
AC 2012-4906: USING EITHER HYDROGEN OR DITHIONITE AS REDUCTANT IN URANIUM CONTAMINATED GROUNDWATER AT POST-LEACH URANIUM MINING SITES, SOUTH TEXAS

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Modeling, Simulations and Studies using Hydrogen or Dithionite as Reductants in Uranium Contaminated Groundwater at Post-Leach Uranium Mining Sites in South Texas

Abstract

This paper summarizes the results of a summer research project conducted by a public high school teacher. The project focused on the impacts of in situ recovery (ISR) uranium mining on groundwater quality in South Texas. Uranium is a major groundwater constituent at ISR mining sites and there is need for more effective post-mining restoration strategies. One promising approach is to add reductants to reduce soluble U(VI) species to insoluble U(IV) species that are permanently immobilized within the aquifer formation. In this research a hydrogeochemical computer program from USGS (PHREEQC) was used to simulate how two different reductants, hydrogen gas (H_2) and sodium dithionite ($Na_2S_2O_4$), induce reduction of U(VI) to U(IV) and groundwater and associated changes in the hydrogeochemistry. The modeling simulation performed with H_2 as the reductant showed that significant reduction of uranium, iron and sulfate was achieved, resulting in very strong reducing conditions. In contrast, the modeling simulation with sodium dithionite as the reductant showed reduction of uranium and iron only. These results have significant implications with respect to the potential effectiveness of H_2 and dithionite as chemical reductants for restoring groundwater quality at uranium ISR mining sites. In particular, while addition of H_2 should achieve stronger reducing conditions near the injection point, the addition of dithionite will likely have a larger zone of influence because it will not be consumed via sulfate reduction reactions.

A learning module based on the legacy cycle concept was developed that challenges the students to think through the processes and steps to determine the level of contamination and the amount of restoration required to return groundwater to safe levels. This learning module will be introduced into high school mathematics and science classes during spring semester 2011-2012 school year. A subsequent assessment of the students' performance will be carried out and reported.

Introduction

In-situ recovery (ISR) mining of uranium (U) has developed into a major mining technology as compared to traditional open pit mining and underground mining for the recovery of U ore because of lower costs, shorter start-up times, greater safety, little disturbance of surface terrain or surface waters, and low labor requirements. Likewise, many of the hazards of working at an ISR mining operation are less significant than for open-pit or underground mining operations. However, the ISR mining of uranium ore has environmental disadvantages because large amounts of groundwater are circulated and there is some withdrawal from an area where aquifers

constitute a major portion of water supply for other purposes. Likewise, injection of an oxidant with the leach solution causes valence and phase changes of indigenous elements such as As, Cu, Mo, Se, S, and V, as well as U, thereby increasing the aqueous concentrations of these species as well. A question of major concern at ISR mining sites is how to restore the groundwater to its original chemical composition. Restoration is necessary to reduce the amounts of undesired chemical constituents left in solution after mining operations and thus to return the groundwater to a quality consistent with pre-mining use and potential use. One promising approach to restoring groundwater quality at ISR sites is to inject reductants that can reduce and permanently immobilize the residual uranium within the aquifer formation. This paper describes a computer modeling study performed to simulate the reduction and immobilization of uranium in groundwater through injection of either hydrogen gas or sodium dithionite solution.

Review of Literature

Geology and Mineralization of Uranium

The Gulf Coast aquifer in Texas is part of the South Texas Uranium (STU) Province, which includes about 20 counties. The uranium deposits in the Gulf Coastal Plain of South Texas were derived from volcanic materials that deposited across an ancient river delta system. Oxidized groundwater leached uranium from the surface sediments into groundwater aquifers. The U-enriched groundwater flowed through the aquifer until it reached an interface between oxidizing and reducing groundwater. At this interface, the U and other elements (including As, Se, V, Cu, and Mo) precipitated out of the solution. The reducing conditions were due to influxes of either oil and gas or H₂S migrating along faults or, less commonly, organic-rich sediments. The reducing conditions changed the redox state of the uranium from a soluble oxidized form, U(VI), to an insoluble reduced form, U(IV). Such deposits are known as “roll-on front” deposits.¹

