NEW MEXICO WATER RESOURSES RESEARCH INSTITUTE
STUDENT WATER RESEARCH

URANIUM ABATEMENT IN WATER

Final Project Report

By
Nicholas G. Beltran
Advisor, Dr. Antonio S. Lara

2008-2009

NEW MEXICO STATE UNIVERSITY
DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY

Table of Contents

Domestic Uranium Contaminated Groundwater Remediation – Sorption and Immobilization Technology via New Mexico Structurally Layered Phyllosilicates

Nicholas G. Beltran, Chemistry and Biochemistry, New Mexico State University, MSC 3AF New Mexico State University, PO Box 30001, Las Cruces, NM 88003-0032, beltrann@nmsu.edu, 575-646-4626

Antonio Lara, Chemistry and Biochemistry, New Mexico State University, MSC 3C PO Box 30001 Las Cruces, NM 88003-8001, alara@nmsu.edu, 575-646-2918

Abstract

Uranium contaminated water is problematic for households and communities in the Four Corners, and the situation will worsen in the near future with projected, re-established mining. Our objective is uranium abatement in water to supply potable water for households in the affected rural areas. Structured layered phyllosilicates will sorb thus removing uranium. The manageable end-product is easy to handle and dispose. The purified water can simply be decanted or drained and the contaminated sorbent removed easily and safely. The overall process is deliberately simple, economic, and a user-friendly small-scale technology. Preliminary tests show the efficacy of this technology. Inductively coupled plasma mass spectroscopy has illustrated uranium uptake to ppb levels by means of sorption isotherms. At constant ambient conditions, the uranium concentration decreased from 500 ppb to 132.40 ppb in the first fifteen minutes. The reduction to 26.13 ppb, a concentration below EPA's safe drinking water limit of 30 ppb, occurred within the next hour and a half. The final uranium concentration was 1.5 ppb after 8 hours of exposure to the layered phyllosilicates. The sorption model was verified with an orthogonal fluorimetric technique. The importance of this technique is that it is non-destructive and most suitable for kinetic modeling (Dolezel et al., 1993). Excitation and emission wavelengths were optimized for analyses in ppm and possibly ppb ranges. Precise uranium calibration curves permit sorption isotherms, kinetic studies and modeling. This project focuses on a New Mexico solution for a New Mexico problem.

Contact: Nicholas G. Beltran, New Mexico State University, beltrann@nmsu.edu, MSC 3C PO Box 30001, Las Cruces, NM 88003-8001

Introduction

Discovery of Uranium – A new versatile element

Martin Heinrich Klaproth, a German chemist, apothecary, lecturer and professor of chemistry discovered uranium, named after the newly discovered planet Uranus, in 1789 while studying the amorphous, dense, black mineral pitchblende (NNDB, 2009). Klaproth passed away New Year's Day in 1817; he was unable to see the isolation of the pure metallic element in 1841 or the discovery of the radioactive properties of uranium in 1896. It was in 1898 that Marie and Pierre Curie explored the radioactive properties linked with uranium atoms. One can only imagine Klaproth's reaction if he knew how his findings would someday drive the modern world's war and energy initiatives. Uranium was being studied extensively around the world during World War II. Scientists found a way to enrich natural uranium ore to initiate a nuclear chain reaction with potential to cause devastating damage. In Albert Einstein's letter to President Roosevelt (appendix A1,A2) (Fehner, 2005), we develop and understanding of how serious the production of uranium would become in the early 1940's. Also, with an ever increasing demand for alternative "green" energy, society has adopted the idea of nuclear energy. Nuclear energy is mainly used to produce electricity in a clean, safe, and cost effective fashion. A nuclear reactors function is similar to coal and gas-fired power supplies, however in a nuclear reactor, nuclear chain reactions are used to produce energy which generates steam to turn a turbine for large scale electricity demands. It is common for companies to report that, "Nuclear power stations do not cause any pollution. The fuel for nuclear power is virtually unlimited, considering both geological and technological aspects."

