STUDENT SUMMER INTERNSHIP TECHNICAL REPORT

Studying the NH_3 Injection Methodology Proposed for Remediation of the Hanford Deep Vadose Zone

DOE-FIU SCIENCE & TECHNOLOGY WORKFORCE DEVELOPMENT PROGRAM

Date submitted:

October 17, 2014

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Submitted to:

U.S. Department of Energy
Office of Environmental Management
Under Cooperative Agreement # DE-EM0000598

FIU | Applied Research Center
FLORIDA INTERNATIONAL UNIVERSITY

ABSTRACT

DOE Fellow, Robert Lapierre, completed a second 10-week internship with Pacific Northwest National Laboratory (PNNL) in Richland, Washington. Under the mentorship of Dr. Jim Szecsody, he studied the influence of NH_3 gas treatment for remediation of uranium in the Hanford vadose zone. The objectives were to assist in ongoing PNNL experiments and develop a working knowledge of the methods being used in order to apply them to the associated research being conducted at Florida International University's Applied Research Center (FIU-ARC). The intern received guidance on the use of supplementary analytical techniques as well as practice with geochemical modeling software that would benefit his ongoing research endeavors. A portion of the research performed was deemed unsuitable for public release at this time and was therefore withheld from the report.

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1. INTRODUCTION

The Hanford Site was the home of the world's first full-scale nuclear production facility which produced the plutonium core that fueled the Fat Man bomb, the second and last nuclear weapon ever deployed in combat. Inspired by mounting Cold War tensions with the Soviet Union, the nuclear weapons complex increased their nuclear fuel output after the end of WWII to expand the American arsenal. The mass production of nuclear fuel at the Hanford Site continued over the course of more than 40 years, resulting in millions of gallons of radioactive waste stored in underground storage tanks. Today, the site is the location of one of the world's largest cleanup efforts due to contamination with the chemicals and radionuclides associated with inappropriate disposal of waste as well as the failure of a fraction of those storage tanks.

As an EPA National Priorities List (NPL) site, scientists from the Pacific Northwest National Laboratory (PNNL) Energy and Environment Directorate (EED) have performed a wide range of studies regarding the current conditions and potential mitigation of the imminent dangers of the Hanford Site. Among the major concerns is the contamination of the vadose zone by the uncontrolled release of waste products into the subsurface. One threat of particular interest is the mobilization of radionuclides, such as uranium, in the subsurface. Though the migration has been found to be slow, the pollutants threaten to reach the Colombia River in the future.

An array of sequestration technologies have been tested on a variety of scales to evaluate their potential for stabilizing the potentially mobile contaminants. Research in support of this task is ongoing at Florida International University's Applied Research Center (FIU-ARC) under the project entitled "*Rapid Deployment of Engineered Solutions for Environmental Problems at Hanford"*. Studies include an investigation into the sequestration of uranium by injection of ammonia (NH_3) gas into the Hanford vadose zone, which is the focus of this report.

The objective of this internship was to further develop an understanding of the prior and ongoing research related to the treatment of the deep vadose zone using reactive gases by working with some of the PNNL scientists most familiar with the project. This included studying the experimental methods and analytical techniques employed in the past. Particular attention was paid to the application of geochemical equilibrium modeling software for the prediction and speciation of the potential species and phases formed. The experience gained will be directly applied to advancing the aforementioned FIU-ARC research.

Additional research and experiments were performed but were deemed unsuitable for public release at this time.

2. EXECUTIVE SUMMARY

This research work has been supported by the DOE-FIU Science & Technology Workforce Initiative, an innovative program developed by the US Department of Energy's Environmental Management (DOE-EM) and Florida International University's Applied Research Center (FIU-ARC). During the summer of 2014, a DOE Fellow intern, Robert Lapierre, spent 10 weeks doing a summer internship at Pacific Northwest National Laboratory (PNNL) in Richland, WA under the supervision and guidance of Dr. Jim Szecsody, Senior Scientist with the Environmental Systems Group. The intern's project was initiated on June 2, 2014, and continued through August 9, 2014 with the objective of performing ongoing research and assisting with experimentation related to the remediation of uranium in the Hanford vadose zone.

3. RESEARCH DESCRIPTION

A portion of the research done over the course of the internship was dedicated to assisting in experimentation related to certain ongoing PNNL projects. Due to the potential sensitivity of the data, this material was not included in the report.

A comparison between the approach currently being implemented in the Florida International University study and those used in related PNNL studies was done in order to revise and advance the methodology of the former. At this point, the research being performed at FIU pertaining to the NH_3 remediation of the Hanford vadose zone is limited in its scope, considering only the pore water in the vadose zone. In the FIU-ARC experiments, synthetic pore water solutions are prepared to imitate key constituents in the Hanford pore water after which the remediation method is applied. Supplementary methods of analysis found to be effective in PNNL research were studied for potential addition to the FIU- ARC experimental plan.

Geochemical Modeling Software

With the emphasis being placed on the products of remediation applied to the aqueous pore water phase, it was proposed that application of geochemical modeling software would allow for the speciation and determination of phase changes in the system. More specifically, the primary aim of the modeling was to identify the most likely uranium-bearing precipitates formed in the post-treatment samples. A prediction based on chemical equilibrium modeling could be used to evaluate the plausibility of any postulated identities based on analysis of the experimental precipitate phase.

Two programs that scientists in the PNNL's Energy and Environment Directorate have recommended for reaction modeling are Visual Minteq (VM) and The Geochemist's Workbench (GWB). Though the former has been used for this project in the past, neither has been utilized in the same manner.

Introduction to The Geochemist's Workbench

The Geochemist's Workbench is a geochemical modeling suite of software modules useful for a multitude of geochemical applications. It makes use of datasets containing the thermodynamic data for a vast library of chemical compounds. In addition to its modeling capabilities, GWB is capable of producing and manipulating graphs and diagrams to represent and describe a variety of chemical processes.