Geochemistry of Uranium in Groundwater

The naturally occurring uranium minerals in nature predominantly exist in one of two ionic states: U(VI) (the uranyl oxidized ion) and U(IV) (the uranous reduced ion). In the oxidized (uranyl) state, uranium is more readily dissolved and is highly mobile in the environment (e.g., in soil, surface water, and groundwater); however in the reduced uranous (U⁴⁺) state, uranium does not readily dissolve in water. Common uranous minerals include uraninite (UO₂), pitchblende (a crystalline variant of uraninite), and coffinite [U(SiO₄)(OH)₄]. Arsenic, molybdenum, and selenium often occur together with uranium at a regional scale because they are derived from the same source (i.e., ash-fall leaching). Radioactive decay of uranium also generates radium and radon.²

Overview of ISR Mining of Uranium Ore

In situ recovery (ISR) mining is the in-place mining of a mineral without removing overburden or the original ore deposits. It is usually done by installing a well and mining directly from the natural deposit via the injection and recovery of a fluid that causes the leaching, dissolution, or extraction of the mineral. The uranium deposits in South Texas are located in porous and confined sedimentary sandstone formations which are very amenable to ISR mining technology. The ISR mining of uranium ore starts with drilling of injection, production and monitoring wells. Once the wells are in place, lixiviant (groundwater amended with dissolved oxygen and sometime sodium bicarbonate) is injected into the ore-bearing aquifer formation to dissolve the uranium mineral. The uranium-laden solution is then pumped back to the surface for extraction and processing into a dry powder-form material consisting of natural uranium, which is commonly called “yellow cake” and is sold on the market as U_3O_8 .³

Groundwater Restoration Techniques

Recognizing that in-situ recovery operations fundamentally alter groundwater geochemistry, the primary goal of a restoration program is to return groundwater quality of the mined ore zone to the pre-mining baseline condition defined by the baseline water quality sampling program. During the groundwater restoration, all parameters, on an average basis, must be returned to baseline or as close to average baseline values as is reasonably achievable. Approaches for restoring groundwater quality at ISR sites typically involves a combination of methods including (1) groundwater transfer, (2) groundwater sweep, (3) reverse osmosis with permeate injection and groundwater recirculation, and (4) stabilization monitoring.⁴

“Groundwater transfer” is the displacement of mining-affected waters in the well field with baseline quality waters from parts of the well field just beginning leaching operations. It involves moving groundwater between the well field entering restoration and another well field where uranium leaching operations are beginning. This results in the groundwater in the two well fields becoming blended until the waters are similar in conductivity and therefore similar in the amount of dissolved constituents. Because water is transferred from one well field to another, groundwater transfer typically does not generate liquid effluents.⁴

“Groundwater sweep” involves pumping groundwater from the all the production and injection wells to the processing plant without reinjection. This pumping causes uncontaminated, native groundwater to flow into the ore body, thereby flushing the contaminants from areas that have been affected by the horizontal spreading of the lixiviant during uranium recovery. Groundwater produced during the sweep phase will contain uranium and other contaminants mobilized during uranium recovery and residual lixiviant. The initial concentrations of these constituents would be similar to those during the uranium recovery operation phase, but would decline gradually with

time. The water removed from the aquifer during the sweep first is passed through an ion-exchange system to recover the uranium and then disposed by deep well injection.⁴

