Decontamination of Radionuclides from Concrete During and After Thermal Treatment

RESEARCH OBJECTIVE

This project will determine the effect of heating concrete on its engineering properties and the potential to aid in removal of common DOE radionuclide contaminants including ^{137}Cs, ^{90}Sr, ^{60}Co, and U. In the chemical properties subtask, effects on direct volatilization of radionuclides during heating, as well as their subsequent extractability behavior, will be established over a range of temperatures up to the melting point of Portland cement. Although not an objective as this project was initially proposed, the serendipitous finding of fixation of radionuclides during heating of common concrete aggregates minerals (quartz, feldspar, and calcite) has led to a breakthrough technique for in situ immobilization of radionuclides and contaminants in soil by thermal treatment. The main objective of the mechanics and thermodynamics subtask of this investigation is to develop a powerful computational capability to evaluate the effects of various regimes of rapid heating of a contaminated concrete wall or slab.

RESEARCH PROGRESS AND IMPLICATIONS

The effect of heating hardened Portland cement paste (the cementitious component of concrete) in aiding the removal of common radionuclide contaminants including ^{137}Cs, ^{90}Sr, ^{60}Co, and U was investigated. Direct volatilization of radionuclides during heating, as well as subsequent behaviors during extractions, were established over a range of temperatures up to the melting point of Portland cement paste. Techniques for spiking pulverized Portland cement paste with shorter-lived radioisotopes (^{134}Cs, ^{85}Sr, and ^{57}Co) and U were developed using gamma-ray spectroscopy to measure their activity nondestructively before and after heating. An extraction procedure (employing five sequential extractions each with water, followed by 0.1*N* $CaCl_2$, followed by 0.2*N* HCl) for pulverized but fully-hydrated Portland cement paste was adapted to contrast behaviors after thermal treatments. Complete volatility of ^{134}Cs was observed at temperatures of 1200°C or greater. Thus, decontamination of ^{137}Cs from cement paste would be feasible by direct heating. However, no volatility of other radionuclides was observed and, thus, their potential for facilitated decontamination will likely depend on their extraction behavior following thermal perturbation. Both ^{134}Cs and ^{85}Sr were readily removed from cement paste during initial water-based extractions for final temperatures <800°C. In contrast, both ^{57}Co and U exhibited negligible extractability into either water or 0.1 *N* $CaCl_2$ probably resulting from their precipitation as hydroxides in the highly alkaline Portland cement paste extracts where pHs were usually greater than 10. The release of both these radionuclides was delayed until sequential 0.2 *N* HCl extracts decreased the pH below 4. Significant patterns in the extraction behaviors of all radionuclides with temperature were observed in ranges where significant mineral alterations are known to occur.

Strontium-90 is a major hazardous contaminant of radioactive wastewater and its processing sludges at many Department of Energy (DOE) facilities. In the past, such contaminated wastewater and sludge has been disposed in soil seepage pits, lagoons, or cribs often under highly perturbed alkaline conditions ($pH > 12$) where ^{90}Sr solubility is low and its adsorption to surrounding soil is high. As natural weathering returns these soils to near neutral or slightly acidic conditions, the adsorbed and precipitated calcium and magnesium phases, in which ^{90}Sr is carried, change significantly in both nature and amounts. No comprehensive computational method has been formulated previously to quantitatively simulate the dynamics of ^{90}Sr in the soil-groundwater environment under such dynamic and wide-ranging conditions. A computational code, the Hydrologic Utility Model for Demonstrating Integrated Nuclear Geochemical Environmental Responses (HUMDINGER), was composed to describe the changing equilibria of ^{90}Sr in soil based on its causative chemical reactions including soil buffering, pH-dependent cation exchange capacity, cation selectivity, and the precipitation/dissolution of calcium carbonate, calcium hydroxide, and magnesium hydroxide in response to leaching groundwater characteristics including pH, acid neutralizing capacity, dissolved cations, and inorganic carbonate species. The code includes a simulation of one-dimensional transport of ^{90}Sr through a soil column as a series of soil mixing cells where the equilibrium soluble output from one cell is applied to the next cell. Unamended soil leaching and highly alkaline soil treatments, including potassium hydroxide, sodium silicate, and sodium aluminate, were simulated and compared with experimental findings using large (10 kg) soil columns which were leached with ^{90}Sr-contaminated groundwater subsequent to treatment. HUMDINGER's simulations were in good agreement with dynamic experimental observations of soil exchange capacity, exchangeable cations, total ^{90}Sr, and pH values of layers within the soil columns and of column effluents.