However, nuclear power has not been a true cradle-to-grave solution as an alternative energy. Uranium mining exposes high concentration levels to mining personnel as well as the environment; this is particularly true in Northern New Mexico. New Mexico has the second largest uranium supply in the nation – Wyoming leads in this respect. With the new surge in uranium mining will certainly increase environmental contamination and human exposure. Unfortunately, exposure and ingestion of uranium is one the leading causes of heavy metal toxicity and death in some uranium mining communities (EPA, 2007). However, there is a New Mexico solution to a New Mexico problem. New technology exists for sorption and immobilization of uranium by means of an appropriate structurally-sound soil sorbent.

Uranium in Nature – Chemical Characteristics

Uranium is a naturally occurring radioactive element found in all areas of the biosphere including the lithosphere, hydrosphere, and occasionally in the atmosphere. On average, most rocks have concentrations of approximately 2 – 4 parts per million (ppm) (Association, 2006). Uranium can be mined in the form of minerals but not in its metallic, elemental state. There are three predominant, naturally occurring uranium isotopes: ^{234}U, ^{235}U, and ^{238}U. Although they are all different isotopes of uranium they all have 92 protons in the nucleus of the atom. What makes each isotope unique is the number of neutrons. ^{234}U has 142 neutrons, ^{235}U has 143 neutrons, and ^{238}U contains 146 neutrons. The natural abundance of the isotopes is 0.0055%, 0.72%, and 99.284% respectively. Each isotope of uranium has a different half-life. The half-life of an element is the amount of time required for half the nuclei in a given sample to undergo

radioactive decay. A shorter half-life time corresponds to a more radioactive isotope. Uranium isotopes have the following half-lives: ^{234}U – 200,000 years, ^{235}U – 700 million years, and ^{238}U has a half-life of 5 billion years. It has been determined that Earth is approximately 4.55 billion years old; therefore, half of the original ^{238}U is still in existence. Uranium is an alpha emitter. The alpha particle cannot penetrate through the skin and it is short lived in the air. However, compared to beta and gamma radiation it is the most ionizing. Therefore, alpha particles are dangerous if ingested.

Uranium isotopes exist in nature heterogeneously, thus the U-235 must be enriched. Several enrichment processes are currently used: Gaseous Diffusion, Gas Centrifugation, and Laser Separation (U.S.NRC, 2007). The objective of uranium enrichment is to separate the ^{234}U and ^{235}U from ^{238}U. U-235 is the primary component which initiate and maintains a nuclear reaction.

Anthropogenic activity – Upsetting nature's equilibrium

If uranium is a natural element that can be found everywhere, how do the natural concentrations exceed safe exposure levels? Uranium can enter the environment through multiple pathways. In mining communities, anthropogenic activities increase human exposure by processing and transporting ore during various weather conditions, for example windy and rainy weather is likely to disperse contaminants throughout the general vicinity. The minerals have now become more mobile compared to their once stationary state. Unbound or mobile uranium particles are susceptible to rainwater and have an increased probability to migrate or leach into the groundwater. As vehicles crush contaminated soil, the particulate matter becomes smaller. The

smaller the particulate matter gets, chances of exposure increases through inhalation. Also, individuals who irrigate their crops and drink contaminated water have an elevated chance of becoming ill by ingesting the contaminated water on a regular basis. With the reestablishment of uranium mining, anthropogenic activity upsets nature's equilibrium. Mining will increase the concentration on a water system in equilibrium if the system is disturbed, it will be incapable of self sustaining to regain its stability if there is continuous activity.

U.S. EPA, WHO, and U.S. NRC – Safe Standards

Uranium has two forms of toxicity, it is radioactive and a heavy metal. Therefore, when setting safe exposure standards both forms of toxicity must be addressed. Certain problems arise when implementing current toxicity tests. Since uranium has an extremely long half-life, it is impossible to carry out an acute toxicity test lasting only 24 hours. Similarly, the 28 – 90 day subchronic toxicity tests will not provide a model of toxicity. Acute and subchronic accidents have been reported and found useful for the highly radioactive isotope of uranium. However, they do not provide any long term expose results for individuals whom are exposed to natural concentration levels. There is currently inadequate data for chemical toxicity for long term exposure of ingesting uranium for humans. Although there is data from animal studies, the radiation doses and chemical toxicity standards are not necessarily comparable for humans. Inhalation data on intermediate duration of soluble and insoluble forms of uranium in dogs has the following results: Concentrations of 0.15 mg U/m^3 in air produced the lowest observable adverse effects. A minimal risk inhalation level for humans is set at 0.4 $\mu g/m^3$ (Uranium

