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Review of Sorption Data for Site Assessment

M.H. Bradbury and N.L. Jefferies

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Chemistry Division, Harwell Laboratory

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DEPARTMENT OF THE ENDERONMENT

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Report Title

Review of Sorption Data for Site Assessment

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Abstract (100-200 words as desired)

This report reviews both the experimental techniques used to generate sorption data and the relevance of available literature data to the assessment of proposed sites for radioactive waste disposal. The factors which lead to a reduction in precision and accuracy of the various experimental techniques are discussed.

It is concluded that the measurement of radionuclide transport properties through intact rock cores yields more conservative data than that obtained by the batch sorption technique. On mineralogical and hydrological criteria it is considered that site specific sorption data will be required for safety assessment analyses. If literature data are to be used, care must be taken to ensure that rock mineralogy, groundwater composition, Eh and pH, and radionuclide concentrations are relevant. Extrapolation of sorption data from experiments with non-relevant variables is unreliable. Appraisal of the sorption data leads us to conclude that the data available, and the characterisation of such variables as mineralogy, water chemistry and detailed experimental procedure, are insufficient to be used with confidence in the prediction of radionuclide migration at specific sites.

Keywords (suggested maximum of five to be taken from DOE standard keyword list provided 299

This work has been commissioned by the Department of the Environment as part of its radioactive waste management research programme. The results will be used in the formulation of Government policy, but at this stage they do not necessarily represent Government policy.

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EXECUTIVE SUMMARY

This report presents an appraisal of the techniques by which sorption data are generated and of the relevance of these data to the UK radioactive waste management programme.

The most widely used method for generating sorption data is the batch sorption technique, in which crushed rock is contacted with a dilute radionuclide solution. A distribution ratio (R_d) is calculated from the partitioning of the radionuclide between the solid and liquid phases. Other experimental methods are termed 'dynamic techniques' since the radionuclide solution flows through the rock, which may either be crushed or intact. Crushed rock column experiments are the most commonly used dynamic technique. More realistic experiments involve the use of intact rock samples, and fall into two catagories - permeability/sorption and diffusion/sorption experiments.

An examination of the literature reveals that batch sorption experiments have poor precision, due to experimental variables such as particle size, water:rock ratio and experiment duration. The precision of dynamic experimental techiques is difficult to assess because of the lack of available data. However, the principal cause of experimental scatter is believed to be due to kinetic effects i.e. the transit time of radionuclide solution through the rock sample is too short for equilibrium to be attained between sorbant and sorbate.

A comparison of R_d values generated by the batch sorption technique with those generated by more realistic dynamic sorption experiments using intact rock cores shows that the former are 10-40 times higher than the latter. This suggests that the batch sorption technique does not yield conservative R_d data. However, both the experimental procedure and the analysis of results in dynamic experiments is more complicated than that in batch experiments, and it is anticipated that the batch sorption technique will remain important for preliminary screening studies.

Ideally, all laboratory experiments should attempt to reproduce groundwater composition, pH and Eh pertaining to the rock 'in-situ'.

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Groundwater composition and pH may be successfully reproduced; however, measurement and control of Eh is very difficult and consequently has been attempted in few experiments.

On mineralogical and hydrological criteria, it is considered that site specific sorption data (obtained by techniques demonstrated to yield 'conservate' R_d values) will be required for safety assessment analyses. If literature data are to be used, care must be taken to ensure that rock mineralogy, water composition, Eh, pH and radionuclide concentrations are relevant. Because R_d typically represents a highly non-linear function, the extrapolation of distribution ratio data from experiments with non-relevant variables is unreliable.

Appraisal of the sorption literature leads us to conclude that the data available, and the characterisation of variables such as mineralogy, water chemistry and detailed experimental procedure, are insufficient to be used with confidence in the prediction of radionuclide migration at specific sites.

(v)

In this introduction, the concentration dependant nature of sorption processes must be emphasized. The distribution ratio (R_d) between the solid and liquid phases typically decreases at higher concentrations of the sorbate. The relationship between R_d and sorbate concentration at constant temperature is known as an isotherm. Several empirical relationships have been developed to describe sorption behaviour, the most widely used of which is the Freundlich isotherm:

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X = KC^N
X = amount of solute adsorbed per unit weight of solid.
C = equilibrium solute concentration in the liquid.
K,N = constants

Clearly, if N = 1, R_d is independent of solute concentration and sorption is said to be linear.

If data existing in the literature are to be used in the modelling of radionuclide transport in rock formations relevant to specific sites (Elstow and Billingham are considered here in particular), then there are two general criteria which must be taken into account in choosing or rejecting any data available:

(1) Rock mineralogy and groundwater chemistry should be as close as possible to those existing at the proposed site. (This implies, of course, that basic geochemical data relating to a specific site(s) are available; likewise for the literature data). With respect to mineralogical characterisation it should be appreciated that minor minerals, present at relatively low levels, can dominate sorption behaviour.

(2) Judgements will need to be made as to the quality and reliability of the data and their suitability to the situation being modelled. It is also necessary to know if the data (and hence any conclusions drawn) can be adequately justified and defended in open debate. This latter point presents perhaps the major difficulty.

Because R typically represents a highly non-linear function, the extrapolation of distribution ratio data from experiments with non-relevant mineralogy, groundwater chemistry and radionuclide concentrations is unreliable.

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1. INTRODUCTION

Sorption is the term given to the various processes by which dissolved components in a liquid phase are transferred onto the surface of a coexisting solid. Such data are required to model the transport of radionuclides away from a repository, since the partitioning between rock and groundwater determines both the rate of movement of the radionuclide and its maximum concentration in the groundwater. This report presents an appraisal of the techniques by which sorption data are generated, and of the relevance of these data to the UK radioactive waste management programme.

The most widely used method presently being used for the determination of radionuclide distribution ratios (R_d) is the batch sorption technique. Crushed rock (generally of an arbitrary mass and particle size) is contacted with a (again arbitrary) volume of the appropriate water which is spiked with the nuclide of interest. Aliquots are taken as a function of time until no change in thE nuclide concentration is measurable when "equilibrium" is assumed. The timescale deemed to be required to attain "equilibrium" is also somewhat arbitrarily chosen: usually 7-10 days for most of the reported data. Distribution ratios can then be calculated knowing the initial and final nuclide concentrations, the mass of rock and the volume of liquid, i.e.

$$R_{d} = \frac{V}{M} \frac{(C_1 - C_2)}{C_2}$$

 C_1 = initial concentration

 C_2 = final ("equilibrium") concentration

V = volume

M = mass of rock.