After a brief introduction to the software, the *React* module was used for modeling our reaction. The experimental conditions, including temperature and component concentrations specific to the system were input into the module for evaluation (Figure 1). For the purpose of optimizing our sample preparation procedures, the module was used to ensure that the sample solutions would be stable. In the cases where the system failed to run our reaction and create a viable solution, concentrations were varied within the model in order to get a workable solution.

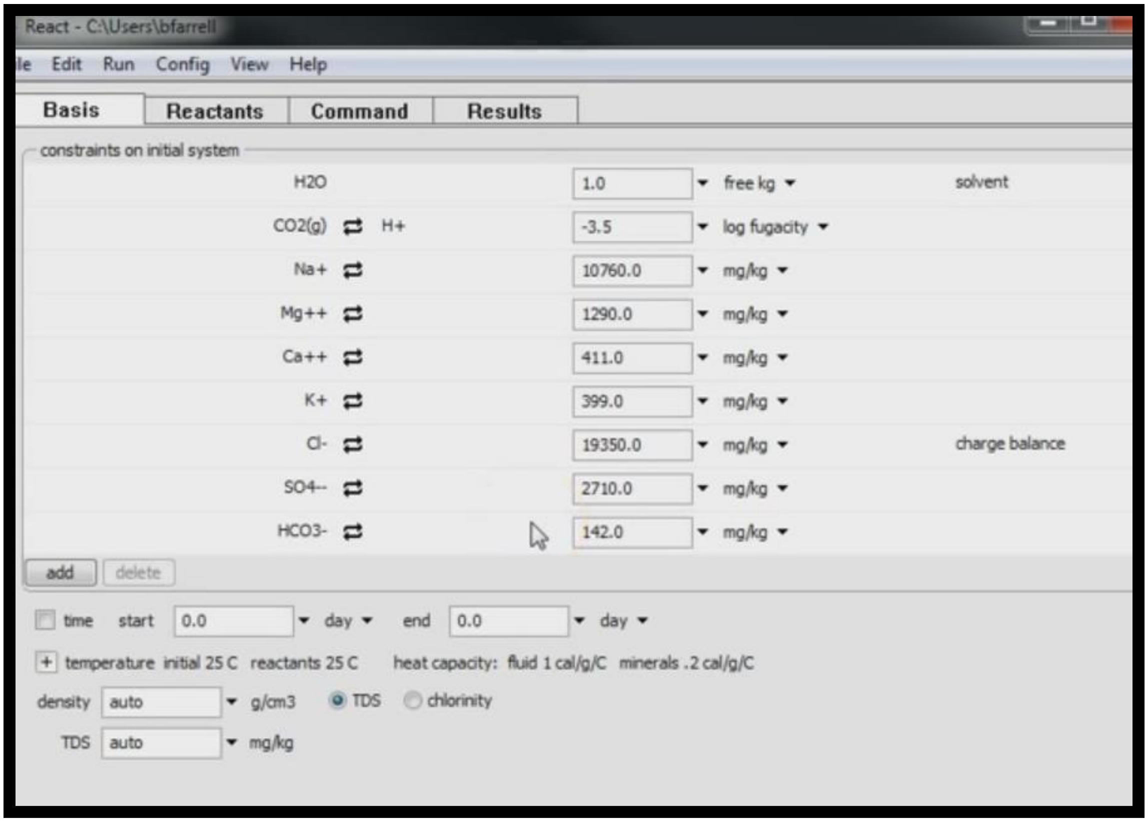


Figure 1. An example of the React component input.

Ideally, modeling our system will provide an idea of the fate and speciation of uranium after the remediation method is applied. This is simulated by a sweep of the pH from an initial value of ~8 to the post-treatment pH of 11 – 12.

Though GWB encompasses many modules, several of which could be relevant to the ongoing FIU-ARC research, *React* was determined to be the most beneficial and the only one considered over the allotted time.

Studying Visual Minteq

Visual Minteq is a chemical equilibrium modeling software that is popular both for its utility as well as for being free to use. Though it does not have the wide range of functionalities that GWB provides, VM provides an application for performing complex modeling for chemicals in water-based systems. The software has been applied in FIU-ARC research in the past, primarily for speciation purposes, though it is also capable of much more.

The initial setup of the system is near identical to the GWB *React* module (Figure 2 & Figure 3). In order to get a detailed look at the speciation of uranium with application of the remediation method, the multi-problem/sweep function was used to run multiple simulations across a range of pH values. It was proposed that this could be accomplished in two ways; allowing the system to vary the pH and varying the aqueous ammonium (NH_4^+) concentration. The latter of the two methods was proposed based on equation [1] to account for any contribution that the added ammonia gas could have on the system.

$$NH_3(aq) + H^+ \leftrightarrow NH_4^+ \qquad [1]$$

To allow for a detailed investigation, the model was programmed to perform the pH change in a series of between 50 and 1000 steps, each of those increments representing a processed problem. The general output data (e.g., component concentrations, distributions, and saturation indices) for each of those steps are available for up to 500 increments. Aside from the general output for each increment, up to thirteen components can be selectively monitored for the duration of the sweep for output. For example: a comparison of the relationship between an increasing pH and aluminum speciation could be done by selecting the possible aluminum bearing components and species to be monitored throughout the sweep and output to a table.

Figure 2. The *Visual Minteq main page* with component input.