Toxicity, 2005). For dogs exposed to insoluble forms of uranium, a uranium concentration of 1.1 mg U/m^3 in air produced no observable adverse effects. A minimal risk inhalation level for humans is set at 8 μg/m^3 (Uranium Toxicity, 2005). Chronic experimentation data from dogs exposed to soluble forms of uranium was reported: 0.05 mg U/m^3 in air produced no observable adverse effects. The minimal risk inhalation levels for humans are set at 0.3 μg/m^3. All results were derived applying a number of safety factors. Several standards have been set for oral ingestion. Reports [Jacob 1997] indicate a tolerable ingestion concentration of 0.7 μg per kg per day. The data reported was based on adverse effects that were observed [McDonald-Taylor 1992] with kidneys of rabbits at resorption rates of 3.2 μg U per kg per day (Uranium Toxicity, 2005). The World Health Organization (WHO) established a Tolerable Daily Intake of 0.6 μg/kg body weight per day. This data is based on adverse effects that were observed [Gilman1998] with kidneys of rats at uptake of 60 μg U per kg per day (WHO). Current Safe Drinking Water Standards are: WHO – 15 μg of uranium per litre, Health Canada – 20 μg per litre, and U.S. EPA – 30 μg per litre (Uranium Toxicity, 2005). Uranium toxicity has been associated with kidney damage but it is not a primary cause of cancer. However uranium decomposes into other elements which are carcinogenic. Toxicity of uranium in water has not been reported.

Current Purifying Methods – Expensive and not a True Cradle to Grave Solution

Generally when we think of water purification we think of large municipal purification systems that produce enough water for large populations. Yet, there exist small rural communities that do not have the luxury of clean water piped into their homes. These individuals must pump

water from wells or else use contaminated groundwater for their families and livestock. Underprivileged communities do not have access to expensive water purification systems. Current methods for purifying water on a small scale are distillation, reverse osmosis (RO), and Whole House Kinetic Degradation Fluxion (WH-KDF). Each of these methods are temporary solutions for a small volume of purified water. Distillation and RO are complex systems that produce a minimal volume of purified water and a highly concentrated byproduct. Some contain filters and membranes that periodically need maintenance and are likely to "plug up" on a regular basis. KDF is defined as a system that requires pH and pE adjustment to convert toxic substances into "harmless components". This system is not full-proof for radioactive nuclei and will not convert uranium into a harmless compound, it just allows separation by precipitation. Elements cannot be converted to harmless compounds. However there is a new technology that is an appropriate solution of water purification for underprivileged communities.

Domestic Uranium Contaminated Groundwater Remediation

Our proposed method is intentionally simplistic to facilitate abatement in any environment where individuals are at risk of ingesting heavy metal contaminated water. This project focuses on a New Mexico solution for a New Mexico problem. Dr. Carmen Melendez-Pizarro modeled lead abatement in her dissertation "Soil/clay pellets to remove lead from water in an efficient and practical method". Soil is a viable resource for sorption of any heavy metal contaminant in its cation state. Uranium contaminated water is problematic for households and communities in the Four Corners, and the situation will worsen in the near future with projected, re-established

mining. Our objective is uranium abatement in water to supply potable water for households in the affected rural areas. Structured layered phyllosilicates sorb uranium thus producing cleaner water. Uranium sorbs to soil through its unique characteristic called cation exchange. Soils are given a cation exchange capacity value which indicate sorption potential, although this value varies between types of soils, all soils have this feature. This distinctive soil trait allows for an appropriate solution for those who have limited resources.

