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RADIONUCLIDE CONTAINMENT IN SOIL BY PHOSPHATE TREATMENT

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ABSTRACT

Radionuclide transport from a contaminant source to groundwater and surface water is a common problem faced by most U.S. Department of Energy (DOE) facilities. Containment of the radionuclide plume, including strontium-90 and uranium, is possible using phosphate treatment as a chemical stabilizer. Such a chemical process occurs in soils under natural environmental conditions. Therefore, the concept of phosphate amendment for radiostrontium and uranium immobilization is already a proven principle. In this presentation, the results of bench-scale experiments and the concept of a field-scale demonstration will be discussed. The phosphate treatment is possible at the source or near the advancing contaminant plume. Cleanup is still the ideal concept; however, containment through stabilization is a more practical and cost-effective concept that should be examined by DOE Environmental Restoration programs.

INTRODUCTION

Contamination of groundwater and surface water is the problem of most concern for the environmental restoration programs of U.S. Department of Energy (DOE) facilities. Stabilization of the contaminants is one of many ways for containing the plume. Containment is not as complete as removal cleanup, but it is a cost-effective remedial solution for certain contaminants. Containment of the plume can be achieved by two principal ways: hydrological isolation using an impermeable barrier or immobilization of contaminants by thermal and chemical stabilization. Vitrification of contaminated soils and rocks in pits and trenches is an example of thermal stabilization (1). Chemical stabilization is a process that induces a change in the chemical states of the contaminants by adding reactive solutions or materials into the contaminated geomedia (2). Themical treatment changes the mobile or exchangeable states of the radionuclides into immobile or nonexchangeable states by chemisorption, precipitation, or chemical reduction. Many radionuclides—including cobalt-60, strontium-90 (radiostrontium), technetium-99, and transuranics (uranium, neptunium, plutonium)—could be immobilized by one of the above chemical processes. For example, organic-bound trivalent radiocobalt and anionic pertechnetate in soil and groundwater could become reduced by ferrous iron. The reduced forms—i.e., divalent cobalt and tetravalent technetium—will be coprecipitated with iron as oxide minerals in soils. Such chemical treatment is also applicable to immobilization of transuranics in soils. Reduction of radiostrontium leachability in soil was also achieved by soda ash treatment (2). The stabilization of radiostrontium in soil by phosphate treatment has been considered previously (3). The strong retention behavior of uranium on phosphate minerals is also well-known. However, such well known chemical principles have not been tested on a field-scale experiment although there are many potential areas at DOE facilities.

The objective of this presentation is to summarize our current efforts at strontium-90 and uranium immobilization by phosphate amendment and to describe its use as a containment approach for reducing the potential risk associated with groundwater and surface water contaminations.

CURRENT DEVELOPMENTS

Phosphate-based immobilization for different metals has been studied sporadically by many scientists and organizations. Since in situ phosphate treatment is based on containment rather than actual cleanup (in situ degradation or excavation for off-site shipping), it has not been an attractive option for many sites. Recent emphasis on cost-effectiveness and risk-based cleanup approaches provides new impetus for the development of containment-based remediation technologies. Thus, our laboratory activities on phosphate treatments for containing strontium and uranium in contaminated soils may be of interest.

Phosphate Amendment for Radiostrontium Containment

Radiostrontium has been recognized as one of the most abundant radionuclides in contaminated areas on the Oak Ridge Reservation and at other DOE facilities in the United States. Furthermore, radiostrontium has a fairly high mobility under neutral and acidic pH conditions of soil and residuum, as evidenced by the common development of strontium seeps around radwaste burial grounds (4). The most commonly applied technology for remediation has been hydrologic isolation by cement grouting. This technology may be effective for a small number of trenches, but it is very expensive for large numbers of trenches at a disposal site. Therefore, phosphate amendment for radiostrontium was proposed as an alternative technology and examined in laboratory bench-scale experiments (5).

The laboratory batch and column experiments were conducted to determine the optimum conditions for use of this technique and to conceptualize the phosphate delivery method for a field-scale application. The column experiment showed that phosphate-treated soils at pH 6 to 9 had considerable reduction of radiostrontium leachability. Tribasic sodium phosphate treatment at elevated pH was the best way to immobilize the radiostrontium in the contaminated soils. The effectiveness of the treatment was increased with increasing phosphate concentration from 0.01 to 0.1 M.

In a batch experiment, varying amounts of metals, including aluminum, iron, and calcium salts, were added to the soils to enhance coprecipitation with radiostrontium. The optimum molar ratio of phosphate to metal was 1:1 for radiostrontium immobilization. The results also demonstrated that reduction of radiostrontium leaching was more noticeable with increasing time of interaction between the phosphate and metals. Soil properties also influenced the effectiveness of the treatments. After calcium-phosphate treatment, an alkaline soil showed a noticeable reduction in radio-strontium leaching, but an acid soil showed no reduction. However, both soils had more than 98% reduction of radiostrontium leaching after phosphate-aluminum and -iron treatments.

