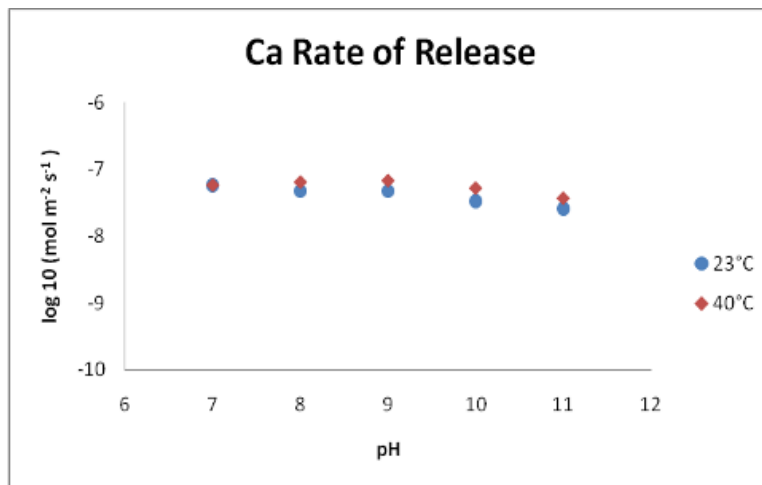


Figure 9. Ca as a function of 50 mM HCO₃⁻.

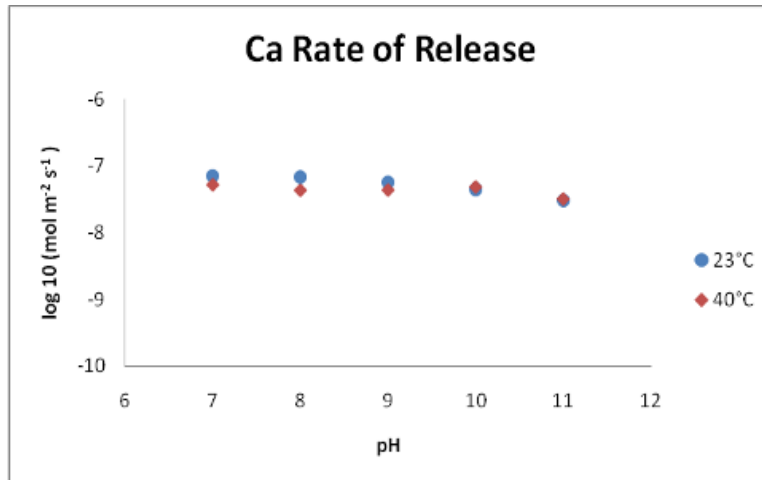


Figure 10. Ca as a function of 75 mM HCO_3^- .

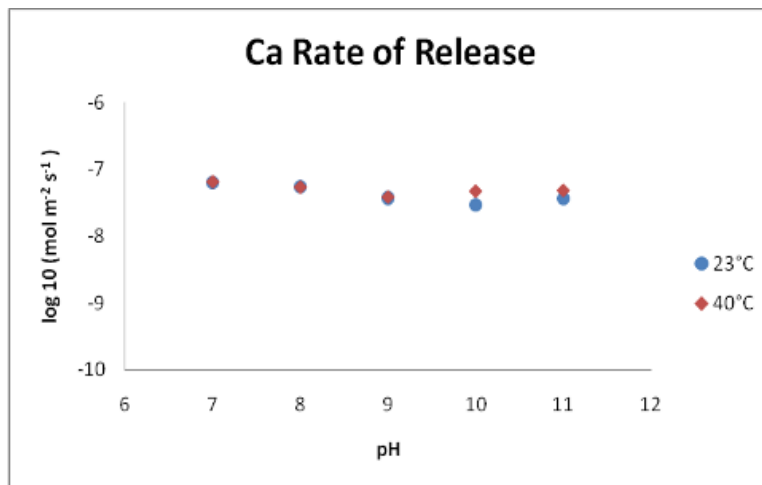


Figure 11. Ca as a function of 100 mM HCO_3^- .

4.2 Phosphorus Rate of Release

4.2.1 Lower Bicarbonate Concentrations

It is shown in figures 12 through 15 how the bicarbonate concentrations were not high enough to overcome the affinity of uranium for phosphate; under these conditions the bicarbonate is not capable of yield highly soluble and mobile uranium species. It was not until the higher concentrations were worked out that bicarbonate had an effect on the dissolution rate of autunite.