Bench-top scale experiments have shown at constant ambient conditions, the uranium concentration decreased from 500 ppb to 132.40 ppb in the first fifteen minutes (appendix 3). The reduction to 26.13 ppb, a concentration below EPA's safe drinking water limit of 30 ppb, occurred within the next hour and a half. The final uranium concentration was 1.5 ppb after 8 hours of exposure to the layered phyllosilicates. The method is well-designed; the entire process can be accomplished in buckets with no moving or mechanical parts. No external power sources are needed at any step of the abatement process. The manageable end-product is easy to handle and safe to dispose. For added disposal protection, the soil sorbents can be vitrified to prevent leaching back into the environment and ultimately back into the water table. The purified water can simply be decanted or drained and the contaminated sorbent removed easily and safely. The sorption model was verified with an orthogonal method (Beltran, 2009). The importance of this technique is that it is non-destructive and most suitable for kinetic modeling (Dolezel et al.,1993). Excitation and emission wavelengths were optimized for analyses in ppm and possibly ppb ranges. Uranium does not leach once bound to the soil sorbents (appendix 4), however

leaching may result at very low pH of 2-5. Such an acidic environment is not likely in New Mexico where the soil conditions are basic. Further studies are necessary to develop leaching models to replicate real world conditions. The overall process is deliberately simple, economic, and a user-friendly small-scale technology. Preliminary tests show the efficacy of this technology. Inductively coupled plasma mass spectroscopy has illustrated uranium uptake for uranium abatement down to ppb levels.

Appendix A-1

Albert Einstein
Old Grove Rd.
Nassau Point
Peconic, Long Island

August 2nd, 1939

F.D. Roosevelt,
President of the United States,
White House
Washington, D.C.

Sir:

Some recent work by E.Fermi and L. Szilard, which has been communicated to me in manuscript, leads me to expect that the element uranium may be turned into a new and important source of energy in the immediate future. Certain aspects of the situation which has arisen seem to call for watchfulness and, if necessary, quick action on the part of the Administration. I believe therefore that it is my duty to bring to your attention the following facts and recommendations:

In the course of the last four months it has been made probable - through the work of Joliot in France as well as Fermi and Szilard in America - that it may become possible to set up a nuclear chain reaction in a large mass of uranium,by which vast amounts of power and large quantities of new radium-like elements would be generated. Now it appears almost certain that this could be achieved in the immediate future.

This new phenomenon would also lead to the construction of bombs, and it is conceivable - though much less certain - that extremely powerful bombs of a new type may thus be constructed. A single bomb of this type, carried by boat and exploded in a port, might very well destroy the whole port together with some of the surrounding territory. However, such bombs might very well prove to be too heavy for transportation by air.

a64a01

Appendix A-2

-2-

The United States has only very poor ores of uranium in moderate quantities. There is some good ore in Canada and the former Czechoslovakia, while the most important source of uranium is Belgian Congo.

In view of this situation you may think it desirable to have some permanent contact maintained between the Administration and the group of physicists working on chain reactions in America. One possible way of achieving this might be for you to entrust with this task a person who has your confidence and who could perhaps serve in an inofficial capacity. His task might comprise the following:

a) to approach Government Departments, keep them informed of the further development, and put forward recommendations for Government action, giving particular attention to the problem of securing a supply of uranium ore for the United States;

