

RADIONUCLIDE ADSORPTION BY MARINE SEDIMENTS

by

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ABSTRACT

The sorption of caesium, europium, americium, neptunium and plutonium by a wide range of deep-sea sediments from natural sea water at 4°C has been studied using a carefully controlled batch technique.

It proved possible to make some interesting correlations between caesium adsorption isotherms and the results of mineralogical analysis and cation exchange capacities and surface areas. The distribution ratio for caesium increased by an order of magnitude as the equilibrium concentration in solution decreased from 10^{-3} M to 10^{-9} M and there was less difference between samples at low than at high concentrations. It seems likely that sorption was by two mechanisms, one having a high sorption capacity which is quickly exhausted and which is not completely reversible.

Europium and americium behaved in much the same way on all the sediments any of which should prove an effective barrier to their migration since distribution ratios were always greater than 10^5 ml/g. The sorption of these two elements did not appear to be reversible.

The sorption of neptunium appeared to be reversible and except for one red clay the distribution ratio was greater than 10^3 ml/g which means that a 30m layer of sediment should prevent ^{237}Np from reaching the sediment water interface. The neptunium in solution remained in the V oxidation state throughout the experiments.

The rate at which different oxidation states of plutonium were sorbed was followed. Pu-IV was sorbed much more rapidly than Pu-V and the rate at which the sediments removed Pu from solution decreased in the order smectite > high-carbonate $\approx$ red clay. There was a strong correlation between these rates and the neptunium distribution ratios for the same sediments. This is presumably because neptunium is in the Np-V oxidation state and the rate controlling step for the sorption of Pu is either the sorption of Pu-V or the reduction of Pu-V to Pu-IV.

At solid/solution ratios below about 40g/l plutonium distribution ratios were greater than 10^4 ml/g but at higher solid/solution ratios the distribution ratio for carbonate sediment dropped to around one hundred which means that carbonate sediments may not be as suitable as red clays for waste disposal. At the high sediment concentrations the plutonium was mainly in the oxidised Pu (V+VI) forms and it is postulated that Pu-V or Pu-IV carbonates were the main species present.

The effect of the solid/solution ratio on measured distribution ratios was investigated. It was shown that the apparent drop in R_d with increasing sediment concentration can frequently be explained by the presence of small amounts of non-separable or "low R_d " species and that by measuring the R_d at different solid/solution ratios it is possible to estimate the proportion of low- R_d species present. These may be colloids or stable complexes.

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CHAPTER 1

INTRODUCTION

1.1. Background

The possibility that high-level radioactive waste (HLW) might be disposed of beneath the sea floor was first considered in the early 1970s when Sandia National Laboratories embarked upon their Subseabed Disposal Program. Since then international interest in subseabed disposal has been growing annually and in 1983 nine nations (Belgium, Canada, Federal Republic of Germany, France, Japan, The Netherlands, Switzerland, United Kingdom, United States of America) attended the Nuclear Energy Agency Seabed Working Group meeting on subseabed disposal.

U.K. involvement in the field followed publication of the Government White Paper (Cmnd 6820) entitled Nuclear Power and the Environment. This report concluded that "There should be no commitment to a large programme of nuclear fission power until it has been demonstrated beyond reasonable doubt that a method exists to ensure the safe containment of long-lived, highly-radioactive waste for the indefinite future". As a result a substantial programme of research into disposal of HLW within geological formations was begun. The options for disposal are burial at depth underground, or emplacement on or below the ocean bed. Feasibility of underground disposal has been established in principle and the U.K. programme is now limited to assessing the applicability of findings from other countries to U.K. conditions (Feates and Richards, 1982). However, research into the other options continues with a number of organisations undertaking research into different aspects of the problem.

In Britain high-level or heat-generating waste has been safely stored as liquid in cooled, stainless steel tanks at Sellafield for the past 25 years. Storage in a solid form is more secure and solids are easier to handle during transport and final disposal. A vitrification plant is, therefore, being built and should be in operation at Sellafield by 1987. The waste will be evaporated to dryness and calcined to produce a fine grained mixture of radioactive oxides. This will then be incorporated into a borosilicate glass by melting 20-30% of calcine together with other added components (mainly SiO_2 , ZnO , B_2O_3 and Na_2O) to form a liquid which is poured into stainless steel cylinders and

allowed to cool to form a glass. These glass blocks in their metal containers will be placed in a store on the surface, probably for a period of at least 50 years before final disposal. At the end of this time heat generation and radiation will be much reduced because of the decay of the shorter lived radionuclides.

If the canisters containing the vitrified waste are disposed of beneath the seabed the main barrier to the final emergence of the radionuclides will be the sediments in the far field. How effective the sediments will be as a barrier will depend upon the extent to which they interact with any nuclides that escape from the waste package. It is very important, therefore, to know as much as possible about sediment-nuclide interactions and in 1981 the Department of the Environment (DOE) commissioned Imperial College to investigate the behaviour of selected long-lived radionuclides in the sediment-sea water system. The work described in this thesis was carried out under this contract and much of it has already been reported in a series of internal reports (DOE/RW/83/129, DOE/RW/83/130, DOE/RW/83/131, DOE/RW/84/084) and two published papers (Higgo et al., 1983 and 1985).

1.2. Why Subseabed Disposal?

Approximately three fifths of the world's surface is covered by deep oceans and it is clearly sensible to consider these areas when choosing sites for the geological disposal of radioactive waste. Some of the reasons that make subseabed disposal an attractive alternative to land disposal are listed in the Sandia 1983 Status Report. These are:-

- i) Some of the most stable geological formations on earth are found underlying the deep oceans. They are often located away from tectonic plate boundaries in geologically stable areas. Sediment samples obtained by coring these regions show that deposition has been continuous and uniform for millions of years. Such records allow the future stability of these areas to be predicted with a high degree of confidence.
- ii) The sediments have low strength and therefore geological disturbances do not produce cracks or voids in the sedimentary structure. Existing permeability data suggest that the natural pore water velocity is in the same range as the sediment accumulation rate (0.1 - 1 mm per thousand years). Pore water from deep within the sediments will therefore not naturally reach the sediment/water interface.

- iii) The sediments have low permeability and high absorbancy. The primary radionuclide transport mechanism is chemical diffusion. This very slow process is slowed further by the tendency of the sediment particles to sorb many of the waste nuclides.
- iv) The deep ocean mid-plate geologic formations and bottom waters are low in known resources. At water depths of 6 km, benthic and pelagic organisms are small and sparsely distributed. The only discernible minerals are manganese nodules that, in the areas of interest are low in the commercially important elements copper, nickel and cobalt.
- v) Temperatures in the deep ocean environment are low (2° - 4° C) and nearly constant which means that chemical processes occur slowly and predictably. Furthermore high pressures (60 MPa) guarantee that the sediments will remain uniformly saturated and the porewaters cannot boil. Ice ages and other climatic changes have little or no effect on the stability and uniformity of the deep-ocean environment.
- vi) Even if some nuclides do escape from the sediments the oceans themselves will act as an additional barrier and have the capacity to dilute and disperse them.
- vii) Areas in international waters could be used as international repositories provided that it were possible to develop an international legal structure that adequately and credibly regulates and monitors a subseabed repository.

1.3. The Subseabed Concept

A subseabed repository cannot be described precisely as some factors have not, as yet, been fully studied. However, for the purposes of this discussion a conceptual description is adequate. The waste canisters are likely to consist of vitrified reprocessed waste (probably in the form of a borosilicate glass containing about 25% radioactive waste) encased in stainless steel and/or titanium containers. Proposed canister dimensions vary from 0.3 m diameter by 3 m long (Sandia, 1983) to 1 m in diameter by 3 m long (Laughton, 1979). The simplest subseabed repository would have individual waste canisters emplaced at some depth in the sediment at 100 m intervals. At this spacing they would be thermally and chemically independent of each other and a square area of 15 km by 15 km would accommodate 20,000 canisters (0.3 m by 3 m). This is the waste volume that would result from the U.S. nuclear power industry by the year 2000 if it remains at its present

size of about 50 GW/yr (Hinga, 1983). The global output will be about eleven times this amount (Laughton, 1979). The depth of emplacement necessary to ensure proper containment of radionuclides will depend on the sediment properties at the repository location and it is essential that site-specific sorption and desorption studies be carried out before a final decision is made about any particular location. The shallowest depth discussed to date has been 30 m.

Emplacement might be achieved by a simple free-fall penetrator or some form of boosted or injector-placed penetrator. If greater burial depths are desired drilled emplacement could be used. Drilled emplacement would be more expensive but it would allow a number of canisters to be placed in a stack in a single hole. Model penetrators 3.25 m long and weighing 1.8 tonnes, have already been dropped. They reached terminal velocities of about 50 m/s and were acoustically tracked to depths of 30 m below the sediment/water interface. Full size penetrators would need to be more substantial than this, perhaps 10 m in length and weighing 20 tonnes (Freeman et al., 1984, Francis, 1984).

1.4. The Multibarrier Concept

Consider a waste canister buried within the sediments of the deep-ocean floor. The multiple barriers of the waste form, the canister, the sediments and the ocean waters will all combine to delay migration of the radionuclides until they have decayed to innocuous levels. The time that each barrier will delay the nuclides can to a certain extent be determined by repository conditions and waste package design and one of the aims of current research is to establish on a cost-benefit basis optimum properties and conditions for each barrier.

i) Canister corrosion:- The first barrier is provided by the metal canister. Using thick canisters of carbon steel or cast iron a corrosion life of 500-1000 years is thought to be attainable and work in the U.K. is concentrating on carbon steel overpacks. During corrosion solid ferrous hydroxide will be formed. Most radionuclides are strongly sorbed to iron hydroxides and this should, therefore, further delay radionuclide migration. Another approach is to use corrosion resistant materials such as Ti-base (e.g. Ticode 12 which is Ti-0.8%Ni, 0.3%Mo and which is favoured by Sandia) or Ni-base (Ringwood, 1979) alloys. These would have longer lives but it is doubtful whether the additional cost would be justified. Sensitivity studies have shown

that a canister with a design lifetime of 100 to 300 years would be sufficient to contain HLW during solidification, transportation and emplacement; to facilitate recovery in the event of an accident or improper emplacement and to isolate the wasteform from the sediment during the thermal period. After the thermal period there is little need for a canister since retardation of radionuclide migration can be better accomplished by deeper emplacement of the waste package (Klett, 1984).

ii) Wasteforms:- Once the integrity of the canister has been breached, the glass containing the waste will be exposed to the pore water of the sediments. The leach resistance of this glass provides the second barrier to the release of the waste. Laboratory measurements of glass leach rates suggest that this process will take a few thousand years. Alternative waste forms such as "synroc" (Ringwood, 1983) that last much longer have been proposed but sensitivity studies indicate that the performance of a subseabed repository depends more on the properties of the sediment than on the leach rate of the waste form (Klett, 1983) and the cheaper alternative will probably be satisfactory.

iii) Transport through the sediment:- Once in solution in the pore water the radionuclides will have to travel through many meters of sediment before they can reach the sea itself. For convenience the sediment barrier is usually considered in two sections, the near field and the far field. The near field is defined as that region where the temperature is $>100^{\circ}\text{C}$. The size of this region varies as the radioactive waste decays and will, of course, be smaller if the waste is stored on land for a long time before disposal. Heat transfer calculations indicate that the near field never extends more than 0.8 m into the sediment. The far field is defined as the sediment between the near field and the sea floor. This region of sediment is the main barrier to radionuclide migration in a subseabed repository. Reliable predictions of transport rates for radionuclides under far-field conditions are, therefore, extremely important in the assessment of repository performance.

iv) The water column:- The intention of subseabed disposal is to prevent radionuclides from reaching the seabed itself in unacceptable quantities. But if they do, or if an accident occurs during transport or emplacement and radioactivity is released directly to the seabed, then the ocean itself will be the fourth barrier, dispersing and diluting it.

1.5. Radionuclide Transport Through the Sediments

The transport of dissolved ions through the far-field sediments differs from the analagous processes in most proposed terrestrial geologic disposal sites in that migration is likely to be almost entirely by diffusion. In the absence of a heat source or severe physical disruption of the disposal site, the only force tending to produce pore water flow is continuing sedimentation which tends to compact underlying deposits. The vertical velocity of the pore waters due to compaction is greatest at the sea floor where pore water velocities are generally less than 10^{-11} cm/s (Heath, 1978). Sedimentation rates in the mid-Atlantic areas being considered for waste disposal range from 10^{-10} cm/s in the CV2 area to 10^{-11} cm/s in the GME area. Advection could therefore never carry dissolved nuclides up to the sea floor since the sea floor grows upward faster than the pore water can migrate.

For an ion diffusing from a source (such as a disintegrating waste package) to a sink (such as the ocean), the characteristic diffusion time is simply the square of the source-sink distance divided by the diffusion coefficient of the ion in the intervening medium. Ions which do not sorb to the sediments have diffusion coefficients in the deep sea sediments of the order of 3×10^{-6} cm²/s (Duursma, 1970). Thus the diffusion time for a burial depth of 30 m is 3×10^{12} s or 100,000 years and an additional 3,333 years will be gained for every additional meter.

If the ion is sorbed by the sediment diffusion times will be longer. The equation

$$D' = \frac{D^0}{[1 + K_d (\frac{1-n}{n})\rho]\theta^2} \quad (1)$$

where D^0 = Diffusion coefficient in pore water at infinite dilution;

D' = Lowered diffusion coefficient due to sorption;

n = porosity; ρ = dry density of sediment; θ = tortuosity;

K_d = Distribution coefficient defined as

concentration of a species on the solid phase at equilibrium
concentration of a species in the liquid phase at equilibrium

is often used to calculate the effect that sorption will have on diffusion coefficients. Use of this equation involves numerous assumptions which are unlikely to be true in the waste disposal situation (Berner, 1980, McKinley and Greenwood, 1980) but it gives an order-of-magnitude idea of the effect that sorption has on the diffusion time. It implies that

the distribution coefficient has a directly multiplicative effect on the characteristic diffusion time of an ion. Thus a K_d of 1000 ml/g implies a diffusion time of 100,000,000 years. The possibility of such long barrier time constants is one of the main reasons that subseabed disposal is considered to be such an attractive method of waste disposal. It also explains why the first two barriers (canister and wasteform) pale into insignificance when compared with the sediment layer and why so much importance has been attached to the determination of K_d values when evaluating possible geological disposal sites.

1.6. The Sorption Process

It is difficult to distinguish among the mechanisms that in complex natural systems govern sorption particularly as many systems exhibit intermediate or hybrid behaviour. Nevertheless, it is convenient to divide ideal sorption processes into four categories (NEA, 1983):-

- i) Physical adsorption: This is due to non-specific forces of attraction involving the entire electron shells of the *ion* in solution and of the adsorbing substrate. This process is rapid, reversible, largely independent of the temperature, the chemical composition, the ionic strength and composition of the solution (provided that the solution is well below saturation). The presence of complexing agents and the pH of the solution have a large influence on physical adsorption. An example of such a process is the uptake of neutral metal hydroxy complexes on surfaces which are also neutral following adsorption.
- ii) Electrostatic attraction: This is due to coulombic forces of attraction between charged solute species and the adsorbing substrate. This process is rapid and largely reversible. It is somewhat dependent on temperature and strongly dependent on the composition of the solid phase as well as on the ionic strength and composition of the solution. An example of an electrostatic controlled process is ION EXCHANGE. The exchange of caesium on clays and zeolites is controlled by this process.
- iii) Specific adsorption: This is due to the sorbate inducing the formation of surface sites of opposite charge when adsorbed and/or due to the sorbate ion as a trace species, occupying some of the small number of surface sites of opposite charge regardless of the net surface charge. This process may be slow or rapid, is highly dependent on the composition of the sorbent as well as on the concentration of

solutes and is temperature dependent. An example of this type of adsorption is the nearly complete adsorption of $\text{UO}_2(\text{OH})^+$ on a ferric oxyhydroxide surface at a pH below the zero point of charge of the oxyhydroxide, where it has a net surface charge.

iv) Chemical substitution, (Coprecipitation or solid solution): This is due to the action of specific chemical forces involving chemical bonding. It may be slow and only partially reversible. It is likely to be highly dependent on the composition of the sorbent and solution and may be temperature dependent. Chemical substitution controls the uptake of ions on a solid containing counter ions that can form a sparingly soluble compound on the surface. It can be considered as a special case of precipitation. Americium acting on the surface of phosphate minerals is an example of this process (Beall et al., 1981).

1.7. The K_d Concept

Numerous attempts have been made to develop theoretical models to explain the adsorption of inorganic material at solid-liquid interfaces (Davis et al., 1978; Harmsen, 1979; Langmuir, 1981; Anderson and Rubin, 1981) and considerable progress has been made in recent years. Nevertheless, because natural systems are so complex, mathematicians modelling the migration of radionuclides through geological materials still rely on empirical K_d determinations and are likely to do so for some time to come. The K_d used in many models assumes that the reaction is reversible, that equilibrium has been established and that the K_d measured is constant over the concentration range of interest. If any of these criteria are not satisfied predictions based on the measured K_d will be incorrect. It has been found that many of the sorption-desorption reactions encountered in the waste disposal situation do not fulfil all of these criteria. The NEA co-ordinating group on geological waste disposal has, therefore, recommended that the term distribution ratio (R_d) should be used when reporting empirical experimental results (NEA, 1983). They define the two terms as follows:

R_d = Distribution Ratio of an element. This is an empirical value that is measured in a laboratory experiment. It is the amount (either mass or activity) of the radioelement which is bound to the solid(s) present divided by the amount remaining in solution. Since this is strictly an empirical value, it does not imply reversibility or equilibrium and no attempt is made to relate it to a specific adsorption mechanism. R_d has the units of $\text{L}_3^3 \cdot \text{M}^{-1}$, such as

$$\frac{\text{g nuclide}}{\text{g solid}} \quad / \quad \frac{\text{g nuclide}}{\text{cm}^3 \text{ solute}} \quad \text{giving cm}^3/\text{g}.$$

K_d = Distribution coefficient of an element. This parameter is similar to R_d but implies that the value represents equilibrium conditions. Such a parameter is appropriate to describe ideal ion exchange for example. The units of K_d are the same as those of R_d .

The work described in this thesis was designed to assess a particular type of repository and, although efforts were made to learn as much as possible about the processes occurring during sorption and desorption, measurements were essentially empirical. For this reason (except in the appendix to Chapter 1 where ideal ion exchange is considered) the term distribution ratio (R_d) is used throughout.

Distribution coefficients or distribution ratios are used to give a quantitative measure of the extent to which radionuclides are sorbed and hence retarded by geological materials. Before any useful assessment can be made of any disposal site it is essential that accurate values be available for all the nuclides of interest and almost every existing computer code for safety assessment relies on the distribution coefficient concept (Serne and Relaya, 1982). At first sight it would appear to be a simple matter to determine an empirical distribution ratio using the batch method. All that needs to be done is to contact the solid with ground water that has been spiked with the nuclide of interest. Then after a predetermined time solid and liquid phases are separated and analysed. In practice, however, it has proved remarkably difficult to obtain meaningful values. In 1978 an inter-calibration exercise involving nine laboratories was conducted under the auspices of Pacific Northwest Laboratories (Relaya and Serne, 1979; Serne and Relaya, 1982). Large quantities of rocks were homogenised and characterised. General guidelines were given to participants on groundwater composition, radionuclides and procedural details. In some cases results differed by three orders of magnitude and it was concluded that several parameters which were uncontrolled may have affected them. The uncontrolled parameters were:- (1) method of tracer addition, (2) solid-solution ratio, (3) initial tracer concentration, (4) particle size distribution, (5) solid-solution separation method, (6) temperature. Other parameters which can have a marked effect on the R_d are (8) pH, (9) Eh, (10) temperature, (11) radionuclide concentration, (12) chemical composition of both solid and liquid phases.

As a result of this intercalibration exercise a detailed standard method for the batch determination of R_d was formulated and issued together with recommendations for supporting data (e.g. mineralogy, surface areas, cation exchange capacities) that should be obtained (Relyea et al., 1980). Since then batch sorption measurements have become more reliable. Computer modelling is becoming increasingly sophisticated and able to cope with R_d that do not even approximate to the ideal K_d . However, because the R_d is an empirical value it is important that conditions used in the laboratory experiments should be carefully controlled and should approximate as closely as possible to actual repository conditions.

Until now one of the greatest limitations of the batch distribution method has been its inability to differentiate multiple species of a radionuclide and it gives only an average R_d for all the chemical forms of the nuclide. Most of the actinides can exist in several oxidation states, sometimes simultaneously, and in a complex medium such as sea water polymers, carbonates and other complexes may exist. These may have positive or negative charges and may all react differently with the sediments and have different migration rates. Column experiments should be able to differentiate between species of different mobilities but are more difficult and time consuming than batch experiments. Furthermore, column experiments like batch experiments do not simulate the conditions that will exist when wastes are buried in the seabed since migration will be by diffusion rather than by ground-water flow. Diffusion experiments have been conducted by Duursma and Bosch (1970), Erikson (1980a) and Schreiner et al., (1982) but are too slow to be practical if the diffusion coefficients are very low. For this reason, it was decided to use the batch method in the present study. At the same time every effort was made to learn as much as possible about the chemical reactions involved in the sorption-desorption process. The effect of oxidation state was investigated and it will be shown (Chapter 5) that by varying the solid-solution ratio it is possible to estimate whether species with widely differing R_d values are present.

