

Immobilization of Radionuclides in Soil Minerals After Thermal Treatment

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Abstract: Heating of common minerals (quartz, feldspar, or calcite) or a soil (from the Hanford DOE reservation) up to 1000°C, after spiking with radioisotopes (⁸⁵Sr, ⁵⁷Co, ¹³⁴Cs, or U), markedly decreased their leachability after cooling using a sequential extraction sequence designed to assess each contaminant's mobility. For example, ⁸⁵Sr was converted from 98% leachable in the ambient Hanford soil to less than 10% leachable, even in the final acid extracts, by heating to 1000°C. The overall effect is consistent with rapid high-temperature ionic diffusion from initially contaminated surfaces into the interior of uncontaminated minerals; subsequent diffusion out of these mineral particles at ambient temperature, as measured by their sequential extraction behavior, would be such a slow diffusion-controlled process that the radionuclides may be considered sequestered for geologic intervals approaching the weathering lifetime of the host mineral. The effect was found to follow an Arrhenius-type relationship with treatment temperature and to be independent of previous thermal treatment of the minerals. Although these results are consistent with a temperature-dependent diffusion process, a general and promising technique for environmental treatment of contaminated soil by high-temperature heating can be extrapolated directly from the empirical leaching information without dependence on any mechanistic explanation. The immobilization technique may be applicable to any non-volatile radionuclide or inorganic contaminant in soil or geologic material and has the potential to achieve high degrees of immobilization for most contaminants.

Previous investigations into the effects of thermal treatment of soil and/or mineral materials on the subsequent leachability of contaminants have usually been incidental to other primary treatment objectives such as thermal destruction or incineration of organic contaminants, volatile removal of organic and certain inorganic contaminants, particulate and gaseous emissions control during incineration, or vitrification processes and their off-gas control. Occasionally, thermally-altered soil within these processes has been noted to exhibit a marked decrease in residual contaminant extractability; this observation is often based on a single extractability test (e.g., the Toxicity Characteristic Leaching Protocol) of a single contaminant and often hypothesized to result from unique contaminant reactivity with component phases in the soil. In an ongoing investigation into the effects of thermal treatment of radioactively-contaminated concrete, we initially focused on changes in radionuclide extractability and volatility following heating of only the hardened Portland cement paste phase (Spalding 2000) which is usually thought to be the most chemically reactive phase, at least when compared to the sand- and gravel-sized aggregates which compose the other 80% of concrete. It was hypothesized that common concrete aggregate minerals (quartz, feldspar, and calcite) would remain inert and unreactive to four major DOE contaminant radionuclides (⁹⁰Sr, ¹³⁷Cs, ⁶⁰Co, and U) during heating up to 1000°C; such thermal treatment can destroy the cement paste's cohesion (strength) and mediate other advantageous

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changes in contaminant extractability resulting in improved concrete removal and decontamination. However, these common aggregate materials, far from remaining inert during heating with spiked radionuclides, have proven so reactive as to warrant thinking of their thermal treatment as a whole new approach to contaminant immobilization in mineral phases. Because these same common concrete aggregate materials, quartz and feldspar, are also ubiquitous and abundant soil components and are chemically similar to the aluminosilicate minerals which compose the common clay-sized minerals of many soils, thermal treatment of soil was also included using one soil from the DOE Hanford reservation, commonly subject to radioactive contamination.

Uniformly sized (-100/+200 mesh) materials (quartz, feldspar, calcite, and Hanford soil) were spiked with one isotope (^{85}Sr , ^{134}Cs , ^{57}Co , or depleted U) and heated in alumina crucibles to increasing temperatures up to 1200°C , using gamma spectroscopy to assay radioisotopic activity before and after heating. The materials were then subjected to a fifteen-step sequential extraction procedure (Spalding 2000) to separate and quantify the functional radioisotopic forms within the thermally-altered minerals or soil among water-soluble, cation-exchangeable (extracted with 0.1 N CaCl_2), acid-soluble (extracted with 0.2 N HCl), and residual forms (assayed in residual solids). Thermal treatment of all four mineral materials at 500 and 1000°C , spiked with any of the four radionuclides, was found to increase the residual or immobilized fraction of the radioisotope; a detailed draft report of these findings for all combinations of isotopes and materials can be found at <http://www.ornl.gov/LANGMUIR/thermalMS.pdf>.