Reverse osmosis and permeate injection are used after groundwater sweep operations. During permeate injection and recirculation, uranium and other chemically associated species are removed by passing the groundwater through a reverse osmosis system consisting of pressurized, semi permeable membranes. The reverse osmosis process yields two fluids: clean water (permeate: about 70 percent) that can be reinjected into the aquifer and water with concentrated ions (brine: about 30 percent) that cannot be reinjected directly. The pH is lowered, and additives called antiscalants are added to the groundwater upstream of the reverse osmosis unit to prevent precipitation of minerals (particularly calcium carbonate). After reverse osmosis, sodium hydroxide may be added to readjust the pH of the groundwater to baseline levels. This process returns total dissolved solids, trace metal concentrations, and aquifer pH to baseline values. The net withdrawal from the aquifer depends on how the rejected liquid (reject) from the reverse osmosis system, which is about 30 percent of the pumping rate, is handled. The reject, which is a brine solution, cannot be directly injected into the aquifer or discharged to the environment but should be disposed directly in an evaporation pond or via a deep well injection in accordance with the discharge limits in a underground injection control (UIC) permit.⁴

The purpose of the stabilization monitoring phase of aquifer restoration is to establish a chemical environment that reduces the solubility of dissolved uranium and other constituents such as arsenic, selenium, molybdenum, and vanadium. To stabilize these metals concentrations, the preoperational oxidation state in the ore production zone should be reestablished as much as is possible. This is achieved by adding an oxygen scavenger or reducing agent such as hydrogen sulfide (H₂S) or a biodegradable organic compound (such as ethanol) into the uranium production zone during the later stages of recirculation. The need for an aquifer stabilization phase will vary on how effectively the sweep and recirculation phases restore the affected aquifer to the required standards at a given site. Following stabilization, the groundwater shall be monitored by quarterly sampling to demonstrate that the approved standards for each parameter have been met and that any adjacent nonexempt aquifers are unaffected.⁴

Groundwater Modeling Approach

Modeling Objective

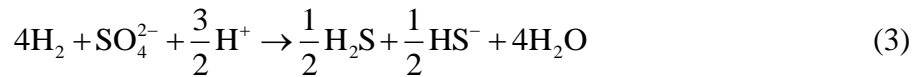
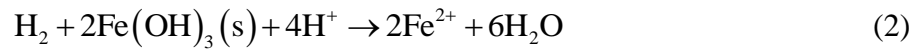
The main objective of this research project was to perform modeling simulations using the USGS PHREEQC software program to compare the theoretical effectiveness of hydrogen gas (H₂) and sodium dithionite (Na₂S₂O₄) for achieving uranium reduction and immobilization from U(VI) to (IV).⁵ In particular, since laboratory soil column studies had shown that sulfate reduction was a significant sink for supplied H₂,⁶ the modeling was performed to compare the degree of sulfate reduction resulting from addition of equal amount of H₂ and dithionite to groundwater.

Stoichiometric Reactions

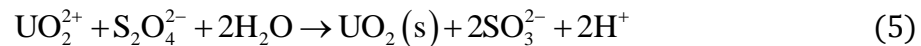
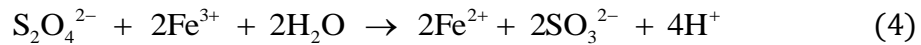
The following equation shows reduction of soluble uranium using hydrogen as the electron donor:



This equation shows that 1 mg/L of hydrogen is required to precipitate 119 mg/L of uranium. However, injection of hydrogen will also promote reduction of ferric iron and sulfate by iron and sulfate-reducing bacteria (IRB and SRB). These types of bacteria may catalyze uranium reduction, but also consume hydrogen as substrate, significantly increasing the demand for hydrogen. The reactions below illustrate the stoichiometry for sulfate reduction and iron reduction.



Dithionite will also reduce uranium and iron according to the following reactions:



In contrast to H_2 , however, dithionite will not reduce sulfate, but will rather generate sulfate through oxidation of the sulfite ions in Equations 4 and 5. In addition, whereas addition of H_2 will generate alkalinity as per Equation (2), addition of dithionite will decrease alkalinity as per Equation (4).