Spent fuel from a nuclear power plant contains a wide range highly radioactive isotopes with vastly differing half lives. Figure 1 (from Searle, 1979) shows how the activity from one tonne of reprocessed uranium decreases with time. One group of elements formed by the

fission of uranium (and plutonium) decays mostly by beta and gamma emission. The most important of these fission products are caesium-137 and strontium-90 and they must be contained for about 600 years before they decay to safe levels. After 600 years the dominant radioactive species are the actinide elements, principally isotopes of plutonium, americium, curium and neptunium. After a million years, the activity of the waste becomes comparable to that of the original uranium which was mined to produce the fuel. Because the canister and wasteform can be expected to contain all nuclides for well over a thousand years only isotopes with long half-lives will have to be retarded by the sediment barrier. Various sensitivity studies (NEA, 1982; Barney, 1980; Sandia, 1983) have suggested that of these the actinides together with Tc-99 and possibly ^{79}Se and ^{135}Cs pose the greatest hazard to man (NEA, 1982). The exact order of ranking according to hazard measures will depend on the particular disposal system used and on the composition of the waste.

Because this work was commissioned by the DOE reports were written after completion of each phase of the research and each Chapter of this thesis is based on a DOE report. For this reason the arrangement is to a certain extent chronological and each Chapter is self contained and with its own summary and conclusions.

Chapter 2 describes the early work using ^{137}Cs and ^{152}Eu . These isotopes were used because, although the main aim of this research was to study actinide/sediment interactions, facilities were not available for studying actinides at the start of this project. Caesium was chosen because it is such an important constituent of HLW and because its chemistry and sorption behaviour have been extensively studied. Europium was chosen because it is a lanthanide and might be expected to have properties similar to the trivalent actinides. The sorption of caesium (unlike that of the actinides) is by ion exchange and distribution coefficients rather than distribution ratios can be used to measure its sorption behaviour. While caesium was being investigated some theoretical studies were made in order to show how the distribution coefficient is related to other thermodynamic parameters used in ion exchange work (e.g. the selectivity coefficient) and results of previous work at Imperial College on pure zeolites were re-interpreted to show how the different parameters are inter-related. This is presented in an appendix to Chapter 2.

As soon as A-grade radiochemical facilities were available work was begun using the actinides americium, neptunium and plutonium. Chapter 3 describes the work with americium and neptunium and Chapter 4 is devoted to plutonium. Finally Chapter 5 shows how the sediment/sea water ratio used in the batch distribution ratio experiments can markedly affect measured distribution ratios. It discusses the reasons for this and points out some important implications.

Table 1.1. Sediment Properties

Property	Calcareous Ooze	Red Clay
Temperature:		
Surface sediment	3°C	3°C
Rate of increase with depth	54°C/100m	54°C/100m
Thermal conductivity (Wm ⁻¹ K ⁻¹)	0.7 - 0.9	0.7 - 0.9
Dry sediment density (gcm ⁻³)	2.6	2.7
Porosity-unconsolidated sediment	65-85%	65-85%
Shear strength in upper 100m (kPa)	10-100	10-100
Porewater diffusion coefficient (cm ² s ⁻¹)	$3 \times 10^{-6} - 5 \times 10^{-6}$	$3 \times 10^{-6} - 5 \times 10^{-6}$
Permeability (cm ⁻²)	$< 10^{-11}$	$< 10^{-11}$
Calcium carbonate content	range: 10-90%	~ 3%
Organic carbon content	range: < 0.1% - 2% (contains more than clays).	range: < 0.1% - 2%
Porewater convection rate (cm s ⁻¹)	$\sim 3 \times 10^{-8}$	$\sim 3 \times 10^{-8}$
Porewater pH	7.7 Range: 5 - 8	7.7 Range: 5 - 8
Porewater salinity (%)	34.5 - 35.5	34.5 - 35.5

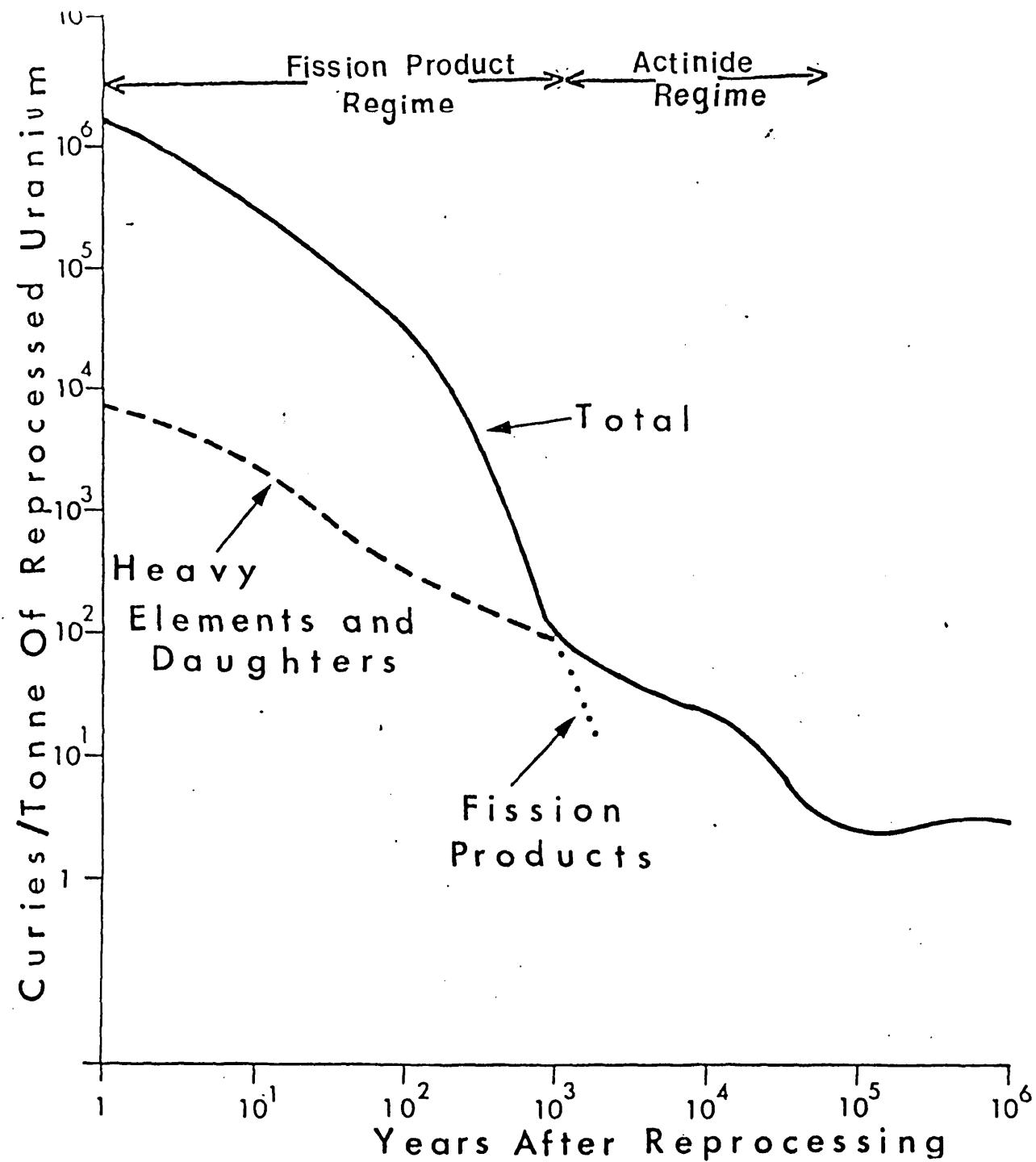


Fig. 1.1

CHAPTER 2

THE SORPTION OF CAESIUM AND EUROPIUM ON MARINE SEDIMENTS

2.1. Introduction

The basic aim of this project was to study the radionuclide sorption properties of deep-sea sediments. These properties are extremely important since the adequacy of the sediments to serve as a barrier to the migration of nuclides away from buried waste will be largely determined by the sorption behaviour of the nuclides.

The samples were chosen to represent a wide variety of sediments occurring in the deep sea. To this end, carbonates, ferromanganese oxides and various types of clays and mixtures of these were obtained. By encompassing several major deep-sea-sediment types it was hoped to cover the range of sediments likely to be selected for deep-sea waste disposal. Three sediments and two manganese nodules were selected for the initial study. Two of the sediments were calcareous oozes containing 87.5% and 44.5% CaCO_3 , respectively. The other was entirely different being rich in smectite (30-40%) and containing large amounts of iron as the oxy-hydroxide (8-15%) as well as amorphous silica. The two nodule samples differed in that one was largely amorphous iron and manganese oxy-hydroxides whereas the other was composed mainly of the manganese minerals, birnessite and todorokite. The reason for including these nodules in this study is that the hydrous oxides of manganese and iron occur in virtually all sediments, both as discrete oxide particles and as partial coatings on other minerals and it is likely that they exert an influence on the sorptive properties of the sediments which is out of all proportion to their concentration. The ion exchange capacities of these oxides is large, but possibly more important is the fact that they are themselves participants in oxidation reduction cycles, and evidence is accumulating that retention of actinides is frequently the result of precipitation during redox reactions rather than by ion exchange.

All the samples were characterised as fully as possible in order to assess whether any particular property had an effect on the sorptive properties. Thus, in addition to the mineralogical analysis, chemical composition surface areas and cation exchange capacities were determined.

2.2. Experimental Methods and Results

2.2.1. Mineralogy and chemical composition

The samples were analysed by X-ray diffraction and Table 2.1. gives details of their mineralogy.

Table 2.1. Mineralogy of Sediments Studied

	Sample No.	Origin	Composition		
			Major	Minor	Trace
Sediments Manganese Nodules	M77-20		Calcite	Quartz	
	S 702	Hellenic Trench	Calcite Quartz	Illite	Smectite Plagioclase feldspar
	SH 1578	Eastern Pacific	Smectite (30-40%) Fe oxyhydroxides (8-10%) SiO ₂ as amorphous silica (10-17%)		
	MV65 I	Mexico	Birnessite Todorokite	Quartz	Plagioclase feldspar
	6269 No. 22	Karlsberg Ridge	Amorphous Mn & Fe oxy- hydroxides	δ -MnO ₂	Plagioclase feldspar Quartz

In addition to analysis by X-ray diffraction the samples were analysed for a number of elements. The major elements were determined by inductively coupled plasma spectroscopy after fusing with LiBO₂. The minor elements were determined by atomic absorption after digestion in HF/HNO₃/HClO₄. In some cases elements were determined by both methods and, except for two aluminium results, agreement is excellent. The quality of the Al data on the plasma spectrograph is good and it is felt that they are more likely to be correct. These results are given in Table 2.2. and tie in very well with the mineralogy. Thus M77-20 and S-702 contain 87.5% and 44.5% CaCO₃, respectively. SH 1578 is high in iron, some of which could be in the montmorillonite lattice. S 702 contains K which is probably fixed in the illite lattice.

Table 2.2. Chemical Composition of Sediments

No	SiO ₂	% Ca		% Al		% Fe		% Mn		Ni	Cu	Zn	Pb	Ti	P	Na	K
	Plasma	Plasma	A.A.	Plasma	A.A.	Plasma	A.A.	Plasma	A.A.	A.A. ppm	A.A. ppm	A.A. ppm	A.A. ppm	Plasma ppm	Plasma ppm	Plasma %	Plasma %
M77-20	7.29	35.0	35.0	1.48	1.4	1.69	1.69	0.124	0.12	21	297	109	8	660	60	0.20	0.32
S-702	17.1	17.8	17.9	4.75	5.1	3.03	3.12	0.134	0.14	165	63	89	9	2500	430	0.44	1.13
SH1578	39.5	1.74	1.8	1.47	2.6	14.6	14.5	3.59	4.26	555	865	435	75	1100	340	0.70	0.34
MV65I			1.4		2.2		2.2		32.9	1800	1200	1340	22				
6269 No 2.			1.7		1.7		13.7		16.8	4680	1580	680	760				

2.2.2. Surface Areas

Surface area measurements were made by the simplified ethylene glycol monoethyl ether (EGME) procedure (Cihacek and Bremner, 1979; Heilman et al., 1965). Before beginning the surface area determinations the clay samples, but not the manganese nodules, were washed twice with distilled water to remove salts. Approximately one gram portions were dried to constant weight over P_2O_5 in a vacuum desiccator. After drying the samples were mixed with approximately 3 ml of EGME to form a slurry and placed in a desiccator over $CaCl_2$ and allowed to equilibrate for 30 mins. The desiccator was then evacuated for about 45 minutes. At intervals (the beginning and end of each working day) the samples were weighed and the desiccator re-evacuated for 45 minutes. When constant weight had been attained it was assumed that the EGME had formed a monolayer over the sample and the total surface area was calculated by dividing the weight of EGME retained per gram of sediment by 0.000286 g/m^2 .

Some difficulty was experienced in attaining constant weight both when drying over P_2O_5 and after equilibration with EGME and the results reported in Table 2.3. are probably not as accurate as one would have liked. However, at this stage it is relative rather than in absolute values that are important and it is felt that they are sufficiently accurate for the present purpose.

The surface areas obtained by the EGME method are given in Table 2.4. and they can be readily correlated with the mineralogy (Table 2.1.) of the sediments. Thus M77-20 which is almost entirely calcite has a low surface area. SH-1578 which contains a high proportion of montmorillonite and Fe oxyhydroxides has a high surface area and S-702 containing less calcite than M77-20 and some illite having a value between the two. Reported values in the literature for the surface area of soils range from $8 \text{ m}^2/\text{g}$ for sandy soils to $300 \text{ m}^2/\text{g}$ for clay-rich soils to $800 \text{ m}^2/\text{g}$ for pure bentonite (Grim, 1968; Bower, 1958; Cihacek, 1979).

The large difference between the two manganese nodule samples is no doubt due to the more highly crystalline structure of MV 65 I as compared with 6269 No. 2. Han (1981) obtained values ranging from $118 \text{ m}^2/\text{g}$ to $287 \text{ m}^2/\text{g}$ and he relates this to the very high porosity of manganese nodules which is about 60%.

2.2.3. Cation Exchange Capacity

Cation exchange is a reversible chemical reaction. The cations held on the surface, and sometimes within the crystal framework of minerals can be reversibly replaced by those of salt solutions and acids. For many years cation exchange capacity (CEC) has been used in the prediction of soil properties and numerous methods for determining the CEC of soils and clays have been developed. In these methods various cations including ammonium, sodium, caesium and magnesium have been used. Of these the ammonium ion has the widest acceptance, although for soils containing carbonates, sodium is preferable because carbonates are soluble in ammonium acetate.

Caesium has a low hydration energy and a relatively low affinity for the aqueous phase. It is selectively adsorbed in preference to Na, Ca and Mg and is therefore, a very suitable cation for use in CEC determinations. Beetem et al. (1962) have described a rapid method using ^{137}Cs and this was used on all the samples. In addition the sodium acetate method (Chapman, 1965) was used on the three clay samples.

(i) The ^{137}Cs method: The sample (between 0.2 and 1.0g, depending on the expected CEC) was weighed into a 15 ml disposable centrifuge tube and 5 ml of a 1.0 M caesium chloride solution containing ^{137}Cs was added. The ^{137}Cs activity was either 40 $\mu\text{Ci/l}$ (high CEC samples) or 120 $\mu\text{Ci/l}$ (low CEC samples). The samples were then shaken on a mechanical shaker for at least four hours. The phases were separated by centrifuging for 25 min at 4000 rpm and the supernatant liquid decanted. This procedure, i.e. addition of 5 ml of spiked 1.0 M CsCl solution followed by shaking and centrifuging was repeated twice more. The excess caesium chloride was removed from the samples by repeated washing with approximately 10 ml portions of 95% ethyl alcohol, agitating thoroughly (10 to 15 min on a mechanical shaker), centrifuging completely and decanting the supernatant liquid after each wash until the decanted alcohol was free from chloride (6-8 washes).

When washing was complete the sample was transferred to a scintillation vial and counted in a well-type gamma scintillation counter. A sample of the solution used to saturate the sample with caesium was counted at the same time and the CEC calculated using the following equation:

$$\text{CEC} = \frac{\text{sample cpm}}{\text{solution cpm/mEq Cs}} \times \frac{100}{\text{sample weight}} \text{ mEq/100g}$$

(ii) The Sodium acetate method: Samples weighing between two and four grams were placed in Oakridge type 50 ml centrifuge tubes. 33 ml of 1.0 M sodium acetate was added and the tubes shaken on a mechanical shaker for five minutes. The samples were then centrifuged for 25 min at 4000 rpm and the supernatant liquid decanted. This extraction was repeated three more times. The sample was then washed in an identical manner with three 33 ml portions of isopropyl alcohol. Alcohol rather than water was used in order to prevent hydrolysis of exchangeable sodium. Bower and Goertzen (1962) have shown that three is the optimum number of washes; the loss by hydrolysis being balanced by incomplete removal of sodium.

Using the same shaking and centrifuging procedure the adsorbed sodium was then replaced by ammonium by shaking with three 33 ml portions of 1 M ammonium acetate. Each wash was decanted into a 100 ml volumetric flask and the solution made up to volume with 1 M ammonium acetate. Standard solutions of sodium in 1.0 M ammonium acetate were prepared and the sodium content of the sample solutions determined by flame photometry.

The results of these determinations are given in Table 2.3. together with the surface areas. Generally agreement between the two methods is good. The caesium exchange method is quicker and seems to give better precision than the sodium acetate method.

As with surface area the results are readily explainable in terms of sample composition. Thus M77-20 being mainly calcite has a very low CEC with S702 which contains some illite being somewhat higher. S702 with its high proportion of montmorillonite has the expected high CEC. Typical CECs given in the literature are montmorillonite 80-150 mEq/100g, chlorite 25 mEq/100g, illite 10-40 mEq/100g, quartz 1 mEq/100g, and limestone 0.5 mEq/100g (Seitz et al., 1980; Duursma and Eisma, 1973) and manganese nodules are said by Stumm and Morgan (1970) to have CECs comparable to clays. They say that sorption of metal ions by hydrous Fe and Mn oxides may be properly interpreted as surface complex formation or ion exchange; hydrogen ions or other cations being released in proportion to the quantity of metal ions adsorbed.

It is interesting to note that whereas in the case of the clays there is a strong correlation between the surface area and the CEC, there is none with the two manganese nodule samples. For these two samples there is little difference in CEC despite a large difference in surface area. Presumably available surface is not the limiting factor as far

Table 2.3. Surface Areas and Cation Exchange Capacities

No	Surface Area m ² /g	CATION EXCHANGE CAPACITY	
		⁺ Na Exchange mEq/100g	⁺ Cs Exchange mEq/100g *
M 77-20	38.5 } 28.4 } 30	12.2 } 9.0 } 11	6.8 ± 0.1 } 6.2 ± 0.1 } 7
S 702	98.1 } 96.1 } 97	18.6 } 18.3 } 18 17.3 }	20.2 } 20.8 } 20 20.11 }
SH 1578	394.9 } 398.8 } 396 394.7 }	116.7 } 125.3 } 113 99.3 }	126 ± 1 } 125 ± 1 } 124 122 ± 1 }
MV 65 I	82 } 85 } 95 119 }	-	101 ± 1 } 100 ± 1 } 100 96 ± 1 }
6269 No 2 (amorphous)	339 } 341 } 340 342 }	-	83 ± 1 } 80 ± 1 } 82 82 ± 1 }

* ERRORS based on counting statistics only.

as sorption is concerned. It may be that the large Cs ion has difficulty diffusing into the pores and only external surface is involved. It is probably worth determining the CEC by the sodium method to see whether this gives higher results.

2.2.4. Distribution Ratios

Distribution ratios are usually determined using batch equilibrations in which a known amount of clay is contacted with a known volume of solution and shaken until equilibrium is reached. The solution is analysed before and after equilibrium and R_d calculated from the formula

$$R_d = \frac{I-F}{F} \times \frac{\text{Vol}}{\text{Wt}}$$

Where I = initial conc. in soln.

F = final conc. in soln.

Any convenient unit, e.g. counts/min may be used.

It is thus unnecessary to analyse the solid phase. This assumes, however, that all the element lost from solution is adsorbed by the solid. This is generally the case, but occasionally adsorption by the container may be significant and it is necessary to analyse the solids.