In most experiments, the reversibility of the sorption processes are not examined. For this reason, we prefer to use the term R_d to denote the distribution ratio rather than K_d , which implies thermodynamic equilibrium and reversible reaction kinetics.

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DATA REQUIREMENTS

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Before examining the sorption data existing in the literature, we first briefly summarise the sort of data that will be relevant to land-based radioactive waste disposal in the UK.

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(i) Rock type

(a) Disposal of low level wastes and of intermediate level wastes containing only short lived radionuclides is envisaged in shallow repositories. One site suggested by NIREX is at Elstow, Bedfordshire, within the Middle Jurassic Oxford Clay. The petrography of this argillaceous formation is summarised in Wilmot and Morgan (1982) and Milodowski & Wilot (1983). This allows a comparison to be made between the Oxford Clay formation and the data on clays presented in the sorption literature. For modelling purposes, data in interbedded sandstones are also necessary.

(b) Disposal of intermediate level wastes containing long lived radionuclides (i.e. actinides) is envisaged in deeper repositories. Prior to February 1985, disposal of this type of waste in the anhydrite mine at Billingham was considered. Sorption data on evaporitic rocks and magnesium limestones relevant to this site are considered.

In the near field, data on concrete, cement and backfill are also required.

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(ii) Groundwater composition.

Since the majority of rocks of interest are aquicludes, groundwaters must, in the main, be prepared synthetically by equilibrating deionised water with crushed rock.

(iii) Radionuclides of interest.

Sorption data are required for the weakly sorbing, long-lived, fission products (Tc, I) and for the actinides (Np, Am, Pu, U, Th). Cs and Sr, the elements most widely examined in the sorption literature because of their single oxidation state and simple aqueous chemistry, are ranked low in lists of hazardous radionuclides (e.g. Barney & Wood, 1980).

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(iv) Concentrations.

Because of the concentration dependant nature of sorption (see Introduction) it is essential to obtain sorption data over a range of sorbate concentrations. In this way it is possible to construct the sorption isotherm for the experimental system. This approach will allow non-linear sorption to be modelled as radionuclides, migrating from a repository, become diluted and dispersed in the groundwaters.

However, since R_d typically decreases at higher radionuclide concentrations, "conservative" sorption data could be obtained from experiments in which the sorbate concentration is the maximum anticipated upon release from the repository. This concentration may be the solubility limit or a value determined by leach rates within the repository.

The methods used to prepare dilute radionuclide solutions for use in sorption experiments involve the addition of the radionuclide, either as a concentrated acid solution or in a solid form, to the groundwater. This technique is known as 'spiking' and is further discussed in Section 4.1.iv.

(v) <u>Eh-pH</u>.

The Eh-pH conditions pertaining to the repository must be known, and where possible experimental conditions must simulate these. The simulation and maintenance of realistic Eh conditions in the laboratory is very difficult.

EXPERIMENTAL TECHNIQUES

This section outlines the experimental techniques most commonly used in the determination of sorption data. There are two broad categories:

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(1) static tests

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(2) dynamic tests.

In static tests, crushed rock or rock coupons are contacted with a volume of the "appropriate" water spiked with the radionuclide of interest. Agitation, to a greater or lesser extent (a variable, see later), is then applied to promote mixing between water and the exposed rock surfaces. In dynamic tests, spiked water is caused to flow over or through the rock which may be either crushed or intact; the former being by far the most common.

(a) Batch sorption

This is the most widely used technique and was briefly discussed in the "Introduction". Details of methodology of this technique are abundant in the literature and have been discussed in detail by Relyea and Serne (1979).

(b) 'Once-through" crushed rock column experiments.

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The most common dynamic method involves a crushed rock column through which a radionuclide-spiked solution is passed. This is the second most common method of measuring R_{d} /retardation.

(c) Recirculation experiments

These are similar to (b) except that the spiked solutions are recirculated through the crushed rock within a closed system until equilibrium is considered to be attained. Methods (b) and (c) should yield very similar results to equivalent batch measurements where the same rock form is used (i.e. generally crushed rock) but in practice often do not. These types of dynamic experiments have been reviewed and discussed in "Sorption", an NEA/OECD publication (1983) and by Serne and Relyea (1982).

(d) Flow through intact rock samples (permeability/sorption experiments)

The classical use of once-through-flow column experiments has been on permeable sediments, soils, disaggregated sands and crushed This has been extended to examine sorption in intact cores rocks. of low permeability rocks (Thompson et al., 1980; Weed et al., 1981). However, in these early experiments on intact low permeability rock cores high hydraulic pressure gradients were applied to promote measurable water flow rates, e.g. Weed et al. applied a pressure differential of ~10 MPa. The use of high hydraulic gradients to generate measurements within a short time can lead to changes in the permeability/ porosity of the rock due to pore flushing or particle movement and re-arrangement within the Also, and more important, erroneous conclusions pore space. regarding retardation/ R_{λ} , values may be calculated if transit times through the sample are insufficient to allow "equilibrium" to be attained between the rock and spiked solution. Irreversible changes in permeability have been observed in granites and sandstones tested at much lower hydraulic heads (~10 KPa) (Bradbury, 1983).

(e) Diffusion/sorption experiments

The simplest type of diffusion/sorption experiment is to allow the diffusion of a sorbing species into a piece of intact rock immersed in a constant volume of a radionuclide solution. The concentration of the solution is followed as a function of time. Such experiments are similar to coupon-type batch experiments but require much longer times (~10" hours is not unusual). The timedependent behaviour of the concentration is analysed in terms of a one-dimensional diffusion equation incorporating sorption. To a large extent the values needed must be independently determined, i.e. diffusion coefficients and sorption isotherms (on crushed rock) but it was generally found necessary to change these in order to obtain a reasonable fit to the experimental curve (see Skagius and Neretnieks, 1982; Atkinson, 1985).

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A variation of this method is to saturate a sample of intact rock with a spiked solution maintained at a constant concentration and then monitor the "out-diffusion" into a constant volume of the appropriate water. The analysis of the concentration-time behaviour is similar to that for the "in-diffusion" experiments.