Heating of fine sand-sized common mineral powders (quartz, feldspar, or calcite) or a soil (from the Department of Energy’s Hanford site) up to 1000°C, in contact with sorbed radioisotopes (^{85}Sr, ^{57}Co, ^{134}Cs, or U), markedly increased each isotope’s immobilization. A sequential extraction procedure was applied after heating the materials to assess the changes in each isotope’s functional form among water-soluble, cation-exchangeable, acid-soluble, and residual phases. The overall immobilization effects were consistent with rapid high temperature ionic diffusion from the initially contaminated surfaces into the mineral matrices; subsequent diffusion out of mineral particles at ambient temperature, as measured by the sequential extraction behavior, would be such a slow process that the radionuclides may be considered sequestered from further potential environmental mobilization. In the Hanford soil, the effect was found to follow an Arrhenius-type relationship with treatment temperature up to 1000°C for ^{57}Co, ^{85}Sr and U and immobilization was independent of previous thermal treatment of the materials. Although ^{134}Cs exhibited its largest immobilization in the Hanford soil after heating to 1000°C, the large immobilization of ^{134}Cs at all temperature and even in unheated Hanford soil made it difficult to observe a strong temperature dependence. A general and promising technique for environmental remediation of contaminated soil by high-temperature heating without melting can be extrapolated directly from the empirical leaching information.

The work in the mechanics and thermodynamics subtask concentrated on effective and realistic computational simulation of the mechanical and thermodynamic aspects of the simulation of concrete spallation induced by rapid heating, both by conductive heating from the surface and by microwave heading within the bulk. The mathematical formulation is now in complete form (although it might still be improved) and a functioning computer program combines the finite element analysis of stresses in the heated surface layer of concrete with energy release fracture analysis, finite volume method for moisture diffusion and heat transfer, and finite difference simulation of microwave heat generation based on Lambert's law, taking into account radiation shielding and scattering by reinforcement bars. The program works and provides meaningful results for the spalling of the contaminated surface layer of concrete engendered by rapid microwave heating.

PLANNED ACTIVITIES

All research activities in the chemical properties subtask have been completed in Fiscal Year 2001.

In the mechanics and thermodynamics subtask during the proposed no-cost extension, the computer program will be finalized and improved in its accuracy and convergence. We will run calculations of many typical configurations and study the effect of various parameters, including microwave radiation power output and duration, pore pressures, movement of the drying front and oversaturation front during the heat treatment, build-up of pore pressure in concrete, development of moisture clog, delamination buckling and explosive spalling of the compressed contaminated layer stresses, effect of initial moisture content of concrete and its other initial parameters, etc. We will ascertain what power input and duration are needed and find out how to control the depth of the spalling layer. With this, the goals of the grant will be satisfied.

INFORMATION ACCESS

A research report has been published in *Environmental Science & Technology* (2000, 34: 5051-5058) summarizing the volatility of radionuclides during heating and their subsequent extraction behavior from the thermally-altered Portland cement. A second research report on the modeling of the extractive behavior of ^{90}Sr in soil, portlandite, and magnesium and/or calcium carbonates under alkaline conditions was also published in *Environmental Science & Technology* (2001, 35: 365-373). A third research report on the fixation of radionuclides in common concrete aggregate minerals (calcite, quartz, and feldspar) and soil has just been published online in *Environmental Science & Technology* (2001, 35: online). Additional details of this important new technique for radionuclide and stable contaminant fixation in soil by heating is also publicly available online.

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