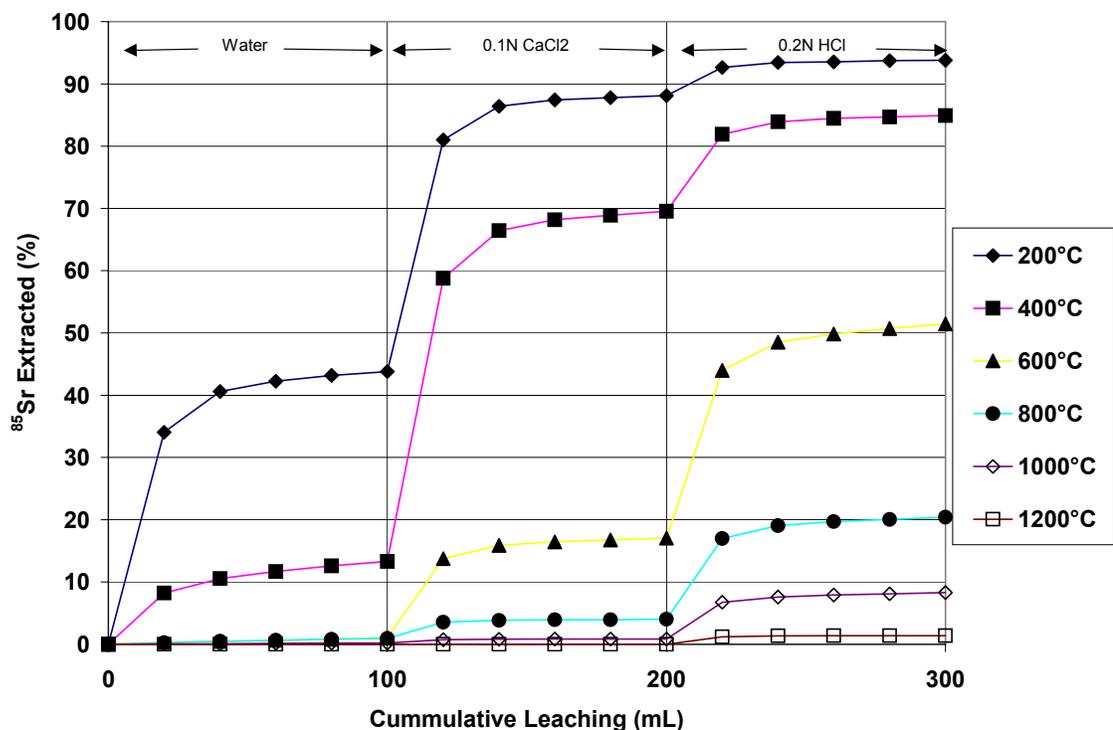


Figure 1. Sequential extraction of ^{85}Sr from Hanford soil following heating to various temperatures.

The generalized effects of heating are illustrated with the results of the ^{85}Sr -spiked Hanford soil in Figure 1.

The degree of contaminant immobilization following heating followed an Arrhenius-type relationship where the logarithm of the amount of residual activity was inversely proportional to the reciprocal of the treatment temperature. Unique thermal chemistry seemed an unlikely explanation because previous soil heating without radioisotope did not affect the immobilization of the radioisotope during subsequent repeated heating. Because radionuclide contaminant immobilization proceeded not only in materials reactive at ambient temperature, like soil and feldspar, but also in arguably inert materials at ambient temperature, like quartz and calcite, the general mechanism can be hypothesized to result from ionic diffusion of radionuclides, initially adsorbed to the surface, into the uncontaminated interiors of the mineral matrices. Using the well-studied Arrhenius-type relationship between diffusion coefficients and temperature for similar ions into materials like quartz, such contaminating radionuclides would be expected to readily diffuse into quartz to distances between 0.001 and 0.1 mm in less than an hour at 1000°C. When these thermally treated materials return to ambient temperature, the same Arrhenius relationship predicts that their diffusion coefficient will decrease 8-10 orders-of-magnitude from its value at 1000°C and result in concomitant transport times approaching millions of years to diffuse back to the surface of the mineral where contaminants would be available for dissolution by groundwater or for extraction by the sequential reagents employed here.

Although arguments for radionuclide immobilization in soil in response to thermal treatment can be conservatively extrapolated to plausible remediation technologies based solely on the present empirical evidence, the diffusive mechanism offers considerable opportunity to speculate about and model the behaviors of additional contaminants in different soils and minerals under widely ranging thermal conditions. Diffusive trapping of contaminants ought to work for any non-volatile soil contaminant in almost any mineral soil. The potential immobilization capacity of soil and minerals for radionuclides via diffusive trapping is enormous because, even at very high activity loadings, the radioactive contaminant would have a negligible mass loading effect on surfaces where self-diffusive tracer conditions would still apply. Unlike all chemical treatments of soil, thermal treatment would be free from the restraints on reactivity which result from a reagent's stoichiometry, mixing, dispersion, or consumption; thermal treatments could be imposed any number of times to varying final temperature without adversely affecting previous degrees of contaminant immobilization. Such thermally-assisted contaminant immobilization may prove beneficial in many applications other than contaminated soil including hazardous waste treatment, high-level radioactive waste disposal, and hazardous off-gas treatment. Indeed, one could envision optimizing the general process to immobilize contaminants based on selection of contaminant- and material-specific diffusion properties, particle size, temperature range, and contact times.

References

Spalding, B. P. 2000. Volatility and extractability of strontium-85, cesium-134, cobalt-57, and uranium after heating hardened Portland cement paste. *Environ. Sci. Technol.* 34: 5051-5058.