A major problem in the latter experimental technique occurs in estimating when the rock is fully saturated with the solution and also when sorption "equilibrium" has been attained.

An alternative technique is to allow radionuclide diffusion into an intact rock sample and, after a suitable time, to section the rock and determine the radionuclide concentration profile (Schreiner et al., 1982). The apparent diffusion coefficient (D_) is calculated from the profile. Since $D = D/\epsilon + pR_d$, (Bradbury, 1985) where D_i = intrinsic diffusion coefficient, ε = porosity, ρ = density and R₄= distribution ratio, it is possible to calculate R₄ from a prior knowledge of D. The intrinsic diffusion coefficient may be determined by studying diffusion rate of a non-sorbing species, for $\frac{1}{2}$ (i.e. $R_{d} = 0$). The R_{d} obtained for a sorbing species which D = is an average sorption parameter over the concentration range of the concentration profile through the sample thickness since R, will probably be concentration dependent. The limitation of the profile method, particularly for strongly sorbed species, is in achieving adequate resolution of the profile (i.e. sectioning thickness).

A fourth method, particularly suited to weakly sorbing species has been described by Bradbury et al., (1982). Diffusion from a constant source is allowed to occur through one face of a sample of intact rock. Concentration as a function of time is monitored in a reservoir at the opposite sample face. Values of the rock capacity factor, α , ($\alpha = \varepsilon + \rho R_d$), can be calculated from the concentration versus time curve. The porosity and density of the rock can be calculated independently, and therefore R_d can be obtained without relying on crushed rock sorption results.

4. AN APPRAISAL OF THE EXPERIMENTAL TECHNIQUES

In this section we attempt to look critically at the sorption techniques discussed previously. For consistency and clarity we will follow the order of Section 3.

4.1 Static Sorption Tests (Batch Sorption)

The vast majority of sorption data existing in the literature has been generated by this method; either on crushed rock, slurried rock (e.g. clays) or on prepared rock coupons.

For crushed rock batch sorption based experiments:

- 1. Crushing the rock creates new fracture surfaces and damages the particles remaining. Surfaces which would never see water when the rock is in the intact state do so in these experiments. What is the influence of these two factors on the magnitude of the distribution ratio measured?
- 2. The rock/water ratio, mainly arbitrarily chosen, influences the value of the distribution ratio, (e.g. McKinley and Greenwood, 1980). As the rock/water ratio increases so does the partition coefficient. What then should this ratio be?
- 3. The rock particle size (for a constant rock/water ratio) markedly influences the distribution ratio (e.g. reference above). As the particle size decreases the sorption often increases; this is a strong effect. What should the particle size be?
- 4. During size sorting to obtain the rock particle size range chosen, strongly sorbing minerals may be concentrated or depleted.

While batch sorption experiments are a quick and easy means of ranking nuclides in terms of their sorption properties, the key question still remains as to their precision under the test situations (arbitrarily) chosen and therefore their validity in real situations; these are points which will be discussed later. In slurry experiments (e.g. on clays) or coupon experiments

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the effect of crushing is replaced by the disaggregation of the rock in the presence of excess water or the effect of manufactured surfaces respectively (sawn, ground, polished) on the sorption behaviour.

In a "round-robin" experiment carried out in the USA, nine laboratories were supplied with homogenised sub-samples of basalt and limestone and the chemical compositions of synthetic limestone and basalt groundwaters (Relyea and Serne, 1979). Exact experimental procedure was not specified. Measurements of R_d were performed for Cs, Sr and Pu. Despite the nine laboratories possessing identical rock and starting water compositions, the measured R_d 's for Cs in limestone varied by three orders of magnitude whilst R_d for Pu in both limestone and basalt varied by two orders of magnitude. The radionuclide concentrations at which these experiments were performed varied by up to 6 orders of magnitude. However, unexpectedly, there was no correlation between radionuclide concentration and R_d . In a subsequent review paper, (Serne and

Relyea, 1982), the experimental parameters which may be responsible for this wide variation in distribution ratio were discussed. They are examined briefly below.

- (i) Particle size An increase in particle size of crushed granite rock leads to a reduced R, (Allard et al., 1977), presumably as a result of the decrease in the ratio of surface area to volume at larger particle sizes. Serne and Relyes (1982) consider that the reduction in R over the size range 1 cm + 50 μ m is of the order of 3-10 times, and sometimes up to two orders of magnitude. However, the surface area of the crushed rock is rarely measured, and therefore sorption distribution ratio data cannot be presented as a function of sorbant area (R_a) instead of weight (R_a) . As sorption is a surface phenomena, the former expression may be more suited to a study of radionuclide sorption. The sieved size fraction will probably not represent the mineralogy of the whole rock - clay minerals and fine grained micas will be enriched in the finer size fraction relative to quartz and feldspars. This may, in part, control the sorption characteristics of the different size fractions used in batch experiments.
- (ii) <u>Agitation of the rock-water mixture during the experiment</u> There appear to be two competing effects. Firstly, a high stirring speed results in particle abrasion, a reduction in particle size and a

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consequent increase in surface area. Brahl (in OECD/NEA report on Sorption, 1983) observed an increase in R_d of greater than one order of magnitude by increasing stirring rates from 0.5 to 100 rpm. The competing effect results from the imperfect separation of solid and liquid phases at the end of the experiment (discussed further in (vi)). There is a greater probability that fine particulate matter generated during abrasion of the crushed rock will remain in suspension and be measured together with the liquid sample, producing lower apparent R_d values.

(iii) Firstly, it must be realised that the The water:rock ratio water:rock ratio during a batch sorption experiment is generally much higher than that in the intact rock where, for example, a typical sandstone porosity of 10% will result in a water:rock ratio The effect of varying this ratio has been examined by of 1:9. several authors, and the causes of variation in R, discussed. Since R_d is calculated as a function of the "equilibrium" concentration (C_2) of the radionuclide in solution and is independent of the water:rock ratio the variation in R_{d} - at constant C, - with change in water:rock ratio cannot be simply explained. Higgo et al. (1984) measured R_{d} values for Am, Np and Pu in deep sea sediments and concluded that the distribution ratio was strongly dependent upon solution/solid ratio, particularly for elements with high R_d values. For example, plutonium contacted with high carbonate sediments had an R_d which decreased from greater than 10^4 to 10^2 with a ten-fold decrease in water:rock ratio, whilst Np - less strongly sorbed onto the clay - had an R, which was essentially independent of water:rock ratio. Similar results were obtained by Daniels (1981); where R, (Cs) increased three-fold and R_{d} (Sr) doubled for an increase in water:rock ratio from 5:1 to 30:1.