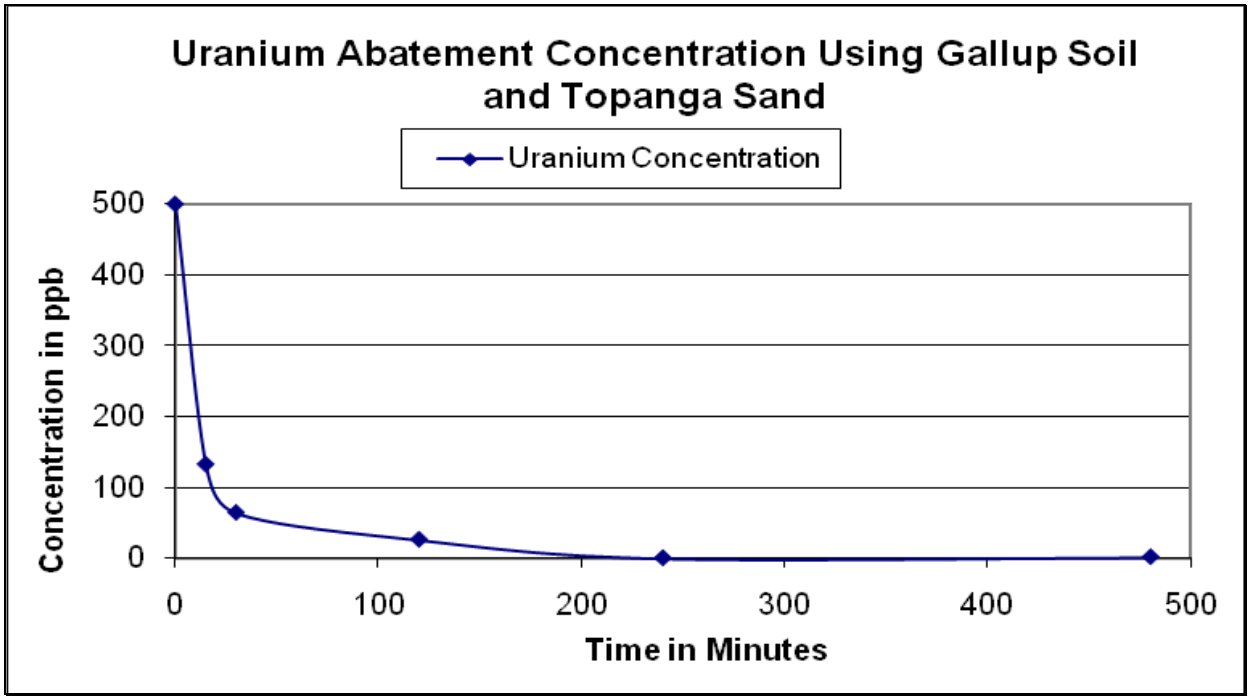
b) to speed up the experimental work,which is at present being carried on within the limits of the budgets of University laboratories, by providing funds, if such funds be required, through his contacts with private persons who are willing to make contributions for this cause, and perhaps also by obtaining the co-operation of industrial laboratories which have the necessary equipment.

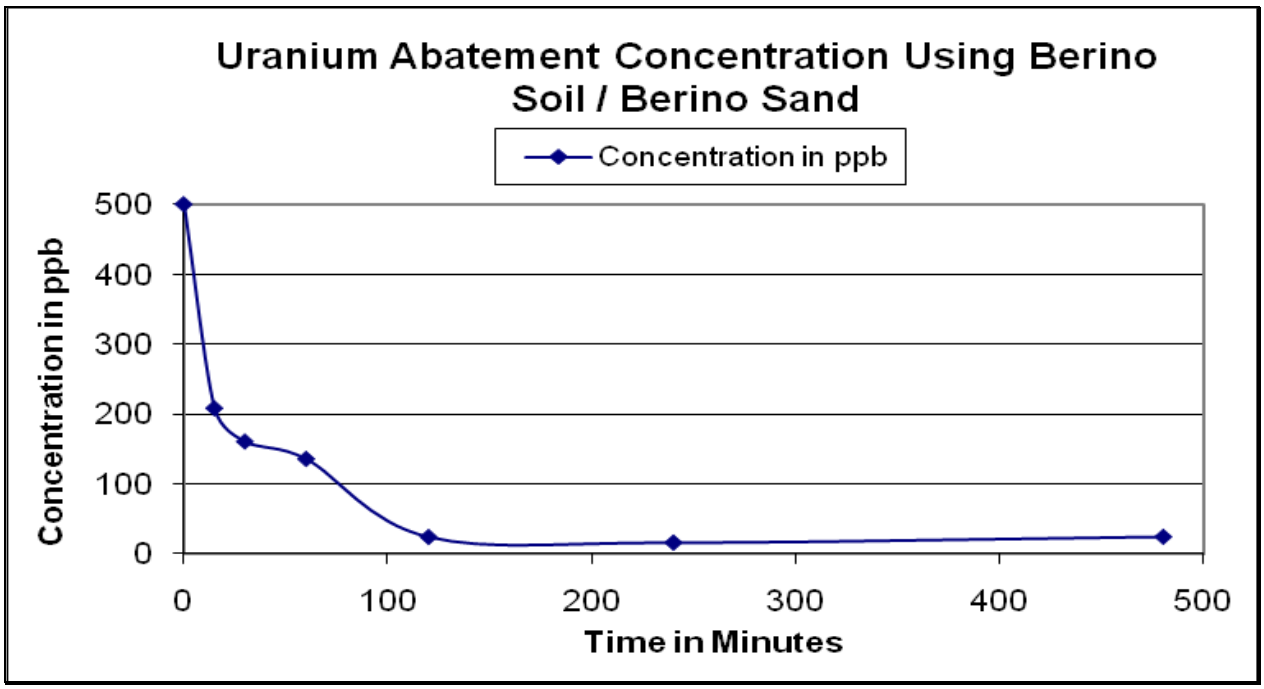
I understand that Germany has actually stopped the sale of uranium from the Czechoslovakian mines which she has taken over. That she should have taken such early action might perhaps be understood on the ground that the son of the German Under-Secretary of State, von Weizsäcker, is attached to the Kaiser-Wilhelm-Institut in Berlin where some of the American work on uranium is now being repeated.