Hydrogeochemical Modeling and Simulations with PHREEQC

PHREEQC was used to simulate and compare the hydrogeochemistry changes resulting for addition of equal amounts of hydrogen and sodium dithionite to a typical aerobic groundwater containing low concentrations of dissolved uranium. The input codes are presented in the Appendix. The equations above show that one mole of H_2 donates $2e^-$ whereas one mole of dithionite donates $6e^-$. Therefore, to facilitate a normalized comparison, the model simulations assumed addition of 0.00550 mole of hydrogen but 0.00183 mole of dithionite (i.e., one-third the amount of H_2) per kg of total solution. In both simulations, the groundwater was assumed to be buffered with 0.01 M bicarbonate. The PHREEQC input files are presented in the Appendix.

Results and Discussion

Figures 1 and 2 show the PHREEQC-simulated changes in (a) oxidized species in solution (Fe^{3+} , U^{6+} and S^{6+}), (b) reduced species in solution (Fe^{2+} , U^{4+} , and S^{2-}), (c) solid-phase species [$\text{Fe}(\text{OH})_3(\text{s})$, $\text{UO}_2(\text{s})$ and $\text{FeS}(\text{s})$], and (d) Eh and pH with increasing addition of H_2 and sodium dithionite, respectively.

Comparing the results for the H_2 and dithionite simulations shows the following results:

- In both cases soluble U(VI) was almost completely reduced to U(IV), which predominantly precipitated from solution as uraninite, $\text{UO}_2(\text{s})$.
- In the H_2 addition case ferrihydrite, $\text{Fe}(\text{OH})_3(\text{s})$, was initially almost completely reduced to dissolved Fe^{2+} . However, as additional H_2 was added, the Fe^{2+} started to precipitate out of solution as pyrrhotite, $\text{FeS}(\text{s})$, until Fe^{2+} was almost completely removed from solution.
- Similarly, in the dithionite addition case, ferrihydrite was almost completely reduced to Fe^{2+} ; however, unlike the H_2 case, there was no sulfide available and consequently the Fe^{2+} remained in solution.
- In the H_2 case sulfate was almost completely reduced to sulfide, with precipitated from solution as pyrrhotite.
- In contrast, in the dithionite case sulfate was generated from the oxidation of dithionite and no sulfate reduction to sulfide (and subsequent precipitation of pyrrhotite) occurred.
- In both cases, solid-phase ferrihydrite almost completely disappeared and almost all the U(VI) was reduced to solid-phase uraninite.
- In the H_2 case, almost all the iron and sulfur present eventually precipitated from solution as solid-phase pyrrhotite.
- In contrast, in the dithionite case there was no precipitation of solid-phase pyrrhotite.
- The addition of H_2 resulted in the pH increasing from 7.0 to 8.5 and the pe decreasing from +4.0 to -5.5.
- In contrast, the addition of an equal amount of sodium dithionite (on an electron equivalent basis) resulted in the pH only increasing from 7.0 to 7.3 and pe only decreasing from +4.0 to -3.2.
- In the H_2 case, there was a significant drop in pe that coincided with the initiation of sulfate reduction. No similar trend was observed for the dithionite case.

The results above were qualitatively consistent with the experimental results observed in parallel batch microcosm studies.⁶