Note i) Since $R_d \propto \frac{1 - F/I}{F/I}$

the graph of R_d against F/I will be hyperbolic. This means that R_d will be very sensitive to small changes in count rates if F/I is small (usually when R_d is high) and very insensitive if F/I is large.

The batch partitioning experiments were carried out as far as possible, following the method described by Relayea et al. (1980) in their "Task 4" Status Report. In addition, an attempt was made to approximate natural conditions as closely as possible. Thus experiments were carried out at 4°C, sediments were kept moist and in contact with sea water at all times and sorption was from sea water.

2.2.4.1. Preparation of spiked solutions

Mid-Atlantic sea water was obtained from the Institute of Oceanographic Sciences. This was deep ocean water of known chlorinity and had been filtered through charcoal. A chemical analysis was not performed but it was assumed to have a composition typical of deep ocean waters.

Solutions spiked with ^{137}Cs were prepared by adding microliter quantities of a stock ^{137}Cs solution. (Amersham; 1.7 mCi/l, 30 ug Cs/mCi) to this sea water. Solutions containing high concentrations of total Cs

were prepared by adding μ l quantities of 1M CsCl. These additions did not alter the pH which remained constant at 8.2.

Europium is known to be unstable in solution, particularly at high pHs. Spiked solutions were therefore prepared several weeks in advance. ^{152}Eu obtained from Amersham was diluted to give a stock solution containing 1 mCi/100 ml and 0.5 mg/100 ml in 0.1 M HCl. 0.15 ml and 1.5 ml portions were then evaporated to dryness at about 30°C and added to 400g of sea water. Five gram samples were counted on a well type NaI scintillation counter. The solutions were left standing at room temperature for five weeks after which time they were centrifuged, filtered through 0.22 μ millipore filters and again counted. There was very little loss in activity (Table 2.4.) and it was assumed that the solubility of europium had not been exceeded. Subsequent work showed, however, that these solutions were unstable when agitated at 4°C (see Section 2.2.6.).

Table 2.4. Preparation of ^{152}Eu Solutions

Date counted	1.5 ml stock per 400g sea water c/min/5g	0.15 ml stock per 400g sea water c/min/5g
5/8/81	317962 $\pm$ 564	27301 $\pm$ 167
10/9/81	307406 $\pm$ 554	21891 $\pm$ 150
Molarity of Final Solution	1.3×10^{-6} M	9.1×10^{-8} M

2.2.4.2. Preparation of solid phases

100g to 200g samples of sediment were taken from cores which had been stored moist and undisturbed. They were mixed with sea water to form a slurry and smaller samples were taken by pipetting while agitating. The solid content of the slurry was determined by washing samples briefly in distilled water and drying at 105°C . All results are reported on a dry weight basis.

The manganese nodules were ground with a mortar and pestle and passed through a 60 mesh sieve. The powder was stored in air at room temperature. The moisture content was determined by drying at 105°C .

Samples were not dried before use but results are reported on a dry weight basis.

2.2.4.3. Caesium batch distribution experiment

It is well known that the fraction of caesium adsorbed by geological materials depends upon the concentration of caesium in the solution phase (Seitz et al., 1980; Erikson, 1978; Barney, 1980). It was therefore decided to determine distribution coefficients over the range 10^{-3} M to 10^{-10} M. This should cover any concentration likely to be met in waste disposal situations. The experimental procedure was as follows:

Samples weighing between 0.2 and 0.4g (dry wt.) were placed in weighed 50 ml Oakridge-type centrifuge tubes and 15g sea water added. The tubes were tightly closed using teflon tape to ensure a leak-proof seal, placed horizontally in a shaking water bath at 4°C, and shaken gently at 120 strokes/min. overnight. This initial prewash was designed to equilibrate the exchange sites of the clay minerals in the sediments and to dissolve any salts which may have precipitated within the sediments during core storage.

The samples were then centrifuged for 25 min. at 4000 rpm and the sea water decanted. They were weighed in order to determine the amount of sea water entrained with the sediment. Sea water, ^{137}Cs and 1.0M CsCl were then added to give the desired concentrations in 30g sea water. When calculating the concentration of Cs present it was assumed that the concentration of Cs in the sea water was 3×10^{-9} M (Goldberg, 1972). The tubes were then returned to the water bath and shaken at 120 strokes/min. After 1 week they were centrifuged and 5g samples of the supernate transferred to a well-type NaI scintillation counter. After counting the liquid was returned to the original centrifuge tube and shaking continued. This sampling and centrifuging procedure was repeated after 13 days and 45 days.

Note. After completion of the experiment at 45 days investigations were carried out to determine whether:

- i) complete separation of solid and liquid phases was obtained by the centrifuging procedure used.
- ii) the fact that the temperature rose from 4°C to about 25°C during centrifuging had any effect on the observed distribution coefficient.

i) Phase separation: If phase separation is not complete observed distribution coefficients will be too low. Various authors (Erdal, 1979,

1980) have reported great difficulty in obtaining complete separation of the solid and liquid phases. Techniques used vary from centrifuging for 20 mins. at 6000 rpm to centrifuging for 4 hours at 1600 rpm followed by filtration through millipore filters. Clearly, exactly what is necessary will depend upon the material being investigated. In all the work described so far, the phases were separated by centrifuging for 25 mins. at 4000 rpm, and the following check was now carried out to see whether filtering through 0.22 μ m filters would have significantly affected the results.

Samples were centrifuged in the usual manner and 5g portions of the supernate transferred to scintillation vials for counting. A further 10 to 20g of supernate were then filtered through double 0.22 millipore filters and 5g portions of the filtered solution counted. Top and bottom filters were counted separately, the difference between top and bottom count rates giving the particulate activity retained on the filter. The solid phase was also counted after it had been transferred to scintillation vials (a correction being made for entrained supernate).

Table 2.5. Phase Separation

Sample	Supernate		Sediment
	Centrifuged only cpm/5g	Centrifuged and filtered cpm/5g	cpm/g
M77-20	36456 $\pm$ 192	34664 $\pm$ 188	553777 $\pm$ 1290
S-702	15623 $\pm$ 127	15753 $\pm$ 128	1109712 $\pm$ 1972
SH 1578	23917 $\pm$ 156	24829 $\pm$ 159	1103119 $\pm$ 2115
MV65-I	10474 $\pm$ 104	10363 $\pm$ 104	871836 $\pm$ 2385

Sample	Filters					
	Top cpm	Bottom cpm	Top- Bottom cpm	Wt. filtered g	$\frac{\text{Wt. Sediment}}{\text{Wt. Liquid}}$	% Sediment retained on filter
M77-20	574 $\pm$ 32	488 $\pm$ 31	86 $\pm$ 45	10.575	0.01137	0.129 $\pm$ 0.068
S702	389 $\pm$ 30	289 $\pm$ 28	100 $\pm$ 41	14.819	0.00963	0.063 $\pm$ 0.026
SH 1578	298 $\pm$ 30	254 $\pm$ 28	44 $\pm$ 41	16.677	0.00867	0.027 $\pm$ 0.026
MV65 I	161 $\pm$ 26	104 $\pm$ 25	57 $\pm$ 36	18.060	0.01427	0.025 $\pm$ 0.016

ERRORS based on counting statistics only.

It can be seen that for the two samples high in calcium carbonate a small amount of sediment was retained on the filters. Caesium does not form colloids in solution and any activity retained by the filter must be due to ^{137}Cs adsorbed on particles of sediment. (In calculating the percent of sediment retained on the filter the assumption has been made that the caesium was uniformly adsorbed over all the particles. This is unlikely to be entirely correct although Eicholz and Croft (1967) report that Cs is one of the elements that have shown a direct relationship between suspended solid concentration and the percentage of the total Cs in the system adsorbed.) However, the effect of this small amount of solid in the solution phase was not detectable and filtering would not have altered the R_d values obtained. Nevertheless, care must be taken if low solution activities are obtained, particularly if the distribution coefficient is high. For the manganese nodule samples and for SH1578 separation seems to have been virtually complete.

ii) Effect of temperature rise during centrifuging

Four samples which had been shaking in the water bath for 47 days were treated as follows:

Shaking was stopped and the samples allowed to stand for 3 hours at 4°C . 5g portions were withdrawn and immediately filtered through 0.22 μ millipore filters. Syringe-type filters were used and filtering took less than a minute. The remainder of the sample was then centrifuged for 25 mins. at 4000 rpm and a second 5g sample extracted and filtered. Both samples were counted. The results of this experiment can be seen in Table 2.6.

Table 2.6. Effect of centrifuging at room temperature.

Sample	after 47 days				after 45 days	
	Filtered Cold cpm/5g	R_d	Filtered after cent. cpm/5g	R_d	Cent. only cpm/5g	
M77-20	51806 $\pm$ 230	39.5 $\pm$ 0.6	54459 $\pm$ 234	33.9 $\pm$ 0.5	54141 $\pm$ 74	33.3 $\pm$ 0.5
S-702	25868 $\pm$ 167	200.4 $\pm$ 0.5	28225 $\pm$ 170	175.5 $\pm$ 1.5	29029 $\pm$ 55	168 $\pm$ 1
SH-1578	27471 $\pm$ 169	247.0 $\pm$ 2.1	30953 $\pm$ 1.7	204.8 $\pm$ 1.8	30115 $\pm$ 56	214 $\pm$ 2
6269	22162 $\pm$ 152	283.5 $\pm$ 2.5	25269 $\pm$ 162	235.0 $\pm$ 2.1	28506 $\pm$ 54	196 $\pm$ 2
Equilibrium Cs concentrations were approximately $2 \times 10^{-9}\text{M}$						

It can be seen that the activity of the solutions that were filtered cold is significantly lower than the activity of the solutions that were filtered after centrifuging and this results in an increase in the calculated R_d value of some 15%. This is presumably due to a shift in the equilibrium with the rise in temperature. Clearly it is desirable to maintain the temperature at 4°C throughout the experiment and later experiments were carried out using a refrigerated centrifuge. The fact that the results obtained for the centrifuged samples are so similar to those obtained after 45 days indicates that this equilibrium shift is reversible.

A decrease in R_d with increasing temperature has been observed by other workers, e.g. Kenna (1980) and Aston (1981), who found a 40% reduction in R_d over the temperature range 1-20°C. Aston was working with intertidal sediments from the Irish sea and caesium concentrations of about 10^{-9} M.

2.2.5. Cs Distribution ratio results

Table 2.7 and Figure 2.1 show the results obtained in the caesium R_d experiments. Two trends are immediately obvious:-

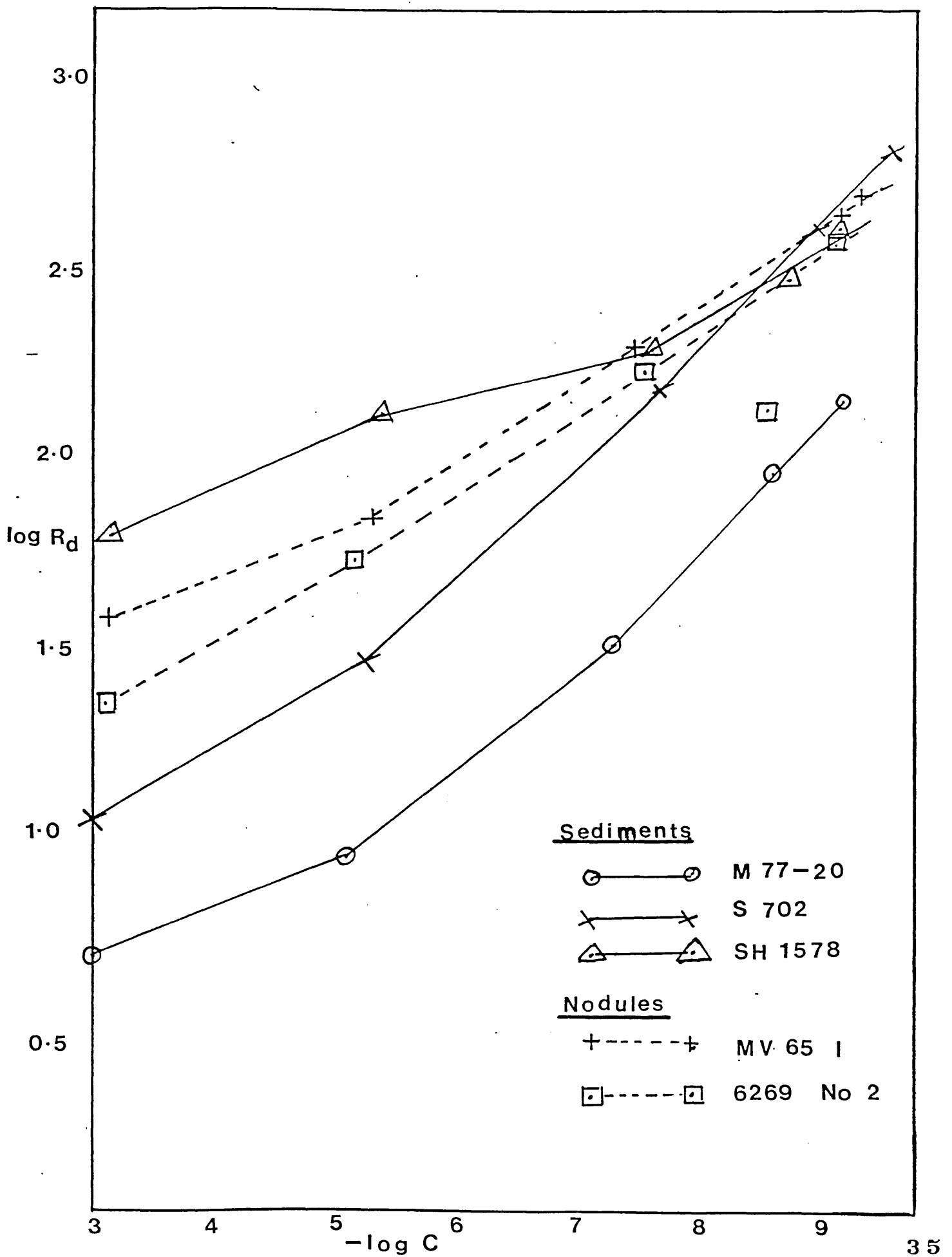
- i) The distribution ratio increases with decreasing caesium concentration.
- ii) The distribution ratio rose slowly with time, this effect being more marked at low than at high concentrations.

These two effects, and the effect of sample composition will be discussed separately, but before doing so it is important to point out that in calculating R_d values, the fact that the samples almost certainly contained significant quantities of caesium has been ignored. Sediments are known to be rich in certain trace elements and our samples were presumably in equilibrium with sea water at the start of the experiment. The concentration of trace elements in sea water is fairly uniform and it was assumed that the caesium concentration was 3×10^{-9} M. The caesium content of sediments is less likely to be uniform, but if one takes the value of 5 ppm given by Martin and Maybeck (1976) as typical, then the calculated value of R_d is 1.2×10^4 ml/g. This is very much higher than the values reported in Table 7. The values obtained in experiments of this nature are not affected by any non-exchangeable Cs in the sediment and it is a moot point whether it would be desirable to include Cs fixed in the lattice of the clay in the solid phase concentration when calculating R_d . From the practical point of view

Table 2.7. Caesium Distribution Ratios

Sample	Initial Cs concentration M	Final Cs concentration M	R_d after		
			7 days ml/g	13 days ml/g	45 days ml/g
M 77-20	3.4×10^{-9}	1.0×10^{-9}	113±4	127±4	156±12
	7.4×10^{-9}	3.4×10^{-9}	76±1	86±1	98±1
	1.0×10^{-7}	7.4×10^{-7}	47±1	29±1	33±1
	1.0×10^{-5}	8.9×10^{-6}	6.7±0.4	8.0±0.5	9.1±0.4
	1.0×10^{-3}	9.4×10^{-4}	3.9±0.5	3.5±0.5	4.8±0.5
S 702	3.4×10^{-9}	3.8×10^{-10}	422±5	482±19	736±16
	7.4×10^{-9}	1.5×10^{-9}	298±3	371±3	464±4
	1.0×10^{-7}	3.8×10^{-8}	122±1	136±1	168±1
	1.0×10^{-5}	6.9×10^{-6}	25±0.5	28±0.5	30±0.4
	1.0×10^{-3}	9.0×10^{-4}	10±0.5	10±0.5	11±0.5
SH 1578	3.4×10^{-9}	8.1×10^{-10}	362±12	381±12	455±9
	7.4×10^{-9}	2.2×10^{-9}	280±3	254±2	318±3
	1.0×10^{-7}	3.9×10^{-8}	194±2	196±2	214±2
	1.0×10^{-5}	4.8×10^{-6}	134±2	131±2	142±1
	1.0×10^{-3}	7.0×10^{-4}		60±1	64±1
MV65I	3.4×10^{-9}	6.7×10^{-10}	485±18	532±18	566±10
	7.4×10^{-9}	9.8×10^{-10}	408±4	413±4	475±5
	1.0×10^{-7}	3.8×10^{-8}	198±2	192±2	211±1
	1.0×10^{-5}	6.1×10^{-6}	69±1	70±1	72±1
	1.0×10^{-3}	7.7×10^{-4}	36±1	35±1	37±1
6269	3.4×10^{-9}	2.7×10^{-9}	306±13	393±13	403±8
	7.4×10^{-9}	7.4×10^{-9}	142±2	148±2	140±1
	1.0×10^{-7}	3.6×10^{-8}	209±2	206±2	196±3
	1.0×10^{-5}	9.9×10^{-6}	53±2	51±1	56±1
	1.0×10^{-3}	9.9×10^{-4}	24±1	24±1	23±1
Errors from counting statistics only					

Fig 2.1 Caesium Distribution Ratios



we are interested in the additional caesium that can be adsorbed and a case can be made for ignoring the initial Cs content of both solid and liquid phases. However, the effect of exchangeable Cs on the sediment could have a marked effect, not on the R_d value, but on the actual Cs concentration associated with a particular value (since ^{137}Cs apparently removed from solution would, in fact, be replaced by stable Cs). An attempt was made to estimate to what extent this may have been happening by using the following reasoning:-

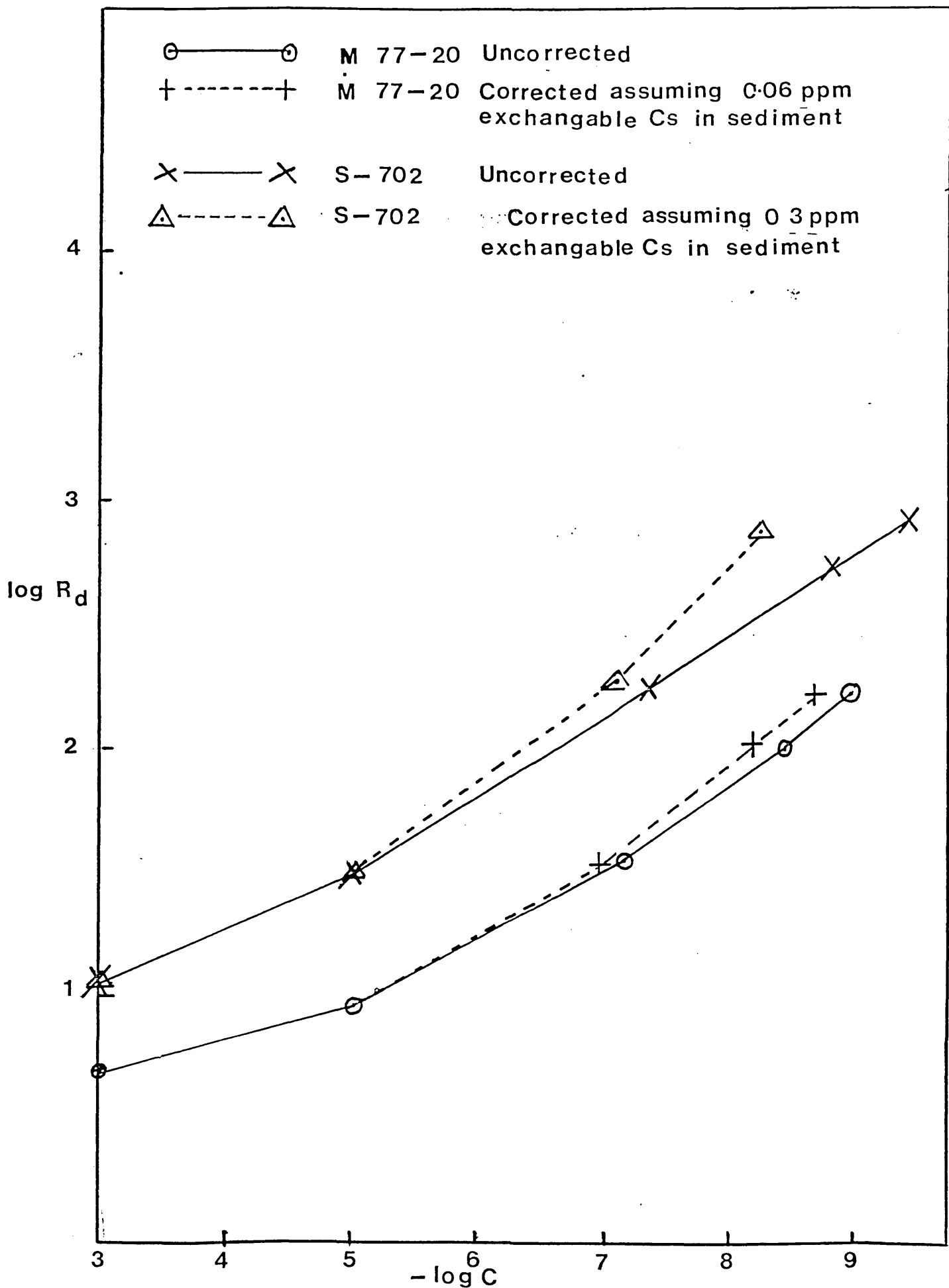
At the beginning of the experiment our samples are in equilibrium with sea water ($3 \times 10^{-9}\text{M}$). In our distribution coefficient experiments the most dilute solution contained only an additional 0.44×10^{-9} moles/l and it is likely that the observed R_d for this dilute solution was not very different from that operating under natural conditions. This is assuming complete isotopic redistribution with exchangeable Cs over the 45 days of the experiment. Knowing R_d and taking the sea water concentration as $3 \times 10^{-9}\text{M}$ it is possible to calculate the concentration in the sediment. Values obtained in this way range from 0.06 to 0.3 ppm for the five samples (Table 2.8.). Duursma (1973) found that only 2.9% of the Cs in a Mediterranean sediment was in exchangeable form and our results are probably of the same order.