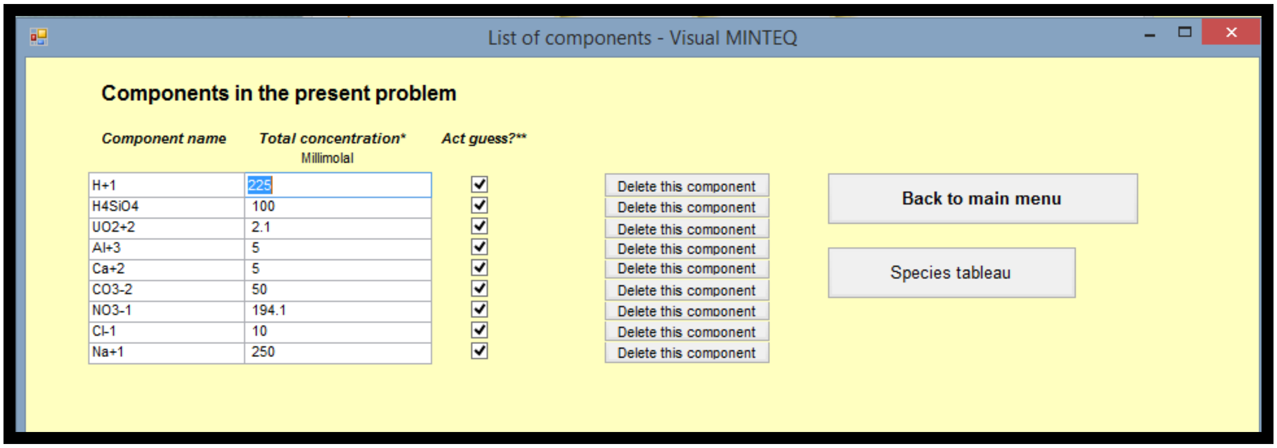


Figure 3. An example of Visual Minteq component list.

Additional Experimental Modifications

In addition to extending the FIU-ARC experimental work to incorporate the use of geochemical modeling software, observation and practice using techniques employed successfully in related PNNL studies has assisted in improving the scope of FIU-ARC's experimental plan. This included learning key points of procedures and devising the best ways to adapt and implement relevant techniques into the project.

The major methodology reviewed for amending the experimental plan was sequential extraction using a group of solutions representing increasingly harsh conditions. This analysis was used to evaluate the mobility of the uranyl phases that were either adsorbed or precipitated after the application of the NH_3 remediation method. This technique was used as an indicator of the effectiveness of the remediation method. The extractions, in increasing intensity, are provided in Table 1.

Table 1. Solutions for Sequential Extraction Experiments

Solution	Time (hrs)	Target
Synthetic Ground Water	1	Aqueous Uranium Phases
0.0144M $NaHCO_3$/0.0028M Na_2CO_3	1	Adsorbed Uranium Phases
1M Sodium Acetate ($C_2H_3NaO_2$)	1	Some Uranyl Carbonates
Acetic Acid (CH_3CO_2H)	120	Majority of Uranyl Carbonates
8M Nitric Acid	2	Difficult Uranium Phases

4. LESSONS LEARNED

Experimental Plan Modifications

Knowledge gained through hours of observation, experimentation, practice, and dialogue will be interpreted and utilized to build upon the existing experimental plans for the ongoing FIU-ARC research. Through communication with the various PNNL scientists experienced with the proposed NH_3 remediation method, several potential supplementary studies and analytical techniques were studied for consideration.

Among those proposed ideas was the application of the sequential extraction technique, previously used for evaluating the mobility of uranyl components in pre- and post-treatment samples. It was determined that the technique could be similarly applied to evaluate the effectiveness of the remediation method under the specific experimental conditions being studied and compared at FIU-ARC. With the general concepts and methods unchanging, applying the technique would require minimal modifications, making it a likely addition to the experimental plan.

Geochemist's Workbench

Though hands-on time with the GWB software was limited, several sets of conditions were tested in the *React* module. Of those sets, relatively few of them successfully completed their host of calculations. The many intricacies of the software limited the ability to resolve the majority of the crashed simulations. Of the functional runs, one particular set of conditions (not shown) was notably effective, producing the speciation diagram for aluminum species shown in Figure 4.

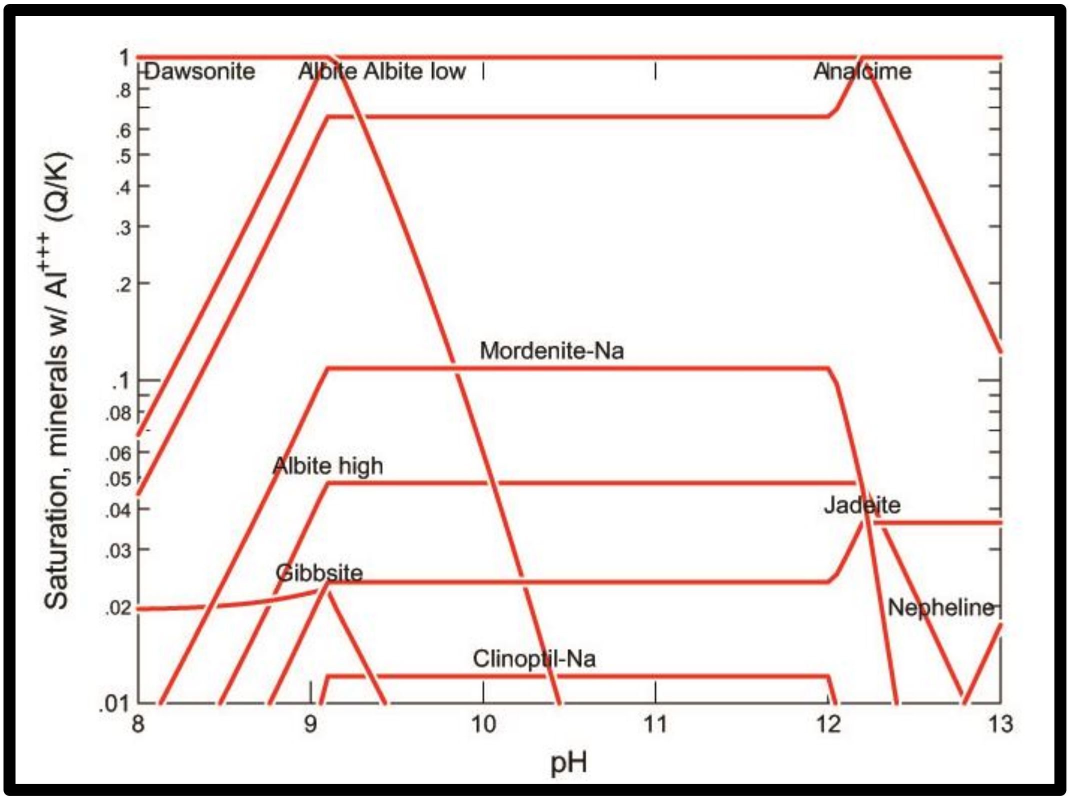


Figure 4. GWB produced speciation diagram for aluminum species.

