

Radionuclide migration in arid soils

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Introduction

Australia is siting and establishing a national radioactive waste repository for the disposal of low level and short lived intermediate level waste. The repository will be a near surface facility located in an arid climate. A code of practice for such a facility in Australia, including site selection criteria, was issued by the National Health and Medical Research Council (NHMRC, 1992). In February 1998, a region in the central north of South Australia (CNSA region) was selected for detailed assessment (BRS, 1997).

The site selection criteria for the repository include requirements that the geological structure and hydrogeological conditions of the site should enable prediction of radionuclide migration times and patterns and that the geochemical and geotechnical properties of the site should inhibit migration of radionuclides. Migration of radionuclides depends on the rate of water movement and the retardation of the radionuclides by chemical reaction with, and adsorption on, the regolith material.

The climate of the CNSA region is characterised by irregular low rainfall with an average of 198 mm.yr^{-1} , low relative humidity, high

evaporation and high summer temperatures. Based on rainfall and evaporation in the region, Harries *et al.* (1999) calculated that the deep drainage for typical soils was between 0.004 mm.yr⁻¹ and 1.3 mm.yr⁻¹ in the presence of vegetation and between 1.4 mm.yr⁻¹ and 7 mm.yr⁻¹ in the absence of vegetation. Limited field measurements were consistent with these estimates. These low water fluxes indicate that the transit time of water moving from the repository towards the water table is expected to be many thousand years.

This paper describes technical studies on the retardation of radionuclides undertaken in support of the site selection and to provide information needed for the safety assessment.

1 Radionuclide retardation

The migration of most radionuclides in groundwater is slower than the rate of water movement because chemical precipitation and adsorption remove the radionuclide from the aqueous phase and deposit it on the solid matrix. Adsorption, by which a solute is bound by the surfaces of minerals and organic matter in the soil, significantly retards the movement of all radioisotopes including those that are relatively or highly soluble. The complex sorption interaction can be expressed as a distribution coefficient (K_d), which is the ratio of the amount of the radionuclide sorbed by the solid (g.g⁻¹) divided by the concentration in the equilibrium solution (g.ml⁻¹). The K_d value is commonly used as a means of assessing the mobility of radionuclides in the environment and for comparing adsorption data obtained from different sources (McKinley and Scholtis, 1992; Sheppard and Thibault, 1990).

The value of the K_d depends on the element in question, the chemical conditions of the regolith solution, and properties of the solid (such as its surface area, surface charge, mineralogy, etc). Some elements (such as iodine) have relatively low K_d values in a range of geochemical environments, whereas others (such as thorium) have very high K_d values and are virtually immobile in most natural environments. However even for a single element, the value of K_d can

cover many orders of magnitude depending on the system in question. We have measured K_d values and retardation over a range of chemical conditions using two different types of experimental procedure: batch and column experiments.

Batch experiments

Batch experiments assess geologic materials in terms of their ability to adsorb radionuclides under a range of experimental conditions. The batch technique measures adsorption of radionuclides from a standard solution at a high liquid-to-solid ratio (10:1 or 100:1). These high solid-to-liquid ratios are dissimilar to field conditions in the unsaturated zone of the arid environment, but the measurement is rapid, reproducible and relatively inexpensive. The column experiments described in Section 4 use liquid-to-solid ratios more comparable to field conditions. In the batch experiment, solid, radionuclide and aqueous phases are mixed for 48 hours, the liquid phase separated by centrifugation and the radionuclide concentration in aqueous phase measured.

Batch experiments have been used to measure the sorption of ^{60}Co , ^{137}Cs and ^{238}U . The experimental duration was three days. In the first 24 hours, the solids were pre-equilibrated with the background electrolyte. The radionuclide, which is supplied in an acid solution, was then added, and the system immediately adjusted to the required pH value. The samples were gently shaken in unsealed centrifuge tubes at room temperature. After 48 hours contact time, the solid and liquid phases were separated by centrifugation and the ^{60}Co , ^{137}Cs and ^{238}U content of the clear supernate was measured by g-spectrometry or kinetic phosphorimetry.

Batch experiments with cesium were performed with two different concentrations of radionuclide. Trace cesium experiments were undertaken with carrier-free cesium-137, and experiments at a higher total cesium (ΣCs) of 1 mmol.l^{-1} were carried out after adding CsCl. The different concentrations of cesium enable chem-

ical controls on sorption of cesium to be measured. The higher concentration value (1 mmol.l⁻¹ total cesium) provided a clear indication of the effect of total concentration, even though this concentration is much greater than would be expected near a repository.

