A REPORT TO THE

REPOSITORY TECHNICAL ASSESSMENT GROUP FOR SITING THE
NATIONAL LOW-LEVEL RADIOACTIVE WASTE REPOSITORY
BUREAU OF RURAL SCIENCES

on

RADIONUCLIDE ADSORPTION AND RETARDATION MEASUREMENTS ON MATERIALS FROM THE CNSA REGION INCLUDING SAMPLES FROM THE PHASE III DRILLING PROGRAM

ANSTO Environment Division

CSIRO Land and Water

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RADIONUCLIDE ADSORPTION AND RETARDATION MEASUREMENTS ON
MATERIALS FROM THE CNSA REGION INCLUDING SAMPLES FROM THE
PHASE III DRILLING PROGRAM

by

John R. Harries, Takashi Itakura, Gordon McOrist and Timothy E. Payne
ANSTO Environment Division

and

David Smiles
CSIRO Land and Water

December 2000

EXECUTIVE SUMMARY

Australia is siting and establishing a national near-surface repository in an arid region for the disposal of low level and short lived intermediate level radioactive waste. The selection of the site for the repository is based on criteria recommended in the "Code of Practice for the Near-Surface Disposal of Radioactive Waste in Australia 1992" issued by the National Health and Medical Research Council (BRS 1997). These criteria require that the geochemical and geotechnical properties of the site should inhibit migration of radionuclides. The 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.

In earlier reports, ANSTO and CSIRO (Harries *et al*., 1998, 1999 and 2000) investigated the hydraulic and radionuclide retardation properties of the vadose zone in the central north region of South Australia (the CNSA region) being investigated for repository siting.

In this report, batch measurements of adsorption and column measurements of adsorption and retardation of the radionuclides cobalt-60 and cesium-137 in regolith samples from the drill program are extended to include samples from all lithologies included in the Phase III drilling program. Results are presented for samples from 10 drill holes and at depths from 1.5 m to 77.5 m. Cobalt-60 and cesium-137 have readily detectable gamma rays, will be present in the waste for disposal at the repository and are each representative of the chemistry of a class of radionuclides.

The results for the range of samples selected gave a good indication of the relative radionuclide retardation in the types of geological material expected in and below the repository zone. The results are for samples that were physically modified by the reverse circulation percussion drilling program which produces relatively clean samples not contaminated by material from above the indicated depth. This comminution of the samples does not affect the mineralogy, although structure is greatly altered. The conclusions presented here assume that comminution does not significantly change the relative adsorptive properties of the materials.

Distribution coefficients measured on these samples show that:

    a) trace cesium-137 is adsorbed in all profiles,

    b) adsorption of trace cobalt-60 on the collected samples is variable and depends on the clay content, pH and salt concentration.

    c) the material of Simmens quartzite formation has a reasonable adsorption due to the many clay bands.

    d) the Bulldog shale has reasonable levels of adsorption, with the adsorption decreasing near the bottom of the formation

    e) the Cadna-owie sandstone has lower adsorption for both cobalt and cesium

    f) the Corraberra formation seems favourable for adsorption of the studied radionuclides, presumably due to the presence of various minor phases such as mica and oxides which have good characteristics.

The relative radionuclide retardation properties of the profiles at sites 40a, 45a and 52a are inferred using comparisons of the Simmens, Bulldog, Cadna-owie and Corraberra formations that appear at these sites.

We conclude that

a) all three sites have sufficient clay and other adsorbers in the profiles to retard trace radionuclides,

b) the radionuclide adsorption and retardation data of the samples analysed do not provide a basis to rank any of the sites 40a, 45a and 52a as significantly more favourable in terms of ability to retard nuclides.

Lack of information on the hydraulic properties of profiles below the soil layer means that the rate of migration of the radionuclides in these profiles cannot be estimated from this data. In the natural soils of the region, however, deep water recharge to ground water, in the maximum recharge case of a non-vegetated surface is only about 0.1% of rainfall and even less for vegetated surfaces (Harries *et al.,* 1998, 1999). As a result, residence times for water in the unsaturated zone above the water table are likely to be very great.

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1.   INTRODUCTION

Australia is siting and establishing a national repository for the disposal of low level and short lived intermediate level waste.   The repository will be designed to minimise the release of radioactivity.   In addition to the engineered barriers, the natural system surrounding the repository is a barrier to the release of radionuclides.   It is important in siting and site characterisation to assess how effectively the natural system acts as a barrier to the migration of radionuclides.

The selection of the site for Australia's National Low-Level Radioactive Waste Repository is based on criteria recommended in the "Code of Practice for the Near-Surface Disposal of Radioactive Waste in Australia 1992" issued by the National Health and Medical Research Council (BRS 1997).   Criteria C and G for site selection are:

> **Criterion C:** The geological structure and hydrogeological conditions should permit modelling of groundwater gradients and movement, and enable prediction of radionuclide migration times and patterns.

> **Criterion G:** The site should have suitable geochemical and geotechnical properties to inhibit migration of radionuclides and to facilitate repository operations.

These criteria relate to movement and fate of radionuclides that might be released inadvertently from the repository.   Rate of movement of radionuclides depends on the rate of water movement and the degree to which the radionuclides are retarded with respect to water movement as a consequence of chemical reaction with, and adsorption on, the regolith material.   ANSTO and CSIRO have assessed samples taken in a drilling program, in terms of criteria C and G.

Preliminary desk-top studies (Harries *et al.*, 1998) identified key desirable vadose zone features of sites in the central north region of South Australia (CNSA region) that is being investigated for repository siting.   Water balance calculations were carried out based on estimated soil properties and 30 years of historical daily rainfall and evaporation data.   In a follow up study, measurements of soil profile properties and near surface soil water profiles from the region were used to confirm water balance and deep recharge predictions of the desk studies (Harries *et al.*, 1999).   Batch and column measurements were carried out on representative samples from the Phase 1 drilling program in the CNSA region (Harries *et al.,* 2000).

In this report, batch and some column measurements are extended to include site specific samples from all lithologies included in the Phase III drilling program including Site 52a where Bulldog Shale was encountered.   The retardation results are also assessed in terms of clay characterisation, which potentially can be used to estimate retardation properties.   These results enable all the sites included in the Phase III drilling program to be compared in terms of radionuclide retardation properties.

ANSTO and CSIRO performed complementary experiments to determine the efficacy of retardation in the regolith material.   ANSTO determined, in batch experiments, points on the adsorption isotherm for cobalt-60 and cesium-137 nuclides.   The slope of the adsorption isotherm, in principle, permits us to predict the degree to which a nuclide is retarded relative to the soil water with which it is associated.

In the column experiments, the relatively unsaturated material absorbs nuclides in solution. This process mimics the behaviour of radionuclides in the unsaturated regolith should an

inadvertent release occur. Column experiments directly measure nuclide retardation during unsteady, unsaturated soil water flow. The column method explicitly confirms behaviour that can only be inferred from the batch method. The results presented in this report are for only two radionuclides and a limited range of geochemical conditions. This limited range of conditions does not cover all conditions that might occur beneath the repository. Nevertheless, the comparison of the behaviour for different materials provides a basis for ranking the materials.

1.1 Basic notions of retardation

Capillary flow in the soil pores provides the simplest model of retardation.

- water flow in a cylindrical capillary has a parabolic velocity profile with zero wall velocity;

- at modest flow rates characteristic of natural soil water flow, solute added to this flow preserves a planar front because of radial diffusion and moves at the average speed of the water;

- if solute is adsorbed onto the walls, the front remains planar but it lags behind the water "front" with the amount of retardation determined by the wall's affinity and capacity for the solute;

- a porous material model composed of interconnected "capillaries" behaves much as a single tube in the same sense that Darcy's Law brings together the average movement of water in a porous material and again, a planar solute front tends to form and retardation of this front relative to the water accompanies adsorption.

In soil materials, adsorption and consequent retardation depends on the clay mineral type, clay content and soil pH and soil solution chemistry because:

- clay mineral type and amount control cation adsorption;

- the great specific surface of clay also adsorbs other nuclides;

- pH is important as is shown in the results reported here for cobalt-60;

- the general solution chemistry affects the exchange isotherm of individual cations; and

- organic matter and oxides, particularly iron oxides can be important

2. SAMPLE SELECTION AND DESCRIPTION

Drill samples representative of the geology and lithology in the CNSA region were selected from material collected in the drilling program being undertaken to assess potential sites for the national repository. The drill samples were collected by cyclone for each one metre interval of drill travel. The reverse circulation technique produces samples that are relatively clean and not contaminated by material from above the indicated depth, but the air hammer drilling modifies the structure of the material. This does not affect the mineralogy. The conclusions presented in this report assume that the physical modification of the samples does not significantly change the relative adsorptive properties of the materials.

A total of 38 samples from the surface to a depth of 78 m were selected for the sorption experiments. The samples selected are considered representative of the materials present at the sites being investigated. The selected samples are listed in Table 2.1 together with a short

summary description. The samples were pulverised during drilling and no further crushing was undertaken. Adsorption experiments were conducted with material that passed a 1-mm sieve.

As reported in Harries *et al.,* (2000), X-Ray Diffraction (XRD) measurements were used to determine the major mineralogy of the samples. Harries *et al* (2000) also describes the significance of the identification of smectite, kaolinite and mica/illite for retardation.