Yours very truly,
A. Einstein
(Albert Einstein)

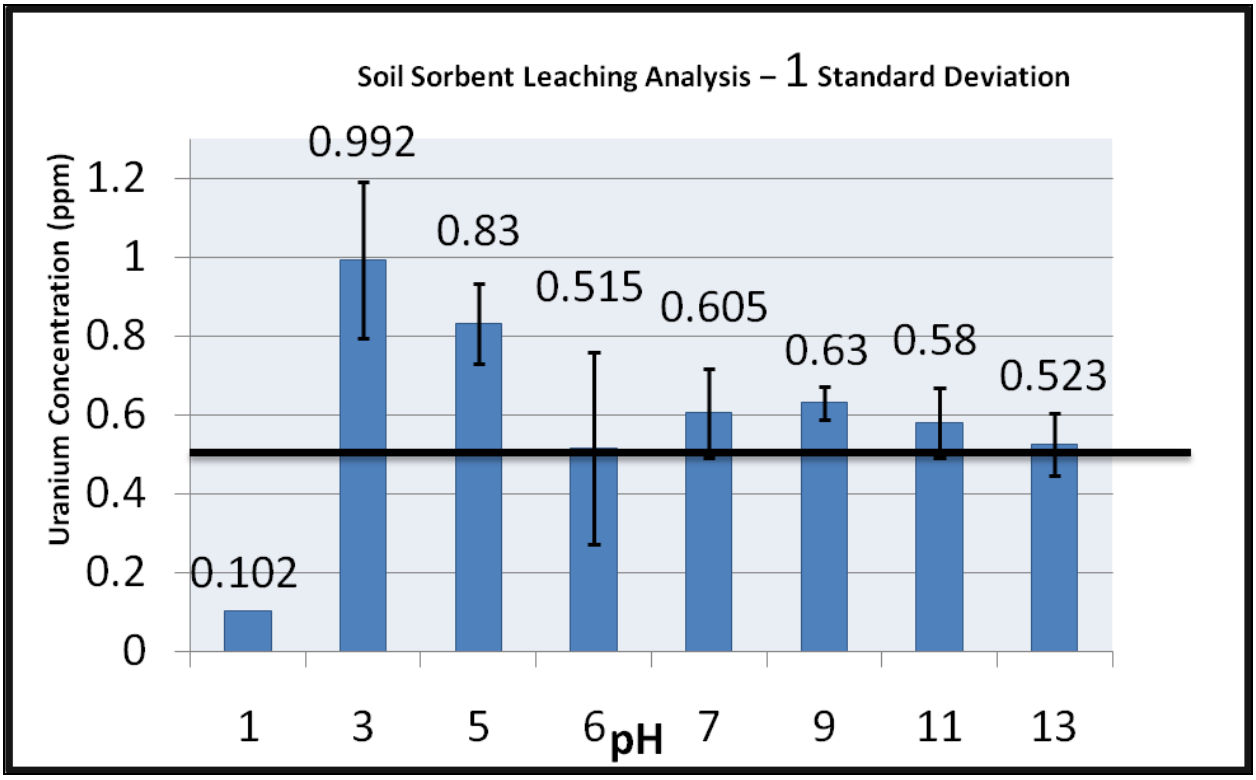
a64a02

Appendix 3


Uranium Abatement Concentration Using Gallup Soil and Topanga Sand
Uranium Concentration
Concentration in ppb
500
400
300
200
100
0
0
100
200
300
400
500
Time in Minutes