Table 2.8. Calculated 'exchangeable Cs' on sediments

Sample	R_d for most dilute solution ml/g	Exchangeable Cs	
		Moles/g	ppm
M 77-20	156	4.68×10^{-10}	0.06
S-702	736	2.21×10^{-9}	0.30
SH 1578	455	1.37×10^{-9}	0.19
MV 65 I	566	1.7×10^{-9}	0.23
6269 No. 22	403	1.21×10^{-9}	0.16

The effect that this small amount of exchangeable caesium has on the calculated equilibrium solution concentration is small as can be seen from the graphs in Figure 2.2. In this Figure the normal uncorrected graphs of $\log R_d$ vs. $-\log C$ (where C = equilibrium concentration in solution) have been plotted together with "corrected" graphs in which C has been corrected for the Cs that exchanged with ^{137}Cs .

Fig 2.2 Effect of Exchangeable Caesium in Sediment



At high solution concentrations the effect is negligible and at low concentrations insignificant in comparison with variations that can be expected because of such variables as sample composition, etc.

2.2.5.1. Sorption isotherms

Figure 2.1. shows plots of $\log R_d$ vs. $-\log C$ for all five samples. In all cases there is a sharp increase in the value of R_d and in the slope of the curve at low concentrations. This effect has been observed by other people working with natural materials and has been ascribed to the sorption of Cs by at least two different mechanisms (possibly on different fractions of the sediment) one having high equilibrium coefficient but low sorption capacity which is quickly exhausted.

In contrast people working with highly purified materials, e.g. Silva (1980) - pure montmorillonite and pure quartz, Shiao et al (1979) - pure montmorillonite and Wahlberg and Fishman (1962) - montmorillonite, kaolin, illite halloysite, found that the distribution coefficient remained constant at low concentrations, only dropping when the loading became significant. In our experiments loading was always less than 5% (except for M 77-20 which has a low CEC and where loading reached 14%) and loading effects would not be expected to come into play. Figure 2.3. shows plots of $\log R_d$ vs. $\log$ (Cs loading). The results of Silva have been included for comparison.

The fact that this change in slope seems to occur with unpurified materials raises the possibility that it is an artefact of the measurements and is due to the presence of Cs in the solution and on the solid phase. It may be significant that the point at which results become sensitive to small changes in the absolute amount of Cs present and to isotopic exchange processes ($10^{-6}M$) is also the point at which the change in slope occurs.

2.2.5.2. Desorption

In order to determine whether or not the adsorption of caesium was reversible, some of the sediments that had been saturated with caesium during the cation exchange determinations, were contacted with 0.5 N sodium chloride for 24 hours and desorption R_d values calculated.

It was found (Table 2.9.) that these values were very similar to those obtained during the adsorption experiments indicating that the

Fig 2.3 Effect of Loading on the Distribution Ratio

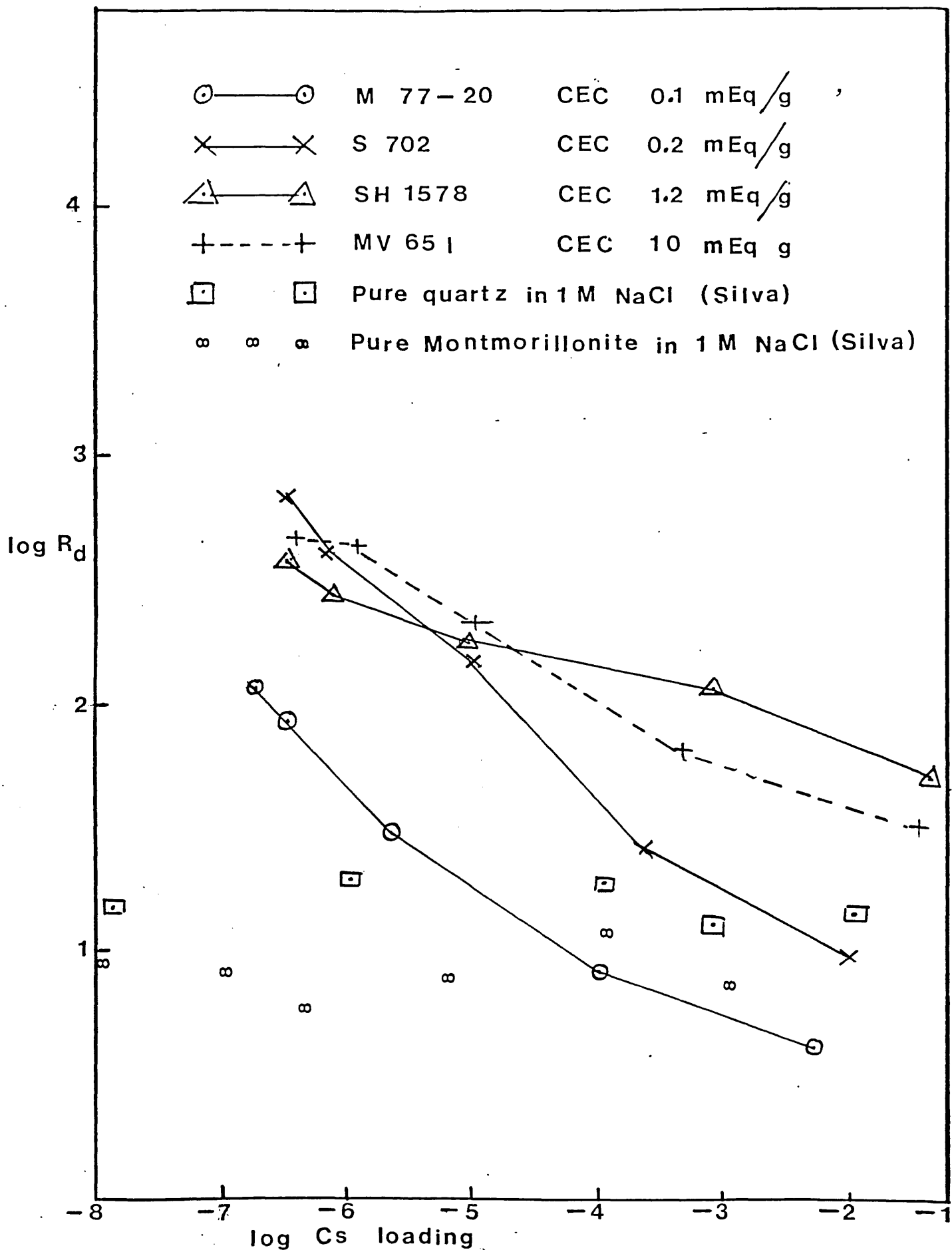


Fig 2.4

Effect of Recalculating R_d (i) on a CaCO_3 free basis
(ii) by normalising to Al

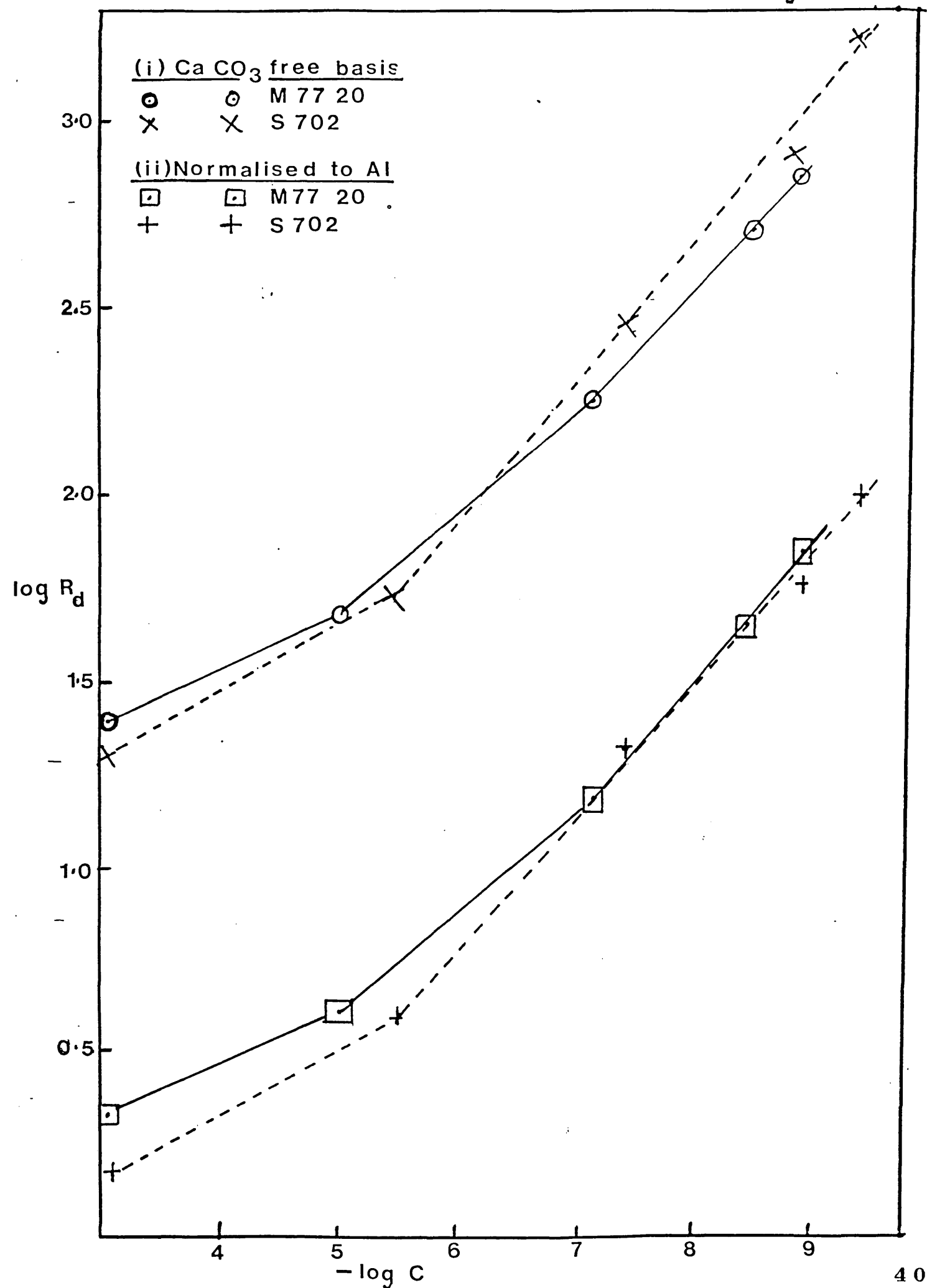


Table 2.7. Caesium Distribution Coefficient

Sample	Initial Cs concentration M	Final Cs concentration M	K_d after		
			7 days ml/g	13 days ml/g	45 days ml/g
M 77-20	3.4×10^{-9}	1.0×10^{-9}	113±4	127±4	156±12
	7.4×10^{-9}	3.4×10^{-9}	76±1	86±1	98±1
	1.0×10^{-7}	7.4×10^{-7}	47±1	29±1	33±1
	1.0×10^{-5}	8.9×10^{-6}	6.7±0.4	8.0±0.5	9.1±0.4
	1.0×10^{-3}	9.4×10^{-4}	3.9±0.5	3.5±0.5	4.8±0.5
S 702	3.4×10^{-9}	3.8×10^{-10}	422±5	482±19	736±16
	7.4×10^{-9}	1.5×10^{-9}	298±3	371±3	464±4
	1.0×10^{-7}	3.8×10^{-8}	122±1	136±1	168±1
	1.0×10^{-5}	6.9×10^{-6}	25±0.5	28±0.5	30±0.4
	1.0×10^{-3}	9.0×10^{-4}	10±0.5	10±0.5	11±0.5
SH 1578	3.4×10^{-9}	8.1×10^{-10}	362±12	381±12	455±9
	7.4×10^{-9}	2.2×10^{-9}	280±3	254±2	318±3
	1.0×10^{-7}	3.9×10^{-8}	194±2	196±2	214±2
	1.0×10^{-5}	4.8×10^{-6}	134±2	131±2	142±1
	1.0×10^{-3}	7.0×10^{-4}		60±1	64±1
MV65I	3.4×10^{-9}	6.7×10^{-10}	485±18	532±18	566±10
	7.4×10^{-9}	9.8×10^{-10}	408±4	413±4	475±5
	1.0×10^{-7}	3.8×10^{-8}	198±2	192±2	211±1
	1.0×10^{-5}	6.1×10^{-6}	69±1	70±1	72±1
	1.0×10^{-3}	7.7×10^{-4}	36±1	35±1	37±1
6269	3.4×10^{-9}	2.7×10^{-9}	306±13	393±13	403±8
	7.4×10^{-9}	7.4×10^{-9}	142±2	148±2	140±1
	1.0×10^{-7}	3.6×10^{-8}	209±2	206±2	196±3
	1.0×10^{-5}	9.9×10^{-6}	53±2	51±1	56±1
	1.0×10^{-3}	9.9×10^{-4}	24±1	24±1	23±1
Errors from counting statistics only					

adsorption of caesium is reversible.

Table 2.9. Desorption of Caesium

Sample	Equilibrium Solution concentration M	R _d
M 77-20	2×10^{-3}	1
S 702	5×10^{-2}	13
SH 1578	7×10^{-3}	28
MV 65 I	2×10^{-2}	14
6269 No. 2	2×10^{-2}	8

Finally, an attempt was made to distinguish between exchangeable and non-exchangeable caesium by desorbing into 1 M CsCl solutions. The results of this experiment are given in Table 2.10.

Table 2.10. Desorption into 1.0 M Caesium Chloride

Sample	Equilibrium solution concentration after loading M	m Eq Cs added to clay	CEC m Eq/g	% loading	% of Cs desorbed into	
					1st wash	1st + 2nd wash
M 77-20	7.1×10^{-8}	2.4×10^{-6}	7	4.9×10^{-5}	29	31
6269 No.2	7×10^{-9}	7.3×10^{-6}	82	8.9×10^{-6}	25	29
SH 1578	3.9×10^{-8}	8.4×10^{-6}	124	6.8×10^{-6}	65	75
SH 1578	3.7×10^{-10}	3.7×10^{-7}	124	3.0×10^{-7}	37	44

Loaded from
 10^{-7} M
Loaded
from
 10^{-9} M Cs

It is difficult to compare samples rigorously because although the first three were all loaded from 10^{-7} M Cs in sea water the final solution concentrations and loadings were all different. However, it would appear that at these loadings:-

- i) A high proportion of the Cs adsorbed onto the montmorillonite-rich sample, SH 1578, was in exchangeable form. In fact about 75% was exchangeable as compared with only 30% on the other two samples.
- ii) A comparison of the two experiments carried out on SH 1578 shows that a higher proportion of the Cs was exchangeable from the sample with the higher loading.

iii) A comparison of the results for the calcareous sample M 77-80 with the results in Table 2.9. shows that about twice as much adsorbed Cs exchanged isotopically with other Cs as exchanged with Na at similar loading.

2.2.5.3. Effect of contact time

It has frequently been observed (Vine et al., 1980; Erdal, 1979) that adsorption ratios determined by the batch technique increase slowly with time. One possible explanation for this effect is that there is self-grinding in the shaking operation which continually exposes new surfaces which adsorb cations. The effect of this addition of a small number of additional sorption sites would be detected at low concentrations but would be negligible at high concentrations and this is probably why we found that there was a much more dramatic increase in R_d for the dilute solutions.

The sediment most affected by contact time was S-702. This sample contains illite. The illites are non-expanding three-layer clays and only the external cations are exchangeable. Smectites (montmorillonites) are also three layer clays but they swell when in contact with water and cations are able to penetrate between the layers. Thus the adsorption properties of an illite are more likely to be affected by changes in the surfaces of the particles than would those of a smectite where a large proportion of the adsorption occurs between the layers. Manganese nodules, with their high porosity would also be expected to adsorb a high proportion of the cations internally and therefore be less sensitive to surface changes. In fact the observed increase in R_d with time could well be due to diffusion effects.

2.2.5.4. Correlation with other properties

It can be seen from Figure 2.1. that at low concentrations the R_d values for all the samples apart from the calcite M 77-20, are of the same order. Moreover, they are similar to those reported by Stanners and Aston (1981) for Ravenglass intertidal sediments (300-500 ml/g) using carrier free ^{137}Cs tracer. This could have important implications with regard to waste disposal as it is expected that the concentration of radionuclides in leach waters will be low, i.e. below 10^{-5}M . At high caesium concentrations, however, there are significant differences between the different sediments, and a number of interesting points emerge if one looks at the lower portions of the curves.

- a) Cation Exchange capacity:- There is a strong correlation between CEC and R_d . This is hardly surprising, particularly as CEC was determined using Cs.
- b) Carbonate content:- Samples M 77-20 and S 702 are both rich in CaCO_3 (87.5% and 44.5% respectively) and have roughly parallel curves. CaCO_3 has a low cation exchange capacity and surface area and it is probable that most of the adsorption occurs on components other than CaCO_3 , either clays or iron and manganese particles or coatings. It is interesting to note that if the R_d values are recalculated on a CaCO_3 free basis or normalised to Al_2O_3 (Figure 2.4.), procedures frequently used by geochemists when it is desired to eliminate the effects of dilution by CaCO_3 (Piper, 1973), then the curves for these two samples coincide almost exactly.
- c) Iron and Manganese content:- The manganese nodules have high distribution coefficients and for the clays R_d increases in the same order as does (Fe+Mn) content. It is highly likely that these elements play an important part in adsorption.

2.2.6. Europium Distribution Ratios

2.2.6.1. Experimental methods and results

(a) Adsorption: Europium distribution ratios were determined using the same procedure as for caesium (Section 2.2.4.3.) except that after each equilibrium the phases were separated by centrifuging for 3 minutes and then filtering through 0.22 μm filters. This was in order to avoid temperature rises.

Sediment weights were between 0.15 g and 0.3 g and they were shaken with 30 g of spiked sea water. Two different europium concentrations [$1.3 \times 10^{-6}\text{M}$ (307406 ± 554 c/min/5g) and $9.1 \times 10^{-8}\text{M}$ (21891 ± 150 c/min/5g)] were used and the solutions were prepared in the manner described in Section 2.2.4.1. The Europium was presumably present as the trivalent cation.

After the first equilibration (6 days) both solid and liquid phases were counted in order to check whether europium was being adsorbed by the container walls. Results indicated that container wall adsorption was negligible when sediment was present but when not, the blank solutions lost a high proportion of their activity. Most of this was retained by the filters indicating that the solutions were unstable and that colloids had formed during shaking at 4°C.

On counting the solutions after 6 days it was found that the ^{152}Eu remaining in the aqueous phase in the experiment using the more dilute solutions was below the limit of detection and the distribution coefficient could therefore only be reported as greater than 5×10^4 . In the experiments using the more concentrated solutions the activity of the final solution, although low, was measurable and R_d values were calculated.

A duplicate set of samples was analysed after 113 days. The increase in R_d (ΔR_d) was small but significant and unlike the absolute values appears to be directly related to the surface area and/or the iron content (Table 2.11.). For part of this time the temperature rose to room temperature but this probably had little effect on the final R_d . Preliminary tests indicate that europium is far less sensitive to temperature changes than is caesium; an indication that the main sorption mechanism for europium is not one of ion exchange.