Table 2.1. Selected Representative Drill Samples

#	Borehole	Depth	General Description	Formation
1	7	9 to 10 m	Simmens Quartzite	Simmens
2	10	23 to 24 m	Simmens Quartzite	Simmens
3	12	1 to 2 m	Surface Clay	Qc
4	12	9 to 10 m	Yellowish clay bands in quartzite	Simmens
5	13	7 to 8 m	Banded quartzite and kaolinitic clays	Simmens
6	13	10 to 11 m	Grey/green clay	Simmens
7	13	21 to 22 m	Grey/green clay	Simmens
8	13	31 to 32 m	Corraberra Sandstone	Corraberra
9	14	13 to 14 m	Green and grey clays	Simmens
10	14	19 to 20 m	Green and grey clays	Simmens
11	14	23 to 24 m	Green and grey clays	Simmens
12	14	28 to 29 m	Corraberra Sandstone	Corraberra
13	14	32 to 33 m	Siltstone	Corraberra
14	14	33 to 34 m	Siltstone	Corraberra
15	14	40 to 41 m	Corraberra Sandstone	Corraberra
16	14	55 to 56 m	Corraberra Sandstone (below water table)	Corraberra
17	16	1 to 2 m	Surface Clay	Qc
18	16	2 to 3 m	Silcrete	Ts
19	16	10 to 11 m	Banded quartzite and kaolinitic clays	Simmens
20	16	24 to 25 m	Shale with trace sulfides	Simmens
21	16	30 to 31 m	Simmens Quartzite	Simmens
22	16	37 to 38 m	Shale with trace sulfides	Simmens
23	16	46 to 47 m	Corraberra Sandstone	Corraberra
24	16	77 to 78 m	Corraberra Sandstone (below water table)	Corraberra
25	40	45 to 46m	Highly micaceous (sericitised) sandstones of the Corraberra Sandstone	Corraberra
26	41	31 to 32 m	Highly micaceous (sericitised) sandstones of the Corraberra Sandstone	Corraberra
27	Surface exposure	surface	Bulldog shale from near site 52a	Bulldog
28	52a NW	3 to 4 m	Yellowish grey siltstone	Bulldog
29	52a NW	15 to 16 m	Yellowish grey mudstone with fine sandstone fragments	Bulldog
30	52a NW	31 to 32 m	Yellow brown and pale grey sandstone	Cadna-owie
31	52a NW	42 to 43 m	Dark bluish grey silty clay	Cadna-owie
32	52a NW	50 to 51 m	Micaceous siltstone / fine sandstone bands	Corraberra
33	52a SE	3 to 4 m	Greenish white siltstone, minor Fe staining	Bulldog
34	52a SE	14 to 15 m	Pale-grey mudstone	Bulldog
35	52a SE	15 to 16 m	Pale yellow-brown siltstone/shale	Bulldog
36	52a SE	31 to 32 m	Mixed material containing drift sands	Cadna-owie
37	52a SE	43 to 44 m	Choc. brown micaceous siltstone and mudstone.	Corraberra
38	52a SE	50 to 51 m	Interbedded shale / sandstone	Corraberra

3. BATCH MEASUREMENTS

Batch experiments compare the different samples in terms of their ability to adsorb radionuclides. The batch technique is described in Harries *et al.,* (2000). Basically, the adsorption of radionuclide is measured by adding to soils a standard solution at a solid/liquid ratio of 1:10 or 1:100 and allowing 48 hours contact time under gently shaking conditions. The batch experiments were undertaken with an initial solution composition of NaCl (0.5 M) or saturated $CaSO_4$. Some cobalt sorption experiments were undertaken with the pH unadjusted and some with pH controlled during the experiment to between 6.5 to 7.0. The NaCl solutions represented the major element composition of infiltration and ground waters. Gypsum ($CaSO_4$) is abundant in some of the profiles in the CNSA region, so some experiments were carried out with saturated $CaSO_4$ solution.

The distribution coefficients, K_d, measured in the batch experiment are listed in Table 3.1. This table includes the results reported in Harries *et al.,* (2000).

3.1 Factors determining Co and Cs sorption

The experimental data for sorption of trace Cs and Co at natural pH values with the two electrolytes are compared in Figure 3.1. The data show that trace Cs is strongly adsorbed by all the materials ($K_d > 30$ mL/g), and there is no significant pH dependence. The K_d values for Cs added in the saturated $CaSO_4$ solution are on average a factor of five higher than those measured when added in 0.5 M NaCl. This is attributed to the higher ionic strength of the NaCl solution leading to greater competition of Na^+ for surface sites and partial displacement of Cs^+ ions.

The main factor determining Co sorption is the pH, with K_d increasing by about an order of magnitude per pH unit. The Co sorption results obtained in the two electrolytes are very similar, although the $CaSO_4$ data appear to be more scattered.

The data in Figure 3.1 relate to samples which have a variety of mineralogical compositions and equilibrium pH values. For a given sample, the pH values obtained with the two electrolytes were similar. The low pH obtained in some experiments may be an intrinsic in-situ property of the materials or may result from oxidation during drilling or storage. Several of the lower experimental pH values were associated with samples indicated in the drill log as containing trace sulfides. The higher pH values (> 7.5) were mostly for shallow samples obtained within 1-2 m of the ground surface.

For some samples from greater than 30 m, the equilibrium pH in the batch experiments was less than 5, suggesting oxidation of contained pyritic material during drilling, storage and/or experiment. Since this oxidation will not occur unless the material is broken up and exposed to the atmospheric oxygen and these samples are from a depth that will not be disturbed in repository construction, it is recommended that the comparison of lithologies be based on the experiments with controlled pH (see Table 3.1). Under the controlled pH conditions, the distribution coefficient for cobalt-60 measured in batch experiments exceeded 40 mL/g for all except two samples.

The observed pH dependence of Co and Cs sorption is similar to that reported on other substrates by various authors (Tewari *et al.,* 1972, Serne and Relyea 1982).
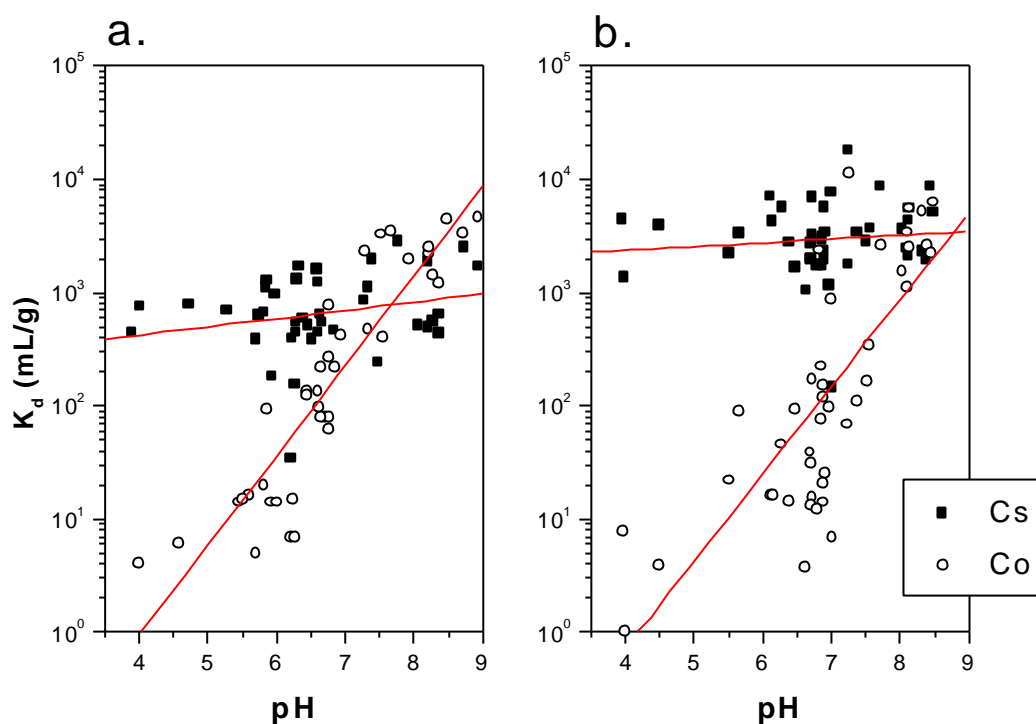
Figure 3.1 Distribution coefficients for trace radionuclides (Co-60 and Cs-137) obtained with samples from the CNSA region of Australia with (a) 0.5 M NaCl and (b) saturated $CaSO_4$. The pH is the equilibrium pH of the sample in contact with the solution.

The general geology of the samples as described by the drill log is indicated for each data point for Figure 3.2, which presents data for both trace Cs and higher total Cs concentration of 1 mmol/L. There is no strong systematic dependence of the K_d for trace cesium on the geology of the sample. Based on the literature, it would be expected that shale or siltstone would have higher values of K_d and hence will retard movement of cesium more than sandstone or quartzite (McKinley and Scholtis 1992, Sheppard and Thibault 1990). However, the data suggest that there is only a slight dependence of K_d on the geological origin of the samples. This may be because the drilling procedure bulks together materials from different layers within the metre sections and the samples are therefore composites over those intervals.

The K_d values obtained with higher total Cs are much lower than those obtained with trace Cs. This commonly observed decrease of K_d with increasing concentration reflects the reduced sorption affinity as the occupancy of surface sites increases.