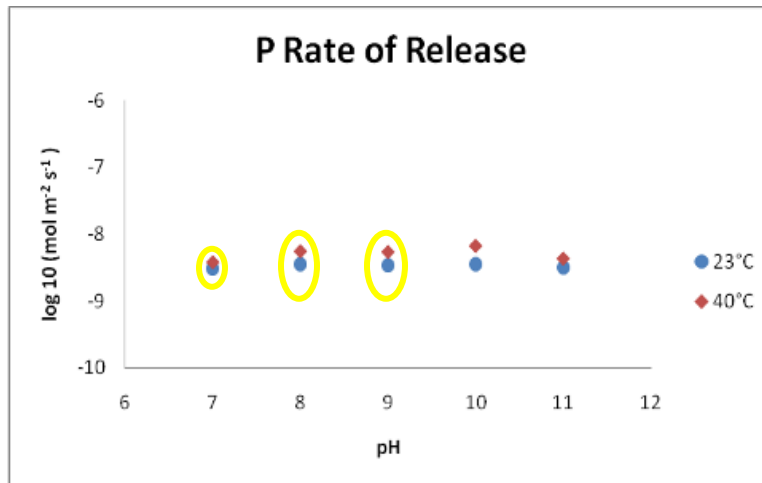


Figure 12. P as a function of 0.5 mM HCO_3^- .

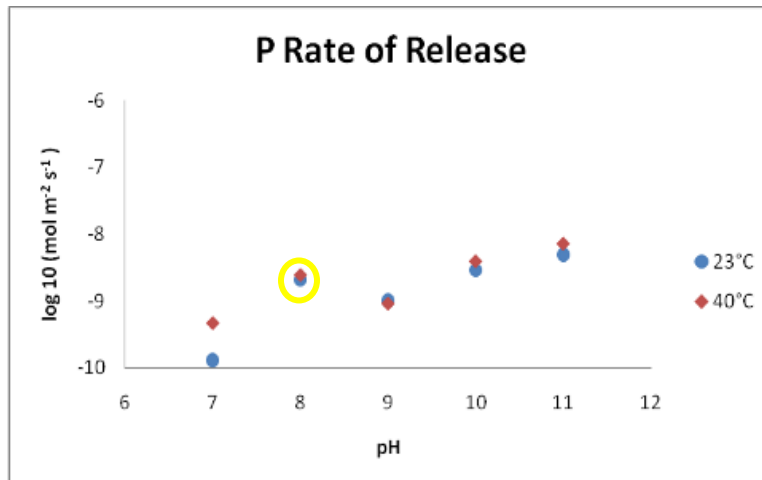


Figure 13. P as a function of 1 mM HCO_3^- .

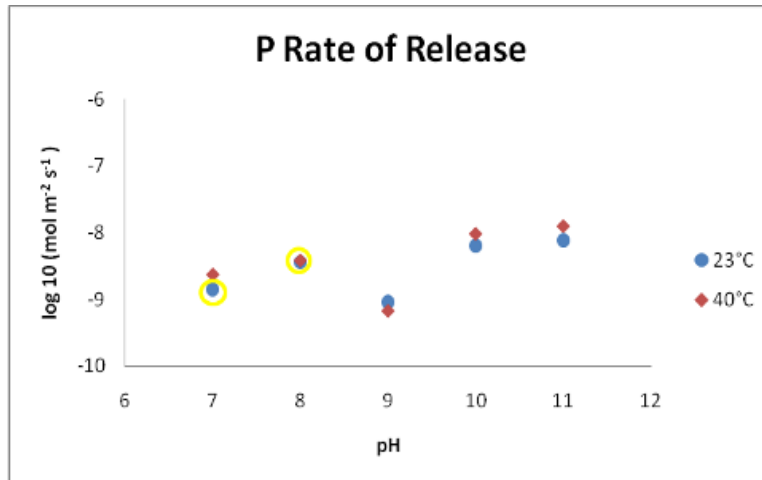


Figure 14. P as function of 2 mM HCO₃⁻.