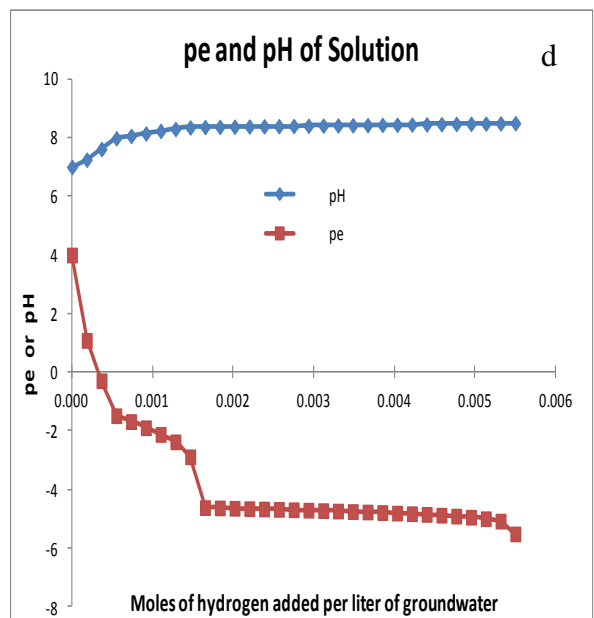
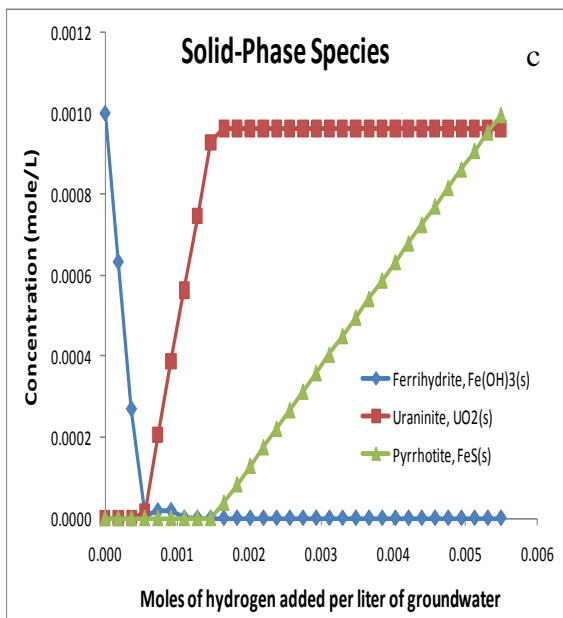
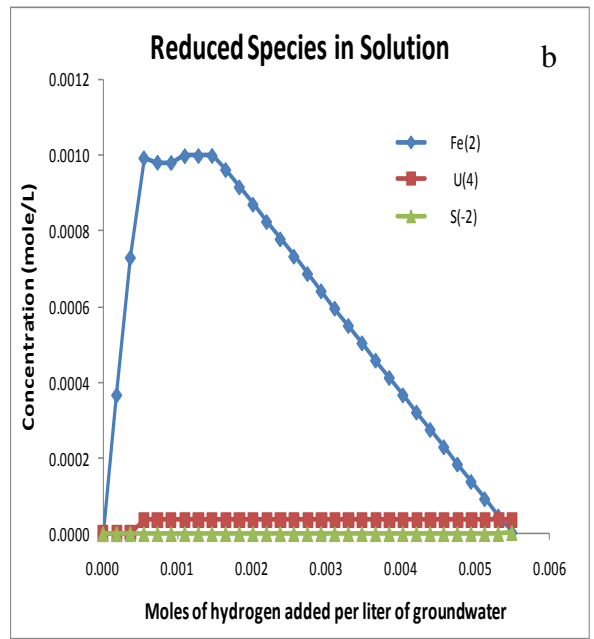
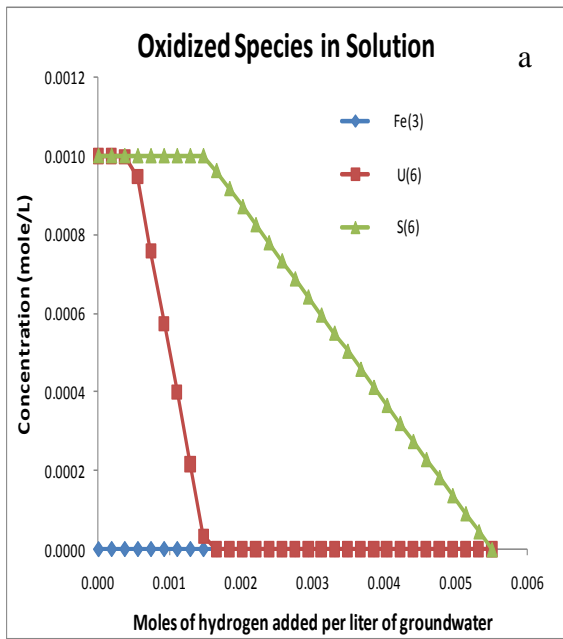


Figure 1: Changes in (a) oxidized species in solution, (b) reduced species in solution, (c) solid-phase species, and (d) Eh and pH with increasing addition of H₂.

