ANALYSIS OF REMEDIATION STRATEGIES FOR RADIONUCLIDE-CONTAMINATED SOILS IN URANIUM MINING[1]

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Abstract. Wyoming is the largest producer of uranium in the United States. An increase in exploration and extraction comes with renewed interest in nuclear power. Associated is a need to be prepared for handling radionuclide-contaminated soils from leaks and surface spills during in-situ recovery (ISR) of uranium.

Uranium mining is controversial in the United States. Consideration of methods for remediating contaminated soils is warranted for economic, environmental, and public health reasons. While uranium is removed in the mining process, radium contamination is of concern when leaks or spills occur. Research exists on treatment strategies for radium in soils, including physical, biological and chemical methods. Commonly, contaminated soils are removed and transported off-site for disposal at Nuclear Regulatory Commission (NRC)-approved facilities. This can be quite expensive and involves the added risk of transport of radioactive material along public highways. Having plans in place for otherwise dealing with soils in the event of contamination would be beneficial to industry from economic, regulatory and public relations standpoints.

A two-phase study has been designed in which an extensive literature review is conducted of methods used to mitigate radionuclide contamination of soils, particularly that of ^{226}radium (^{226}Ra), and then lab results are used from radium-contaminated soils specific to a Wyoming mine site to determine a remediation strategy for implementation. Feasibility of strategies are analyzed in relation to soil and vegetation characteristics typical of Wyoming uranium mine lands, so that operators will have access to this information when deciding the best course of action for handling radionuclide-contaminated soils.

Preliminary results of the first stage of this project show a dearth of studies on radium in soils, but that some physical, biological and chemical methods have been used and may warrant further consideration.

Additional Key Words: ISR (in-situ recovery), radium, radiochemistry

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Introduction

Developments in the uranium (U) mining industry over recent years include the advent of in-situ leaching (ISL) of U. This recovery technique is currently being used at Cameco Company's Highland and Smith Ranch in northeastern Wyoming. In-situ recovery (ISR, also known as in-situ leaching or ISL) uses a group of injection wells surrounding a production well. Modern ISR involves the circulation of naturally occurring and benign groundwater, fortified with oxygen and bicarbonate, through a U ore body. This fortified natural water is pumped into injection wells, through the ore, where the U in the host sandstone is oxidized and solubilized. This solubilized U moves through the sandstone to the extraction wells, where the U-bearing groundwater is pumped to the surface (Uranium Producers of America 2010). During this process, excess pressure can cause cracks and leaks in recovery pipes, which can lead to contaminated soil. While U is leached out in the process of mining, the daughter element ^{226}Ra remains. Radium-226 is of primary concern to operators (Wichers 2010) because of its 1600-year half-life, decay to radon gas, and radio-toxicity (Nathwani and Phillips 1979).

Uranium mine land reclamation is addressed by the Wyoming Department of Environmental Quality Land Quality Division (WDEQ-LQD) Non-Coal Rules and Regulations under Chapter 8, Exploration by Drilling, which specifies that each drill site will be restored to as near its original condition as possible (WDEQ 2009). Additionally, US Nuclear Regulatory Commission (NRC) regulations stipulate that areas of land over 100 square meters on average which contain Ra as a byproduct material may not exceed background level by more than 5 picocuries per gram (pCi/g) of ^{226}Ra averaged over the top 15 cm below the surface, and 15 pCi/g averaged in 15 cm thick layers below that initial 15cm under the soil surface (NRC 2010).

Currently, Wyoming operators remove and dispose of radionuclide-contaminated soils from surface spills during ISR U mining at NRC-approved sites, removing soil to at least a depth of 6 inches (approximately 15 cm.). Though NRC regulations, generally followed by WY DEQ, address the top 15 cm separately from deeper soils, in terms of expectations for meeting background levels of radiation, operators acquire baseline gamma levels in the permitting process. In the event of a surface spill, they are required by WDEQ to return soil below the top 15cm to the same standards as the initial depth when addressing contamination (Ingle 2010.)

Soils are complex media for materials to move through, and radionuclides interact with the various chemical, physical and biological components in several ways. Radionuclide transport in soils is not simple to predict, given these varying characteristics of soils. For instance, ^{226}Ra has been shown to vary in concentration in soil solution in relation to cation exchange capacity (CEC), organic matter (OM) content and pH (Vandenhove and Van Hees 2007.)