The sorption data obtained with higher total Cs also have little or no pH-dependence. However, the near-surface clay materials yielded higher K_d values in these experiments (Figure 3.2), and reached a higher equilibrium pH value than the other samples. Based on analysis of XRD data reported by Payne *et al* 2000, the higher cesium K_d values are likely to be due to higher smectite content of the surface soils.
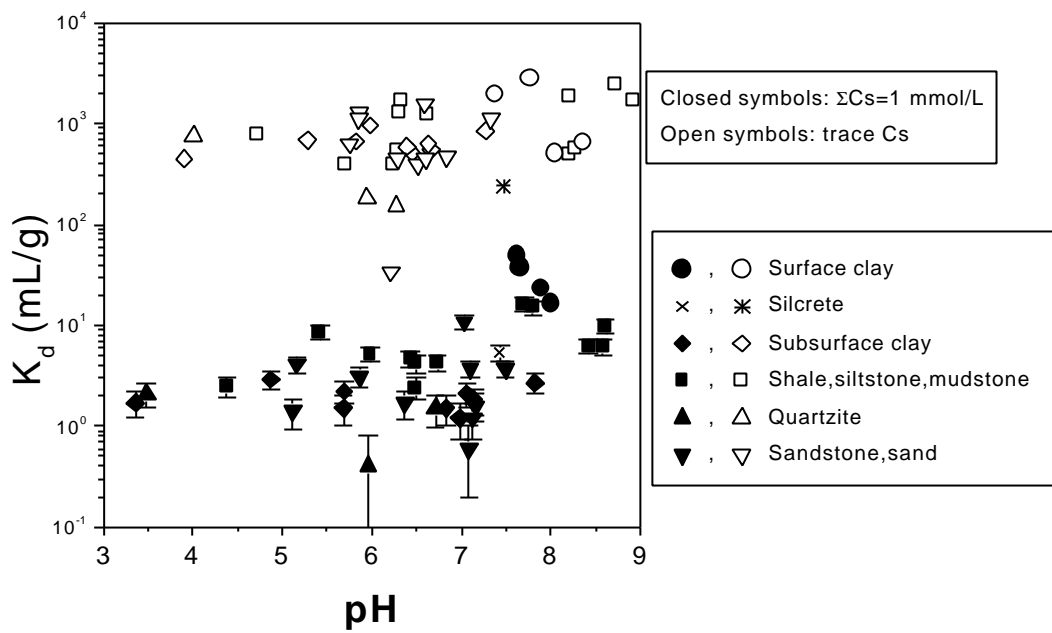
Figure 3.2 Distribution coefficients for trace Cs-137 and total Cs of 1 mmol/L obtained with samples from the CNSA region of Australia with 0.5 M NaCl. The pH is the equilibrium pH of the sample in contact with the solution. Each data point represents an experiment with a different sample, carried out at the pH attained by the samples. The symbol shape indicates the general geology of the samples from the drill log.

Table 3.1 K_d values (mL/g) measured using the batch technique, samples ordered by formation. The initial solution added was 0.5 M NaCl or saturated $CaSO_4$. The pH is the pH of the sample in equilibrium with these solutions, and in one experiment the pH was controlled to between 6.5 and 7.

Hole	Depth	Formation	Description	K_d Trace Cs in NaCl	K_d Trace Cs in CaSO$_4$	K_d 1 mmol/L Cs in NaCl	pH Trace Co in NaCl	K_d Trace Co in NaCl	K_d Trace Co pH controlled in NaCl	pH Trace Co in CaSO$_4$	K_d Trace Co in CaSO$_4$
13	7.5	Sim	Clay in Qz	513	1776	2.1	6.77	79	79	7.24	68
16	10.5	Sim	Clay in Qz	854	2812	2.7	7.54	395	142	7.51	164
12	9.5	Sim	Clay in Qz	633	3379	1.8	6.71	79	79	7.38	110
13	10.5	Sim	Clay in Qz	586	1963	1.2	6.76	61	61	6.89	20
13	21.5	Sim	GreyGrnClay	545	2704	1.5	6.63	95	96	6.71	31
14	13.5	Sim	GreyGrnClay	959	2734	2.2	5.82	20	79	6.38	14
14	19.5	Sim	GreyGrnClay	671	3281	1.5	6.00	14	43	6.72	16
14	23.5	Sim	GreyGrnClay	690	6969	2.9	5.61	16	93	6.11	16
7	9.5	Sim	Qzite	154	1155	1.5	6.43	122	197	6.97	97
10	23.5	Sim	Qzite	182	1042	0.4	5.92	14	23	6.63	4
16	30.5	Sim	Qzite	747	4392	2.1	4.00	4	56	3.96	8
16	24.5	Sim	Shale / sulf	1231	6879	4.3	6.95	424	423	6.72	168
16	37.5	Sim	Shale / sulf	789	3911	2.5	4.57	6	191	4.49	4
52aNW	3.5	Bul	Siltstone	489	2473	15.1	8.21	2231	1458	8.09	3381
52aSE	3.5	Bul	Siltstone	557	1917	8.5	8.28	1418	1299	8.38	2603
52aSE	14.5	Bul	Mudstone	550	2359	16.2	6.28	6	54	6.89	14
52aNW	15.5	Bul	Mudstone	388	2017	4.2	5.70	5	82	6.70	13
52aSE	15.5	Bul	Siltstone	390	1720	2.4	6.23	15	44	6.79	12
52aNW	31.5	Cad	Sandstone	34	144	0.6	6.21	6	13	7.01	7
52aNW	42.5	Cad	Blue clay	447	1359	1.7	3.90	0	44	3.99	1
52aSE	31.5	Cad	Sdstone/sand	1112	3681	3.7	7.33	467	352	7.56	337

Table 3.1   Continued

Hole	Depth	Formation	Description	K_d Trace Cs in NaCl	K_d Trace Cs in CaSO$_4$	K_d 1 mmol/L Cs in NaCl	pH Trace Co in NaCl	K_d Trace Co in NaCl	K_d Trace Co pH controlled in NaCl	pH Trace Co in CaSO$_4$	K_d Trace Co in CaSO$_4$
14	28.5	Cor	Sdstone	1290	4200	4.1	5.46	14	134	6.14	16
13	31.5	Cor	Sdstone	449	1964	1.7	6.65	80	80	6.69	39
14	40.5	Cor	Sdstone	628	2222	1.4	5.50	15	122	5.51	22
16	46.5	Cor	Sdstone	1107	3326	3.1	5.87	92	269	5.66	88
14	55.5	Cor	Sdstone	466	1668	1.6	6.77	271	271	6.47	94
16	77.5	Cor	Sdstone	447	1721	1.2	6.85	219	219	6.87	120
14	32.5	Cor	Siltstone	1706	5660	5.2	6.60	133	139	6.28	45
14	33.5	Cor	Siltstone	1304	5666	4.7	6.45	135	213	6.89	154
40	45.5	Cor	Mica sandst	1590	7645	10.7	6.77	771	771	6.99	870
41	31.5	Cor	Mica sandst	386	2942	3.7	6.65	221	308	6.86	223
52aNW	50.5	Cor	Siltstone	2502	3571	9.9	8.72	3347	1029	8.03	1518
52aSE	43.5	Cor	Siltstone	1883	5464	6.2	8.21	2487	1330	8.13	2519
52aSE	50.5	Cor	Shale	1680	8585	6.1	8.93	4652	877	8.44	2226
16	1.5	Qc	Clay	647	4299	16.7	8.49	4464	1543	8.12	5530
12	1.5	Qc	Clay	512	5062	23.3	7.93	1962	1315	8.48	6234
16	2.5	Ts	silc	239	1754	5.3	7.28	2268	1776	6.81	2349

Sim – Simmens

Bul – Bulldog

Cad – Cadna-owie

Cor – Corraberra

Qc – Quaternary (surface clay)

Ts – silcrete

4. COLUMN EXPERIMENTS

Solutes in the regolith are advected with, and diffuse relative to, the soil water. These processes are moderated by chemical reaction on the reactive surfaces of the regolith matrix. Ion exchange theory predicts that retardation of the ion, *relative to the water*, will be proportional to the slope of its exchange isotherm in the chemical environment of the flow.

The use of space-like material coordinates, based on the distribution of the solid and of the water, in the analysis of the column experiment, provides useful insights that are not immediately evident in physical space, into distribution and movement of solutes. The flexible use of these coordinates also helps analyse chemical reactions and, in this case, the retardation of nuclides. The approach seeks to generalise absorption/chemical reaction measurements and hydraulic properties.

Full theoretical detail is found in papers accepted by *MRS2000* (Smiles and McOrist 2000) and by the *Australian Journal of Soil Research* (Smiles 2001). The methods and discussion that follow are restricted to the properties that are relevant to the site selection criteria.

4.1   Experimental method

Smiles and Philip (1978) and Harries *et al.* (2000) describe the method. A uniform, relatively dry, horizontal column of soil absorbs aqueous solution from a source at constant water potential and the solutes in the solution react with those in the soil. The invading solution appears to displace soil solution originally present like a piston, and hydrodynamic dispersion spreads the solute on the "piston front". Retardation of the solute is seen as a "delay" of the solute concentration front relative to the movement of the piston front. This delay is predictable using the slope of the adsorption isotherm for conditions relevant to the absorption experiment.

Soil at an initial low water content was packed into a sectioned cylindrical column of internal diameter 20 mm. The soil was added in increments of 2-3 grams and packed using a small drop-hammer to ensure uniformity. Saturated $CaSO_4$ solution containing radionuclides was applied at zero water potential to one end of the column. The experiments were terminated after a specified time and the columns sectioned. Each moist section was weighed and then counted using gamma and or beta spectrometry to determine the amount of radionuclide present. Water soluble salts, conductivity and tritium were then measured in a water extract based on 2.5 parts water to 1 part soil. Dilutions were tracked by weighing and all quantities were referred to the oven dry weight of soil in each section which was determined following these measurements. Concentration data were graphed as a function of distance divided by the square root of time at which the profiles are measured (Smiles and Philip 1978). The water content and solute profiles fall on single curves (are self-similar or reveal similarity) when graphed in this way if the theory is correct and the initial and boundary conditions are realised.

Three sets of experiments were performed:

a)   Preliminary experimental sets for Site 14:19-20m and Site 16:1-2m and 10-11m were described in Harries *et al*. (2000). These experiments used saturated $CaSO_4$ containing Co-60, Cs-137 and H-3, and critical data are tabulated here for completeness. Two further sets of experiments were conducted as a result of these experiments.

b)   Experiments to assess the effect of clay mineral concentration in the regolith material. These experiments were intended to establish whether a clay-based coordinate would permit generalization of behaviour across regolith materials of varying clay content. Material from a depth of 10-11m at Site 16 was mixed with three different amounts of acid washed sand.

c)   Comparison of regolith material from 4 levels from Site 52aNW in terms of their ability to retard movement of nuclides.