The measured K_d values for cesium on the near-surface materials from the CNSA region are summarised in Table 1. Over the range of variables considered in the present study, pH had almost no effect on cesium adsorption. This is because the aqueous speciation of cesium is limited to the Cs⁺ species under most environmental conditions. These results indicate that the migration of trace cesium in these materials would be greatly retarded relative to water movement. For K_d values greater than 200 ml.g⁻¹, the radionuclide would be retarded by at least 3 orders of magnitude compared to water flow. At a total concentration 1 mmol.l⁻¹ total cesium, the results in Table 1 indicate that the efficiency of adsorption is reduced. The increase of total cesium by several orders of magnitude greatly reduced the measured K_d values.

The pH is a significant factor influencing the adsorption of uranium (Figure 1). This reflects the speciation of U(VI), which is strongly dependent on pH and on the presence of carbonate. The very weak sorption of U at high pH values under these conditions is a consequence of the stability and weak sorption of aqueous uranyl carbonate complexes. As with cesium, the sorption of U(VI) also decreases at higher radionuclide concentrations, although the effect is significant only in the low pH region, at pH values below about 5 (Figure 1). This effect has been attributed to the presence of a range of sorption sites of varying affinity for adsorbing uranyl (Waite *et al.*, 1994). A similar dependence on total uranium may occur near the high pH desorption edge, but this pH edge is very steep and the experimental uncertainty precludes identifying a concentration effect.

The results of batch sorption experiments with ⁶⁰Co with materials from the CNSA region indicate that the K_d for cobalt is strongly pH dependent. The K_d of cobalt increases from approximately 1 ml.g⁻¹ at a pH of 4.0 to 1000 ml.g⁻¹ at pH of 8.0. In addition to the role of pH, there is some dependence on mineralogy.

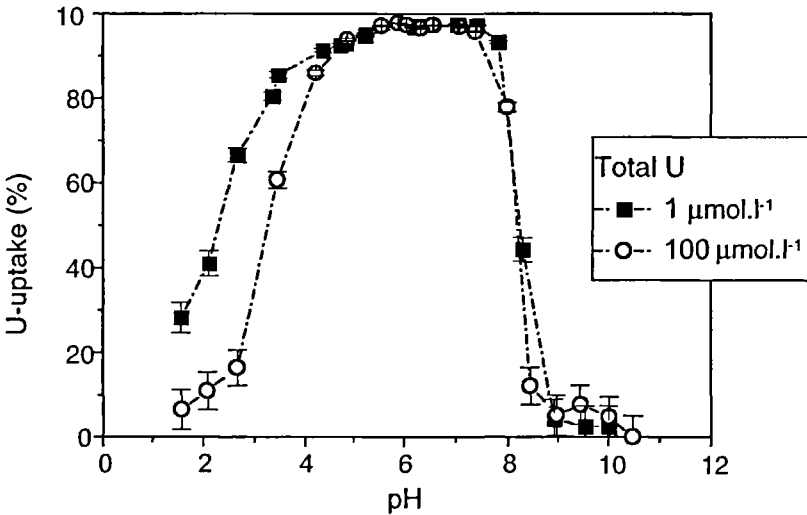


Figure 1
Percentage of uranium adsorbed on the W2 soil sample from the CNSA region as a function of pH and total uranium (ΣU). Data were obtained in 0.02 M NaCl and equilibrated with air ($p\text{CO}_2 = 10^{-3.5}$ atm.). Note the very strong pH dependence and the effect of ΣU on the position of the low-pH edge.

Column measurements

The column experiments are based on a liquid-to-solid ratio of about 0.3:1. In these experiments, saturated CaSO_4 solution containing radionuclides (^{60}Co , ^{137}Cs and ^3H) was absorbed by a uniform and relatively dry soil column. The advance of the wetting front was observed and, at different elapsed times, experiments were terminated to measure the spatial distributions of water and solute. The chemical conditions in the experimental column are expected to be similar to conditions in the field.

The column experiments were conducted with material that passed a 2-mm sieve. The CaSO_4 was used to maintain the structural sta-

bility of these materials; it is expected to be present in the field. All experiments involving nuclide traces in solutions are therefore based on saturated CaSO_4 (≈ 30 millimoles of charge $\cdot \text{l}^{-1}$).

Some swelling occurred in the experiments, which makes a physical space coordinate system unreliable. The experiments were analysed in terms of both solid based space and a material coordinate based on the distribution of the water in the soil. The solid-based coordinate is the cumulative mass of solid per unit area of cross section, measured away from the inflow surface. A water-based coordinate system is used to compare mobility of nuclides. The use of these coordinate systems (Smiles, 2000) gets over the swelling problem; it also reduces the effects of inevitable slightly different column packing. The data are scaled in terms of material distance divided by the square root of time. The coherent set of data for experiments terminated at substantially different times indicates that basic initial and boundary conditions on the experiments are realised and that diffusion equation theory can be applied to extend the experimental data in both distance and time.