The aluminum speciation diagram was produced using example conditions very similar to the desired experimental set up but excluding the uranium source [uranyl nitrate, $UO_2(NO_3)_2$]. The free sodium (Na^+) ions were selected as the component for balancing the simulated reaction. The system was programmed to monitor the saturation of the aluminum species as the pH was slid from 8 to 13.

The diagram produced with these example conditions offer promise for what could be expected with genuine experimental conditions and practice with the software. Once the GWB suite is available to FIU-ARC, it is anticipated that additional modules will be investigated and applied to the research where appropriate.

Visual Minteq

Though VM modeling has been applied in past studies, the understanding of the software was greatly expanded. Similar to the GWB applications, the multi-problem sweep function was used to simulate the geochemical changes that occur with a pH shift from 8 to 13. The results of initial example simulations run using this function showed promising results that corroborated earlier predictions.

The execution of the sweep function is very similar to the more general use of VM. The sample's components are added in the typical manner, corresponding to the desired starting conditions (Figure 3). From this point, the "Multi-problem/Sweep" tab is selected (Figure 5) revealing the menu wherein the details of the sweep are set (Figure 6). For the purpose of this example, a single parameter, total concentration sweep, was selected with that variable being NH_4^+. The menu shows that the ammonium concentration would start at 0 and change in increments of +10 over the course of 50 problems. Carbonates were selected for monitoring in order to observe the speciation through the reaction, though any relevant components or products could be selected. Figure 7 shows the general output page for the simulation with the option to select one of the 50 problems to display their results. Additionally, clicking the “Selected Sweep Results” button will reveal the sweep data for the selected species over the range of problems (Figure 8). This data is easily exported into excel for data analysis and plotting, as seen in Figure 9 – Figure 12.

Figure 5. Visual Minteq main page (Sweep option circled).

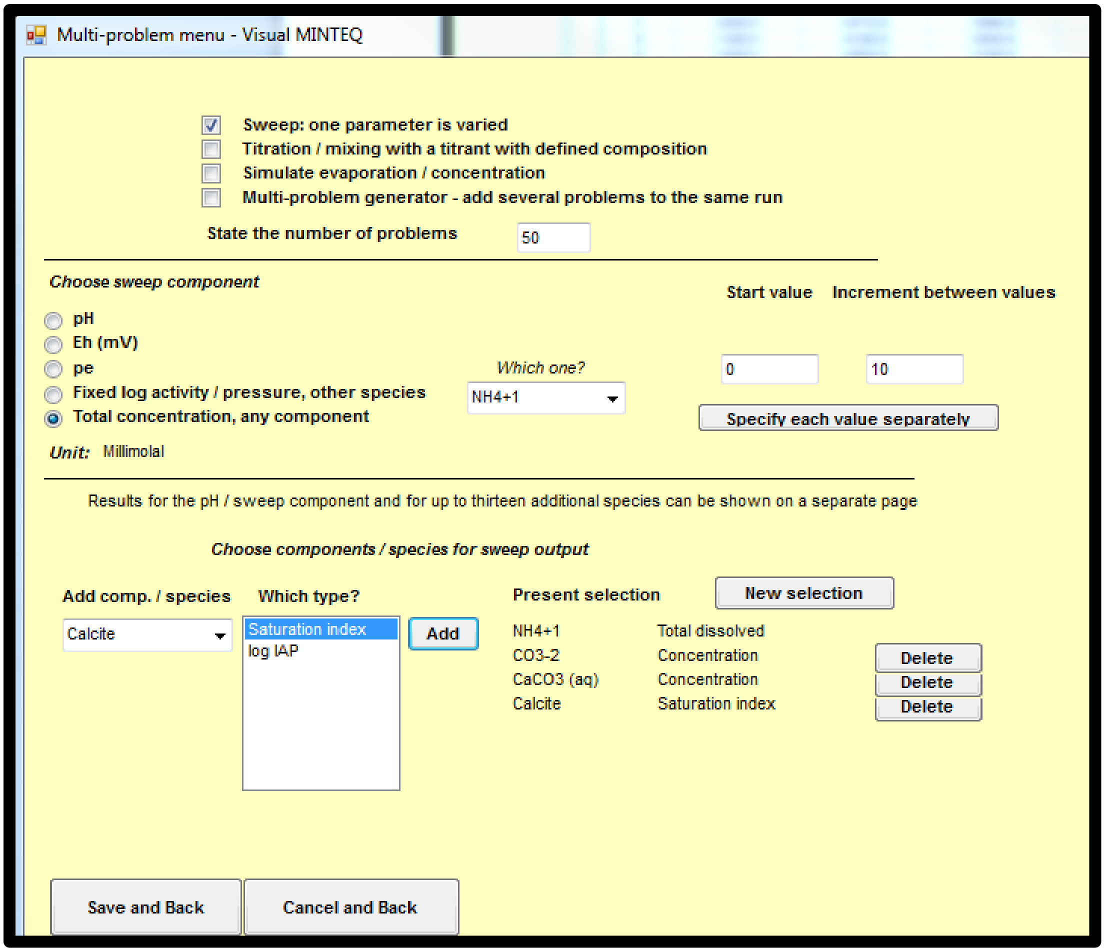


Figure 6. Visual Minteq Multi-problem/Sweep menu.