Experiments in (b) and (c) focussed on tritiated water and Co-60 in saturated $CaSO_4$. Gypsum was used because it tends to high concentration in these materials and, because it is relatively insoluble, it tends to maintain chemical saturation for a considerable time during the passage of most absorbed waters. Gypsum also ensures that structural stability is maintained.

Tables 4.1(a), (b), and (c) respectively summarise salient features and derived results of experimental sets (a), (b), and (c) above.

4.2   Results and discussion of column experiments

A minimal experimental data set is presented to indicate characteristic forms of behavior. These data provide sufficient detail to derive key numbers in the summary Tables 4.1. Full explanation is presented in Smiles (2001).

4.2.1   Preliminary experimental set for Site 14:19-20m and Site 16:1-2m.

We recall from Harries *et al* (2000) that tritiated water moves as does ordinary water so H-3 is not retarded relative to the water. Cs and Co are however retarded with the magnitude of the phenomenon proportional to *b*, the slope of the Cs and Co adsorption isotherm. *b* is the distribution coefficient identified by the symbol K_d in the batch experiments. We use a different symbol because of the different conditions under which it is estimated. In addition, in the column experiments we use a molal convention to define solution concentration so the dimensions of *b* are (g of solution/g of soil) rather than (mL of solution /g of soil) for Kd. Approximate and minimum values of *b*, for Cs and Co are found in Table 4.1. They are *minimum* values for samples from Site 16:1-2 and Site 16:10-11 because the cations did not move beyond the first section in the columns and the location of the front within the section is unknown. As can be seen from Figure 4c of Harries *et al* (2000) for the sample from Site14:19-20 the cesium barely moved into the second section, whereas cobalt had a clear profile. These preliminary results led us to focus on Co in the sample from Site 14:19-20 as the radionuclide that is least retarded.

It is important to make two comments because they apply both here and to the later column data.

a)   These *b*-values represent chemical conditions that arise during invasion of these solutes under conditions, where the initial soil solution is swept ahead by the incoming solution.

b)   As a rule of thumb (but see eg Freeze and Cherry 1979), retardation of the nuclides will be approximately 4-5 times *b*. A *b* value of about 2 will therefore reduce the movement of the nuclide relative to the water by a factor of about 10.

4.2.2   The effect of clay mineral concentration in the regolith material.

Figure 4.1 shows the water content profiles observed in these experiments. Here, q_g, the mass fraction of the water is graphed as a function of solid space (*m*) divided by the square root of

time (t). The solid-based coordinate is the cumulative mass of solid per unit area of column cross section measured from the origin of the column. In a non-swelling soil, it is simply related, through the bulk density, to physical space. In a swelling soil, it provides the rational basis for analysis of 1-dimensional water flow.

In Figure 4.1, the profiles with the same clay content but sectioned at different times preserve similarity and thus confirm that basic flow laws are obeyed and that the initial and boundary conditions are realised. Those materials containing different amounts of sand differ systematically with the sorptivity, S (g/cm^2.s$^{1/2}$) increasing with sand content. The sorptivity is the cumulative volume of water absorbed in unit square root of time: it is a characteristic of the flow process and of the material (Philip 1957).

Figure 4.2(a) shows the ^{3}H profiles as functions of $M = mt^{-1/2}$ for each experiment. The data set determined in the "natural soil" preserves similarity, the others are systematically different, with the displacement of the inflection points reflecting the differing sorptivities evident in Fig. 4.1. The concentration of ^{3}H expressed per unit mass of soil solid reflects the water content profiles shown in Fig. 4.1, and the area under each curve equals C_i´S (Bq/cm^2 s$^{1/2}$), the total amount of tritium absorbed by each column. The "centres-of-mass" of the ^{3}H fronts (see Table 4.2) lie behind the water fronts shown in Fig. 4.1 as the piston displacement model requires.

Figure 4.2(b) shows the ^{60}Co concentrations as functions of $M = mt^{-1/2}$. This is the *total* Co; that is the water soluble plus adsorbed components. Again, the integral under these curves equals the total amount absorbed. The notion of a ^{60}Co front is more difficult to visualise with these "concave upwards" profiles but the "centre of mass" of the profile provides a useful surrogate. The centres of mass (CM in Table 4.2) lie well behind the water front of Fig. 1 and also behind the ^{3}H and soluble salt "fronts" of Figs 2(a) and (c). The variation in location of the front evident in Fig. 4.2(b) arises because chemical retardation decreases with clay content and the solution also travels further as the sorptivity increases with decreasing clay content. We show how these different effects can be dealt with below.

Figure 4.2(c) presents corresponding water-soluble salt profiles. It is evident that the inflowing solution displaces the soil solution originally present. The "retreating" salt front corresponds with the advancing tritium front as theory anticipates. It is important to note the very high solution salt concentrations that initially existed in this material and that nuclide exchange and adsorption occurs in a chemical environment that approximates that of the invading solution.

Figures 4.3(a) and (b) show the ^{3}H and the ^{60}Co concentrations presented in a water-based space-like coordinate system. This coordinate has, as its origin, the notional piston front that separates the invading water from that originally present were displacement of the latter by the former perfect. The coordinate is positive ahead of the front and negative behind it, it is numerically equal to the cumulative amount of water per unit area measured in either direction away from the piston front.

The advancing "front" for ^{3}H is located at the origin of this system and is distributed about it because of diffusion relative to the water. This is consistent with the notion that the tritiated water behaves like water. The ^{60}Co profiles are significantly retarded relative to the origin of the water-based coordinate. This effect is related to the retardation factor (eg Bolt 1976, Freeze and Cherry 1979, Hashimoto *et al.* 1967, Lai and Jurinak 1972); it reflects the average slope of the adsorption isotherm for ^{60}Co *in the chemical environment of the soil during this displacement process*. The ratio of the locations of the nuclide fronts in water space and solid space is equal to -$\boldsymbol{b}$ (Smiles 2001). Values calculated from these data are found in Table 4.2

The distinct effects of sorptivity and clay content on retardation of Co can be dealt with if we graph the Co concentration in terms of a clay based space like coordinate which we normalise with regard to the sorptivity. Figure 4.4 shows the data of Figure 4.2(b) regraphed by

a) expressing the ^{60}Co concentration data in terms of *unit mass of clay* rather than unit mass of *soil*. The material coordinate must then be expressed as the cumulative mass of *clay* per unit area of cross section rather than unit mass of *soil*.

b) normalising this clay based space-like coordinate according to the sorptivity, *S*. As before, this accounts for the different amounts of ^{60}Co in each column because different amounts of solution and hence ^{60}Co are absorbed in each experiment.

This procedure brings the different data sets together within reasonable experimental error. It reveals quantitatively:

a) that high clay content at the inflow surface results in a high total amount of [60]Co *per unit amount of soil* and greater retardation and that a lower clay content proportionally reduces the retardation and the amount of ^{60}Co per unit amount of soil, and

b) that effects of hydraulic properties of the system can be dealt with quantitatively and independently.

4.2.1. Properties of selected material from Site 52aNW.

Figure 4.5 corresponds to Fig. 4.1 above and sets out the water content profiles observed during these experiments. The pairs of experiments again preserve similarity when graphed in terms of *M* although each set is different. The disturbed material will have quite different hydraulic properties and hence sorptivities to that *in situ*.

Figures 4.6(a) and (b) show the Co-60 profiles in solid-based material space, normalised with regard to the sorptivity for Site 52a:Top and 5m (a), and Site 52a:16m and 31m (b). Figures 4.7(a) and (b) correspondingly show these data graphed in normalised water-based space. Note the quite different behavior of the surface 5m when compared with the material at depth.

Analysis of these data lead to the values of *b* shown in Table 4.3.

Table 4.3 in concert with the particle size data and water soluble salt data, suggest that:

a)   The surface 5 m or so appears basically similar with modest clay contents, soluble salt contents of 2-4% by weight, and values of $b \approx 18$ (g/g).

b)   Site 52a:15m however has quite high clay contents and high salt contents (4% by weight) but $b \approx 0.6$ (g/g), that is 30 times less than the surface. We have no explanation for this without further experiments.

c)   Site 52a:31m has $b \approx 0.3$ (g/g). This may be attributed to the very low clay content.

4.3   Discussion of column results

4.3.1   General issues

The column procedure determines the fate of a nuclide during absorption of solution containing that nuclide into soil. Data should be qualitatively consistent with results from the batch experiments described in Section 3 above; the issue is discussed in more detail below. The column measurement is made in association with the cation and anion suite actually initially in the soil during the displacement reaction process.

Where experiments such as these are used, normalization of data provides useful ways to identify and generalise behaviour across different soil materials. The procedures used here are physically based and, qualitatively, one would expect them to lead to substantial unification of data. It is useful to enumerate them:

a) Use of water based material coordinates permit us to discriminate between the hydrodynamic process of advection ["passive" transport of solute] and dispersion [the redistribution of solute as a result of concentration gradients in the soil water]. Each element permits independent analysis and subsequent synthesis. We use this approach

b) Normalization based on the sorptivity is a physically-based and powerful procedure that ensures that the total amount of a solute that has entered the soil during absorption is comparable across systems. It does not obscure retardation relative to the piston front for the water due to adsorption. It permits extension of laboratory experience to the field provided reliable field data is available.

c) The results show that, generally, the clay content of the material is a critical selection characteristic *but*

d) Behaviour of the sample from Site 52a:15m, which has significant clay but which has a low retardation for Co-60 is exceptional and requires further examination to understand the processes occurring.