Table 2.11. Effect of time on europium distribution coefficient

Sample	Iron content %	Surface area m^2/g	CEC $\text{mEq}/100\text{g}$	$R_d/10^5$ after		$\Delta R_d/10^5$
				6 days	113 days	
M 77-20	1.7	30	7	2.0 ± 0.1	2.3 ± 0.1	0.3
S 702	3.1	98	20	1.3 ± 0.1	1.9 ± 0.1	0.6
SH 1578	14.5	396	124	1.5 ± 0.1	3.5 ± 0.1	2.0
MV 65 I	2.2	95	100	3.0 ± 0.2	3.6 ± 0.2	0.6
6269 No.2	13.7	340	82	2.5 ± 0.5	4.8 ± 0.4	2.3

When the samples were counted after six days it was observed that the europium concentration was similar for all the solutions irrespective of sample size or nature. The europium concentration was about 8×10^{-10} M and it seemed likely that the solution chemistry rather than the nature of the solid phase was the dominating factor. In order to check whether or not this was the case further aliquots of stock ^{152}Eu were added to the samples and shaking continued. After six days the solutions were counted and found to be 8×10^{-10} M once again. This procedure was repeated several times and the results of these experiments are given in Table 2.12. Because it was considered important not to exceed the solubility of europium in the initial solutions and because the distribution ratios are so high, the count rates of the

Table 2.12. Europium distribution Ratios - Effect of successive addition of Eu.

Date counted		22/9/80		28/9/80		1/10/80		5/10/80		7/10/80		15/10/80	
Days since previous addition of Eu		6		6		3		4		2		10	
Cpm ¹⁵² Eu added to system		1,850,000		2,671,110		3,492,990		5,136,750		7,595,550		7,595,550	
	Sample	cpm/5g liquid	$\frac{R_d}{10^5}$	cpm/5g liquid	$\frac{R_d}{10^5}$	cpm/5g liquid	$\frac{R_d}{10^5}$	cpm/5g liquid	$\frac{R_d}{10^5}$	cpm/5g liquid	$\frac{R_d}{10^5}$	cpm/5g liquid	$\frac{R_d}{10^5}$
	M 77-20	173±13	2.0±0.1	204±10	2.2±0.1	234±11	2.8±0.1	332±11	3.4±0.1	438±12	3.3±0.1	405±11	3.6±0.1
	S 702	259±11	1.3±0.1	232±10	2.2±0.1	230±11	2.9±0.1	319±12	3.6±0.1	393±12	3.7±0.1	256±10	5.7±0.2
	SH 1578	395±12	1.5±0.1	234±11	3.6±0.2	315±12	3.5±0.1	645±0.1	2.9±0.1	1021±14	2.4±0.1	364±11	6.6±0.2
	MV 65I	201±11	3.0±0.2	213±11	4.1±0.2	359±12	3.2±0.1	831±14	2.3±0.1	1348±14	1.8±0.2	339±11	7.3±0.3
	6269 No.2	180±11	2.5±0.5	125±13	5.2±0.5	162±11	5.3±0.4	370±12	3.9±0.1	193±11	9.6±0.5	251±10	7.4±0.4

Errors from counting statistics only.

final solutions are low (about one and a half to two times the background). Nevertheless, after 20 minute counts, reasonable counting statistics were obtained and the following conclusions can be drawn from these results and the results in Table 2.11.

i) The distribution ratio for all the samples was between 1×10^5 and 8×10^5 . This is very high and clearly any of the sediments studied would form a satisfactory barrier to the migration of europium provided that the Eu is attached to the sediment and not present as colloidal particles which could conceivably be negatively charged, and hence free to travel unhindered through the sediment.

Heath and Laine (1978), Ericson (1980), and Ericson et al., (1980) have also reported distribution ratios of greater than 10^5 for deep sea sediments even though they were working mainly with pHs below 7 and in 0.68 N NaCl. In all our experiments the pH was that of natural sea water, i.e. 8.0 - 8.2.

ii) Although the difference is only a factor of two, it does appear that the manganese nodules adsorbed europium to a greater extent than did the sediment samples. This might indicate that the iron and manganese oxides present in all of the samples are involved in the removal of europium from solution. Apart from this, sample mineralogy, cation exchange capacity and surface area seem to have little effect on the initial distribution ratio.

iii) As europium was successively added to the system a greater proportion of the additional europium deposited on or with the sediment than would have been the case if the distribution ratio was constant. Thus after the final addition the sediment contained four times as much europium as after the first equilibration but the solution concentration increased by only one to two times. The calculated R_d is therefore greater by a factor of up to four. At the end of the experiment the loading of europium on the sediment was still only about 10^{-4} mEq/g so only a fraction of the exchange sites have been occupied, if they are involved. It does appear however, that the concept of a fixed concentration in the solid phase corresponding to a particular equilibrium concentration in the liquid phase is not valid and R_d values obtained in this type of experiment must be used with caution.

(b) Desorption: After 113 days the samples were centrifuged and the supernatant liquid decanted. 30 g of unspiked filtered (0.1 μ m filters)

sea water was added and the samples were shaken for five days at room temperature. The aqueous phase was then counted and the "desorption R_d " calculated.

During the next four months the samples were kept at 4°C and shaken only occasionally except for the last three days when they were returned to the water bath and shaken at 120 strokes/min. Finally, they were centrifuged at 7000 rpm in a refrigerated centrifuge and filtered through double filter paper (0.22 μ above 0.10 μ) and the solutions counted.

The results of the desorption experiments are given in Table 2.13. and it can be seen that:-

Table 2.13. Desorption of Europium

Sample	Adsorbed on to solid	ADSORPTION		DESORPTION			
		Conc. in solution	R_d	1 week		4 months	
				conc. in solution		conc. in solution	
				mEq/g	R_d	mEq/g	R_d
	$\frac{\text{mEq/g}}{10^{-4}}$	$\frac{\text{mEq/g}}{10^{-10}}$	$\frac{R_d}{10^5}$	$\frac{\text{mEq/g}}{10^{-10}}$	$\frac{R_d}{10^5}$	$\frac{\text{mEq/g}}{10^{-10}}$	$\frac{R_d}{10^5}$
M 77-20	6.1	17.1	3.6 0.1	6.2	10.0 0.7	3.6	16.8
	1.6	6.9	2.3 0.1	1.9	8.2 1.8	2.1	7.6
S 702	6.2	10.8	5.7 0.2	10.8	5.7 1.0	6.3	9.9
	1.6	8.2	1.9 0.1	2.6	5.9 1.0	2.5	6.4
SH 1578	10.2	11.5	6.6 0.2	6.3	16.2 1.1	5.0	20.5
	2.2	6.2	3.5 0.2	2.0	11.4 2.5	0.9	25.6
MV 65 I	10.4	14.3	7.3 0.3	7.6	13.8 0.8	8.2	12.7
	1.8	5.1	3.6 0.3	1.5	12.0 3.4	1.6	11.6
6269 No.2	7.8	10.6	7.4 0.3	3.2	24.2 3.3	3.4	22.7
	2.6	5.3	4.8 0.4	1.0	24.2 9.7	0.4	17.2

- i) Desorption R_d after four months were not significantly greater than after one week.
- ii) The desorption distribution ratios are two to three times the adsorption distribution ratios indicating that either the reaction is only partially reversible or that desorption is slower than adsorption.
- iii) The desorption R_d is the same for both loadings (one four times the other). This indicates that an equilibrium had been set up and that the solution concentration depended on the concentration in the solid phase. This is in contrast to the adsorption experiments when the R_d increased as the loading increased.
- iv) The samples most reluctant to lose europium, i.e. those with the highest desorption R_d , are the two manganese nodules and SH 1578, which has a high iron concentration. This is another indication that the europium may be associated with the iron and manganese phases.

When the filter papers were counted it was found that, as with Americium (see Chapter 4), a significant amount of Eu was retained by the top 0.22 μ papers but there was no detectable activity on the lower 0.10 μ papers. The activity on the top papers is almost certainly due to fine sediment particles and the fact that no europium passed through the top papers indicates that any colloidal Eu that may be present is firmly attached to these particles.

2.3. Summary and Conclusions

Sorption studies using caesium and europium have been carried out on five widely differing sediments. It proved possible to make some interesting correlations between caesium adsorption isotherms and the results of mineralogical analysis, cation exchange capacities and surface areas. Europium, on the other hand, appeared to behave in much the same way on all five sediments, any of which should act as an effective barrier to the migration of this element as in all cases the distribution ratio was greater than 10^5 . The distribution ratio for caesium increased by an order of magnitude as the equilibrium concentration in solution decreased from 10^{-3} M to 10^{-9} M and there was less difference between samples at low than at high concentrations. It seems likely that sorption is mainly by ion exchange but a small proportion may be sorbed by a second mechanism which has a high sorption capacity, is quickly exhausted and is not completely reversible.

APPENDIX TO CHAPTER 2

THE RELATIONSHIP BETWEEN THE DISTRIBUTION COEFFICIENT AND OTHER EQUILIBRIUM QUOTIENTS USED IN ION EXCHANGE STUDIES

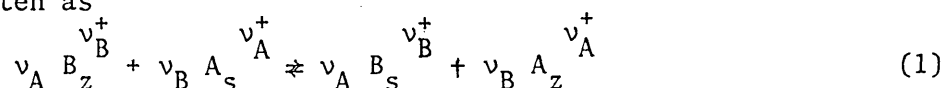
2A1. Introduction

Although, for the sake of consistency, the term "distribution ratio" (R_d) has been used throughout this thesis, the sorption of some of the nuclides in high-level waste, e.g. Cs and Sr appears to be governed mainly by ion exchange. Equilibrium is reached and the sorption-desorption reactions are reversible. It might, therefore, have been more appropriate to use the distribution coefficient (K_d) when discussing caesium.

At Imperial College a large amount of fundamental work on ion exchange in zeolites has been done (Barrer et al., 1956, 1963, 1974; Barri, 1980; and Barri and Rees, 1980) and it was felt that a better understanding of distribution coefficients would be obtained if we could see how the distribution coefficient is related to the thermodynamic parameters used in ion-exchange work. Therefore equations were derived relating K_d to the selectivity coefficient (K_c). Using the data of Barri and Rees (1980) it was then possible to plot graphs of $\log K_d$ against the cation fraction (A_z) in the zeolite and to plot graphs showing how K_d and K_c vary with the different types of exchange isotherms.

2A2. Ion exchange equations

Exchange of ion $A^{v_A^+}$ in solution for ion $B^{v_B^+}$ in a zeolite may be written as



where v_A and v_B are the valencies of cations A and B whose charges are v_A^+ and v_B^+ , respectively. The subscripts Z and S denote "in zeolite" and "in solution", phase respectively. Three equilibrium quotients are of interest. The thermodynamic equilibrium constant, K_a ; the Kielland quotient K_c ; and the mass action quotient, K_m :

$$K_a = \left(a_{B_S}^{v_A} \cdot a_{A_Z}^{v_B} \right) / \left(a_{B_Z}^{v_A} \cdot a_{A_S}^{v_B} \right) \quad (2)$$

$$K_c = \left(a_{B_s}^{v_A} \cdot A_z^{v_B} \right) / \left(a_{A_s}^{v_B} \cdot B_z^{v_A} \right) \quad (3)$$

$$K_m = \left(B_s^{v_A} \cdot A_z^{v_B} \right) / \left(B_z^{v_A} \cdot A_s^{v_B} \right) \quad (4)$$

where the a with appropriate subscripts denote activities of the ions A and B in solution(s) or in the zeolite (z) and A and B with appropriate subscripts denote equivalent fractions of A and B in solution or in zeolite.

K_a can be re-written as

$$K_a = A_z^{v_B} m_{B_s}^{v_A} f_A^{v_B} \gamma_B^{v_A} / B_z^{v_A} m_{A_s}^{v_B} f_B^{v_A} \gamma_A^{v_B} \quad (5)$$

where the f's are activity coefficients in the zeolite on the equivalent cation fraction scale and the γ 's are these coefficients in the solution phase on the molality scale. K_a and K_c can also be expressed as

$$K_a = \frac{K_c f_A^{v_B}}{f_B^{v_A}} ; K_c = \frac{A_z^{v_B} m_{B_s}^{v_A} \gamma_B^{v_A}}{B_z^{v_A} m_{A_s}^{v_B} \gamma_A^{v_B}} \quad (6)$$

Since dilute solutions are usually used, molalities may be replaced by molarities and introducing the equivalent fractions of the cation in the solution A_s and B_s , we get

$$M_s^A = \frac{A_s}{v_A} (v_A m_{A_s} + v_B m_{B_s}) = \frac{A_s}{v_A} \cdot N \quad (7)$$

$$M_s^B = \frac{B_s}{v_B} (v_A m_{A_s} + v_B m_{B_s}) = \frac{B_s}{v_B} \cdot N$$

where $M_s^A + M_s^B$ are the molalities of the ions A and B, respectively, and N is the total normality of the equilibrium solution phase

$$K_c = A_z^{v_B} B_s^{v_A} \Gamma / B_s^{v_A} A_s^{v_B} Q \quad (8)$$

where

$$\Gamma = \gamma_B^{v_A} / \gamma_A^{v_B} \quad (9)$$

and

$$Q = \frac{v_B^A (\gamma_N)^{(v_B - v_A)}}{v_A^{v_B}} \quad (10)$$

In equation 8 the quantities A_z , B_z , A_s and B_s are determined experimentally by analysing cation concentrations at equilibrium. The activity coefficients γ and f are not directly measurable and have to be determined by other methods.

The activity coefficients γ_A and γ_B are individual ion activity coefficients, and as such cannot be determined. Their ratio Γ (equation 9) can however be evaluated (Barri 1980) and is given by

$$\Gamma = \frac{\gamma_B^{v_A}}{\gamma_A^{v_B}} = \frac{\gamma_{BX}^{v_A(v_B + v_X)} / v_X}{\gamma_{AX}^{v_B(v_A + v_X)} / v_X} \quad (11)$$

In the case of two univalent cations and a common univalent anion this reduces to

$$\Gamma = \frac{\gamma_B}{\gamma_A} = \frac{(\gamma_{BX})^2}{(\gamma_{AX})^2}$$

In the case of a divalent cation A, univalent cation B and a common univalent anion X, the expression becomes

$$\Gamma = \frac{\gamma_B^2}{\gamma_A} = \frac{(\gamma_{BX})^4}{(\gamma_{AX})^3} \quad (12)$$

The activity coefficients γ_{BX} and γ_{AX} are those for the salts AX and BX in mixed solution. They may be taken from the literature or determined experimentally (For a full discussion see Barri, 1980).

In a few cases the ratio f_A/f_B is constant, i.e. independent of the relative amounts of the competing species A and B in the zeolite. For uni-univalent exchanges where Γ is also constant we have from equations 6 and 8

$$\frac{A_z B_s}{B_z A_s} = \text{constant} \quad (13)$$

In this case the selectivity coefficient is constant. Such ideal behaviour is the simplest form of the law of mass action and has been found to apply to some exchanges, e.g. Na-Li, Na-K and Na-Ag in basic sodalite (Barrer and Falconer, 1956).

In most cases, however, the selectivity coefficient is not constant, but is a function of the proportion of the ions A and B in the zeolite. Kielland (1935) found the following empirical equations to express the solid phase activity coefficients as a function of cation loading:

$$\log f_A = C B_Z^2 ; \log f_B = C A_Z^2 \quad (14)$$

where C is an empirical constant and the logarithms are to the base 10. Substituting in the mass action equation (6)

$$\log K_a = \log K_c + C(1 - 2A_Z) \quad (15)$$

Thus a plot of $\log K_c$ versus A_Z should, by this theory, produce a straight line of gradient $2C$ and intercept on the $\log K_c$ axis of $(\log K_a - C)$. This equation was found to hold for some exchanges in zeolites, e.g. Na-Li, Na-K, Na-Rb and Na-Cs in zeolite A.

Barrer and Falconer (1956) have used statistical thermodynamics to derive an equation which is successful in interpreting the linear Kielland plots. However, the Kielland approach does not apply to many exchanges. In the general case the plot of $\log K_c$ vs. A_Z is neither horizontal nor in fact a straight line.

A simplified thermodynamic approach to the evaluation of activity coefficients in the solid phase and of the thermodynamic equilibrium constant has been developed by Gaines and Thomas (1953). They regarded the solid phase as a binary solid solution of (A,B)Z. The standard states of the exchanger were the mono-ionic exchanger in equilibrium with an infinitely dilute solution of the same ion. The standard state for water was chosen so that the activity of the water is the same in exchanger and solution. The standard state for the electrolytes is the hypothetical 1M solution in which the mean activity coefficient of the solute is unity.

Having made these assumptions they deduce

$$\begin{aligned} \log f_A^{v_B} &= 0.4343 (v_B - v_A) B_Z - B_Z \log K_c + \int_0^{B_Z} \log K_c d A_Z \\ \log f_B^{v_B} &= -0.4343 (v_B - v_A) A_Z + A_Z \log K_c - \int_0^{A_Z} \log K_c d A_Z \end{aligned} \quad (16)$$

The integrals required in equation 16 can be evaluated either by graphical integration or by obtaining, using the least squares method, a curve which represents the best fit of experimental points.

The standard free energy of exchange, ΔG^0 , per equivalent of exchange, is

$$\Delta G^0 = - \frac{RT}{v_A v_B} \ln K_d \quad (17)$$

2A3. Ion-Exchange Isotherms

Ion-exchange equilibria can be characterized by the ion-exchange isotherm. This isotherm is a graphical representation which, in principle, covers all possible experimental conditions at a given temperature. Various ways of representation can be used. For convenience, the equivalent cationic fraction, A_s , of the entering ion A in the solution is plotted as a function of the equivalent cationic fraction A_z in the zeolite.

In a hypothetical system in which the zeolite shows no preference for A or B, the equivalent cationic fractions in the zeolite are the same as those in the solution. Here, the ion-exchange isotherm is linear and is the diagonal in the diagram A_s vs. A_z . If the ion A is preferred throughout, the isotherm is concave and lies below the diagonal, and if B is preferred, the isotherm is convex and lies above the diagonal. S-shaped isotherms are also found demonstrating reversal of ion selectivity. The overall selectivity is determined by the sign of ΔG .

In most noncrystalline exchangers, the isotherms terminate at lower left and upper right corners of the diagram. In zeolite, however, there are many exceptions due to exclusion of the entering ions or trapped cations in the zeolite structure. This is referred to as the ion-sieve effect, that is, the entering ions cannot reach all of the sites occupied by the ions initially in the zeolite. The isotherm then terminates at a point where the degree of exchange A_z is less than one.

2A4. Dependence of the Exchange Selectivity on the Total Solution Concentration

From equations 6 and 10 we have

$$K_a = \frac{f_A^{v_B}}{f_B^{v_A}} K_c = \frac{A_z^{v_B} B_s^{v_A}}{B_z^{v_A} A_s^{v_B}} \cdot \frac{A^{v_B} N^{v_A - v_B}}{v_A} \cdot \frac{f_A^{v_B}}{f_B^{v_A}} \cdot \Gamma = \frac{A_z^{v_B} B_s^{v_A}}{B_z^{v_A} A_s^{v_B}} \cdot \frac{f_A^{v_B}}{f_B^{v_A}} \cdot \frac{\Gamma}{Q}$$

For a given A_z , $f_A^{v_B}/f_B^{v_A}$ should be nearly independent of the external electrolyte concentrations normally used with zeolites, and thus for a given A_z

$$\frac{B_s^{v_A} \Gamma}{A_s^{v_B} Q} = K_c \frac{B_z^{v_A}}{A_z^{v_B}} = K_a \frac{B_z^{v_A} f_B^{v_A}}{A_z^{v_B} f_A^{v_B}} = \text{constant} \quad (18)$$

All these ratios should be independent of the total normality, N , of the external solution.

In equivalent exchanges (i.e. $v_A = v_B$), Q in the quotient $B_s^{v_A} / A_s^{v_B} Q$ is always unity and the ratio $B_s^{v_A} / A_s^{v_B}$ for fixed A_z can then vary with the total concentration only in so far as Γ changes. However in dilute solutions normally used in exchanger studies, Γ varies little from unity so that in this range there is little change in A_s , for any fixed A_z at different N 's. All isotherms must therefore be very closely grouped.

In the case of $v_A \neq v_B$ for a chosen A_z and two different N 's we must have from equation 17

$$A_{s1} = \frac{A_{s1}^{v_B} Q_1}{(1 - A_{s1})^{v_A} \Gamma_1} = \frac{A_{s2}^{v_B} Q_2}{(1 - A_{s2})^{v_A} \Gamma_2} = \text{constant} \quad (19)$$

where A_{s1} , Q_1 and Γ_1 refer to N_1 and A_{s2} , Q_2 and Γ_2 to N_2 . It has been shown that the change in Q is larger than that of Γ and accumulative i.e. as Q increases Γ decreases. Therefore the value of $A_s^{v_B}/(1 - A_s)^{v_A}$ must change to satisfy equation 19. Thus for fixed A_z at different N 's A_s changes and hence the isotherms are strongly dependent on the total concentrations. Furthermore, according to equation 18 for a fixed A_z , A_s should decrease as N decreases and thus the isotherm appears more selective for the cation with the higher valency A (i.e. the isotherm becomes more and more concave with respect to the diagonal) as the solution becomes more dilute. Barri and Rees (1980) determined exchange isotherms for Na-Mg and Na-Ca exchange and found that the experimental isotherms agreed well with theory.

