
ADVANCES IN TREATMENT METHODS FOR URANIUM CONTAMINATED SOIL AND WATER

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ABSTRACT

Water and soil contaminated with actinides, such as uranium and plutonium, are an environmental concern at most U.S. Department of Energy sites, as well as other locations in the world. Remediation actions are on going at many sites, and plans for cleanup are underway at other locations. This paper will review work underway at Clemson University in the area of treatment and remediation of soil and water contaminated with actinide elements.

Key words: actinides, radionuclides, contamination, soil, remediation

INTRODUCTION

Depleted, enriched and natural uranium contamination in soil and water has been identified at many sites worldwide including the United States. In soil, uranium is typically in an oxidized form, and in water, it is usually present as a uranyl hydroxyl carbonate complex. A variety of treatment methods are available to remove uranium from soil and water. Many methods are commercially available. This paper will review some work in progress at Clemson University on actinide contaminated soil remediation methods and relate these studies for uranium contaminated soils. The Clemson work on inexpensive methods to remove uranium from water will also be highlighted.

SOIL TREATMENT

In the United States, the Nevada Test Site (NTS) possesses widespread soil contamination caused by deposition of uranium, plutonium and other radionuclides from defense related nuclear test operations. Clean up efforts are ongoing using conventional remediation techniques. However, the U.S. Department of Energy (DOE) desires to obtain technologies that can further reduce risks, reduce clean up costs, and reduce the volume of remaining contaminated soil.

Clemson University and teaming partner Waste Policy Institute, through a cooperative agreement with the National Environmental Technologies Lab in Morgantown, West Virginia, are assisting the NTS in evaluating possible technologies that have the potential of

reducing risks and clean-up cost. Physical, chemical and biological treatment processes are being evaluated. Our technology assessment includes the following sub-tasks:

A description of soil contamination problems at the NTS including a description of contaminant distribution, soil characteristics and adhesion/absorption characteristics of contaminants on soil particles.

An evaluation of physical, chemical and biological processes that have potential to remediate radioactive contaminated soils.

Ranking of technologies based on technical merit, potential experience and ease of implementation.

An engineering evaluation of technologies to determine scale-up potential and cost effectiveness.

Identification of secondary waste treatment needs for full-scale implementation.

Identification of barriers and research needed to overcome technology limitations.

Preparation of a comprehensive final report that will provide a road map for developing and demonstrating an optimal treatment approach for soils at the NTS.

The removal of actinides from NTS soils has been attempted using various combinations of attrition scrubbing, size classification, gravity based separation, flotation, air flotation, segmented gate, bioremediation, magnetic separation and vitrification [1-6]. Attrition scrubbing was used extensively as a pretreatment step to break up agglomerated materials, to remove surficial coatings from larger soil particles, and hopefully to make the contaminated soil more amenable to processing. Size separation, based on wet sieving of the contaminated soil, showed that the contamination was associated with the smaller particles. Attrition scrubbing and wet sieving of NTS soil was able to achieve a 70% volume reduction.

Gravity-based processes work on the principle of Stokes' law; heavy particles settle faster than light particles. However, the size of the particle also influences the rate of settling, thus, gravity based separation is not very effective for fine particles, typical of the NTS soils. Gravity and centrifugal separators utilize the terminal velocity of a particle for the basis of separation, which depends on the combination of density and size. Thus, the fine (size) and heavy (density) actinide oxide particles will be separated and report together to the same concentrate product stream with the large (size) and light (density) soil matrix particles.

Flotation separation is highly dependent on using the correct reagent in the slurry, which would permit air bubbles to attach to contaminated mineral grains. More work is needed to identify the best reagents to produce better separations of soil and contaminants. Carrier flotation has the advantage over air flotation of use of a carrier, which is especially important if the contaminant of interest is present at very low concentrations.

The segmented gate system separates contaminated soil from clean soil according to a preset radioactivity criterion. Poor results were obtained in a recent field test of the technology performed at the NTS: only 61% of the plutonium activity ended up in the "concentrate" with a volume reduction of 2:1 (weight of feed to weight of clean).

Bio-leaching of plutonium oxide occurs with sulfuric acid produced from elemental sulfur in the presence of sulfur oxidizing bacteria. This technology is also based on a precipitation of plutonium sulfate complex ($\text{PuO}_2(\text{SO}_4)_3^{4-}$) as plutonium oxide sulfur (PuO_2S) in the presence of sulfate reducing bacteria. Good results of field testing at the

NTS were obtained and the technology has been evaluated as promising. The unit processes are based on sound scientific concepts that have been proven in the acid leaching of uranium oxides with sulfuric acid and oxygen, and in the precipitation of metal ions in wetland-treatment of acid-mine drainage.

Early studies with magnetic separation indicated that the magnetic susceptibility of fine soil is very low. Wet magnetic separation was being tested and indications were that wet magnetic separation might work. Although results to date have not been encouraging, there is the potential to further optimize treatment and reduce the amount of material that is held up.

Vitrification and fixation are expensive and do not achieve soil volume reduction. It does not meet DOE programmatic goals of volume reduction; instead, it provides only immobilization of the contaminant. However, it is possible that vitrification may be an acceptable form of treatment on certain locations, especially for uranium contaminated soils.

Leaching methods may be more attractive for uranium contaminated soils than plutonium soils. Carbonate leaching at pH above seven has shown to work extremely well to solubilize the uranyl ion as a carbonate complex while not significantly leaching any of the soil constituents [7].