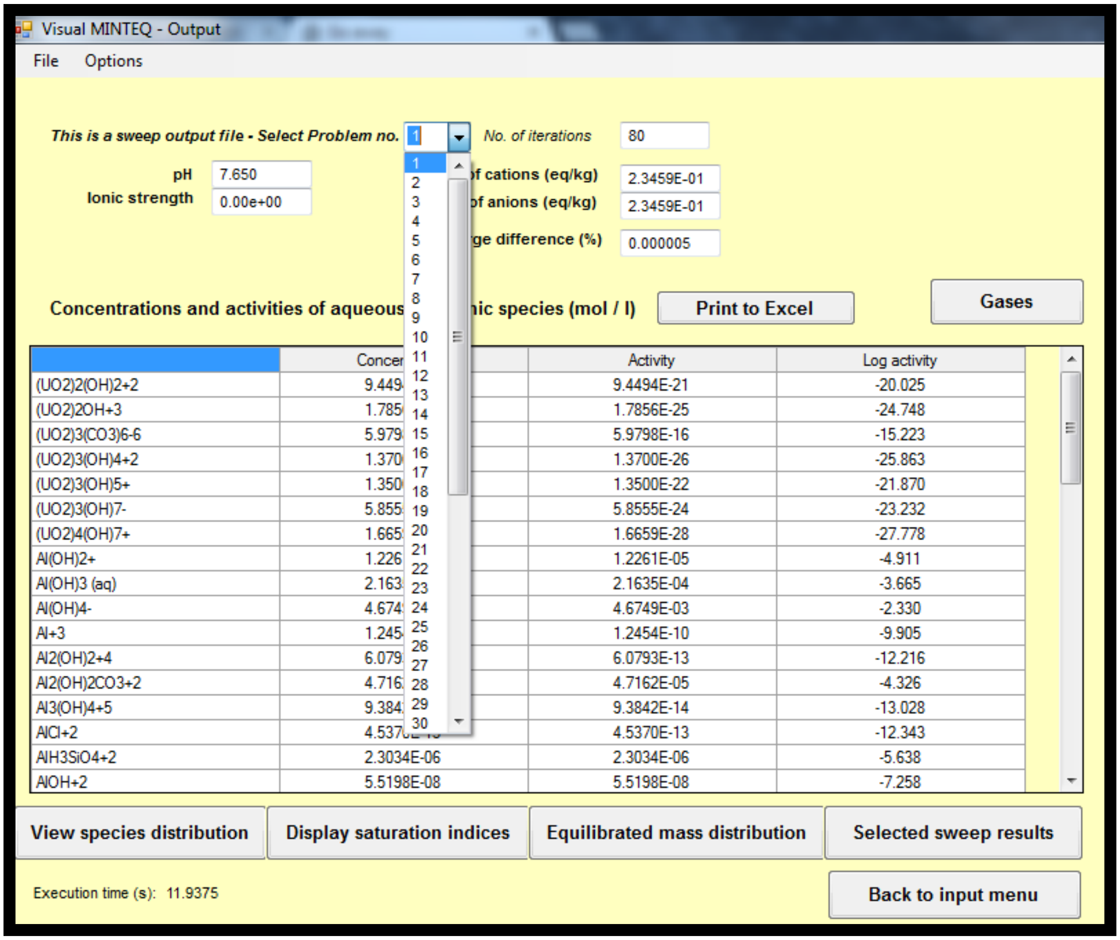
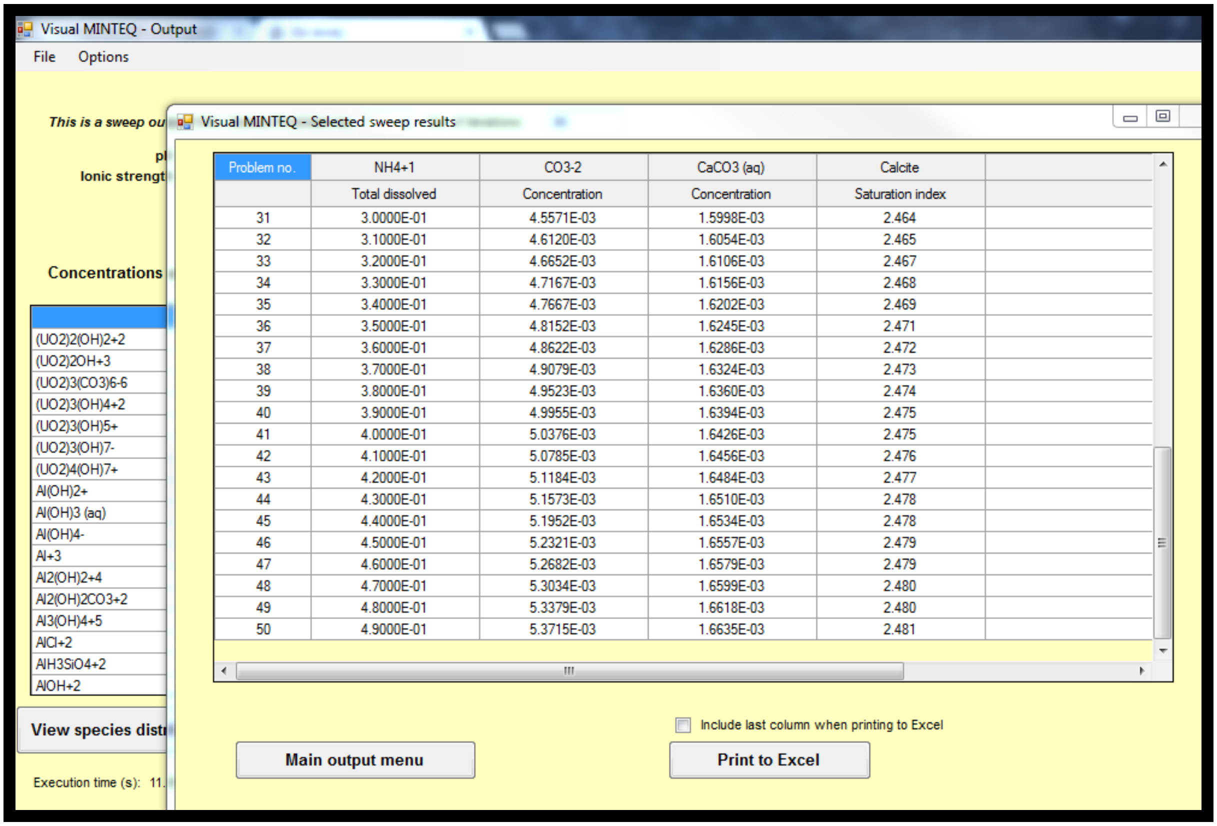


Figure 7. Visual Minteq output showing the various problems in the sweep.