Nathwani and Phillips (1979) found OM to adsorb approximately 10 times the Ra of clays in the soils they tested, attributing the retention power of both to CEC . When measuring ^{226}Ra activity in different soil size fractions, Misra et al. (2001) found highest ^{226}Ra activity in smaller size fractions, with 44% found in soil particles of -5 microns or less. Fernandes et al., in studying a U mine site in a semi-arid region of Brazil, noted that despite potential higher availability of Ra in those soils, lack of precipitation limited leaching and mobilization (2006).

Table 1. Radium contamination results, Ottawa soil

Contaminated Soil Fraction	Weight %	Average ^{226}Ra Activity (PCi/g)
+300 micron	43	26.2
-300 +10 micron	33	92.3
-10 micron	24	180

Radium contamination results by soil fraction found at Ottawa, IL, contaminated site near Chicago. (Misra et al. 2001)

Although Wyoming soils are highly variable (Munn and Arneson 1998), ISR of U takes place in areas with similar characteristics in terms of the five soil forming factors: parent material, climate, biota, topography and time. A predominance of sites slated for development lie in the Powder River, Laramie, Wind River and Green River Basins. These are generally aridic in moisture regime, but the moisture regime intergrades towards ustic, meaning soils have limited moisture but that moisture normally occurs primarily during the growing season (Munn 2009.) Thus, soils support more vegetation and contain more organic matter here than do those of typically aridic regimes. These soils may also contain secondary carbonates like calcium carbonate ($CaCO_3$), or lime, which are common in arid and semi arid environments, and tend toward a high pH. These landscapes host predominantly sagebrush or grassland habitat. Big sagebrush (*Artemisia tridentate*), blue grama (*Bouteloua gracilis*), common buffalograss (*Bouteloua dactyloides*), wheatgrass (*Agropyron spp*.) and other typical prairie vegetation may be present in a mining area.

The Highland Ranch project permit of 1991(PRI) characterizes the terrain as "nearly flat to gently rolling hills dominated by sagebrush and grassland" with highly variable populations of the abovementioned species, as well as prairie junegrass (*Koeleria macrantha*), needle-and-thread (*Stipa comate*), and threadleaf sedge (*Carex flilifolia*) recorded. Topsoil texture was very fine for all samples taken by Stahl et al., and were classified as clays or silty clays, while at the Irigary site to the northwest, soils sampled had slightly less fine textures; they were silty clays (2002). Soil pH ranged from 6.4 to 8.0 and OM content from 1.08 to 2.4% for non-stockpiled soils (Stahl et al. 2002).

Table 2. Examples of pH and organic matter content (%) on WY uranium mine sites

Property	HUP Wellfield C Native	HUP Wellfield C In situ	HUP Wellfield F Native	HUPWellfield F In Situ	Irigary Native	Irigary In Situ
pH	6.7	7.2	6.4	7.9	8.0	7.8
Organic Matter content (%)	2.4	2.28	2.48	1.71	2.01	1.77

Soil sample results from Stahl et al. (2002) Highlands Uranium Project and Irigary Mine sites, in the east central part of Wyoming.

The objective of this study is to use Wyoming soil specific data, combined with a comprehensive literature review, to help operators determine possible in-situ remediation methods in the event of an ISR U mine surface spill, thus decreasing the economic costs and potential public health hazards of transporting contaminated soils, and enhancing future reclamation efforts.

Materials and Methods

Gavrilescu, et. al., (2008) address several techniques for remediation of radionuclide-contaminated soils: natural attenuation, physical processes, and chemical methods including extraction and permeable reactive barriers (PRBs), biological methods including phyto-remediation and biosorption, and electrokinetics. While their paper pays particular attention to U, Ra is a daughter product of that element, and these methods can be considered for remediation of soil contaminated with ^{226}Ra as well.

Additionally, US Environmental Protection Agency (EPA) and Department of Energy (DOE) projects concerned with radionuclide-contaminated soils discuss remediation strategies for such soils, which may be applicable to ISR U mine surface spills. These projects are concerned primarily with 1) government sites contaminated during defense and weapons testing programs and 2) residential and commercial sites contaminated by industrial activity (Misra et al. 2001).

Phase one of this project utilizes numerous studies in the above categories. We use a flow chart model to determine the feasibility of specific methods in Wyoming soils and in remediating ^{226}Ra in particular. This model considers physical, chemical and biological methods of in-situ soil remediation (natural attenuation being ruled out as discussed in the next section) from economic and ecological standpoints, separating active from passive strategies.

Current and historic literature pertaining to mitigation of radionuclide-contaminated soils has been researched, with a particular emphasis on studies which address soil, vegetation and other aspects similar to those found on U sites in Wyoming. Communication has been made with those in other areas who have conducted studies to provide further information as warranted. Remediation methods are prioritized in accordance with data available from previous studies and implementation, with those providing the most comprehensive information of primary interest. Costs to implement strategies are considered in categorizing methods potentially feasible for use in Wyoming.