The effect of water:rock ratio on sorption of I, Sr and Cs onto sulphate resisting Portland cement has been investigated by Atkinson (1985). By varying the water:rock ratio from 2:1 to 100:1, the calculated R_d 's for Cs and Sr increased by factors of 30 and 4 respectively, whilst that for I decreased by a factor of 9. (The latter result remains unexplained).

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Several possible causes for the dependence of R_d upon water:rock ratio have been discussed. The water used in the cement experiments was analar water, and therefore the range of R_d 's was attributed to the differing water chemistries existing during the experiments as a result of progressive cement: water interactions. An alternative cause was suggested by Higgo et al. (1984) for their experiments based upon the presence of several radionuclide complexes in solution which possessed widely differing sorption characteristics. There is a great deal of conjecture regarding the effect of water:rock ratios on sorption. However, there is no generally accepted and tested explanation. The experimental observations that R_d values increase with increasing water:rock ratios is well substantiated. Since virtually all experiments are carried out at unrealistically high water:rock ratios, this, in general leads to non-conservative, "high" R_d values.

- (iv) The method of tracer nuclide addition This is identified as one of the major causes of poor precision in batch experiments by Serne and Relyea (1982) (but would also apply to any other method). The radionuclide can either be added to the groundwater in the form of a strongly acid solution, after which the pH of the system can be adjusted, or the acid solution may first be evaporated to dryness and then dissolved in the groundwater. In the former case, because of poorly-known solubility limits in groundwaters, there is a possibility of supersaturation or colloid formation with pH changes, either during addition of the radionuclide to the water or during the final pH adjustments. Erdal et al (1980) observed that the method of tracer addition caused order of magnitude differences in calculated R, values of Am and Pu.
- (v) Variable adsorption onto the container walls Again, this is seen by Relyea and Serne (1982) as an important source of variability. Partial corrections may be obtained by running a 'blank' experiment in which the change in concentration of a spiked solution is measured after contact with an empty container. However, recent

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studies for Am, Pu and the lanthanides indicate that this correction biases R_d results to low values because competition for radionuclide adsorption onto the rock is not considered. The problem may be overcome if the radioactivity in both the solid and liquid phases are measured; however, because of the extra time involved, this is rarely done.

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- (vi) <u>The method of separating the solid and liquid phases</u> There are two principle methods of separation employed: either centrifuging or filtration. The centrifuge method generally leads to greater variability in the experimental results and lower R values (Erdal et al., 1980).
- (vii) The duration of the experiment The time required for "equilibrium" to be attained depends upon the mechanism by which the radionuclide is transferred to the solid phase for example, ion exchange, precipitation, adsorption. A recent review of fission product sorption (Andersson and Allard, 1983) identified time as an important parameter in batch experiments. Slow adsorption was identified for Co sorption on bentonite, where a steady increase occurred over 144 days, whilst Cs adsorption on argillites reached "equilibrium" in 10-30 days. Contact time for the standardised batch procedure presented in Relyea and Serne (1979) was only seven days.

The particle size also seems to have a strong influence on the time at which "equilibrium" is attained. Swedish workers (quoted in NEA-OECD sorption report, 1983) reported that equilibrium for Cs and Sr sorption on granite was attained after 100 hours for 0.1 mm sized particles, whilst 5 mm thick partricles only achieved equilibrium after 10^{4} hours (i.e. greater than 1 year).

Since precise experimental details are rarely presented in the literature, poor precision when comparing data must, unfortunately, be accepted. There seem to be strong influences on the values of R_d obtained due to minor variations in experimental technique and procedures, e.g. agitation rate, particle size range etc.

Furthermore, due to some questionable practices inherent in the technique, e.g. crushing, the accuracy of the technique with reference to real situations must be regarded as being somewhat dubious; R_d results seem to be biased "high", without any real indication as to how "high". The above comments would apply equally to "slurry" type experiments on unconsolidated materials such as clays.

Finally, a word concerning batch coupon experiments. Where surface sorption only is being considered, e.g. sorption onto the surfaces of fissures in fractured media, then such experiments could be relevant if they are compared with sorption on actual fissure surfaces. A comparison between the two types of sample can then be made and conclusions drawn as to whether the results on the more readily available machined coupons are conservative or not. However, such measurements may not be applicable at all if bulk sorption processes (i.e. matrix sorption on the surfaces of the pores) are being considered.

4.2 Dynamic Sorption Tests

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(a) Recirculation experiments

These experiments are essentially similar to batch tests with flow providing the mixing instead of agitation. Experiments are mainly performed on columns containing crushed rock. The same reservations apply to this technique as those listed previously for batch tests.

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(b) Once-through column experiments

Because relatively few of these experiments have been performed it is not possible to quantitatively assess precision. However, a recent review paper (Serne and Relyea, 1982) has summarised the position with regards to column experiments.

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For the majority of column experiments the column consists of crushed rock or unconsolidated material and the applied hydraulic gradient is mainly chosen to provide data on a "reasonable" time scale. This normally implies a very unrealistic pressure gradient with respect to that found in nature. This is especially true of the very few experiments which have been conducted on intact porous rocks (e.g. Weed et al., 1981; Thompson et al., 1980).

Radionuclide retardation is evaluated by measuring the activity profile of the outflowing water and/or the residual activity profile in the column itself. Experimental difficulties increase as the rock permeability decreases. The main problem in column studies is the analysis of results, since flow, dispersion, sorption (including non-linear sorption) and kinetic effects are involved.

The residence time in "once-through" column experiments (whether on crushed or intact porous rock) may be a very important factor determining the retardation coefficient calculated. In many experiments it is possible that the transit time across the sample is insufficiently long for "equilibrium" to be attained between sorbant and sorbate, i.e. indeterminate sorption kinetics may play an important role (Serne and Relyea, 1982).