2A5. The Distribution Coefficient

The sorption properties of materials are frequently represented mathematically by the equilibrium distribution coefficient, K_d , which is defined as

$$K_d = \frac{[A]_z}{[A]_s}$$

where $[A]_z$ and $[A]_s$ are the equilibrium solid phase and liquid phase concentrations of cation A.

If we work with cation fractions and the unit of concentration is m Eq/g then

$$A_z = \frac{\text{m Eq/g on zeolite}}{\text{CEC}} = \frac{[A]_z}{\text{CEC}}$$

$$\text{and } A_s = \frac{\text{m Eq/ml in solution}}{N} = \frac{[A]_s}{N}$$

where A_z and A_s are cation fractions in zeolite and solution, respectively.
CEC = cation exchange capacity in m eq/g of hydrated zeolite.
and N = Total normality of equilibrium solution phase in m Eq/ml.

$$K_d = \frac{A_z}{A_s} \cdot \frac{\text{CEC}}{N} \quad (20)$$

We will now consider the case of uni-univalent exchange and uni-divalent exchange separately. From equation 8 we can show:

a) Uni-univalent exchange

$$K_c = \frac{A_z}{A_s} \cdot \frac{B_s}{B_z} \cdot \frac{\gamma_{\pm BY}^2}{\gamma_{\pm AY}} \quad (21)$$

$$K_d = K_c \cdot \frac{B_z}{B_s} \cdot \frac{\text{CEC}}{N} \cdot \frac{1}{\Gamma}$$

$$\log K_d = \log K_c + \log \frac{B_z}{B_s} - \log N + \log \text{CEC} - \log \Gamma \quad (22)$$

b) Uni-divalent exchange

$$K_c = \frac{A_z}{(B_z)^2} \cdot \frac{(B_s)^2}{A_s} \cdot 2N \cdot \frac{\gamma_{\pm BY}^4}{\gamma_{\pm AY}^3} \quad (23)$$

$$K_d = K_c \cdot \frac{(B_z)^2}{(B_s)^2} \cdot \frac{\text{CEC}}{2N^2} \cdot \frac{1}{\Gamma}$$

$$\log K_d = \log K_c + 2 \log \frac{B_z}{B_s} - 2 \log N + \log \frac{\text{CEC}}{2} - \log \Gamma \quad (24)$$

Using these equations it is possible to investigate the relationship between K_d and K_c .

2A6. Calculation of K_d for Exchange Between Various Ions and Sodium in Zeolite A

Barri and Rees (1980) determined exchange isotherms for Ca-Na and Mg-Na exchange in zeolite A. They then calculated the corrected selectivity coefficients, K_c , from equation 23 and fitted the experimental points in the plot of $\log_{10} K_c$ vs. A_z to a polynomial of the form $\log K_c = C_0 + C_1 A_z + C_2 A_z^2 + C_3 A_z^3$.

Values of Γ were obtained from the data of Moore and Ross (1965).

Using this data it is possible to calculate values of K_d for all values of A_z and to plot graphs $\log K_d$ vs. A_z . Figures A6-A9 show these graphs together with the experimental exchange isotherms and plots of $\log K_c$ vs. A_z . In addition graphs of $2 \log \frac{B_z}{B_s} - 2 \log N$ were drawn in order to show the effect of the individual terms in the equation on the shape of the $\log K_d$ vs. A_z graph. For the purpose of these calculations Γ was taken as 1.6. Barri (1980) has shown that for variations in N from 0.05 to 0.2 and in A_s from 0.05 - 0.9, Γ lies between 1.4 and 1.8 whether the data of Moore and Ross or of Gleuckhoff (1949) are used. A change in Γ simply causes a vertical shift in the graph of K_d vs. A_z .

In the same way it is possible to calculate $\log K_d$ for uni-univalent exchange and this has been done for Li, K, Rb and Cs using the data of Barrer, Rees and Ward (1963) and equations 21 and 22. Γ was assumed to be 1.0 for these calculations. These graphs are shown in Figures A10-A13.

The most important fact to emerge from a study of these graphs is that at low loadings the $\log K_c$ term is the dominating term in equations 22 and 24, whereas at high loadings the $\log B_z/B_s$ term dictates the shape of the graph. From the point of view of radioactive waste disposal A_z will always be low and K_d will therefore be proportional to K_c .

It should be noted that unlike K_c , which does not change with N , K_d increases as N decreases.

The effect of a change in total normality, N , is considerably greater for the divalent cations than for the monovalent cations. This is because of the effect of the N^2 term in equation 22.

A study of the graphs for the four univalent elements shows how K_d and K_c vary with the different types of exchange isotherm. Thus the exchange isotherm for potassium is almost the ideal diagonal and hence the $\log K_c$ graph is nearly horizontal. $\log K_d$ therefore changes very little as the loading decreases. In contrast, the caesium exchange isotherm deviates markedly from the diagonal. The $\log K_c$ graph has a slope of -4.5 and $\log K_d$ therefore increases dramatically as the loading decreases. Lithium and rubidium fall between these two extremes.

2A7. Distribution Coefficients at Low Loading

a) Uni-univalent exchange

$$\log K_d = \log K_c + \log \frac{B_z}{B_s} - \log N + \log \text{CEC} - \log \Gamma \quad (21)$$

For a particular zeolite if $A_z \approx 0$ and is fixed then $\log K_c$ is constant

$$B_z = B_s = 1 \text{ and } \log \frac{B_z}{B_s} = 0$$

$\log \text{CEC}$ is constant

$\log \Gamma$ is not constant but the change with A_s for a particular N is small. It will tend to zero for low N .

$$\therefore \log K_d \approx -\log N + \text{const.}$$

So the graph of $\log K_d$ vs. $\log N$ at a fixed low loading will be a straight line of slope -1 and intercept $\log K_c + \log \text{CEC} - \log \Gamma$.

Shiao et al (1979) have determined K_d at specific low loadings for different normalities of sodium chloride on pure montmorillonite and obtained gradients very close to -1 for Cs, Sr and K.

Using the values for K_c given by Barrer, Rees and Ward (1963) we can calculate the values for K_d at various normalities for zeolite A at very low loadings and these are given in Table A1.

Table A1. K_d at zero loading for zeolite A

Uni-univalent exchange with sodium in a sodium chloride solution.

Element	$\log (K_c)_0$	$\log (K_c)_0$ + $\log \text{CEC}$	$\log K_d$ for N			K_d for N		
			1	0.68	0.1	1	0.68	0.1
Li	-0.75	-0.034	-0.034	0.295	0.966	0.29	1.97	9.2
K	0.1	0.816	0.816	0.983	1.816	6.55	9.62	65.5
Cs	0.9	1.616	1.616	1.783	2.616	41.3	60.7	413
Rb	0.2	0.916	0.916	1.083	1.916	6.5	12.1	65

NOTE

- (i) CEC for zeolite A = 5.2 m Eq/g of hydrated zeolite.
- (ii) $(K_c)_0 = K_c$ at zero loading.
- (iii) $N = 0.68$ has been included as this is the approximate value for sea water.

b) Uni-divalent exchange

$$\log K_d = \log K_c + 2 \log \frac{B_z}{B_s} - 2 \log N + \log \frac{CEC}{2} - \log \Gamma \quad (23)$$

For a particular zeolite if $A_z \approx 0$ and is fixed then

$$\log K_c = \text{constant}$$

$$\log \frac{CEC}{2} = \text{constant}$$

$$B_s = 1 \text{ and } \log \frac{B_z}{B_s} = \log B_z = \log (1 - A_z)$$

which is constant for a particular loading and if changes in Γ can be neglected then $\log K_d = -2 \log N + \text{constant}$ and the graph of $\log K_d$ vs. $\log N$ at a fixed A_z will be a straight line of slope -2. Figures A9 and A10 show how this gradient deviates from the ideal as the loading increases and as N increases. It can be seen that at low loadings the gradient ≈ -2 . It is also close to -2 at low N and high A_z but deviates markedly from the ideal when N increases and Henry's law is no longer obeyed.

Shiao determined the values of K_d at fixed low loadings for different normalities of NaCl in pure montmorillonite and obtained gradients very close to -2 for Ca, Mg and Ba.

Using the values of K_c given by Barri and Rees (1980) we can calculate the values of K_d at various normalities for zeolite A at very low loadings and these are given in Table A2.

Table A2. K_d at zero loading for zeolite A.

Uni-divalent exchange with sodium in a sodium chloride solution.

Element	Temp. °C	log K_d for N			K_d for N		
		1	0.68	0.1	1	0.68	0.1
Ca	25	3.45	3.78	5.45	2.8×10^3	6.1×10^3	2.8×10^5
Ca	65	4.03	4.36	6.03	1.0×10^4	2.3×10^4	1.0×10^6
Mg	25	2.03	2.41	4.08	1.2×10^2	2.5×10^2	1.2×10^4
Mg	65	3.23	3.56	5.23	1.6×10^3	3.6×10^3	1.6×10^5

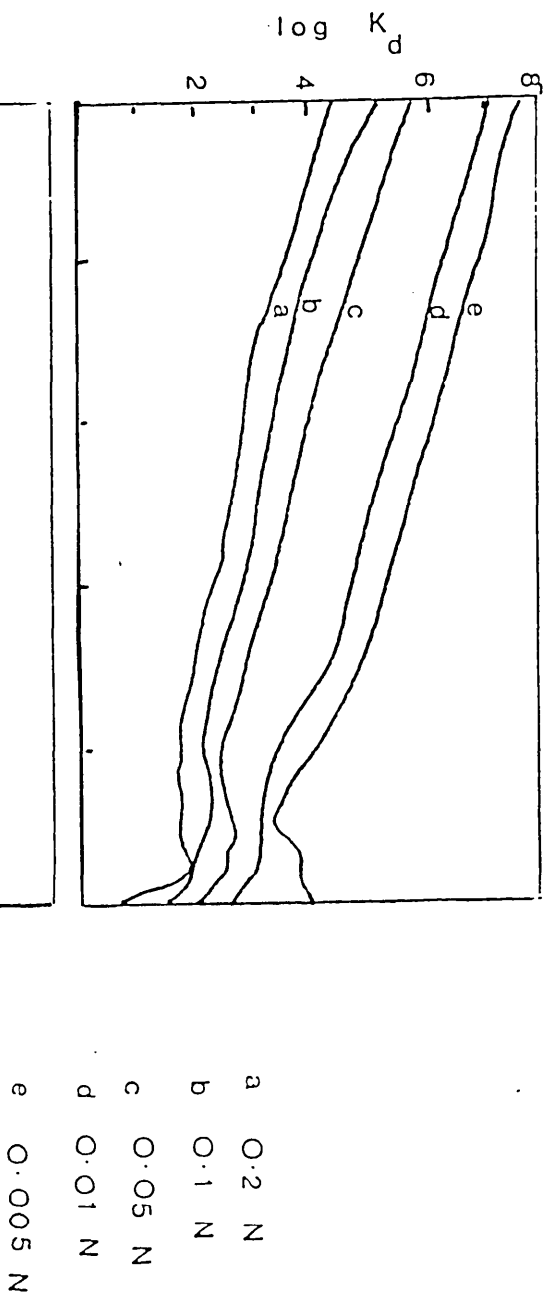
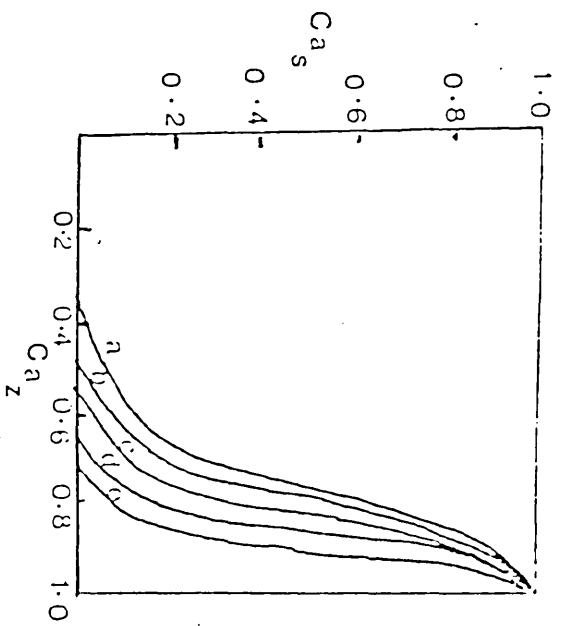
NOTE

- (i) K_d (and K_c) increase with increasing temperature.
- (ii) ΔG° is negative when Na^+ ions are replaced by calcium and magnesium indicating that they are the preferred ions when exchanging with sodium. This is in contrast to the exchange of Na^+ ions by Li^+ , K^+ , Rb^+ and Cs^+ , where ΔG° is positive indicating that these elements have a smaller standard affinity for the exchange than does Na. Nevertheless at low loadings the isotherms for K^+ , Rb^+ and Cs^+ show a selectivity of the solid crystals for these ions as compared with sodium.
- (iii) The K_d for divalent cations is several orders of magnitude higher than that for univalent cations.

2A8. Summary and Conclusions

It has been shown that for ion exchange reactions the distribution coefficient can be calculated from the selectivity coefficient and at low loadings is almost directly proportional to it. The selectivity coefficient can be determined accurately, and once it is known, the exchange isotherms for any total normality can be calculated (Barri and Rees, 1980).

Fig. A1 Calcium at 25 °C



- a 0.2 N
- b 0.1 N
- c 0.05 N
- d 0.01 N
- e 0.005 N

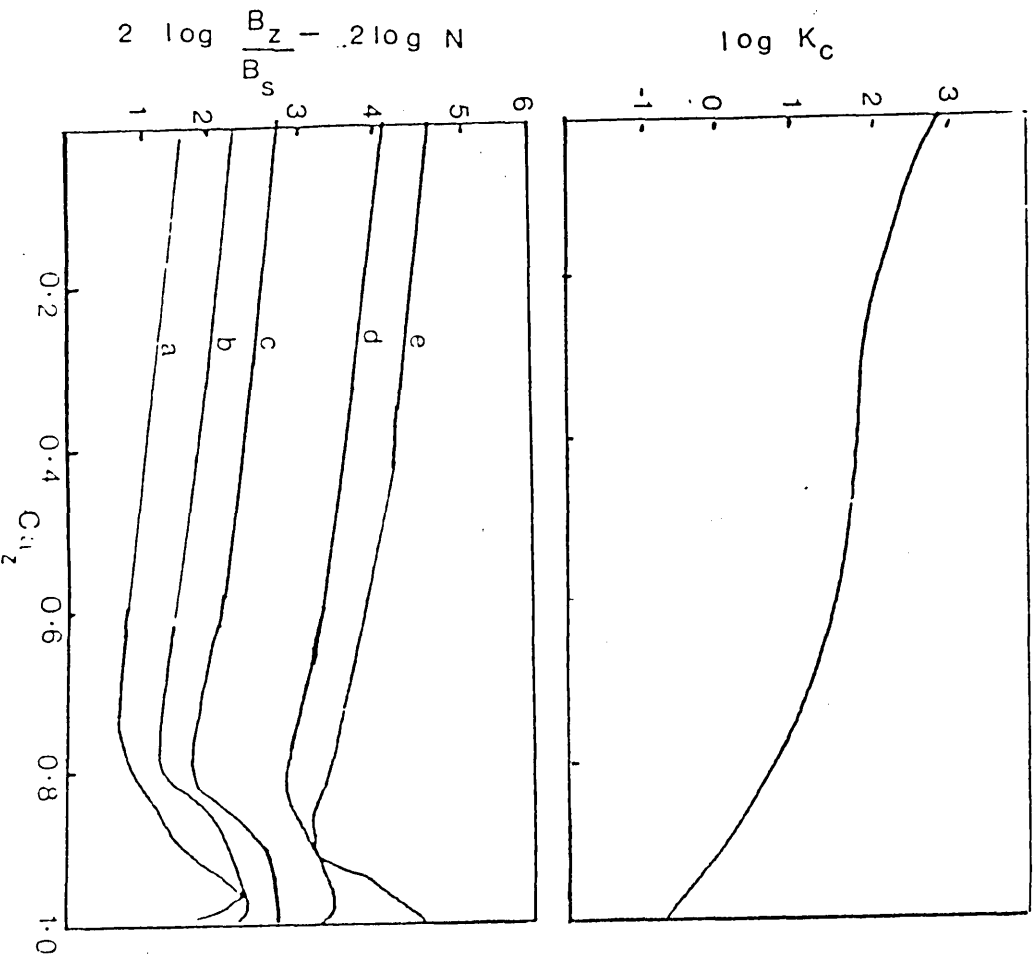


Fig.A2 Calcium at 65 °C

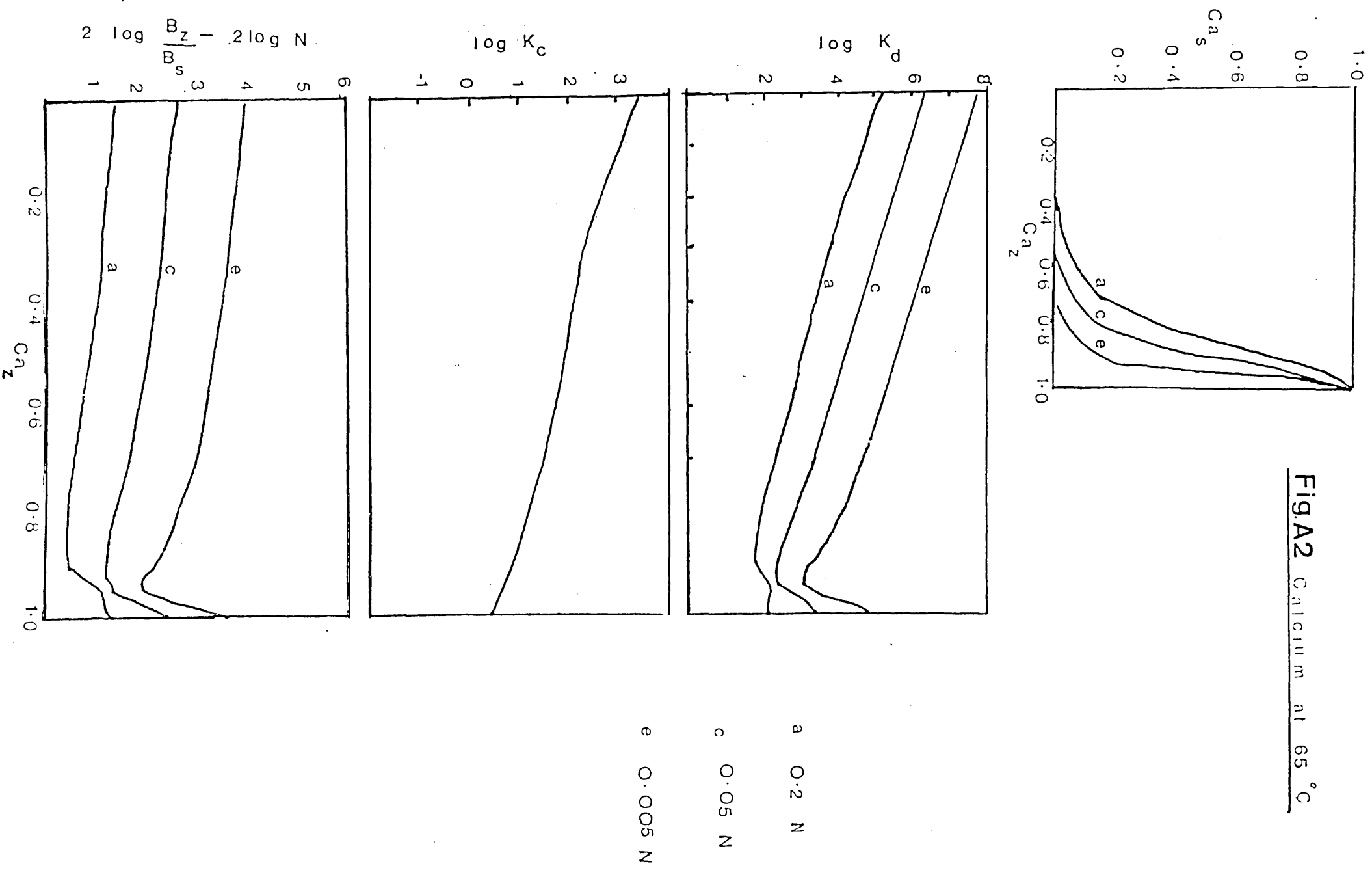
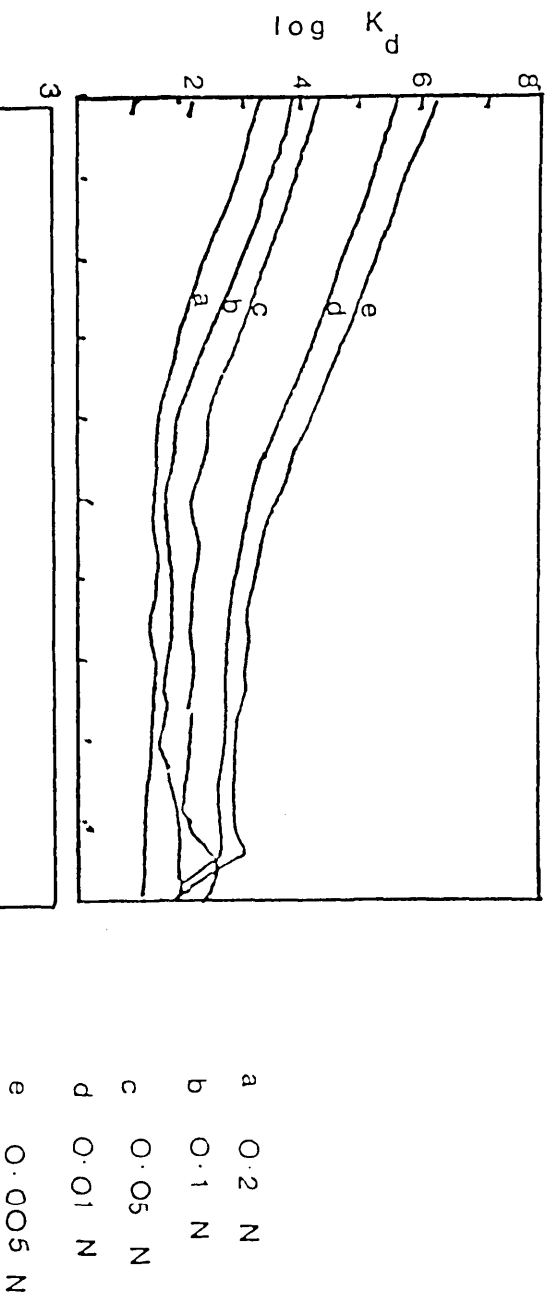
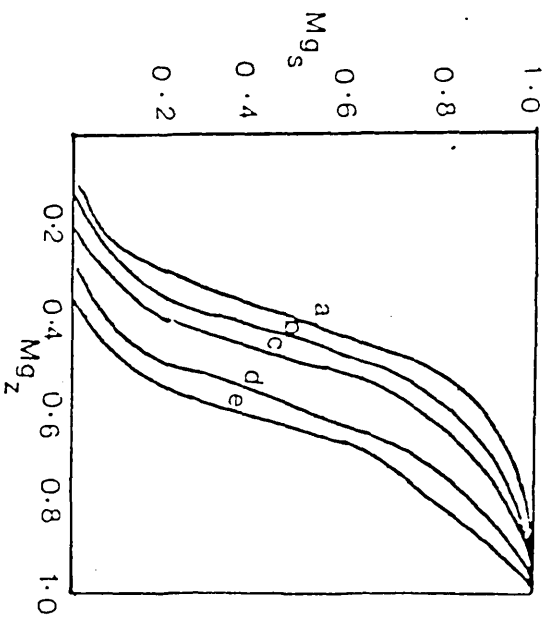