In summary, size separation helps as an initial soil decontamination step and is especially useful for smaller sized particles. But there can be significant variability in contaminant distribution in the soils and any successful treatment process must address this drawback. Attrition scrubbing appears to help although there is limited data to compare results with and without scrubbing – most studies used either one or the other. Carbonate leaching may improve these systems as well as be totally effective as a primary method. None of these processes have been fully optimized, so significant improvement may be realized by more in-depth studies.

WATER TREATMENT

Naturally occurring uranium has contaminated numerous private domestic water wells in South Carolina at levels exceeding the U.S. Environmental Protection Agency's (EPA) drinking water standard of 30 ug/L for uranium concentration. This is based on nephrotoxicity, rather than on radiological hazards. Other areas of the U.S., such as California and New Mexico, also have natural uranium in well water that exceeds the EPA standards.

In Simpsonville-Greenville, South Carolina, high amounts of uranium (30 to 9900 ug/L) were found in 31 drinking water wells. The contamination of uranium in the well water was most likely the result of veins of pegmatite, running east of Greenville to southwest of Simpsonville. In addition to the elevated uranium concentration, elevated radon levels have also been discovered. All the wells that have been tested (currently 111) are above 300 pCi/L in radon. The South Carolina Department of Health and Environmental Control (SC DEHC) requested homeowners to discontinue the use of the well water since chronic ingestion of this water may result in an increased risk of cancer. In addition, SC DEHC is beginning a program to test the levels of radon in air in this community.

The purpose of our work at Clemson University was to determine the form of uranium present in the well water and to test the effectiveness of common household treatment

devices to remove uranium and radium. Batch tests with activated carbon, iron powder, magnetite, anion exchange resin and cation exchange resin were used to characterize the form of uranium in the drinking water. In the tests, water and the separation materials were first equilibrated, filtered and then analyzed by alpha spectrometry. The results of the batch tests showed that it is possible to remove greater than 90% of the uranium and radium in the drinking water by using any of the sorbants listed above. Simple filtration with a 0.1 μm filter had little to no impact on uranium removal. Testing of two household treatment devices was performed and found not to be totally effective.

A magnetic field-enhanced filtration/sorption device is also being evaluated for removal of actinides from water [8-10]. The device consists of a column of supported magnetite surrounded by a movable permanent magnet. The mineral magnetite, or synthetically prepared iron ferrite ($\text{FeO}\cdot\text{Fe}_2\text{O}_3$), is typically supported on various materials to permit adequate water passage through the column. In the presence of the external magnetic field, enhanced capacity was observed in using supported magnetite for removal of actinides and heavy metals from wastewater. The enhanced capacity is primarily due to magnetic filtration of colloidal and submicron particles along with some complex and ion exchange sorption mechanisms. The loaded magnetite can easily be regenerated by the removal of the magnetic field and use of a regenerating solution.

One inexpensive device for containing supported magnetite is simply some type of static-bed column with screens at the entrance and exit for holding the support in place while permitting the flow of smaller magnetite particles in and out of the column. The first step in operating the column would be to pass a slurry of activated magnetite down the column containing a support material such as glass beads. Once the column is loaded with magnetite, the magnets would be placed around it to hold the magnetite in place. Then water to be treated would be passed upflow through the column until contaminant breakthrough is reached. Then the magnetic field would be removed and an additional amount of fresh magnetite slurry added to the top of the column to displace a portion of loaded magnetite and the captured contaminant particles. Then the magnets would be replaced around the column and more water passed upflow. The spent magnetite could be regenerated or discarded depending on the contaminants and operational situation. Discarding the material would be useful for contaminants that sorb strongly onto the adsorbent material (thus perhaps serving as a favorable waste form for final disposal).

In some cases it may be advantageous to have the magnetite bonded to the support and to use a normal fixed-bed column operation with regenerating solution. There are several methods available to adhere or bond the magnetite particles onto supports. For example, crushed glass and glass wool may be mixed with the support in the presence of a solution of an alkali or alkaline hydroxide (this process would also activate the magnetite); heating may also assist the process, as well as raising the temperature to near the melting point of the glass without the solution present. Grinding the glass wool (or waste fiberglass insulation) with the magnetite may also bond the materials, as would the use of silica gel, resins and other bonding adhesives.

Many processes have utilized iron oxides for the treatment of liquid wastes containing radioactive and hazardous metals. These processes have included adsorption, precipitation and other chemical and physical techniques [11-12]. For example, a radioactive wastewater precipitation process includes addition of a ferric hydroxide floc to scavenge radioactive contaminants, such as uranium [13-15]. Some adsorption processes for wastewater treatment

have utilized ferrites and a variety of iron containing minerals, such as akaganeite, ferrosite, ferrihydrite, goethite, hematite, lepidocrocite, maghemite and magnetite. Ferrite is a generic term for a class of magnetic iron oxide compounds. Ferrites possess the property of spontaneous magnetization and are crystalline materials soluble only in strong acid.

Besides ferrite treatment, wastewater could also be pretreated with standard flocculation/precipitation and filtration steps to remove gross amounts of actinides from solution. The magnetic filtration/sorption device would then be used as a polishing step for the water to remove colloids, small particles and complex ions not removed in the precipitation/filtration steps.

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