4.3.2 Specific conclusions based on column experiments on samples from Sites 14 and 52a.

We focus on the value of b, and note, subject to general disclaimers set out earlier in relation to the effects of comminution, that

a) Material from Site 52aNW 0-5m (and also the topsoil of Site 16) is much more retentive of Co-60 ($b \approx 18$ units), than is material from Site 16:9-10m ($b \approx 1.6$ units), and this is in turn much more retentive than material from Site 52aNW at 15m or 31m ($b \approx 0.6$ and 0.3 units respectively),

b) A corollary of these data for Site 52aNW is that 1m of the surface material is equivalent to 18/0.6 (=30) m thickness of the material at 15m or 18/0.3 (=60) m of the material at 31m at that site. It follows that 1 m of the local "topsoil" at Site 52a will be a very effective in retaining Co-60.

c) The surface material from Site 52aNW is as retentive as any we have measured in the survey to date for Co-60. Its capacity to retain the Cs-137, inferred from batch experiments and exploratory column experiments, is greater than that for the Co-60.

d) Tritiated water moves as does water and its retardation is related solely to the hydraulic properties of the regolith.

Table 4.1 – Key preliminary experimental details with Site 16 and 14 material [see Harries *et al*. 2000 for more detail]

Sample	Nuclide	Time [min]	q_l	b $g_{wat} \cdot g_{sol}{}^{-1}$
#14:17-20	Co	32.5 and 169	0.06	1.2-1.6
	Cs			4.8-6.4
#16:1-2	Co	1285 and 380	0.12	>4
	Cs			>4
#16:10-11	Co	180 and 900	0.07	>2
	Cs			>2

Table 4.2 (a) – Key Experimental details with Site 14:17-20 material. Experiments 1, 2 and 3 were with the sample as collected from the field, in experiments 4,5 and 6 the clay content has been reduced by addition of silica sand to the sample

Expt	%Clay	% Silt	% Sand	Time [min]	q_i	r g cm^{-3}	S g cm^{-2} s$^{-1/2}$	b $g_{wat} \cdot g_{sol}{}^{-1}$	$b/clay$ $g_{wat} \cdot g_{sol}{}^{-1}$
1	14	11	75	43	0.07	1.83 ±0.07	1.56×10^{-2}	1.58	11.3
2	14	11	75	180	0.07	1.85 ±0.05	1.4×10^{-2}		
3	14	11	75	414	0.07	1.84 ±0.05	13.6×10^{-2}		
4	11.2	8.8	80	57	0.06	1.72 ±0.07	5×10^{-1}	1.31	11.7
5	9.1	7.2	83.7	32	0.05	1.64 ±0.07	7.8×10^{-2}	1.07	11.8
6	8	6.3	85.7	13	0.04	1.61 ±0.05	1.12×10^{-1}	0.96	12.0

Table 4.3 Clay mineralogy of Site 14:17-20m

Measured by X-ray diffraction on the less-than 2µm sample. The values in parenthesis are the errors in the last significant figure reported from SIROQuant. SIROQuant is a statistical package that integrates beneath an XRD trace to provide a semi-quantitative estimate of the relative amounts of different minerals in a sample.

Illite	Kaolinite	Smectite	Quartz	Anatase
71 [2]	9 [1]	13 [1]	6 [1]	<1

Table 4.4 – Key Experimental details with Site 52aNW material

Expt	%Clay	% Silt	% Fine Sand	Time [min]	q_i	Salts $g/100g$	r $g\ cm^{-3}$	S $g\ cm^{-2}\ s^{-1/2}$	b $g_{wat}\text{-}g_{sol}^{-1}$	$b/clay$ $g_{wat}\text{-}g_{clay}^{-1}$
Top	30	29	24	7	0.06	2.17	1.54 ±0.09	1.19×10^{-1}	18	60
				16	0.05	2.18	1.52 ±0.06	1.16×10^{-1}		
3-4m	21	29	27	24	0.02	4.10	1.35 ±0.02	3.82×10^{-2}	18	72
				68	0.02	4.08	1.38 ±0.04	3.53×10^{-2}		
15-16m	28	21	28	22	0.35	0.410	1.71 ±0.05	4.10×10^{-2}	0.6	2
				60	0.35	0.360	1.69 ±0.05	4.30×10^{-2}		
19-20m						0.348				
						0.346				
31-32m	3	6	32	18	0.01	16.4	1.78 ±0.05	5.82×10^{-2}	0.3	20
				50	0.01	16.7	1.75 ±0.09	6.2×10^{-2}		
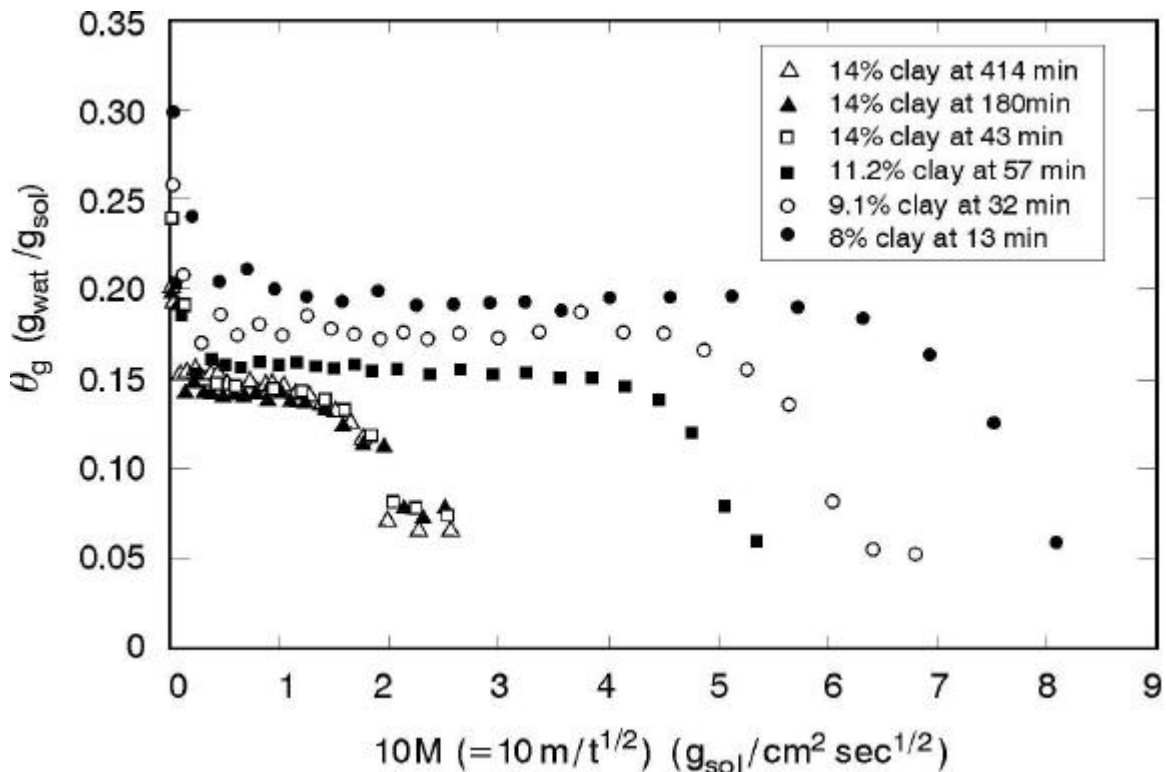
Figure 4.1.　Water content profiles for different soil and mixtures and determined at different times as shown on the figure. The water content, q_g, is expressed as the mass fraction (relative to oven dry weight); the space coordinate $M = m/t^{1/2}$, is the cumulative *mass* of oven dry soil per unit area of cross section, divided by the square root of the time at which the profiles were measured.
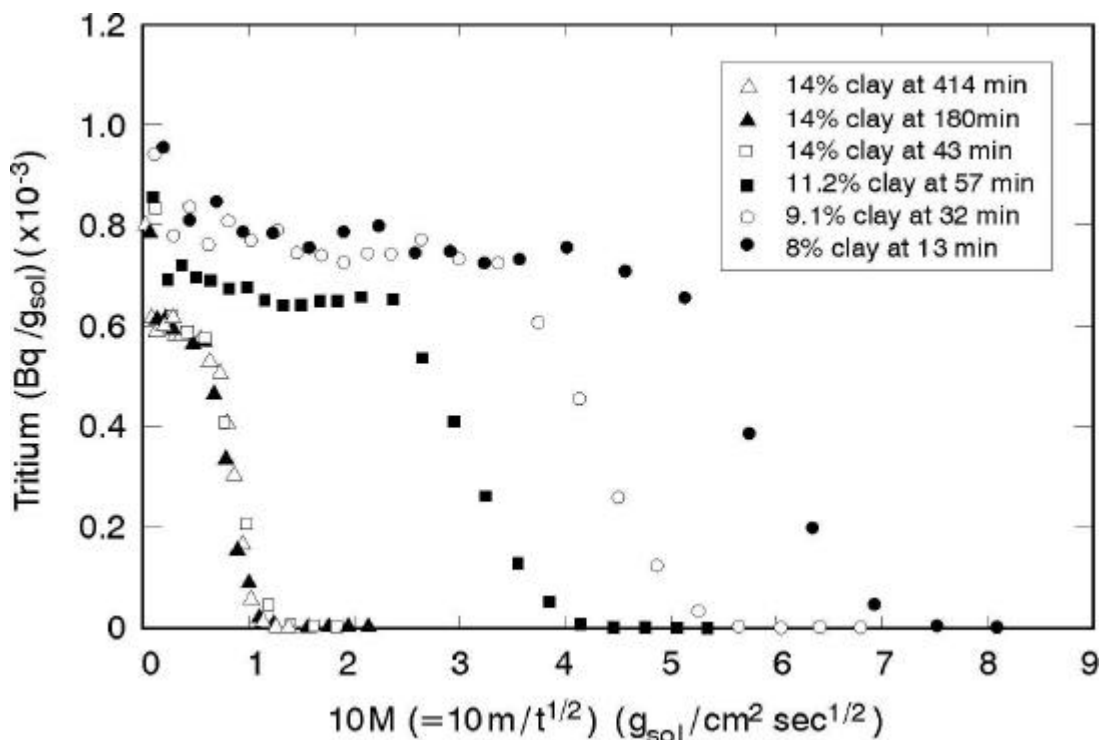