Problem no.	NH4+1	CO3-2	CaCO3 (aq)	Calcite
	Total dissolved	Concentration	Concentration	Saturation index
31	3.0000E-01	4.5571E-03	1.5998E-03	2.464
32	3.1000E-01	4.6120E-03	1.6054E-03	2.465
33	3.2000E-01	4.6652E-03	1.6106E-03	2.467
34	3.3000E-01	4.7167E-03	1.6156E-03	2.468
35	3.4000E-01	4.7667E-03	1.6202E-03	2.469
36	3.5000E-01	4.8152E-03	1.6245E-03	2.471
37	3.6000E-01	4.8622E-03	1.6286E-03	2.472
38	3.7000E-01	4.9079E-03	1.6324E-03	2.473
39	3.8000E-01	4.9523E-03	1.6360E-03	2.474
40	3.9000E-01	4.9955E-03	1.6394E-03	2.475
41	4.0000E-01	5.0376E-03	1.6426E-03	2.475
42	4.1000E-01	5.0785E-03	1.6456E-03	2.476
43	4.2000E-01	5.1184E-03	1.6484E-03	2.477
44	4.3000E-01	5.1573E-03	1.6510E-03	2.478
45	4.4000E-01	5.1952E-03	1.6534E-03	2.478
46	4.5000E-01	5.2321E-03	1.6557E-03	2.479
47	4.6000E-01	5.2682E-03	1.6579E-03	2.479
48	4.7000E-01	5.3034E-03	1.6599E-03	2.480
49	4.8000E-01	5.3379E-03	1.6618E-03	2.480
50	4.9000E-01	5.3715E-03	1.6635E-03	2.481

Figure 8. Sweep output data from the # of problems for the selected components.

Figure 9 was prepared to prove that increasing NH_4^+ concentration could be used to ramp up the pH for subsequent simulations. It was theorized that this method would be a superior simulation of NH_3 gas injection. Alternatively, it is possible to have the model manipulate the pH without considering any additional contribution that the aqueous ammonia would have.

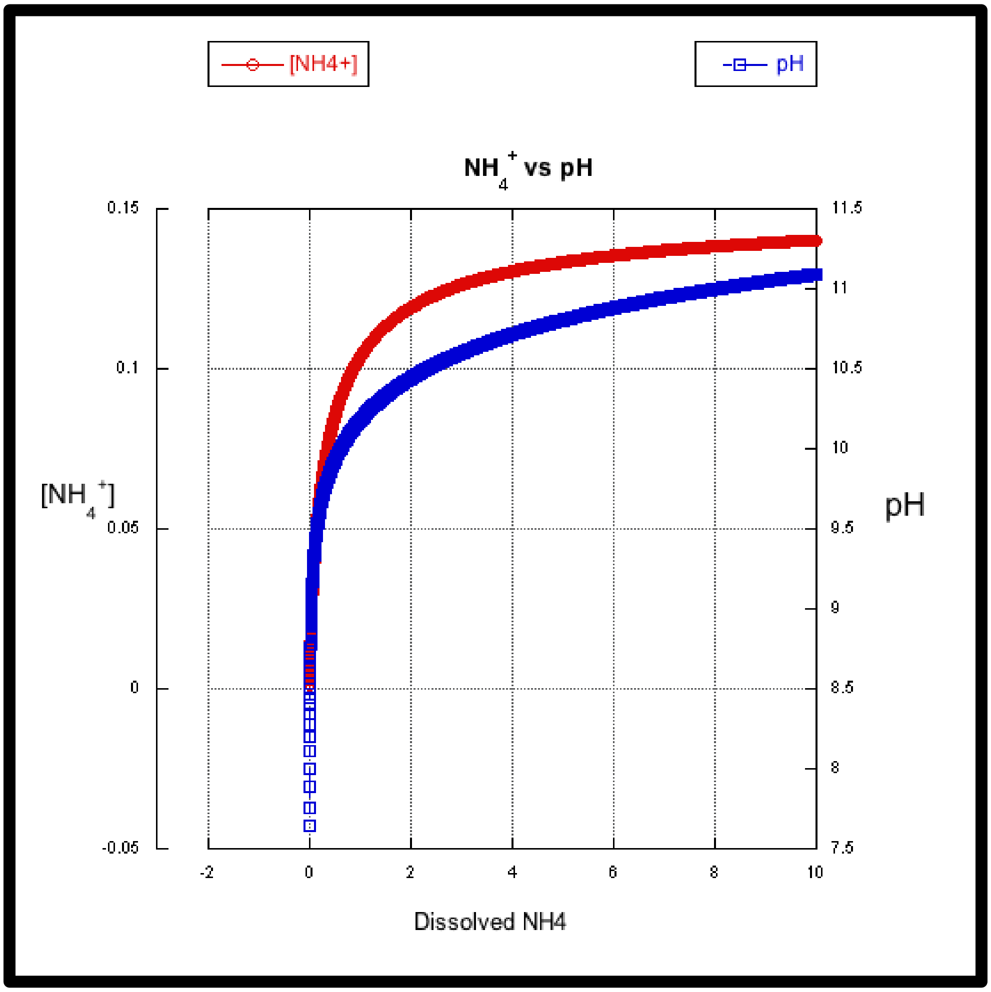


Figure 9. Visual Minteq plot of dissolved NH_4 vs pH.