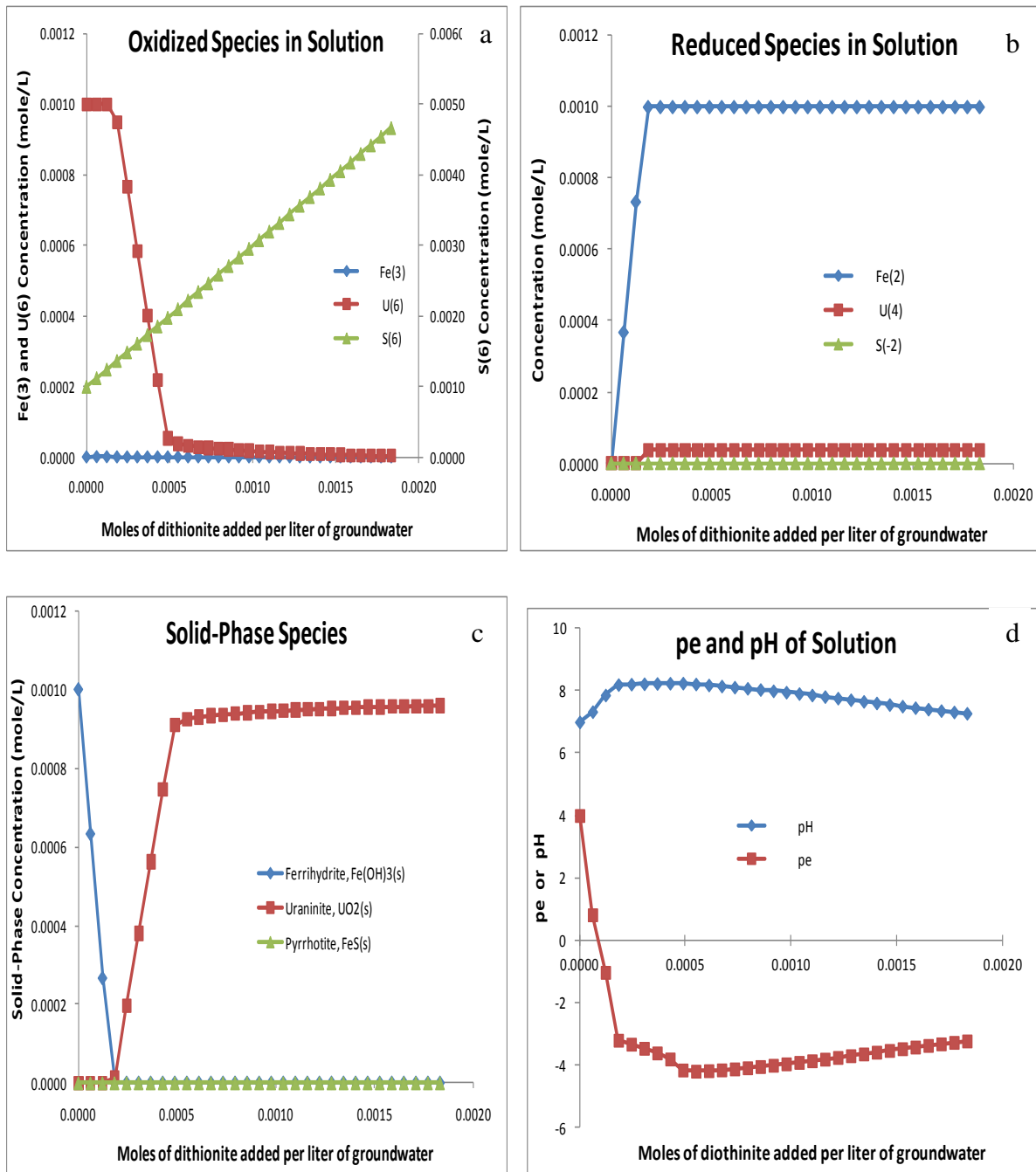


Figure 2: Changes in (a) oxidized species in solution, (b) reduced species in solution, (c) solid-phase species, and (d) Eh and pH with increasing addition of sodium dithionite.