Fig. A3 Magnesium at 25 °C



- a 0.2 N
- b 0.1 N
- c 0.05 N
- d 0.01 N
- e 0.005 N

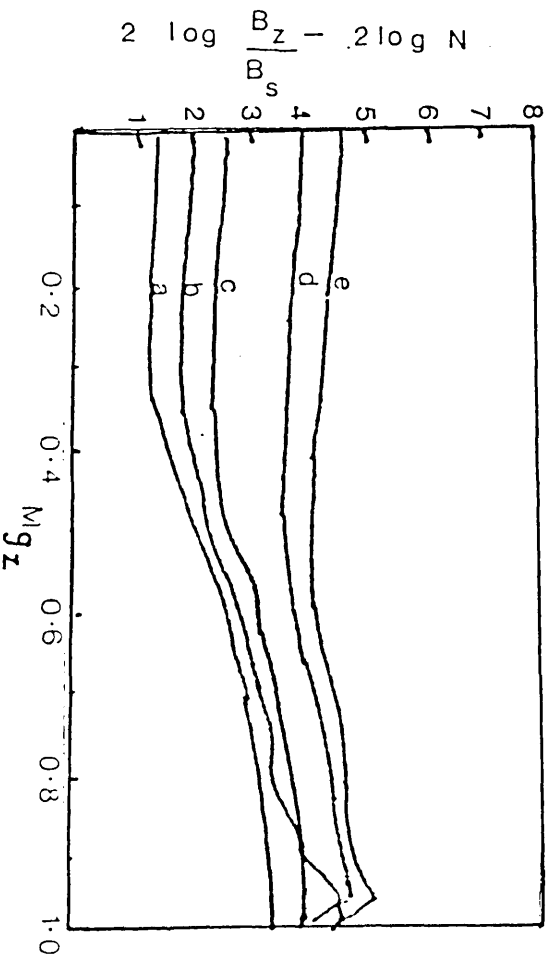
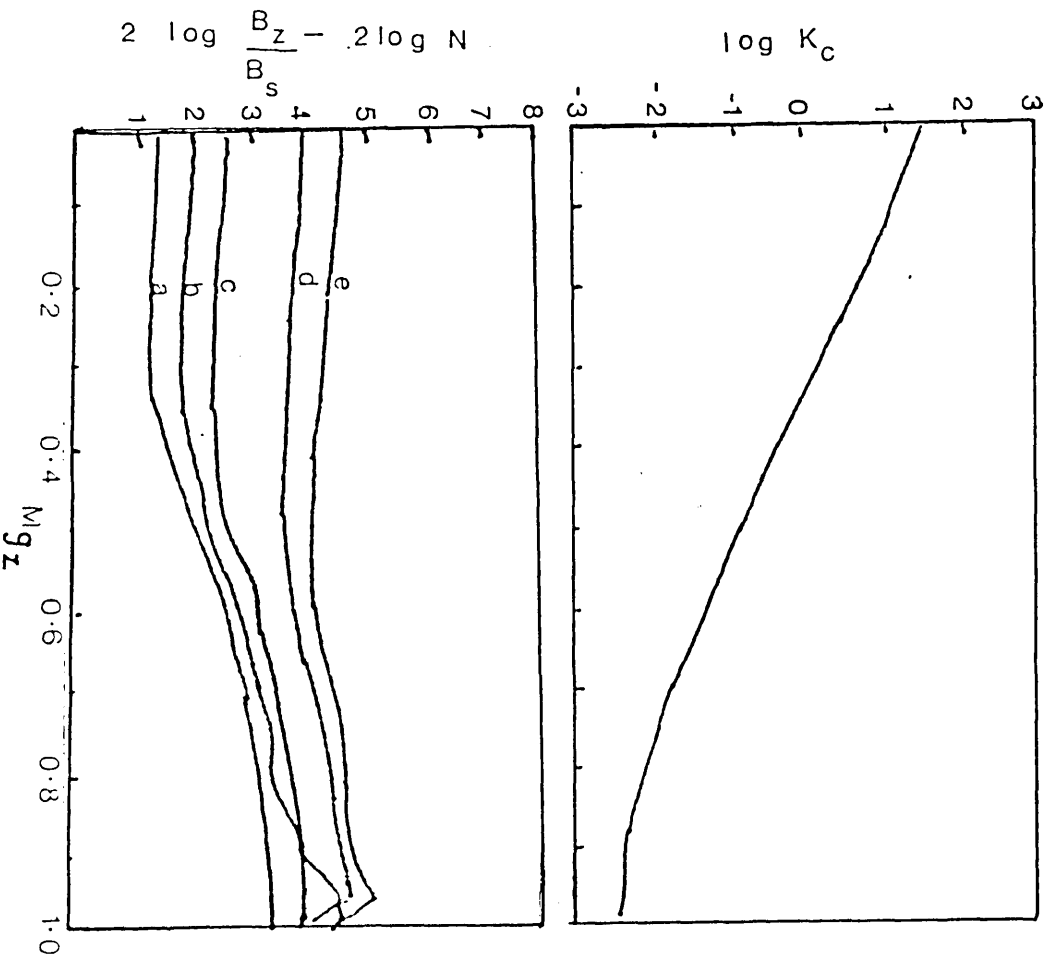


Fig.A4 Magnesium at 65 °C.

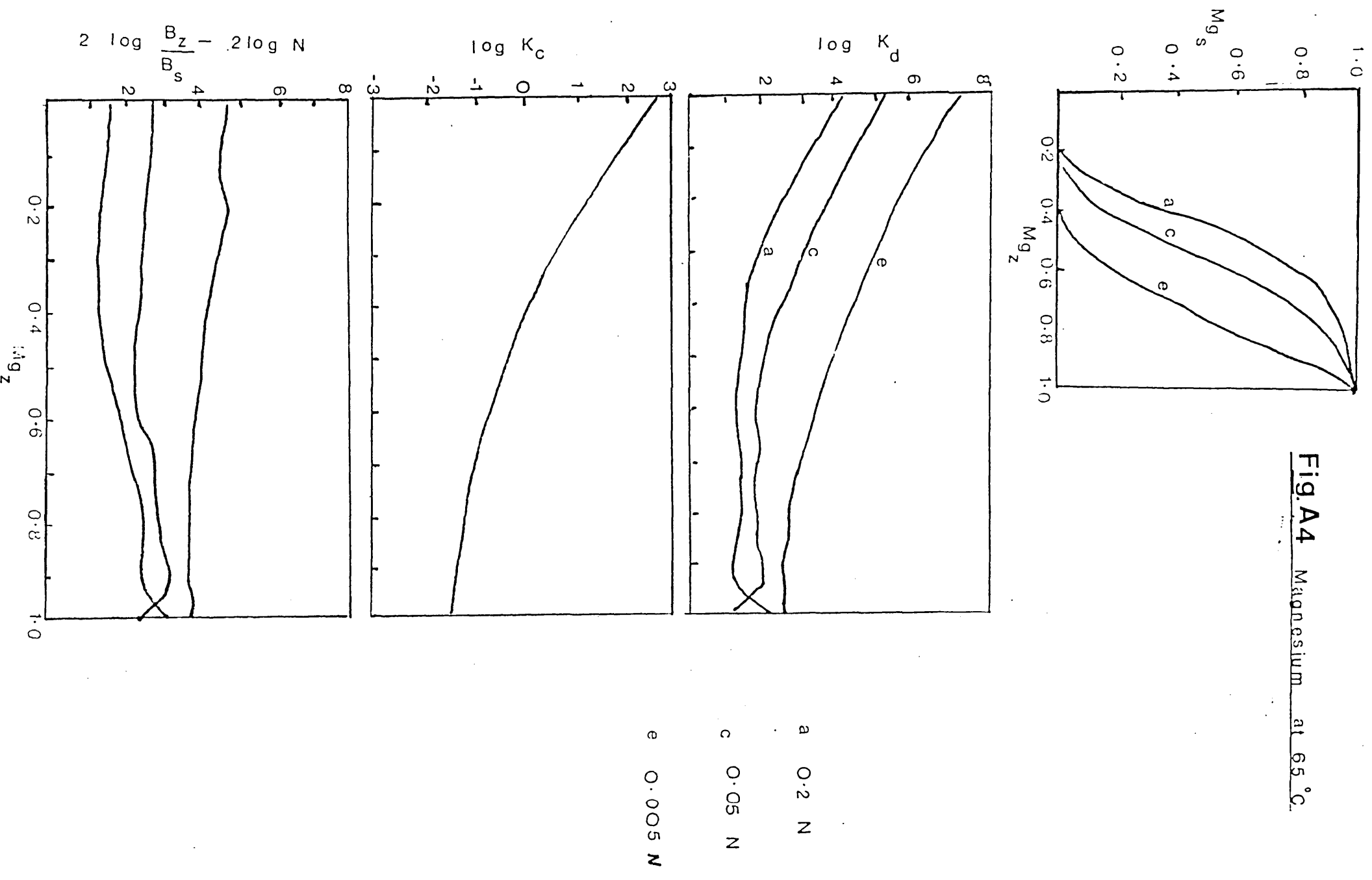


Fig. A5 Cesium

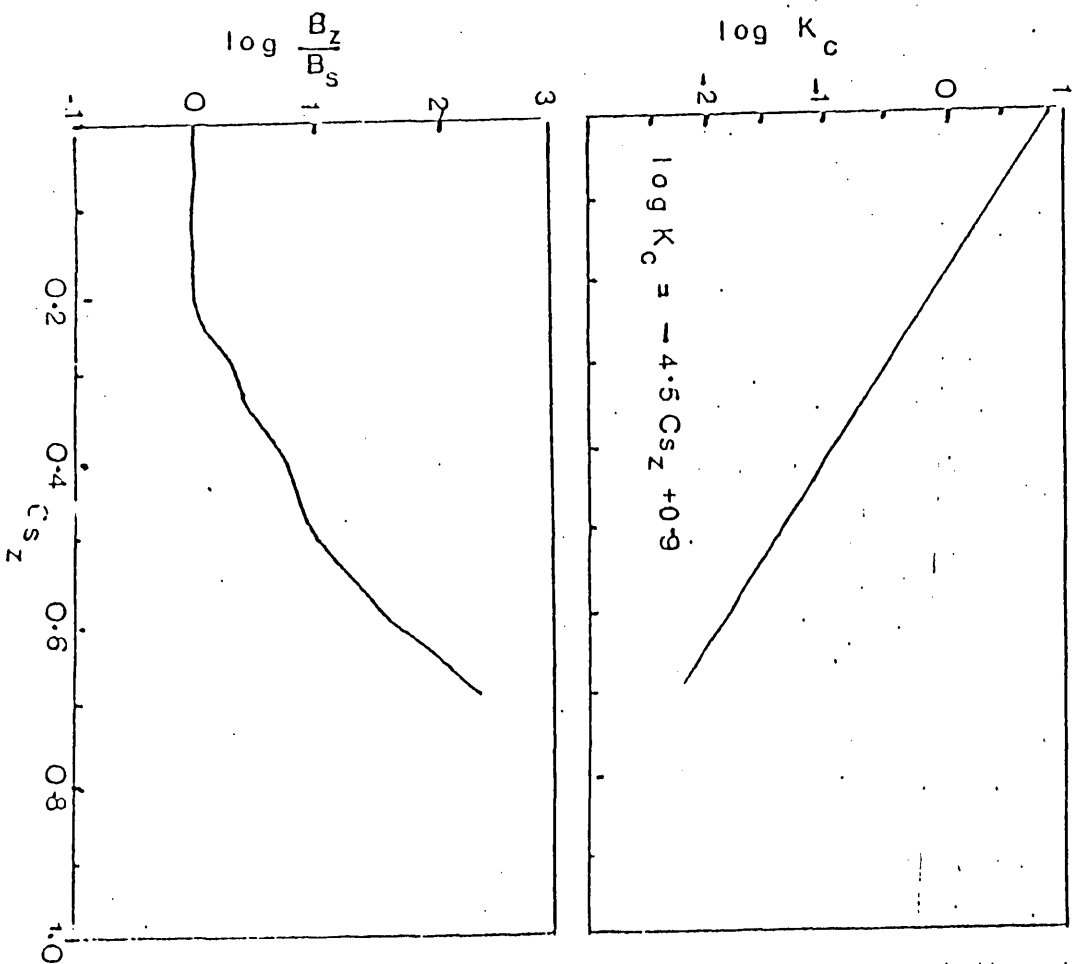
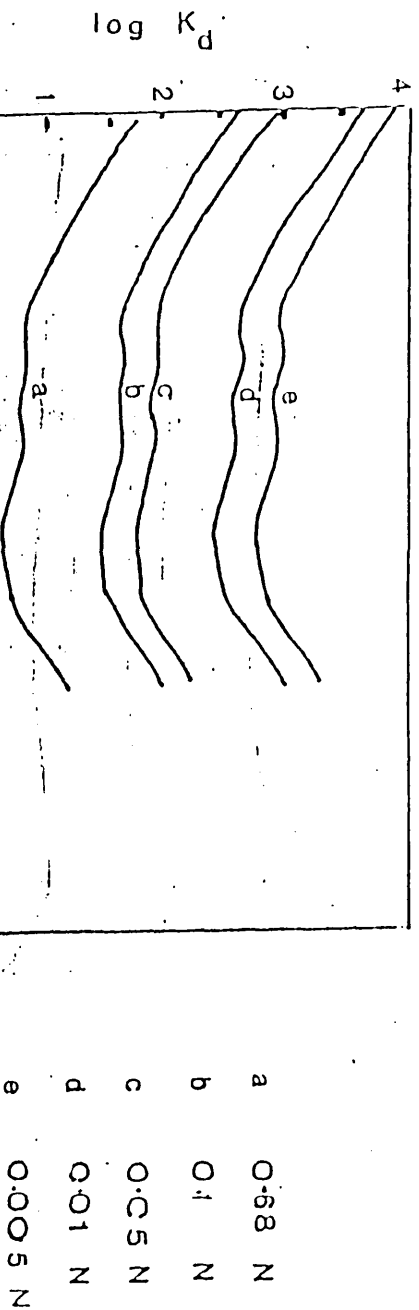
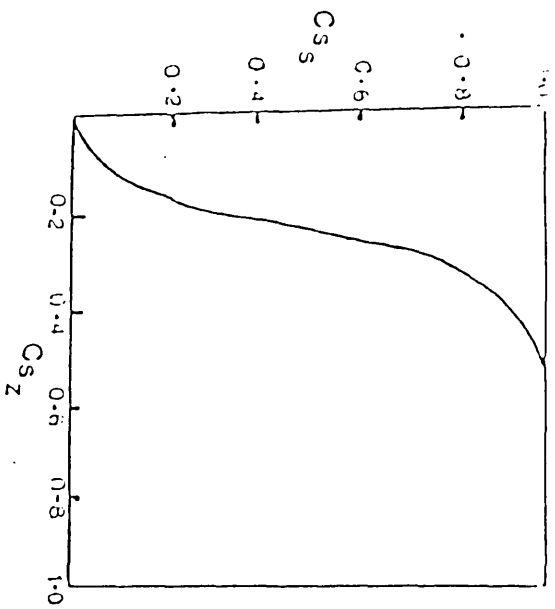
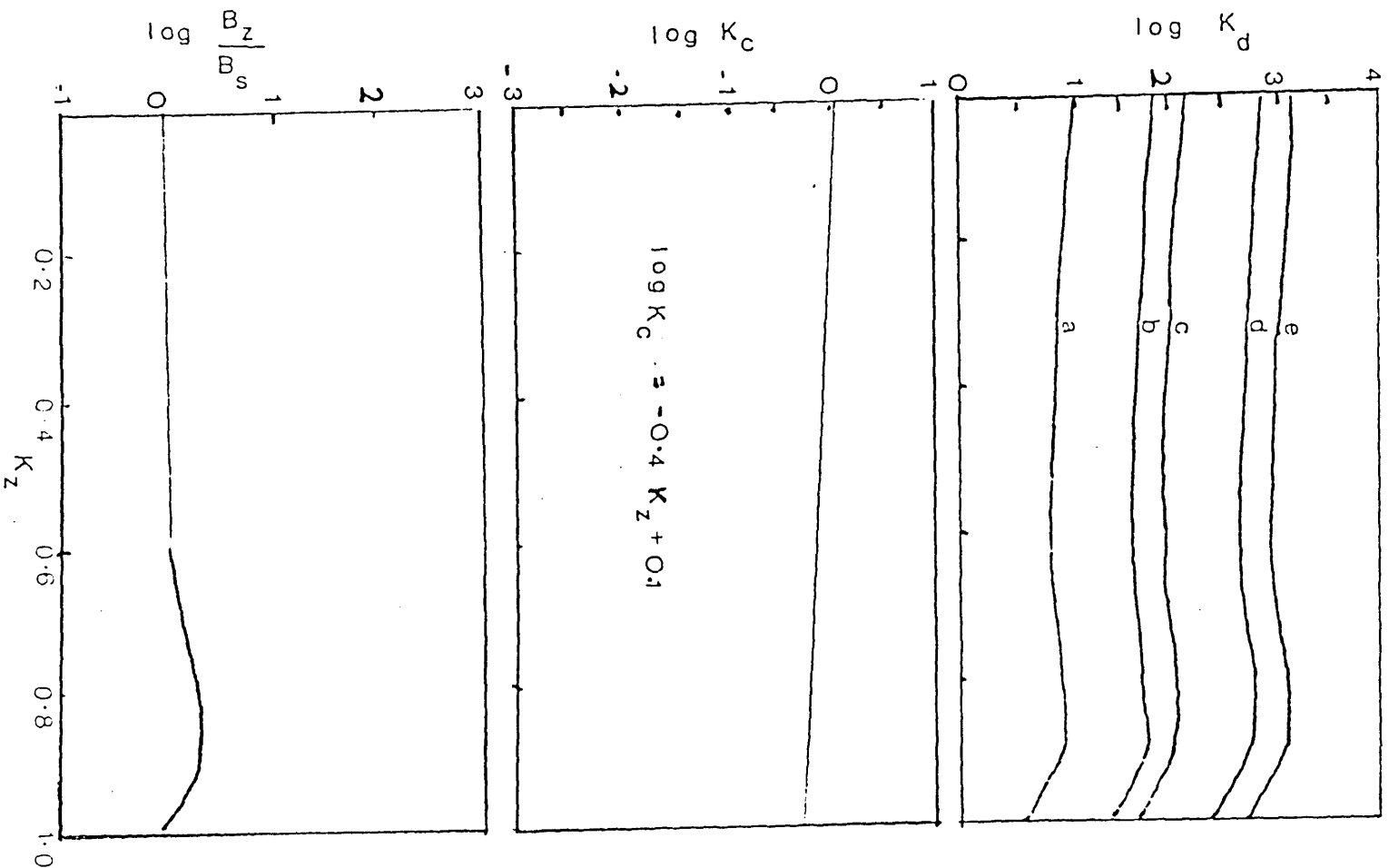
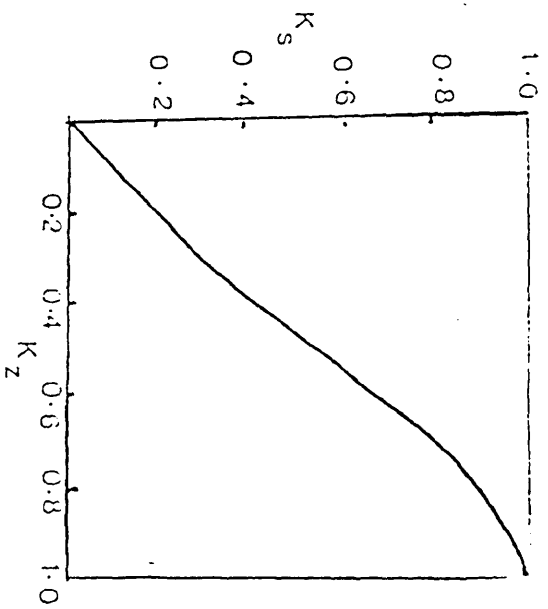