Figure 4.2(a) Tritium concentration measured in 1:2.5 extracts from the sections shown in Fig. 4.1 and graphed as a function of M (the mass-based coordinate of that figure). The activity of the ^3H is expressed as Bq per unit mass of dry soil.
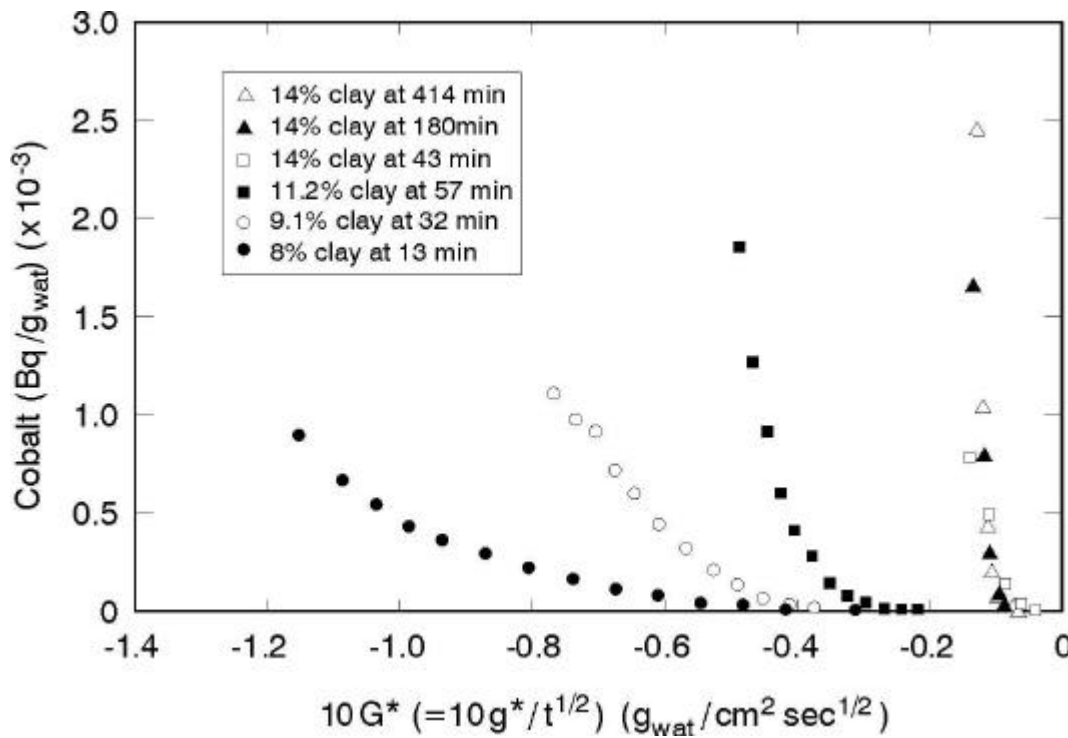
17
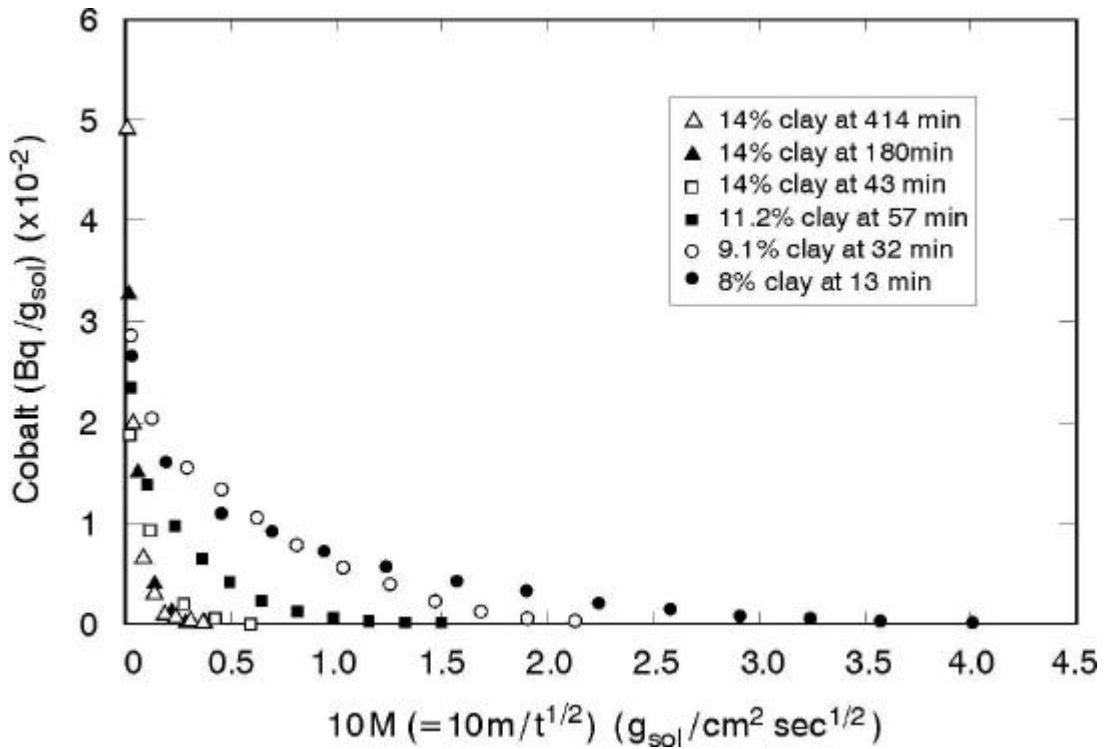
**Figure 4.2 (b)** Cobalt (as ^{60}Co) measured by gamma spectroscopy on the soil from the sections shown in Fig. 4.1 and graphed as a function of *M*. The activity of the Co is expressed as Bq per unit mass of dry soil.
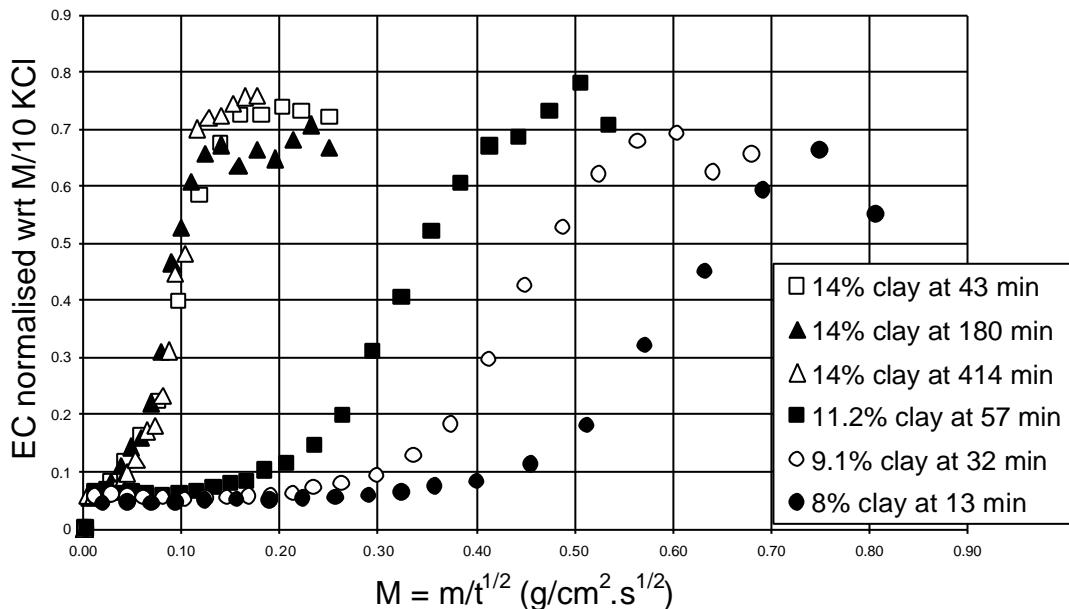
Figure 4.2(c). Water soluble salt normalised in 1:2.5 extracts from the sections shown in Fig. 4.1 and normalised with regard to M/10 KCl. M is the mass based coordinate of that figure.
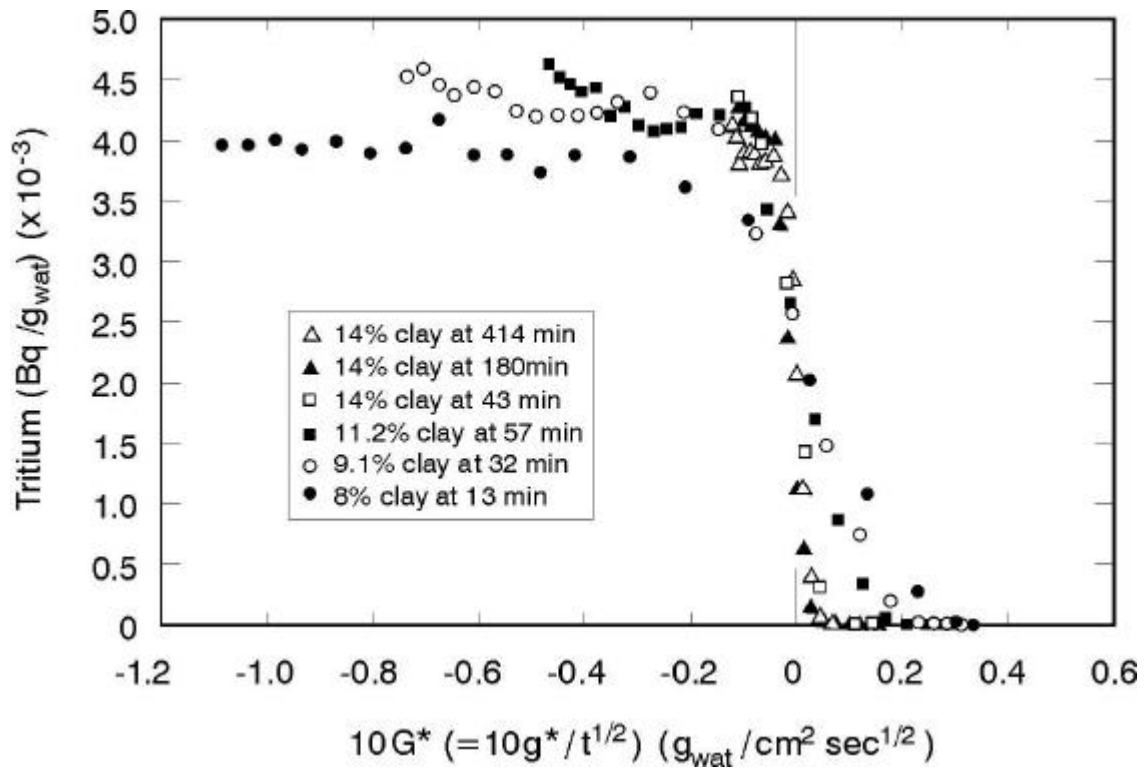
Figure 4.3(a) Tritium concentration measured in 1:2.5 extracts from the sections shown in Fig. 4.1 and graphed in terms $G*$ a water-based coordinate.