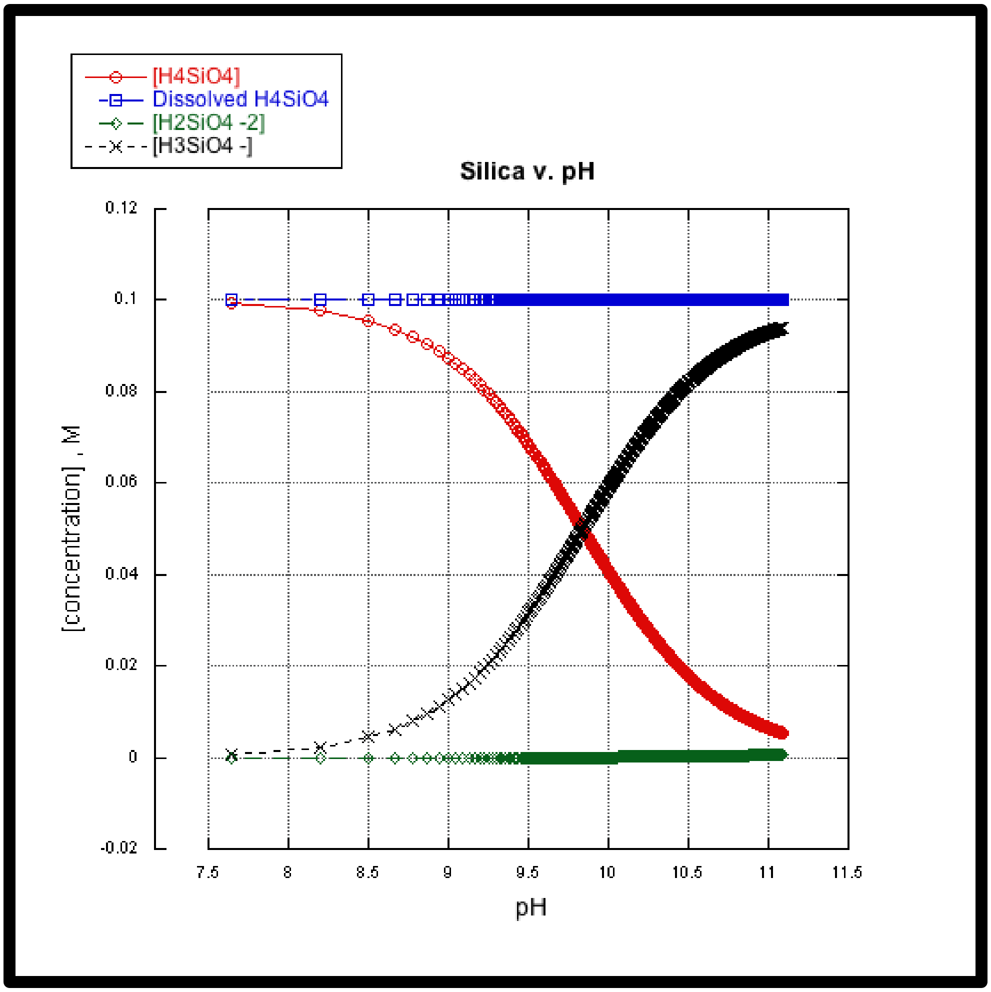


Figure 10. Visual Minteq reaction path for silica species with increasing pH (by NH_4 increase).