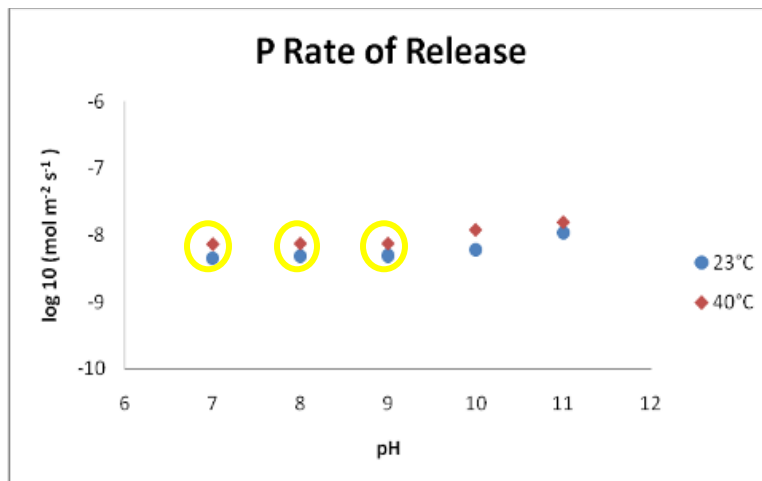


Figure 15. P as a function of 3 mM HCO₃⁻.

4.2.2 Higher Bicarbonate Concentrations

Phosphorus shows the expected pattern where its rate of release increases with increase in pH and temperature and also as a function of bicarbonate. As the bicarbonate increases, it is first to complex the uranium in solution, so it shifts the saturation state of the system with respect to uranium so that more uranium can be released. Figures 16 through 19 show the rate of release for phosphorus over varying pH at different concentrations of HCO_3^- .

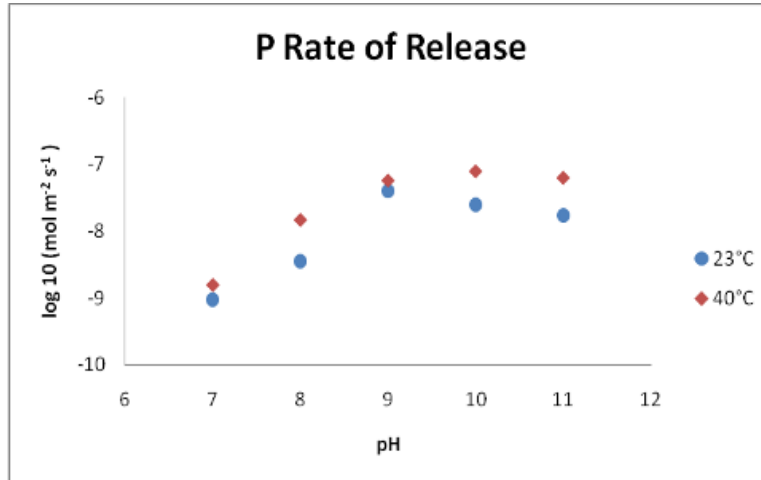


Figure 16. P as a function of 25 mM HCO_3^- .

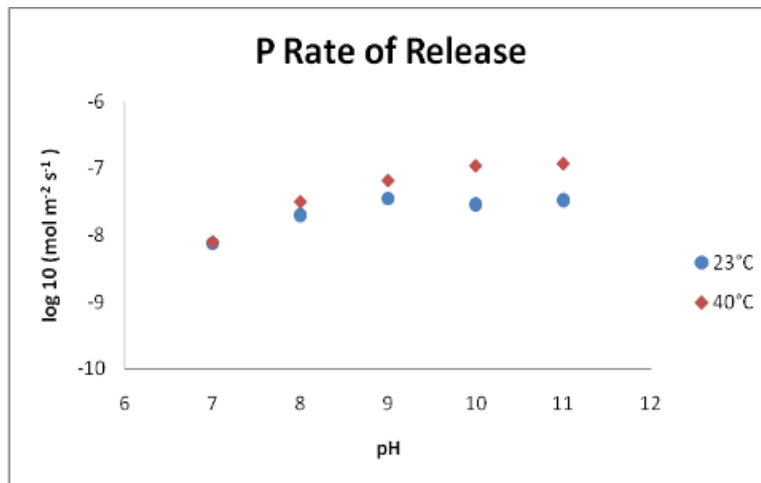


Figure 17. P as a function of 50 mM HCO_3^- .