Figure 4.3(b) Cobalt (as ^{60}Co) measured by gamma spectroscopy on the soil from the sections shown in Fig. 4.1 and graphed as a function of $G*$.
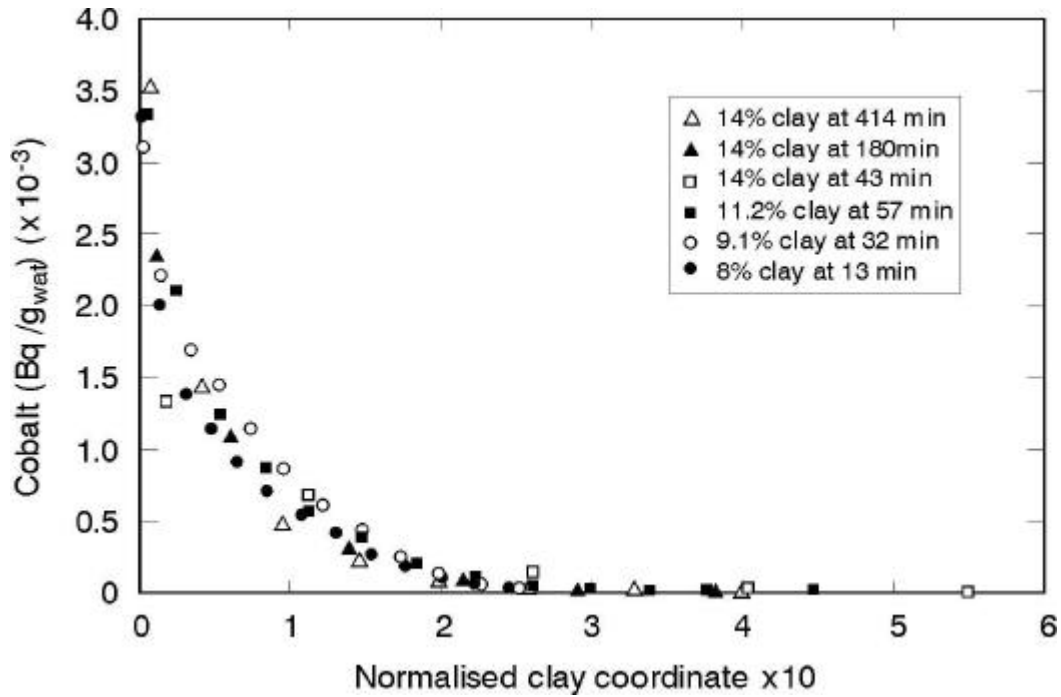
Figure 4.4. ^{60}Co data of Fig. 4.2(b) regraphed after expressing the Co concentration as Bq per unit mass of clay, and recalculating the space coordinate so that it is clay-based rather than soil-based, and normalizing this coordinate according to the appropriate value of the sorptivity, S.
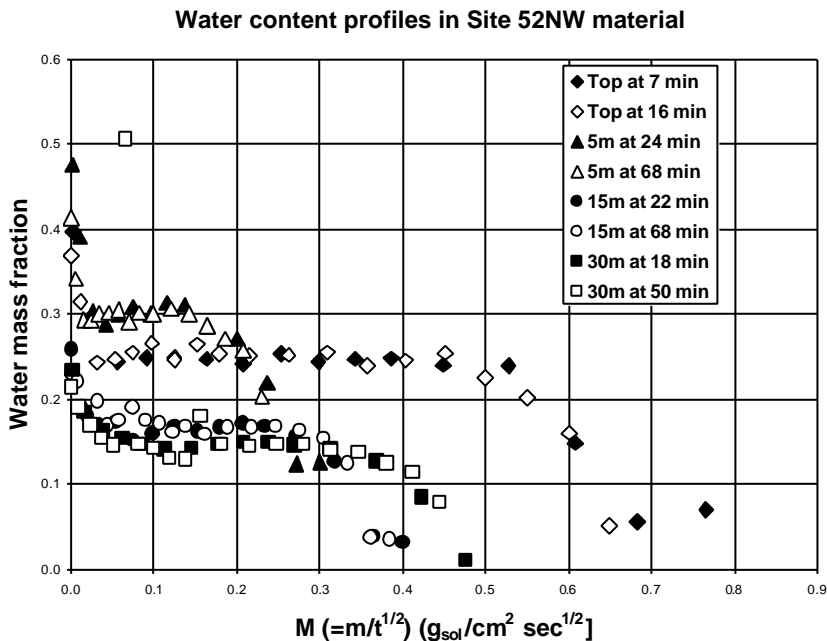
Figure 4.5

Water content profiles for different soil and mixtures and determined at different times as shown on the figure for Site 52aNW samples. The water content, q_g, is expressed as the mass fraction (relative to oven dry weight); the space coordinate $M = m/t^{1/2}$, is the cumulative *mass* of oven dry soil per unit area of cross section, divided by the square root of the time at which the profiles were measured.
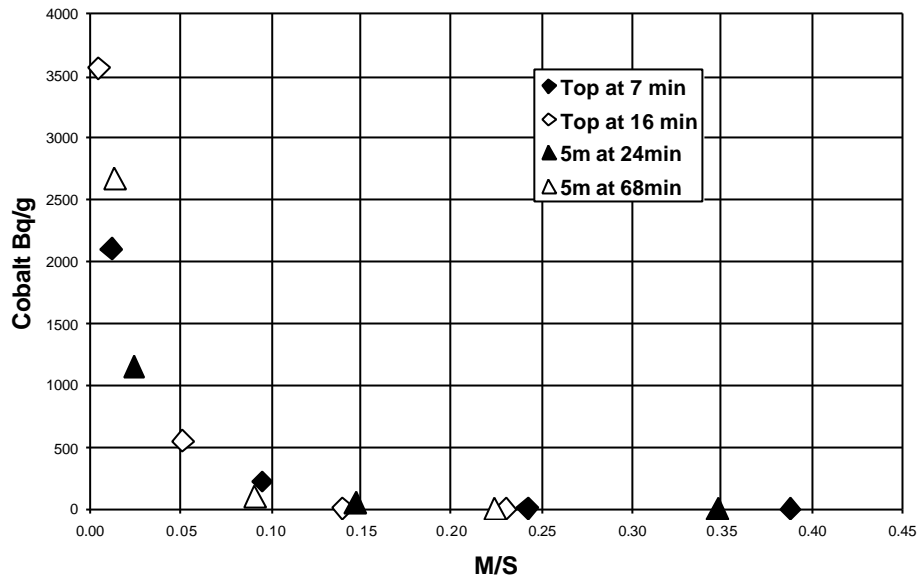
Figure 4.6(a). Cobalt profiles in normalised solid based space for the Top and 5m samples of Site 52aNW. These graphs are similar to those for Site 16 shown in Fig. 4.3(b)
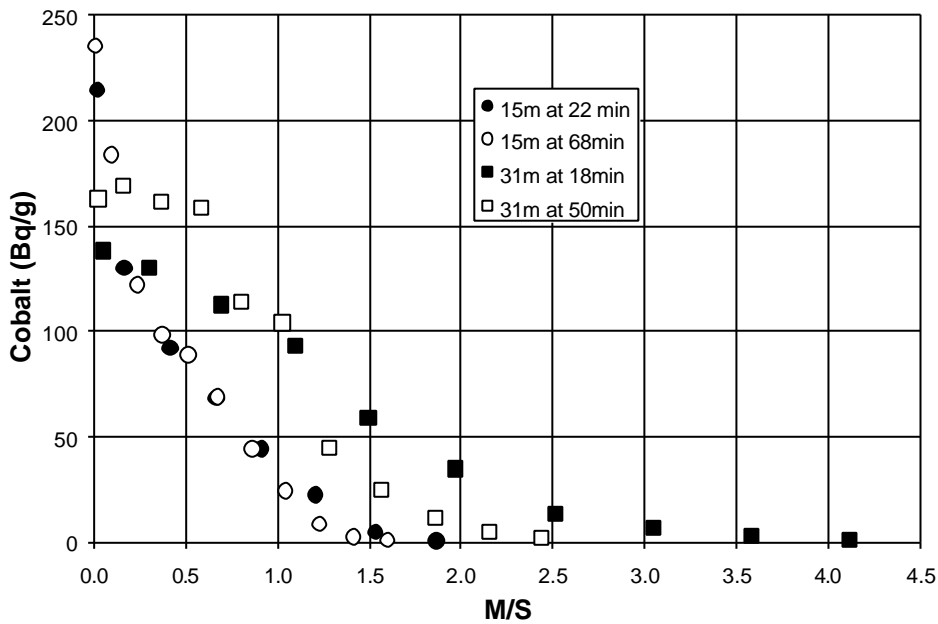