Several experimenters have examined the effect of groundwater velocity Seitz et al. (1979) calculated the retardation through intact rock cores. factor for ¹³/Cs on crushed basalt columns for varying water velocities. At a water velocity of 3800 m/y the retardation factor was approximately four times lower than that calculated with a flow rate of 430 m/y. In addition, dispersion effects were much greater at the higher water velocities due to non-equilibrium between sorbant and sorbate. In experiments in which water flowing through the column was spiked with a sorbing radionuclide and the elution curve measured, for "equilibrium conditions" (slow water flow rate), the curve was symmetrical with a small spread about the mode. In contrast, the elution curve for what were considered to be "non-equilibrium conditions" (with reference to sorption) was asymmetric with a long tail. Non-ideal chromatographic peaks present a problem in the calculation of retardation factors. Although attempts have been made to produce solutions for peakless or asymmetric breakthrough curves this remains one of the major problems in column tests with unrealistically high flow rates (Serne and Relyea, 1982).

A further difficulty experienced with high pressure intact core column experiments is that of water leakage between the core and the sample holder, resulting in short-circuiting of the rock core by the spiked water (Weed et al., 1981).

More recently, column experiments on low permeability rocks (intact cores ~ 20 mm thick) have been developed using a much lower pressure differential of between 1 and 10 kPa (equivalent to a head of between 10 cm -1 m of water). This procedure required the development of techniques to measure very low flow rates through the sample (as low as 0.15 cm³ day⁻¹). These techniques either relied upon capillary tube measurements of the flow through the sample or measurements of the concentration change of I⁻ (a non-sorbed species) in a measurement cell (Bradbury, 1983). Therefore, the difficulties presented above are largely overcome by the use of low hydraulic gradients across samples, promoting low flow rates and thus minimising kinetic effects. Even at these very low flow rates kinetic effects have been observed. Thus a "low" flow rate does not automatically imply the absence of kinetic effects.

4.3 Diffusion/Sorption Experiments

The main problems associated with diffusion/sorption experiments, listed in Section 3, are

- (i) long experimental times (for strongly sorbing species this may be so long as to make the experiments impractical)
- (ii) sawn, abraided or polished surfaces may have very different sorption properties from internal pore surfaces. This may complicate the interpretation.
- (iii) concentration gradients are set up within the sample. Where steady state concentration profiles are established, the calculated R_d's are mean values valid between the concentration limits used. Where non-steady state conditions apply, it will probably be necessary to take into account non-linear sorption in interpreting the profiles, though exactly how this is done remains unclear to us.

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A corollary to this statement is that, during radionuclide migration from a repository, concentration gradients will exist during transport by diffusion/permeability processes. Therefore a single R_d value is not useful for representing sorption in migration models: the dependence of R_d on radionuclide concentration in solution must be known, i.e. sorption isotherm data is preferable to single R_d values.

In the case of "membrane" type experiments in which a constant source concentration is required, a closed loop circulation system between the high concentration side of the cell and an external (large) reservoir is necessary. Circulation via an external reservoir enables the source concentration to be maintained at a constant value, required as a boundary condition for the solution of the diffusion differential equation. The size of the reservoir necessary will depend on the magnitude of sorption.

The main advantage of such sorption experiments on intact rock are that they are probably the best that can be achieved in the laboratory to simulate bulk sorption processes occurring in the field. Very few such experiments have been attempted to generate sorption parameters (Bradbury, 1985).

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A COMPARISON BETWEEN STATIC AND DYNAMIC SORPTION MEASUREMENTS

Different types of "sorption" experiments measure different parameters. For dynamic experiments, where all retardation is assumed due to sorption, and static batch experiments where a sorption parameter is measured directly, the values of retardation and sorption are simply related. However, as pointed out previously, the biggest difficulty in dynamic experiments (e.g. crushed rock columns) is the analysis of results since retardation is the product of a large number of individual processes which may vary both in time and space. (The analyses of experimental data is often simplistic and may involve unjustified assumptions; NEA Sorption 1983).

Intuitively it might be expected that R_d 's calculated from crushed rock batch tests and R_d 's calculated from crushed rock "once through" column tests should yield very similar values. However, comparison of the two techniques demonstrates that "once through" column R_d 's are consistently lower than batch R_a 's by a factor of up to five times (Erdal et al., 1980).

Some of the reasons for the discrepancies between the two techniques may lie in the choice of variables used to measure R_d 's in batch tests (see Section 4.1; particularly W/R ratios). Other reasons may be

- (1) the method of analysis used to interpret column experimental results (see earlier)
- (11) concentration dependent sorption effects during migration through the column. (i.e. any injected pulse will tend to broaden due to dispersion/diffusion)
- (111) kinetic effects if the transit time for the sorbing radionuclide is not sufficiently long for equilibrium between sorbant and sorbate to occur during migration (Seitz et al., 1979)
 - (iv) time scale effects. Batch sorption tests are normally completed in a relatively short time (~5-10 days) whereas column tests may take very much longer.

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Walton et al. (1982) investigated the kinetics of sorption onto fresh surfaces of granite over a period of five months. Leaching of these fresh surfaces was detected throughout the experimental period, and this alteration was observed to effect the sorption behaviour of both 137 Cs and 60 Co.

Close agreement has been obtained between column and batch techniques in the case of unconsolidated material (such as soils and sandy tills). Comparison of batch and column experiments on unconsolidated montmorillonite (for Cs: Meyer et al., 1977) and disaggregated soils (for ⁶⁰Co: EDTA, ⁸⁵Sr, ^{95^m}Tc and ¹²⁵I: Gee and Campbell, 1980; for Am: Bidoglio et al., 1984) produced very similar R_d measurements: however, the precision of the column technique is reported to be greater than that for the batch technique for the measurement of relatively mobile radionuclides (Gee and Campbell, 1980). The reasoning behind this statement is unclear to us.

However, agreement between batch and column experiments or reasons for any discrepancies may to some extent, be a side issue. Discussion and experimentation on the above may be academic unless there is strong evidence to indicate that such experiments are providing sorption/retardation data which can be used with confidence in migration models. Moreover, the magnitudes of the sorption parameters used (or upper and lower bounds on their values) must be justifiable. In tests on unconsolidated rocks (see before) batch-type experiments probably can be justified since the in-situ rock is in a disaggregated form. (There merely remains the problem of resolving the "correct" W/R ratio, and whether W/R ratio variations have significant effects on R, values). For the case of consolidated rocks (granites, limestones, anhydrites, sandstones, concretes etc.) the effect of crushing or surface preparation remains, as yet, indeterminate. Therefore, even high precision in batch experiments is no criterion for accuracy. Alternative experimental techniques must be developed and used to obtain data with which to evaluate batch derived sorption parameters.