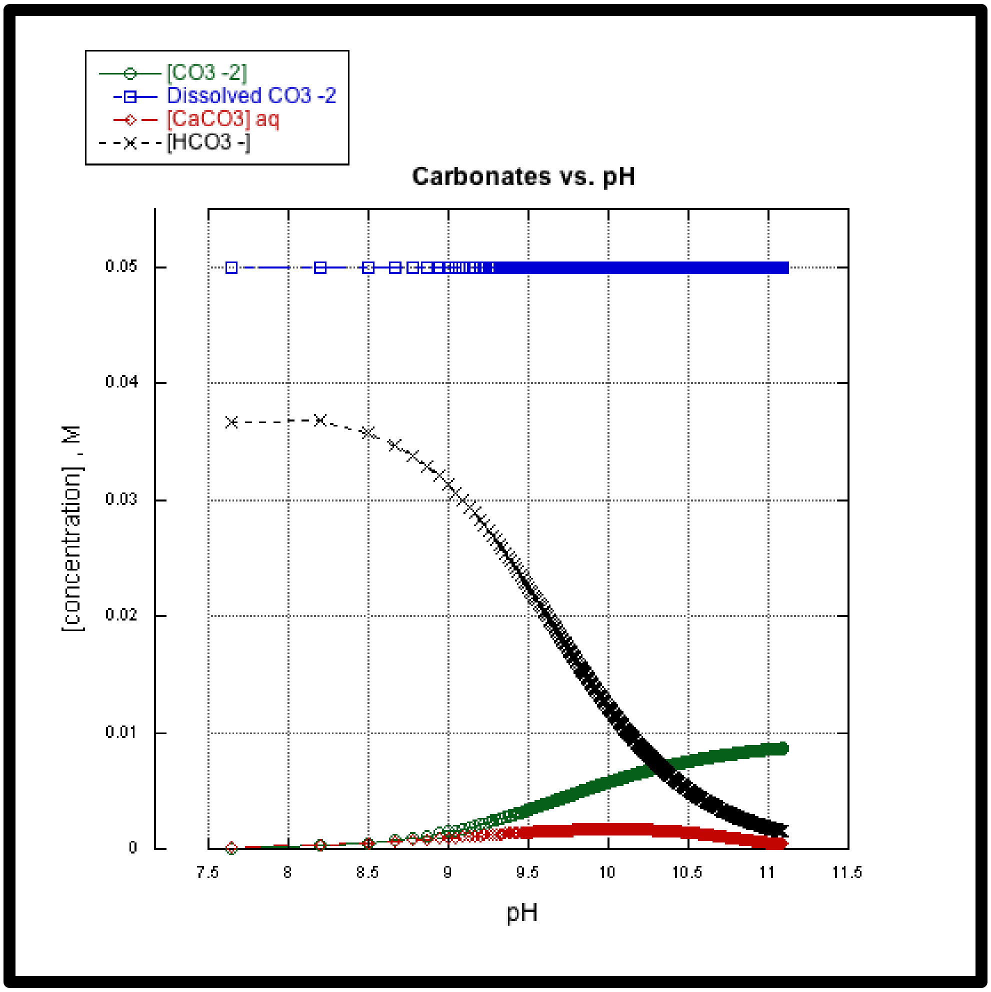


Figure 11. Visual Minteq reaction path for carbonate species with increasing pH (by NH_4 increase).

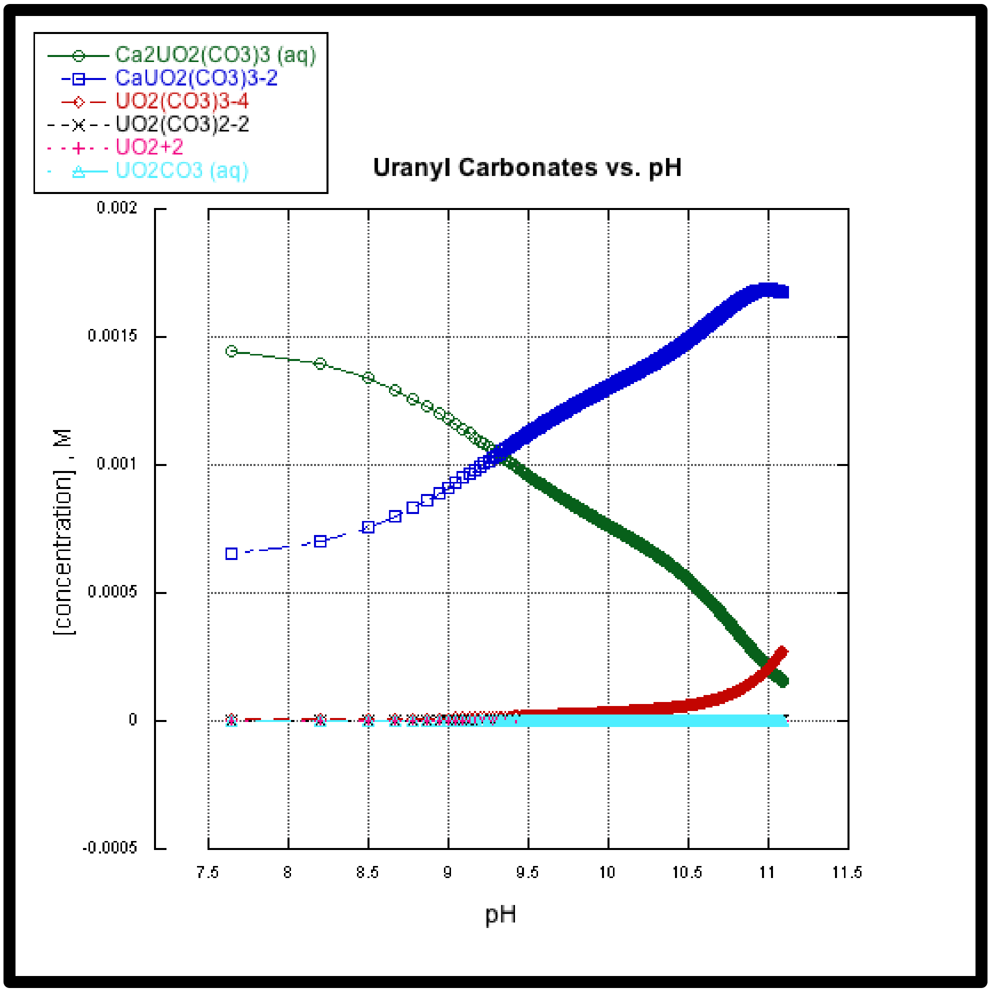


Figure 12. Visual Minteq reaction path for uranyl-carbonate species with increasing pH (by NH_4 increase).

Figure 10 – Figure 12 show the interrelationships between selected species as the pH is artificially increased using the aforementioned [NH_4^+] manipulation. The analysis did not show any of the anticipated solid uranyl phases within the Visual Minteq database and was therefore omitted from Figure 12. One of the predicted forms, Cejkaite ($Na_4(UO_2)(CO_3)_3$), was not even found in the VM library. Attempts to find the thermodynamic information for that compound and add it to the database are ongoing.

Despite the advances made regarding the application of Visual Minteq, there are functions and capabilities of the software that have yet to be figured out (i.e.: solid phases, adsorption, and surface complexation). Of those functions, some progress was made with the precipitate function, though it has yet to reach the point at which it could be added to the study. Within the scope of the project, further investigation into the software is planned to unlock its full capacity and potential application.

5. CONCLUSION

The experimental approaches favored by Pacific Northwest National Laboratory (PNNL) scientists were studied to determine how they could be applied to the complementary research being conducted by FIU-ARC researchers. Geochemical modeling software was studied to determine its use how it can be applied as the project moves forward. Though the results of The Geochemist's Workbench modeling were not as expected, the opportunity to become familiar with the program will be extremely beneficial once the software suite has been acquired. Prior understanding of Visual Minteq was significantly enriched in ways that will result in a significant improvement in the way that the modeling data is collected and represented. A handful of analytical methods used in related PNNL projects were also studied for their potential application to the ongoing FIU-ARC research of the same ilk.

Additionally, experience was gained by assisting Dr. J. Szecsody with experimentation and analysis of his ongoing projects. The information related to this portion of the internship was omitted as it was deemed unsuitable for release at this time.

6. REFERENCES

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