Figure 4.6(b). Cobalt profiles in normalised solid based space for the 16m and 31m samples of Site 52aNW. Note the greater penetration of Co in these profiles when compared with Fig. 4.7(a).
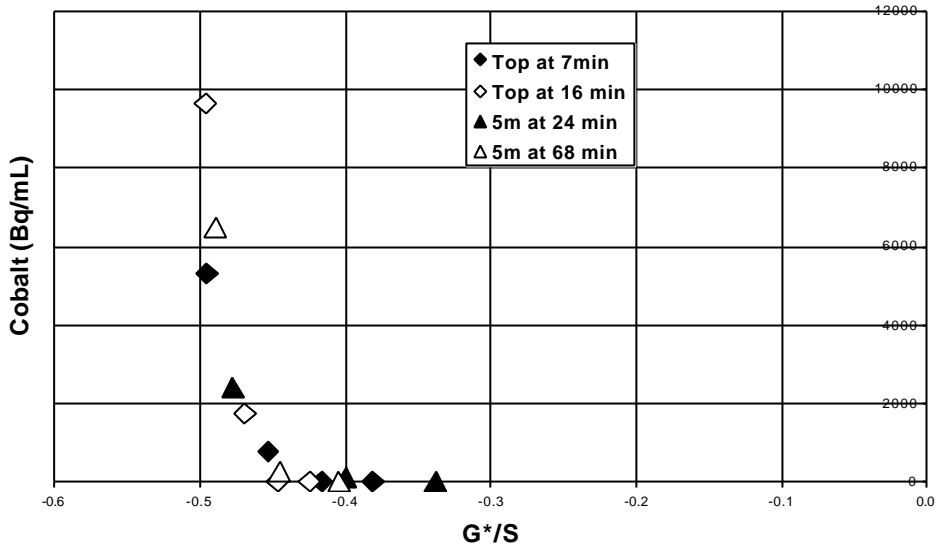
Figure 4.7(a). Graph showing Co profiles in normalised water based space (cf Fig. 4.4(b) for the Top and 5m samples of Site 52aNW
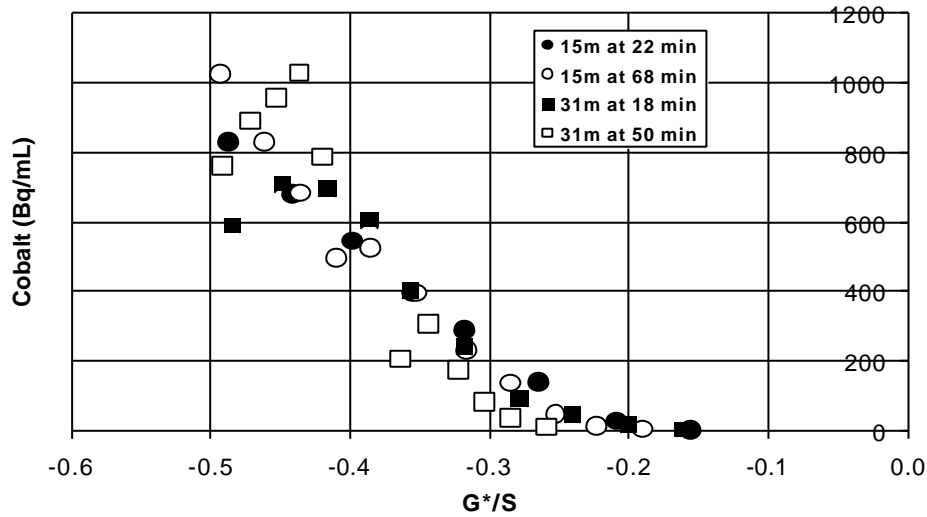

Figure 4.7(b). Graph showing Co profiles in normalised water based space (cf Fig. 4.4(b) for the 16m and 31m samples of Site 52aNW. Note again the difference in retardation of the co in the two sets of data.

5. DISCUSSION

The ability of the geologic materials to adsorb radionuclides and to retard their movement relative to water movement is an important criterion for siting the repository. Sections 3 and 4 report results of batch and column experiments on representative samples seeking to estimate these effects.

5.1 Comparison of batch and unsaturated column experiments

The batch and column experiments in these studies are different and care is required in their interpretation and comparison. Any measure of adsorption and consequent retardation of nuclides is a function not only of the particular species but also the chemical environment of the adsorption process. The appropriate solution for the adsorption or retardation experiment depends on the circumstances of release. For example, if the radionuclide release occurs when unsaturated ground water infiltrates the repository, dissolves nuclides and proceeds on into the regolith, then the ambient soil solution is the appropriate chemical environment in which to assess K_d and to infer retardation. These conditions approximate to the batch experiments reported in Section 3. If however, rainwater saturated in $CaSO_4$ infiltrates the repository, dissolves radionuclides and this solution proceeds into the regolith displacing the high saline existing pore water, then the conditions correspond to those in the column experiment reported in Section 4.

A simple comparison of the result obtained by the batch and the column experiments is therefore difficult and inappropriate. What does emerge from such a comparison is the general qualitative consistency between the two and that Co is more mobile than the Cs.

Table 5.1 compares the distribution coefficient K_d measured in the batch experiments with the adsorption isotherm β measured in the column experiments. If these experiments were measuring the same process under the same geochemical conditions, the numerical values of both parameters would be expected to be the same. The column **b** values are much less than the batch K_d values, however. This reflects the different conditions in the two sets of experiments. In the column experiments, incoming water displaces the highly saline water and adsorption occurs in the chemical environment determined by the invading solution. In the

Table 5.1. Comparison between K_d measured in batch experiments and β measured in column experiments for trace cobalt in a saturated $CaSO_4$ solution

Sample	Batch Kd mL/g pH uncontrolled	Batch Kd mL/g pH controlled ~ 6.75	Sample	Column β g_{wat}/g_{soild}
Site 14:19-20m	16	43	Site 14:17-20m	1.58
Site 52aNW 3-4m	3400	1460	Site 52aNW:top	18
			Site 52aNW:5m	18
Site 52aNW 15-16m	13	82	Site 52aNW:15-16m	0.6
Site 52aNW 30-31m	7	13	Site 52aNW:30-31m	0.3

batch experiments the salinity remains in the sample and adsorption occurs in the presence of higher concentration of NaCl and other soluble salts originally present in the material. Another complicating factor is the strong pH dependence in of cobalt adsorption evident in Figure 3.1. Both sets of experiments were carried out at the pH established by the sample with no attempt to control pH. The inflow pH in the columns was 6.0. The rankings of materials by the two methods, however, are qualitatively consistent.

We reiterate that results are for samples that were physically modified by the reverse circulation percussion drilling program and our conclusions presume that the comminution of the samples does not significantly change the relative adsorptive properties of the materials.

5.2   *Comparison of sites*

5.2.1   Chemical issues

The distribution coefficients measured in the laboratory batch experiments show that:

 a) trace cesium-137 is adsorbed in all profiles,

 b) adsorption of trace cobalt-60 on the collected samples is variable and depends on the clay content, the pH and the soil solution salt concentration.

 c) the material of Simmens quartzite formation has a reasonable adsorption due to the many clay bands.

 d) the Bulldog shale has reasonable levels of adsorption but this decreases near the bottom of the formation

 e) the Cadna-owie sandstone has lower adsorption for cobalt and cesium

 f) the Corraberra formation seems favourable for adsorption of the studied radionuclides, presumably due to the presence of various minor phases such as mica and oxides which have good characteristics.

The relative radionuclide retardation properties of the profiles at sites 40a, 45a and 52a are compared using the range of distribution factors determined for samples of the Simmens, Bulldog, Cadna-owie and Corraberra formations that appear at these sites. Overall, the three sites appear to have reasonable retardation properties and include surface layers of highly retarding material.

5.2.2   Hydrology issues

Water balance calculations based on the measured properties of a material very similar to the top 2m of Site 52a, together with historical daily rainfall and evaporation data over a period of 29 years at the site indicate that cumulative deep drainage is of order 0.14 cm/year if there is no vegetation (Harries *et al.,* 1998, 1999). This corresponds to less than 0.1% of average annual rainfall. Deep drainage is even less if there is vegetation. Lack of information on the hydraulic properties of profiles below the soil layer, however, means that estimates of the rate of migration of the radionuclides in these profiles is uncertain. Nevertheless, with a water table at 40 metres and an average water volume fraction through the regolith of 0.2, this represents a residence time for water from 15 m to 40 m of approximately 3,500 years. This calculation assumes a porosity of at least 0.2 throughout the regolith. It would overestimate residence times were the regolith of greater density with limited fracturing.

High concentrations of water soluble salts at depths up to 19m at Site 52aNW and low values at 31m (see Table 4.3) suggests that these recharge estimates are conservative and that very little water passes these depths in this profile.

6. CONCLUSIONS

Radionuclide adsorption and retardation parameters on materials from the CNSA region have been measured using batch and column experiments. The results suggest that the regolith profiles at all sites have reasonable retardation and would be considered suitable for repository siting. There are some layers where the adsorption of Cobalt-60 is low, but there are other layers in the same profiles that have higher adsorption.

All three sites have sufficient clay and other adsorbers in the profile to retard trace radionuclides and provide an effective natural barrier to the migration of radionuclides. The long transit time to the water table will provide sufficient time for most radionuclides to decay to very low levels. The radionuclide adsorption data of the samples analysed does not provide a basis to rank any of sites 40a, 45a or 52a as significantly more favourable in terms of ability to retard nuclides.

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