Uranium Abatement Concentration Using Berino Soil / Berino Sand
Concentration in ppb
Concentration in ppb
500
400
300
200
100
0
0
100
200
300
400
500
Time in Minutes

Appendix 4


Soil Sorbent Leaching Analysis – 1 Standard Deviation
Uranium Concentration (ppm)
1.2
1
0.8
0.6
0.4
0.2
0
0.992
0.83
0.515
0.605
0.63
0.58
0.523
0.102
1
3
5
6
pH
7
9
11
13

Scope of Research and Development for Uranium Abatement at Diné

Uranium and Heavy Metal Contamination - Quantitation and Abatement

I. Establish procedures for accurate and reproducible measurements of uranium in contaminated water and soil samples
   A. Establish and confirm uranium concentration levels at various sites, these sites determined by Diné personnel (See item II below)
   B. Provide sampling, sample transport, analysis, calibration, data handling, and data interpretation and uranium safety training for all staff and students from Diné and NMSU
   C. Test handheld X-Ray Fluorescence (XRF) detector for usefulness in screening material sources sites and contamination sites
   D. Use ICP/MS for uranium measurements less than 30 ppb - NMSU
   E. Use phosphorescence analysis to model uranium adsorption from water - NMSU

II. Identify uranium contaminated water sources and U-free soil zones in Northwestern New Mexico
   A. Develop working groups between Diné and NMSU based on each institution's resources and availability(e.g. Diné sends water samples to NMSU)
   B. Review Diné College's contaminated site data from Summer 2008 (GPS)
   C. Correlate Diné data with 2007 EPA maps of uranium mining and processing sites
   D. Correlate NMSU selective site measurements with Diné and EPA data

III. Design a uranium-abatement, user-friendly, inexpensive method specifically for remote households, based on the technology developed in the NMSU laboratory
   A. Develop the first prototype for a household unit (see item II.B. for Diné collaboration) and establish SOPs for the first prototype
   B. Address the safety issues for safe disposal
      1. Conduct desorption studies to determine whether uranium is bound irreversibly or if leaching may occur from sorbent and under what conditions
      2. In collaboration with Diné, establish suitable disposal sites

IV. Optimize the method and materials for uranium sorption and abatement
   A. Reiterate item III and produce sorption models to improve the efficacy
   B. Conduct kinetic studies once the thermodynamic, saturation, equilibrium time has been determined – this information is needed for implementation
   C. Use thermodynamic equilibrium data to propose sorption models and possibly binding energy distributions which can be compared to other metal sorption energies for comparison
   D. Optimize sorbent material design and composition

V. Test the uranium adsorption efficacy in the presence of actual local water matrixes

A. In collaboration with Diné data, sorption studies will be conducted with spiked uranium water and also water from the local communities with U-affected areas.
B. NMSU will conduct analyses on samples collected by Diné research interns, both soil and water

VI. Test a remote household prototype for uranium abatement efficacy
A. Diné and NMSU will jointly develop a SOPs for using the method
B. SOPs will be revised and improved as needed for optimal local use
C. Diné and NMSU will continue collaboration to ensure sustainability of the program, especially as it pertains to student training for water sampling and analysis
D. In our lab, we strongly desire "water testing" continue indefinitely as part of the monitoring program. However, we still need to work on the monetary sustainability of this aspect

VII. Disseminate information about uranium chemistry as it pertains to human health and the environment; this with approval from Diné College and the NNIRB

A. Diné and NMSU will conduct workshops that are educational, culturally sensitive and improve safety for local communities
B. Public Forums will be conducted at Diné and NMSU

Timeline for Uranium Abatement at Diné

Uranium and Heavy Metal Contamination - Quantitation and Abatement

I. Workshops / Dissemination at Shiprock [**1 June 2010 – 31 July 2012]**
   E. Second week 1 in July for 2010, 2011, and 2012; after DINÉ/BRIDGES student program at NMSU
   F. 1st year: health and project goals
      2nd year: prototype description