As long ago as 1979 this comparison, between the batch technique and the intact rock column technique, was considered to be of prime importance (Serne et al., 1979) in order to assess the accuracy of batch sorption data for use in modelling radionuclide transport. However, despite this there is very little

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literature data available. Data reviewed in Serne and Relyea (1982) indicates that R_d (Sr) values obtained from a tuff were four times higher for batch than for intact column experiments. A general conclusion from these experiments is that if slow water velocities and low hydraulic gradients are used in intact rock column experiments then the R_d 's obtained are lower than those determined by batch techniques.

Experiments currently underway to measure sorption of Cs, Sr and Tc in intact rocks by diffusion/sorption and permeability/sorption techniques (Bradbury and Stephen, 1985) in sandstones, anhydrites and limestones indicate that R_d values (for Cs and Sr) derived by column techniques are between 10 and 40 times lower than those obtained from corresponding batch measurements.

Conversely, retardation factors for 85 Sr, determined by Weed et al., (1981) on intact sandstone columns, gave R_d values ranging from 1-3 compared with values of unity determined from batch measurements. However, possible disequilibrium factors were involved as evidenced by the asymmetric form of the eluted radionuclides.

In a review paper, Serne and Relyea (1982) have suggested that batch data may be corrected to "conservative" values in the following manner. For elements which exhibit moderate sorption ($R_d \sim 50 \text{ ml/g}$) then the batch R_d could be reduced by a factor of three, whilst for R_d 's between 50 and 300, and greater than 300, reductions by factors of 5 and 10 respectively could be applied. At present there is insufficient comparative data to justify such an arbitrary reduction.

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6. THE EFFECT OF MINERALOGY ON R, VALUES

In an earlier section on 'Data Requirements' it was stressed that if data in the literature is to be used, then it must be from rocks of similar mineralogy to those of relevance at named sites. Clearly the sorption characteristics of a granite or sandstone would not be used to model radionuclide transport in a mudstone, because of the obvious differences in mineralogy between these rock types. However, it is commonly assumed that all mudrocks have similar sorption characteristics and that as long as literature data on clay rocks is used, then this will be adequate for modelling purposes. This is incorrect.

Clay minerals are members of the phyllosilicate group - minerals which possess (A1,Si)205 sheets with various interlayer cations. The two-dimensional aluminosilicate sheets are responsible for the platy aspect of these minerals. The sorption characteristics of the clay mineral species depends upon variables such as the cation exchange capacity, oxidation-reduction reactions with the radionuclide, and the charge state of the clay surface. R, values for various radionuclides on different clay minerals have been determined using the batch technique and this data is summarised in a recent review (Andersson and Allard, 1983) and reproduced in Table 1. Because in this work only relative R_{d} 's were of interest, the experimental parameters are not given. It is important to note, however, that the data in Table 1 and also in Table 2 are generated from clays either contacted with dilute ionic solutions or distilled water, which will not be in equilibrium with the clay rock. The problem of disequilibrium between groundwater and rock probably exists in all sorption experiments regardless of experimental technique, but is particularly acute with regard to clay minerals. This is because of the ease with which interlayer cations, in particular the alkali metals, are leached from the clays, resulting in a transformation from one mineral to another. The data presented in Table 1 indicates that such transformations may have profound effects on sorption characteristics.

In addition, sorption data for Cs onto a series of clay rocks mixed with distilled water is presented in Table 2. The data indicates that the R_d values of the clays investigated varied by two orders of magnitude. Clearly, if data for clay rocks is to be taken from the literature it is essential that the mineralogy is as close as possible to that of the rocks at the proposed disposal site.

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The effect of trace minerals upon the sorption characteristics of evaporitic rocks has been examined by Swiss researchers (Glassmann et al. 1979). These authors conclude that the sorption properties of anhydrites are controlled by the presence of minor clay and micacous minerals in the rock. This is because Sr and Cs are, at most, only very weakly sorbed upon anhydrite and gypsum whilst they are strongly adsorbed onto clay mineral impurities.

In view of the above it should not be assumed that sorption on Swiss anhydrite is relevant to the sorption properties of anhydrites from other localities, e.g. Billingham. Swiss anhydrites occur in metamorphic terrains and consequently original clay minerals have been transformed to phlogopite, chlorite and talc. In the anhydrite formation at Billingham, which has not been metamorphosed and recrystallised, the minor minerals are illite and kaolinite.

Table 1

		•	$R_{\rm A}$ (m ³ /kg)
Co	Illite	1. T.	10.0 + 1.00
	Montmorillonite		 0.1 + 3.2
	Kaolinite		$0.003 \div 0.32$

(Skytte Jensen, 1980; cation conc. $10^{-3} - 10^{-1}$ M)

Sr	Illite	0.5
	Montmorillonite	1.2
	Vermiculite	1.0
	Kaolinite	0.2

(Relyea et al., 1977; 0.03 N NaHCO₂)

Cs	Biotite		64.7
	Illite		43.01
	Montmorillonite	•	1.22
	Vermiculite		7.18
	Kaolinite		0.75
	(Quartz)		0.057

(Relyea et al., 1977; 0.03 N NaCl)

Table 2

Rock mineralogy	R _d (m ³ /kg)
corrensite, illite, quartz	50
illite, calcite, chlorite, quartz	50
dolomite, illite, muscovite, vermiculite, quartz	40
montmorillonite, illite, kaolinite	20
calcite, illite, quartz, feldspar	20
illite, kaolinite, chlorite	10
kaolinite. Fe oxyhydroxide	3
kaolinite	0.5

(Laske, 1979; distilled water)

LITERATURE SORPTION DATA

A preliminary sweep of the literature was made in order to obtain a first estimate of the potential relevance of existing sorption data to the requirements of the UK radioactive waste management programme. Information was sought on

(1) rock types: mudstones, anhydrites, limestones, cements and concretes.