The experimental methods, based on sectioned columns of unsaturated but uniformly moist fine soil, and the theoretical analysis, are described by Smiles *et al.* (1981) and Bond *et al.* (1982).

Illustrative results for a set of column experiments terminated after various time intervals are shown in Figure 2. The tritium is a tracer for water. Thus, the tritium front, identified with an inflection in the concentration curve, corresponds to an inflection in the receding soil solution salt profile (Figure 2). This is consistent with the notion that the tritium front should correspond with a "piston front" which would exist if the invading solution displaced, in its entirety, the soil water originally present. Displacement of solute front relative to the "piston front" reflects the degree to which the solute is retarded relative to the moving soil water.

Comparison of the profiles for ^{60}Co with the tritium indicates the rate of movement of cobalt relative to the water. The column experiments involved both ^{137}Cs and ^{60}Co . However, the cesium experimental data are not shown because the ^{137}Cs did not travel past the first section of the column. This is consistent with strong association of cesium with the soil indicated in the batch experimental data

(Table 1) where typical K_d values for trace cesium exceed 10^3 ml.g⁻¹. In contrast, cobalt does progress through the column to some extent, as is shown by the profile in Figure 2.

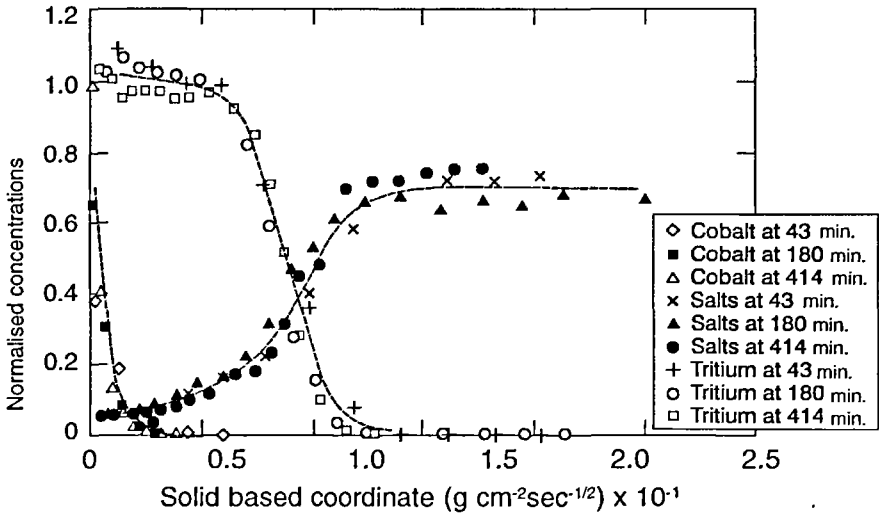


Figure 2

Illustrative results from a set of column experiments. Water-soluble salts, tritium and ⁶⁰Co concentrations are graphed as functions of solid distance divided by the square root of time. To facilitate presentation on the same diagram, the concentrations are normalised (Smiles and McOrist, 2000).

Preliminary batch experimental data for materials from the CNSA region indicate that the K_d for cobalt is strongly pH dependent, with the K_d increasing with increasing pH. The input tracer solution for the column experiments has a pH of 6.0, and measured K_d values in batch experiments for these materials in the pH range from 5.5 to 6.5 were between approximately 10 and 100 ml.g⁻¹. Thus the batch experiments and column experiments both indicate that the cobalt should be more mobile than the cesium, but substantially retarded relative to the tritium. This behaviour is illustrated in Figure 2.

Total Cesium	pH	Measured range of K_d
Trace Cs	7.0	4000 to 9000 ml.g ⁻¹
Trace Cs	8.0	2000 to >10000 ml.g ⁻¹
Trace Cs	9.0	3000 to > 10000 ml.g ⁻¹
$\Sigma Cs = 1 \text{ mmol.l}^{-1}$	various	170 to 330 ml.g ⁻¹

Table 1

Summary of K_d ranges for 11 experiments with Cesium on W1 and W2 soils from the Australian arid zone (mass loading 0.3 g/30 ml). Note the lack of significant pH dependence but a strong effect of total cesium (ΣCs).

Conclusions and recommendations

Measurements of radionuclide adsorption in batch experiments, and measurements of nuclide retardation during absorption of water by columns of relatively dry soils, have been undertaken. The batch experiments enable dependence of retardation on geochemical conditions to be investigated, whilst the column experiments enable retardation under specific conditions to be measured under unsaturated conditions similar to field conditions.

Repository safety assessment requires prediction of the behaviour of any radionuclides released from the repository. For an arid zone repository, this needs to be based on knowledge of water flow and radionuclide retardation in materials at the site. A combination of batch and column experiments can provide the required information on radionuclide retardation for site specific samples.

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