      3rd year: prototype results

      (Note: At each of the summer workshop sessions, Diné student participants are identified and disclosed)

II. Startup **[1 August 2009 —28 February 2010]**
   1. Set up subcontract
   2. Identify student(s) for research (see IB) (Diné / NMSU)

III. Sorbent characterization **[1 June 2010 – 31 December 2010]**
   A. Characterize the control soils – Gallup / Berino soils
   B. Collect soils from Northern New Mexico for developing local structured sorbent materials
   C. Begin characterization of soil minerals and find unique soil characteristics
   D. Correlate the above soils to the control Gallup and Berino soils
   E. Correlate soil samples to Diné student GPS soil data and other documented soil classification schemes
   F. Start uranium abatement characterization

IV. Continue soil processing and characterization to include robustness, pH, saturation, and leaching **[1January 2011 –31 July 2011]**
   A. In conjunction with Diné travel to Shiprock and locate and collect uranium contaminated water samples
   B. Sorbent characterization for physical management
   C. Test uranium abatement efficacies using ICP/MS and fluorescence

V. Model sorption for iterative improvements **[1 August 2011 - 31 December 2011]**
   A. Fit fluorescence data to sorption isotherms and kinetic models
   B. Characterize for sorption efficacy
   C. Analyze structured soil materials (LIBS/XRF/ ICP-MS/fluorescence)

VI. Prototype design and implementations
   A. Designate a Northern NM location for a small scale uranium abatement prototype trial and measurement process
   B. Begin implementation at designatied site and disseminate information to communities (with NNIRB approvals)

VII. Present research at a national conference as approved by NNIRB and Diné
   [1 January 2012 – 31 July 2012]

Works Cited

Agency, E. P. (2006). *Uranium Location Database Compilation.* Retrieved from U.S. EPA: http://www.epa.gov/radiation/docs/tenorm/402-r-05-009.pdf

Association, W. N. (2006, June). *What is uranium? How does it work?* Retrieved from World Nuclear Association: http://www.world-nuclear.org/education/uran.htm

Beltran, N. G. (2009, August). Domestic Uranium Contaminated Groundwater Remediation - Sorption and Immobilization Technology via New Mexico Structrually Layered Phyllosilicates. Las Cruces, New Mexico.

Duff, M. C. (1998). Comparison of acid and base leach for the removal of uranium from contaminated soil and catch-box media. *Canadian Journal of Soil Science* , 675.

Ebbs, S. D. (1998). Soil Processing and Chemical Transport: The Effects of Acidification and Chelating Agents and the Solubilization of Uranium from Contaminated Soil. *Journal of Environmental Quality* , 1486.

EPA, U. (2007, September 18). *Analysis of Uranium Exposure in the Eastern Agency of Navajo Nation*. Retrieved from U.S. Environmental Protection Agency: http://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.abstractDetail/abstract/8499/report/0

Fehner, F. G. (2005, October). *The Manhattan Project*. Retrieved November November 2, 2009, 2009, from U.S. Department of Energy Office of History and Heritage Resources: http://www.mbe.doe.gov/me70/manhattan/einstein_letter.htm

Martin Heinrich Klaproth. (2009). Retrieved 2009, from NNDB Tracking the entire world: http://www.nndb.com/people/533/000097242/

Nyer, E. (2001). In situ treatment technology. 63, 391-433, 426-427.

Parra, R. R. (2004). Soil Amendment Effects on the Mobility of Depleted Urnaium and the Desorption of Lead in Calcareous Soils of the Southwest U.S. *Dissertation* , 8, 16.

Shatalov, V. V. (2001). Ecological Safety of Underground Leaching of Uranium. *Energy-New York-C/C of Atomnaia Energiia* , 1009.

U.S.NRC. (2007, Septemper 20). *Uranium Enrichment.* Retrieved from United States Nuclear Regulatory Commission: http://www.nrc.gov/materials/fuel-cycle-fac/ur-enrichment.html

Uranium Toxicity. (2005, June 1). Retrieved from WISE Uranium Project: http://www.wise-uranium.org/utox.html