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(2) radionuclides: I, Tc, Np, Pu, Am, Cs, Sr (particularly sorption isotherm data).

(3) groundwater chemistry (water composition, pH and Eh).

(4) experimental techniques and procedures (W/R ratios, particle size distribution, experimental time scale).

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on (5) Mineralogy. On contractional teachership de tractical grade and electronic contractions and electronic of the second

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Some of the results of this data gathering exercise have been included in previous sections.

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The conclusion of this study was that very little data on the rock types and radionuclides listed, particularly under realistic water chemistry conditions, was available.

for the data obtained form the ISIRS adata banks may be summarised as follows: the perfection of a summarised as

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(a) The data bank comprises of a total of 2300 data sets, largely on natural rocks but also on pure minerals. 1700 are for Cs and Sr under oxidising conditions.

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(b) There is only very limited data available on other rocks for other radionuclides. (c) and (c) are the second second

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- (c) 95%+ of the data was generated by the simple batch sorption method.
- (d) No data of any sort was available for cements/concretes.
- (e) In general, the mineralogical information supplied for the solid phase was inadequate.
- (f) A list of ~350 data sets for sediments possessing porosities between 10-30% (mudstones and some sandstones) was obtained. However, the relevance of this data for our purposes was in doubt because of (e) above and water chemistry considerations.

McKinley and West (1982) have published batch sorption Freundlich isotherm data for Cs, Sr and Co on Gault, Oxford and Kimmeridge clays obtained from the Harwell site. One set of these data was on Oxford Clay which outcrops at Elstow. The groundwater used for this study was obtained from the underlying limestone aquifer and was therefore not in equilibrium with the clay. Furthermore, later hydrogeological studies (Alexander and Holmes, 1983) showed that this water was contaminated by drilling and well completion procedures. The sorption experiments were seen as <u>a screening study only</u> and no claims were made as to the relevance and applicability of the data with regard to modelling.

The Swiss results on anhydrites were discussed in the previous section . and the conclusion from these measurements and those given above is the same, i.e. use of such sorption values in migration models applied to UK sites is not justifiable (indeed the authors themselves do not claim their measurements to be appropriate even for modelling of radionuclide movement specific to the sites from which the samples were obtained).

The data available on cements and concretes is very sparse indeed. Recent reports have been concerned with the leaching of Cs and Sr from Portland cement (Atkinson et al., 1984), sorption and diffusion of I and Cs in cements and concretes (Andersson et al., 1983) and the effect of Cs adsorbing additives on Cs sorption characteristics (Glasser et al., 1984; Atkinson et al., 1984). Because concretes and cements are "man-made" it should in principle be easier to work with these materials under well defined conditions, and to compare and

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contrast their sorption characteristics for different radionuclides using a variety of techniques. Most experimenters are still relying on batch techniques though Atkinson et al. (1984) are attempting to make comparisons using different experimental methods.

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8. CONCLUSIONS

1. It is apparent from the foregoing discussions that batch sorption data from the general literature must be used with great caution when input data for migration model calculations is sought. Points to bear in mind are:

- (i) the data should be obtained on rocks having similar (if not identical) mineralogy.
- (ii) contacting water chemistries (composition Eh, pH) should be those pertaining to the rock formation. For example, contacting clays with distilled water can result in drastic alterations to the sorption properties of the clay, because of mineralogical transformations. (Such changes and corresponding changes in water chemistry will be time-dependent.)
- (iii) attention must be paid to the technique(s) used and judgements made as to whether the data generated is justifiable and "conservative".

2. For the various reasons outlined in sections of this report, there is a general and growing realisation that batch sorption (particularly on crushed rock) may not be providing the sort of input data required for mathematical models. Attention has been drawn to the poor precision and dubious accuracy of R, values obtained by batch methods. Many authors have advocated that batch tests be used for preliminary screening purposes only or to investigate particular chemical effects (e.g. Serne et al., 1979; Henrion, 1984). Other authors, in papers on their batch sorption tests, have stated their views more explicitly. For example, Glassman et al. (1979) concerning batch data on anhydrite rocks, states: "... it is clearly indicated that the absolute values of these experimentally defined distribution coefficients are only valid for the particle size of the test material ... the water volume to solid volumes also has a great influence on the expriments. Buetzker (1975) [the author of the work reviewed] necessarily concludes that his measurements should only be used as a comparison.".

Similarly, Higgo et al. (1984) in their recent work on marine sediments conclude: "... R_d values obtained in this way [batch tests] should be used with extreme caution in migration modelling. ... results obtained in situ or from diffusion experiments approximating as closely as possible in situ conditions are likely to provide the more reliable figures.".

3. For the rocks pertinent to named sites and the radionuclides of major importance (actinides, Tc, I) it is concluded that relevant sorption data does not exist in the ISIRS data bank. Data does exist for Cs and Sr, under oxidising conditions; however the mineralogical characterisation given for the sorbates is so inadequate as to make the application of such data to UK sites highly questionable.

4. Our general conclusion for sorption data existing in the literature (predominantly batch data) is that it cannot alone be justifiably used in safety analyses related to specific UK sites. Site specific sorption data is required.

5. However, batch-type tests remain the only practical means of conducting a large number of experiments on a variety of rocks and radionuclides under different water chemistry conditions and radionuclide concentrations. The allure of this simple technique lies in the number of measurements which can be completed and is the reason why it is still so widely used. Precision can be determined but the accuracy remains questionable. There is little or no sorption data generated by other techniques with which batch data can be compared. Field tests are expensive and notoriously difficult to perform and interpret, so this means of testing and providing a comparison and/or a validation of the laboratory batch data seems remote. The only feasible means of comparison/validation is to develop alternative more realistic laboratory techniques on intact rock to measure sorption.

Comparison of batch sorption data with that generated by alternative, more realistic, methods will give a guide as to:

(1) the most appropriate parameters to be used in batch tests, i.e. particle size, water/rock ratio and methodology, which will give the most "conservative" values. (ii) the "safety factors" which may need to be applied to batch data in order to ensure that the values used in modelling studies are realistically conservative, and can be justified as such.

The application of somewhat arbitrary reductions factors, as suggested by Serne and Reylea (1982), is unjustifiable and would prove to be a very vulnerable aspect of the presentation of any safety case in the future. The problem is exactly that stated above, i.e. at present we have no means of judging the validity of batch sorption results (comparisons between crushed rock tests and crushed rock column tests is, in our view, meaningless in this respect).