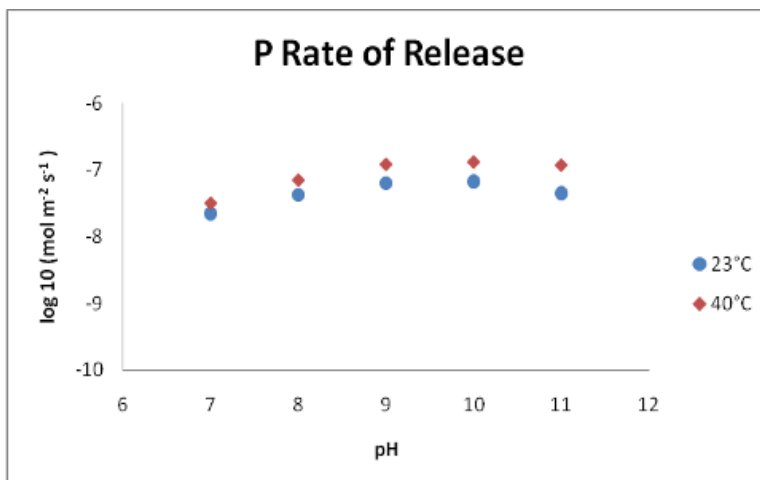


Figure 18. P as a function of 75 mM HCO_3^- .

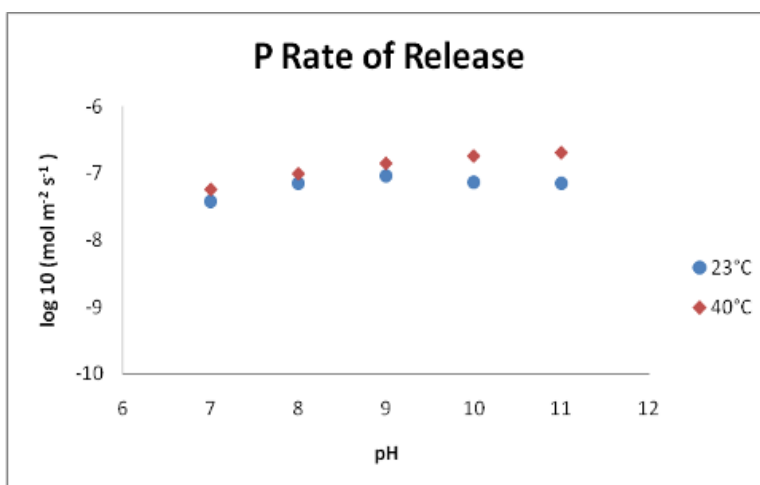


Figure 19. P as a function of 100 mM HCO_3^- .

5. CONCLUSION

The conclusions that can be drawn from the results of the two lower temperatures (23 and 40 °C) are only for calcium and phosphorus. It is clearly demonstrated in the graphs that carbonate is the dominant variable in the case of calcium and phosphorus rate of release; it is expected to have an effect in the rate of release of uranium as well. Calcium rate of release only shows ion exchange and the different temperatures and pH do not show an impact on the dissolution rate. For phosphorus, the rate of release tends to increase as the pH becomes more basic; it was also observed in the graphs that an increase in the temperature causes a higher rate of release.

The lower bicarbonate concentrations do not show a noticeable effect on the rate of release of Ca and P, the bicarbonate concentrations (0.5 – 3 mM) are not high enough to overcome the affinity of uranium for phosphate. In the higher concentrations of bicarbonate (25 – 100 mM), it shows clearly the effect of bicarbonate concentrations on the rate of release. In the future, some geochemical modeling will be done in order to confirm if there is any potential impact from the bicarbonate being present and with the calcium.

6. REFERENCES

1. Bernhard G, G Geipel, T Riech, V Brendler, S Amayri, and H Nitsche. 2001. "Uranyl(Vi) Carbonate Complex Formation: Validation of the $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ (Aq) Species." *Radiochimica Acta* **89**:511-518.
2. Casas I, J De Pablo, J Gimenez, ME Torrero, J Bruno, E Cera, RJ Finch, and RC Ewing. 1998. "The Role of Pe, Ph, and Carbonate on the Solubility of UO_2 and Uraninite under Nominally Reducing Conditions." *Geochimica et Cosmochimica Acta* **62**(13):2223-2231.
3. Cinneide SO, JP Scanlan, and MJ Hynes. 1975. "Equilibria in Uranyl Carbonate Systems-I the Overall Stability of Constant of $\text{UO}_2(\text{CO}_3)_3^{4-}$." *Journal of Inorganic and Nuclear Chemistry* **37**:1013-1018.
4. Elless MP, and SY Lee. 1998. "Uranium Solubility of Carbonate-Rich Uranium-Contaminated Soils." *Water, Air, and Soil Pollution* **107**:147-162.