Direct application of laboratory batch and column results to a field-scale demonstration is difficult, but the laboratory results proved the known chemical principle that radiostrontium could be immobilized by phosphate treatment with or without aluminum and iron additions as coprecipitators.

Phosphate Amendment for Residual Uranium Immobilization

Cleanup of uranium-contaminated soil is another major problem faced by the DOE Environmental Restoration Program. In response to this problem, the Office of Technology Development has initiated a Uranium Soil Integrated Demonstration (USID) program at the Fernald Environmental Management Sitein Fernald, Ohio. Most surface soils inside the production areas at the Fernald site are contaminated by uranium (6). The leading cleanup concept of the USID program is an exsitu lixiviant leaching (soil washing) of uranium from soils. The goal of the program is to remove uranium from soil and return the cleaned soil to its original place. Detail development of the technology was discussed in a technical memorandum (7).

After more than a 2-year investigation, we concluded that removal of contaminated uranium from these soils to background levels is impossible without critical damage to the soil and the generation of large volumes of secondary wastes. Under the best conditions, the residual uranium concentration was noticeably higher than the targeted technology screening level of 50 mg/kg. Furthermore, solubility measurements of residual uranium in the treated (cleaned) soils indicated that uranium levels of the groundwater that passes through the buried cleaned soils will be higher than the proposed acceptable drinking water limit of uranium concentration (20 μg/L). The observed higher uranium concentrations in the leachates indicated that carbonates in the groundwater or dissolved from indigenous carbonate minerals in the soil reacted with and removed uranium from residual uranium-bearing mineral surfaces in the cleaned soils (8).

To reduce uranium solubility, two cleaned soils samples from the Fernald pilot-scale soil leaching test runs were equilibrated with phosphoric acid solution and dried to enhance phosphate fixation. The total residual uranium concentrations of the cleaned soils were <50 to 125 mg/kg. The phosphate-amended soils were leached for 77 days with synthetic groundwater, formulated on the basis of the average composition of site groundwater (8). The leaching experiment showed that the uranium concentration of the phosphate-amended soil leachate was only less than 10% (<1 mg/L) that of unamended soil. While the uranium concentration was still higher than the proposed level, it will not pose a problem because the uranium in the leachate is removed by soil minerals (retardation) along the transport pathway.

The phosphate fixation stabilizes not only uranium, but also calcium, iron, and aluminum in soil. Chemisorption of phosphate on calcium, aluminum, and iron generates new active sorption sites for soluble uranium. Therefore, the uranium fixation capacity of the soil will be increased with aging of the phosphate treatment. This is an irreversible chemical reaction and, as noted earlier, is a well-known natural chemical process occurring in soils.

FUTURE DEVELOPMENTS

At the present time, our investigations are limited to batch and column tests for both radiostrontium and uranium immobilization. We are planning a scale-up of the laboratory experiment to evaluate and develop phosphate delivery methods. For full-scale field application, detailed site characterization is also needed to develop and execute the site-specific plan.

In the past, low-level radioactive liquid and solid waste was disposed of in pits and trenches. The plumes generated by leaching of radwaste passed through the surrounding soil and residuum. For in situ applications, we can introduce phosphate in two different ways: (i) by injecting phosphate solution or mixing soil with phosphate minerals both within and in front of the plume pathway, and (ii) by building a permeable low-grade phosphate mineral wall around the plume. Both radiostrontium-contaminated and uranium-contaminated sites are available at the Oak Ridge Reservation for demonstration.

For ex situ applications, the soils cleaned by soil washing technologies, including both physical separation and chemical leaching, could be amended by the addition of phosphate solution or by mixing with phosphate minerals at the end of the treatment process. This particular process will be demonstrated for uranium-contaminated soils at the Fernald site as a part of the scale-up pilot or full-scale soil chemical leaching demonstration planned in a year.

SUMMARY

Soils contaminated with both radiostrontium or uranium occur throughout DOE sites. Laboratory results showed that phosphate amendment for in situ containment and ex situ stabilization of the radionuclides could be an effective and economical remediation technology. However, we must understand the physicochemical and mineralogical properties of the cleaned soil for ex situ application and site characteristics including hydrogeology, geochemistry, and soil mineralogy for in situ application. Fortunately, most soils and residuum have very high phosphate fixation capacities. Therefore, environmental degradation caused by unreacted phosphate discharge from the demonstration site is not expected. Application of industrial grade phosphoric acid and basic phosphate solutions will effectively contain the radionuclides without the addition of metal coprecipitants. Also, low-grade phosphate rock (hydroxyapatite with other minerals) is commonly available at relatively low cost.

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