6. It is important to realise that diffusion/sorption and permeability/ sorption dynamic methods (the alternative techniques suggested here, although there are others) are more difficult to perform and are "long term" experiments $(10^3 - 10^4 \text{ hours})$. It will require time to fully understand the processes occurring and therefore to interpret these experiments. Because of the above, only a limited number of experiments can be carried out in a given time period. (We would estimate, in terms of the number of experiments completed, one to two orders of magnitude less than for batch tests.) Also for certain strongly sorbing radionuclides such experiments will be virtually impossible to cary out because of the long times involved.

7. The conclusions stated above relate to bulk sorption. If sorption onto the surfaces and infill material in fractured systems is considered to be important then batch-type tests on machined rock coupons (e.g. Vandergraaf et al., 1982) may be justifiable. This is simply because comparisons can be made between the sorption characteristics of prepared rock coupons and actual samples of fissure surfaces. However, geometric surface areas are often used to calculate R values (area distribution ratios) and the actual surface area of coupons and fissure surface samples may be drastically different. Obviously true surface area measurements are required in order to make real comparisons. The time-scale of the experiment may also be important since diffusion and sorption onto the surfaces of pores within the matrix may play a (important?) role in the R values measured. The extent to which "near surface bulk sorption" contributes to "surface sorption" measurements will depend on the sorbing species; i.e. the contribution from bulk sorption to the (assumed) surface sorption measurements will be greater for weakly sorbing species than

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for strongly sorbing species which will hardly penetrate the bulk pore space at all. In addition the above will be influenced by the diffusion properties of the near surface region of the coupon or fissure surface. In diffusion experiments on UK granites fissure surfaces have exhibited porosities and diffusion rates many orders of magnitude greater than "good" rock (Bradbury, 1985). It should not, however, be assumed that R values measured on the surfaces of samples are valid in the bulk of the sample; the two may be entirely different.

8. In our view it is highly unlikely that the above arguments relating to batch tests on crushed consolidated rocks (see point 5) can be applied to clays. Clays, in an unconsolidated state and in contact with excess water, can swell, leach strongly (changing the charge state on the clay layers), disaggregate and change their mineralogical form. This may lead to the development of vastly different sorption properties to that of the clay in situ. The only justifiable and realistic means available for measuring the sorption properties of clays is to perform diffusion/sorption or permeability/ sorption measurements on intact clay samples which have been re-consolidated and re-saturated, i.e. returned to their in situ state as far as is possible in the laboratory. (After approx. 8 years research on the transport properties of Boom Clay. Mol. Belgium, this is the definitive conclusion reached by Henrion He is in the process of setting up a laboratory solely devoted to (1984). diffusion/sorption measurements).

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9. FINAL COMMENTS AND RECOMMENDATIONS

- (1) However sophisticated the mathematical models developed to predict the migration of radionuclides at specific sites, they are only as valid as the input data provided. In spite of the general conclusions reached in the NEA report on the sorption workshop (OECD-NEA "Sorption", 1983) it is our view that the quality of sorption data currently available is insufficient and inadequate, particularly for the named UK sites. It is anticipated that this will also be the case for any other sites named in the future. Therefore, field work, sampling and carefully selected laboratory studies on site specific samples will be an essential prelude to site selection.
- (ii) It is not satisfactory that sorption data which "seems" vaguely relevant is used in site assessment studies. The data which exists, if chosen without due consideration to the points raised in this report, can give rise to misleading conclusions. Therefore, close interaction between experimentalists and modellers is important.
- (iii) Competition between sorbing radionuclides, or between sorbing radionuclides and dissolved salts in the groundwater, is rarely considered in experiments in which distribution ratios $(R_d's)$ are calculated. However, this may be an important mechanism by which R_d 's for particular radionuclides may be markedly decreased. For example, Henrion (1982) has considered the effect of competition between trivalent lanthanides and Am, both of which may be considered to be in the trivalent state.
 - (iv) Time, finance and available experienced manpower will ultimately determine what can be achieved on any given timescale. Therefore research priorities need to be clearly, realistically and coherently defined with respect to sorption measurements in any site specific investigation study. The points raised in this report, which have highlighted the inadequacy of the currently

available data and the requirement that the data must be justifiable, (possibly by the development of alternative comparative techniques) must at all times be clearly held in mind.

(v) For the majority of cases reducing conditions are assumed to exist within both the repository and the host rock soon after closure. The reasoning behind this is largely based on theoretical The determination of Eh in the field is a considerations. notoriously difficult measurement to make. The creation. maintenance and measurement of reducing conditions in laboratory experiments is likewise exceedingly difficult. In our view these difficulties are often understated in the literature and the Eh state of the solution is often assumed to be that theoretically expected rather than that reliably measured (see for example Chatt et al., 1983). The Eh condition of the water is very important in determining the sorption behaviour of the radionuclides of prime importance (e.g. actinides and Tc). We feel that more detailed attention needs to be applied to this important parameter than has hitherto been paid; particularly to the creation and reliable measurement of Eh conditions in laboratory experiments which claim to mirror those existing in situ. This is almost a research topic in its own right.

(vi) There is an abundance of theoretically based calculations in the literature regarding speciation of the actinides (solubilities, charge stage, complexes) under given (mainly theoretical) groundwater chemistry conditions. It was recently brought to our attention (P Tasker, 1985) as to whether the thermodynamic data base used to calculate speciation for the actinides is reliable. If the experimental data base is inadequate then this may lead to erroneous calculations and incorrect conclusions regarding the most effective directions research should take. The thermodynamic data base should be looked at most carefully before calculations and the ensuing conclusions are made. By looking critically at the basic existing data reseach priorities can be set at an early stage. It could be very misleading to accept data quoted in the literature without looking critically at its source and making judgements as

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to its validity with regards to our current requirements. It may even be worthwhile to institute a project to appraise the value of the existing thermodynamic data base used for speciation and solubility calculations for the actinides.

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(vii) Our current view is that models, and the data requirements for them, are far in advance of the reliable experimental data available. At present the data available for use with models is often of dubious credibility, and this situation needs to be rectified as soon as possible if we are to assess potential repositories with reasonable confidence.

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