Learning Module

A learning module based on the legacy cycle concept was developed that challenges the students to think through the processes and steps to determine the level of contamination and the amount of restoration required to return the concentrations of contaminants in groundwater to safe levels. This learning module will be introduced into high school mathematics and science classes during the spring semester of this school year (2011-2012). A subsequent assessment of the students' performance will be carried out and reported.

The Legacy Cycle lesson format consists of six stages: (1) Challenge Question, (2) Generate Ideas, (3) Multiple Perspectives, (4) Research and Revise, (5) Test Your Mettle (6) Go to Public. A two-day Legacy Cycle workshop was presented to the teachers as part of the RETainUS program. The workshop provided the framework for the teachers to develop their instructional materials that formed part of the legacy cycle based on current learning theory in how people learn through mind, brain, experience, and school. The learning module being developed was based on the above research project and will be implemented for Mathematics and Science classes at LBJ Middle School, PJSA in Pharr, Texas. At the time of the writing this paper, the legacy cycle had not been yet implemented and hence results from applying the learning module below were still pending. Table 2 below describes the components of the learning module in the form of the legacy cycle.

Table 1: Components of the Legacy Cycle: Inquiries in Science about Water Pollution

Component	Elements
Challenge Question	People in your neighborhood are complaining about the foul odor coming from the water in the open drainage canal. Their children and other members of the community have gotten sick. Students are employed by a local water district to study and assess the water and subsequently make recommendation on how to solve the problem. Students will conduct experiments and develop a model to describe on what are the effects of water pollution on living organism?
Generate Ideas	<ul style="list-style-type: none"> ▶ What information do you need to know to solve the problem? ▶ What is the chemistry of drinking water? ▶ Nutrients in drinking water ▶ Standards for drinking water ▶ What is the usual chemical composition of water being used for irrigation? ▶ Why is water being recycled? ▶ What is the chemical composition of recycled water? ▶ Do you have to just let the rain water stay for a while in your container before you drink it? ▶ Is there any kind of natural filtration using the natural sands and gravels in the area? ▶ What are the instruments used in testing water pollution? ▶ What are your findings and recommendations?

<p>Multiple Perspectives</p>	<ul style="list-style-type: none"> ▶ Invite and interview a chemist from the Water District ▶ Show video clips on different water filtration processes ▶ Students will identify 3 things learned from these video clips ▶ Update the Generated Ideas Master List ▶ Some hazardous elements in drinking water ▶ Tolerable limits of chemical water intake to our body ▶ How much water does a human body need for 1 day? ▶ Test local water for pollutants ▶ Design and create aquatic community ▶ Introduce pollutant ▶ Do comparison to the water pollution problems in global perspectives ▶ Compare the effects to a controlled community
<p>Research and Revise</p>	<ul style="list-style-type: none"> ▶ Allows the students to develop and realize relationships between knowledge points <ul style="list-style-type: none"> – Group items and have students label the group <ul style="list-style-type: none"> • Drinking water chemical composition • Chemistry of local water and how the pollutants affect the environment in general ▶ Students to go back to Generate Ideas if they anything to add <ul style="list-style-type: none"> – Why is water recycled? – Why others chemicals are allowed in the drinking water? – What are the pollutants in the local water (canal)? ▶ Research local, national, and international water pollution
<p>Test Your Mettle</p>	<ul style="list-style-type: none"> ▶ Formative Assessments with an open-ended question: Describe the chemistry of drinking water and rain water and compare their composition. ▶ Students will answer the question: What are the pollutants in local water and why is it is giving a foul odor? ▶ Students will answer the question: Why is there a universal need for recycling water? ▶ Students will answer “What are the existing standards for a safe drinking water?” ▶ What are the students and the recommendations?
<p>Go public</p>	<p>Students will display the results: (1) Water Testing and Pollution Kit, (2) Poster /Design Project, (3) Oral presentation</p> <p><u>Conclusion:</u> <i>Water pollution affects living organisms, therefore the better we understand the consequences of our actions, the better equipped we are to make decisions that support <u>sustainable and environmentally-friendly practices.</u></i></p>