Phase two of this project will involve taking contaminated soil samples at two depths to determine whether a lesser depth of soil than is currently standard practice may be removed in the event that removal and disposal is the chosen option to comply with regulation.

Core soil samples will be taken, including background samples, on a site contaminated by an ISR surface spill at 5cm and 15cm (2” and 6”) depth. These samples will be taken on areas of differing topography and vegetation within the spill and will include bulk samples as well, and will be sent to Energy Labs in Casper, WY, or another similar lab which conducts radiochemical analyses. Results will be used to determine whether removing 5cm of topsoil from this specific site will meet regulatory expectations, or whether the standard 15cm will be required.

Results and Discussion

This project eliminated some in-situ radionuclide-contaminated soil remediation options quickly from consideration. For example, as the half-life of ^{226}Ra is ~1600 years, natural attenuation is not a feasible strategy. Additionally, while studies of bioremediation of heavy metals in soils and Ra in wastewater have been conducted, little data has been uncovered on bioremediation of Ra contaminated soil, although it has been applied to U.

Early research indicates phyto-remediation may be a potential strategy for use in Wyoming. Several studies worldwide have looked at Ra uptake in a variety of plant species, from grasses to trees. For example, in southeastern China, soil-to-plant transfer of ^{238}U, ^{226}Ra and ^{232}Th were studied in nine different plant species; it was found that root-uptake of each radionuclide was plant-specific (Chen et al. 2005.) Often conducted to predict Ra entry into the food web, this type of research is also valuable in evaluating whether phyto-remediation may be a feasible option for cleaning ^{226}Ra-contaminated soils on U mine sites. While several studies have involved woody species not native to Wyoming, some using grasses and one in which sagebrush uptake of Ra was analyzed were conducted at Colorado State University in the 1980s (Simon and Fraley 1986). These provide a basis for further examination.

Another strategy, which is now being employed in south Texas, is that of homogenization of contaminated soils. Here, soil affected by U mine surface spills is homogenized horizontally across the permit area, with topsoil remaining in the upper part of the profile (McClendon 2010). The aim of homogenization is to reduce contamination to a desired level relative to background by mixing those contaminated soils to homogenize and then homogenizing the resulting contaminated soil with the remainder of the unaffected soils in the treatment area. Thus, soil remains on site, but diluted in radioactivity to background levels or below, in order to meet regulations.

Chemical means of addressing Ra-contaminated soils also provide possibilities. For example, chelation, in which polydentate ligands attach to multiple electron receptors on metals, has been studied specific to radionuclides (Chao et al. 1998). Chelation is used to prevent customary reactions of metal ions, without removing them from solution. Chelating agents that can be precipitated out of complex with a change in pH would be reusable and, according to Chao et al. (1998), can therefore be more cost effective (1998).

Shah et al. (2007) found that chelating ligands formed complexes with different metal ions dependent upon specific pH conditions, indicating an increased selectivity and specificity of chelating groups on different metals. Wyoming soils tend toward a higher pH and associated CEC, thus having an affinity for adsorbing Ra. However, given variations in optimum pH conditions for complexation, study of chelating agents specifically on Ra-contaminated soils may be warranted.

The second part of this study may indicate less than the current customary 15cm, or 6 inches, of soil could be removed from the surface of a mine spill area on an ISR U mine site and still remain within regulatory standards. Soil characteristics gathered thus far from U sites in Wyoming show low organic matter and relatively high pH. Though organic matter (OM) has been seen in the literature to absorb more Ra than clay, these Wyoming soils tend toward a smaller size fraction (silty clay and clay). Furthermore, depending on the time of year a spill occurs and how quickly operators respond, being in an aridic to ustic moisture regime, these soils are likely to mobilize radionuclides and leach much more slowly than in a wetter climate. (Nathwani et al. 1979; Misra et al. 2001; Fernandes et al. 2006).

Results of this research will provide site-specific options for management decisions on implementation, as soils are tested for Ra content and soil characteristics (pH, CEC, texture, and OM content) pertinent to Ra transport within them, as well as a comprehensive set of strategies for industry consideration on a case-by-case basis when contending with Ra-contaminated soils in the future. The addition of in-situ remediation options as possible alternatives to removal and disposal of contaminated soil is expected to be more economical to U operators, more supportive of future reclamation efforts, and reduce transport of hazardous wastes on public roadways, thus increasing environmental safety and public health protection.

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