Summary and Conclusions

This modeling study confirmed that both H_2 and $Na_2S_2O_4$ should promote significant reduction and immobilization of U^{6+} to U^{4+} when added to groundwater as chemical reductants. However, the modeling simulations also indicated that a significant amount of sulfate reduction (and subsequent FeS deposition) should occur when groundwater is amended with H_2 , whereas no sulfate reduction should occur when groundwater is amended with dithionite. Concomitantly, the modeling also showed that H_2 addition should achieve significantly lower pe than the addition of an equivalent amount of dithionite. These results have significant implications with respect to the potential effectiveness of H_2 and dithionite as chemical reductants for restoring groundwater quality at uranium ISR mining sites. In particular, while addition of H_2 should achieve stronger reducing conditions near the injection point, the addition of dithionite will likely have a larger zone of influence because it will not be consumed via sulfate reduction reactions. Further experimental research must be carried out confirm that this will be the case.

A learning module that share some of the basic concepts used for the research experience has been designed. The module targets students in Mathematics and Science classes at LBJ Middle School and is based on the Legacy Cycle methodology. It will be implemented in the spring of 2012 at a public school with 98% Hispanic students.

Acknowledgements

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Appendix – PHREEQC Program Input Files

USING HYDROGEN	USING DITHIONITE
<p>SOLUTION 1</p> <p>Temp 25</p> <p>pH 7</p> <p>pe 4</p> <p>redox pe</p> <p>units mol/kgw</p> <p>density 1</p> <p>Cl(-1) 0 charge</p> <p>Na 0.01</p> <p>Ca 0.01</p> <p>C(4) 0.01</p> <p>U(6) 0.001</p> <p>S(6) 0.001</p> <p>__water 1#kg</p> <p>EQUILIBRIUM_PHASES 1</p> <p>Fe(OH)₃ 0 0.001</p> <p>Pyrrhotite 0 0</p> <p>UO₂(am) 0 0</p> <p>REACTION 1</p> <p>H₂ 1</p> <p>0.0055 moles in 30 steps</p> <p>INCREMENTAL_REACTIONS True</p> <p>SELECTED_OUTPUT</p> <p>_file L:\PHREEQC\PHREEQC 7-9_11\test1.sel</p> <p>_totals Fe(3) U(6) Fe(2) U(4) S(-2)</p> <p>__equilibrium phases Fe(OH)₃ Pyrrhotite UO₂(am)</p> <p>END</p>	<p>PHASES</p> <p>Dithionite</p> <p>Na₂S₂O₄ = 2Na⁺ + (S₂O₄)²⁻</p> <p>Log_k -4.58</p> <p>Delta_h -0.109</p> <p>SOLUTION 1</p> <p>Temp 25</p> <p>pH 7</p> <p>pe 4</p> <p>redox pe</p> <p>units mol/kgw</p> <p>density 1</p> <p>Cl(-1) 0 charge</p> <p>Na 0.01</p> <p>Ca 0.01</p> <p>C(4) 0.01</p> <p>U(6) 0.001</p> <p>S(6) 0.001</p> <p>water 1# kg</p> <p>EQUILIBRIUM__PHASES</p> <p>Fe(OH)₃ 0 0.001</p> <p>Pyrrhotite 0 0</p> <p>UO₂(am) 0 0</p> <p>REACTION 1</p> <p>Dithionite 1</p> <p>0.0018333333333333 moles in 30 steps</p> <p>SELECTED_OUTPUT</p> <p>_file F:\PHREEQC 7-9__11\test1__2304.sel</p> <p>_totals Fe(3) U(6) S(6) Fe(2) U(4) S(-2)</p> <p>__equilibrium phases FE(OH)₃ Pyrrhotite UO₂(am)</p> <p>END</p>

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