Fig. A6

Potassium



- a 0.68 N
- b 0.1 N
- c 0.05 N
- d 0.01 N
- e 0.005

Fig. A7

Lithium

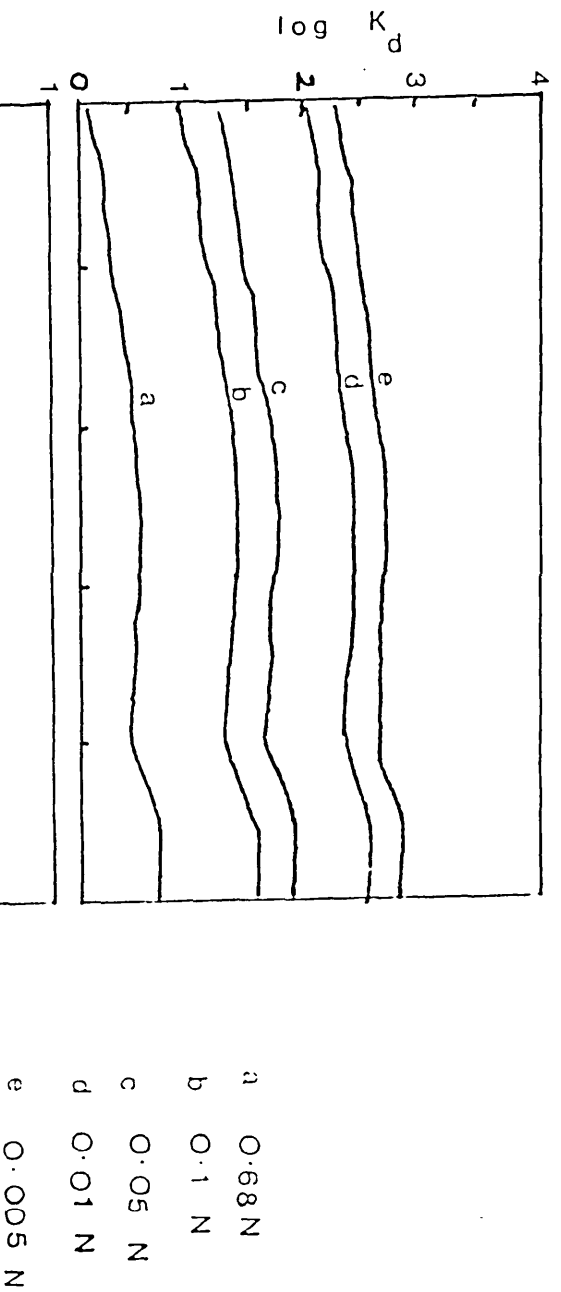
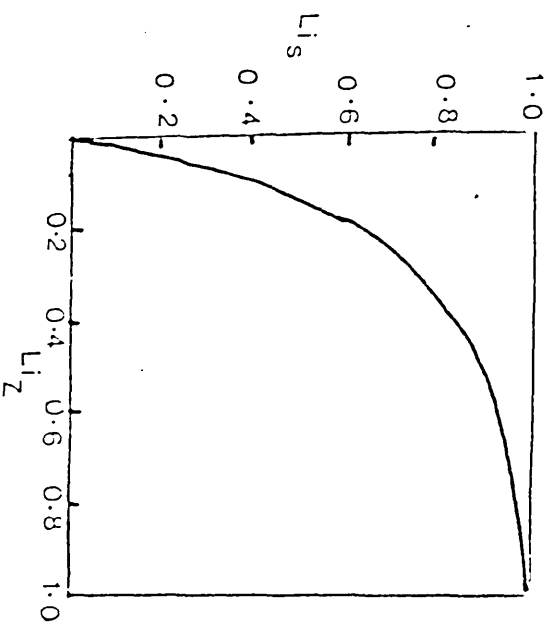
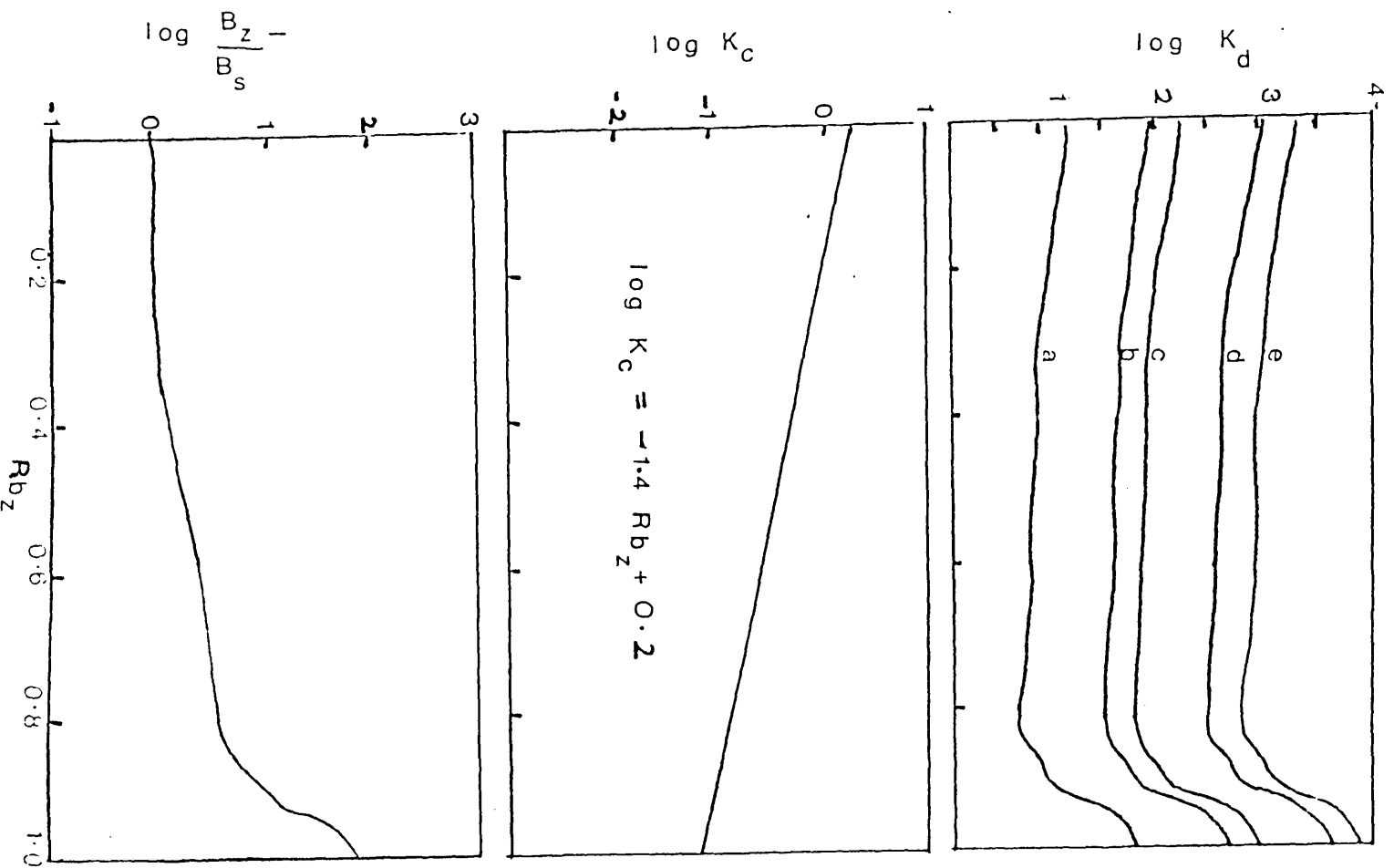
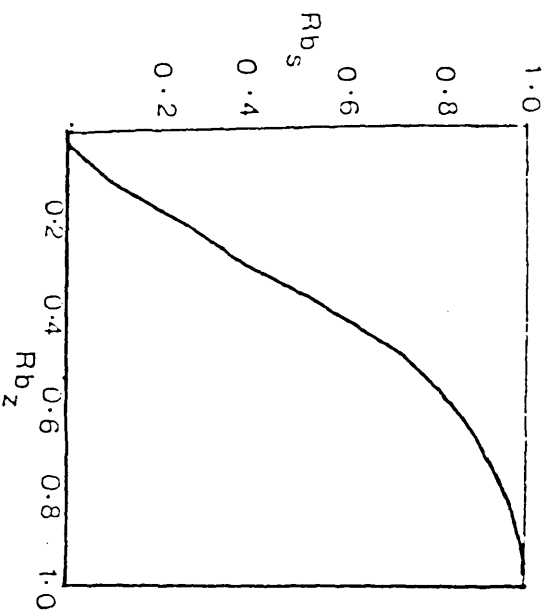


Fig A8 RUBIDIUM



- a 0.68 N
- b 0.1 N
- c 0.05 N
- d 0.01 N
- e 0.005 N

Fig.A9 · Effect of loading on graph of $\log K_d$ vs $\log N$ for M_g at 25 °C

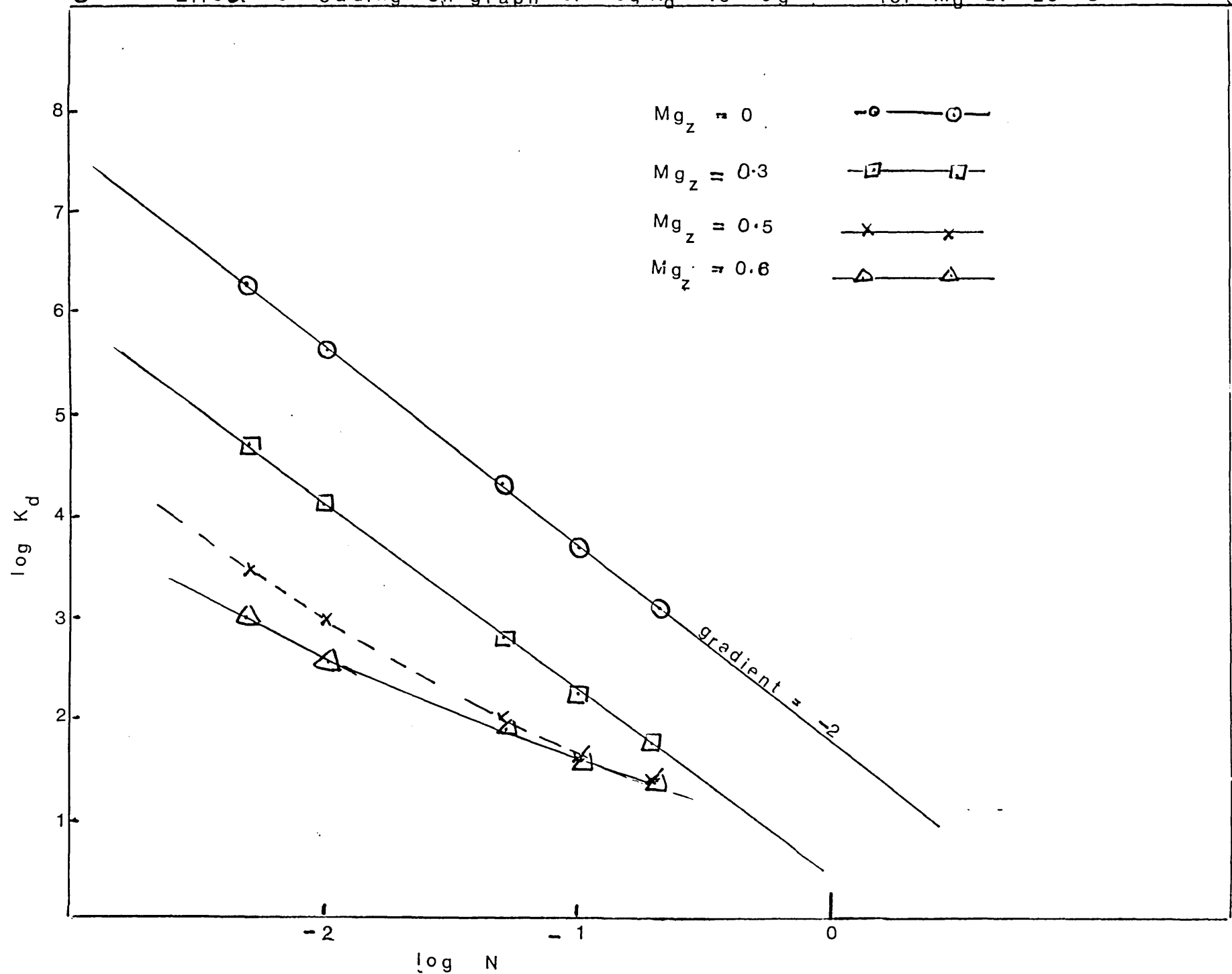
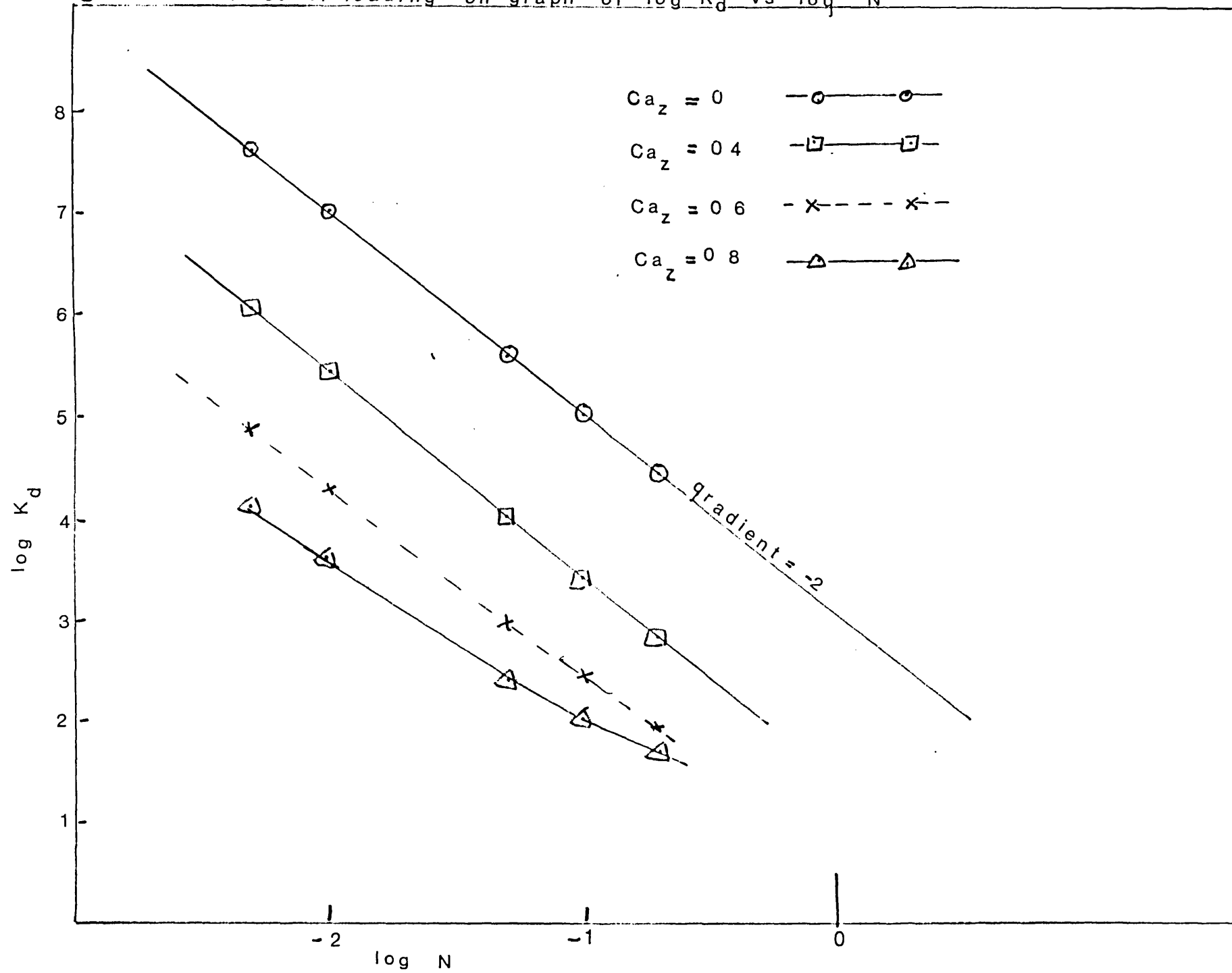


Fig. A10

Effect of loading on graph of $\log K_d$ vs $\log N$



CHAPTER 3

THE SORPTION OF AMERICIUM AND NEPTUNIUM ON MARINE SEDIMENTS

3.1. Introduction

As soon as A-grade laboratory facilities became available work was begun with americium and neptunium. A cooled centrifuge was purchased and all work with these nuclides was done at 4°C. An additional eight sediments from the Atlantic sea bed were included in the study. Two of them were site specific in that they were taken from the area that is now favoured for U.K. high-level-waste disposal. They were collected by the Institute of Oceanographic Sciences (IOS) from an area in the Cape Verde distal abyssal plain/mid-Atlantic Ridge foothills during their February 1982 cruise. Figure 3.1. shows the ship's track during this cruise. The samples were taken from stations 10399 (25°15'N, 25°28'W, water depth 5235m) and 10400 (25°42'N, 30°58'W) and were a sediment rich in carbonate and a red clay, respectively. They were taken with a box corer and, from the time of collection until sampling (by usual slurry technique) were kept at 4°C and in sealed containers to prevent evaporation of the pore waters. These two sediments 10399#7K and 10400#8K were obtained later than the other six (IOS-1 to IOS-6) and were studied in a separate set of experiments in which the emphasis was placed on reproducibility (all R_d determinations were done in triplicate) and on the effect of solid/solution ratio.

All the new sediments were characterised in exactly the same way as the original five samples. Thus they were subjected to mineralogical and chemical analysis and surface areas and cation exchange capacities were determined using the methods described in Chapter 2. For completeness the results for all thirteen samples are given in Tables 3.1. to 3.3. The samples fall into two main categories, those high in calcium carbonate and containing only minor amounts of montmorillonite, illite, kaolinite and quartz, and those containing little calcium but high in iron and/or manganese. The calcium carbonate content of the calcitic samples ranges from 45% to 89% and, as many of the other variables show a direct relationship to this value, the samples have been arranged in order of decreasing CaCO_3 content. It can be seen from Table 3.2. that both cation exchange capacity (CEC) and surface area (SA) vary inversely with CaCO_3 content. Furthermore, several of the major and minor constituents, e.g. SiO_2 , Fe, Al, K, Ni, and Mg, all increase steadily as the CaCO_3 content decreases (Table 3.3.).

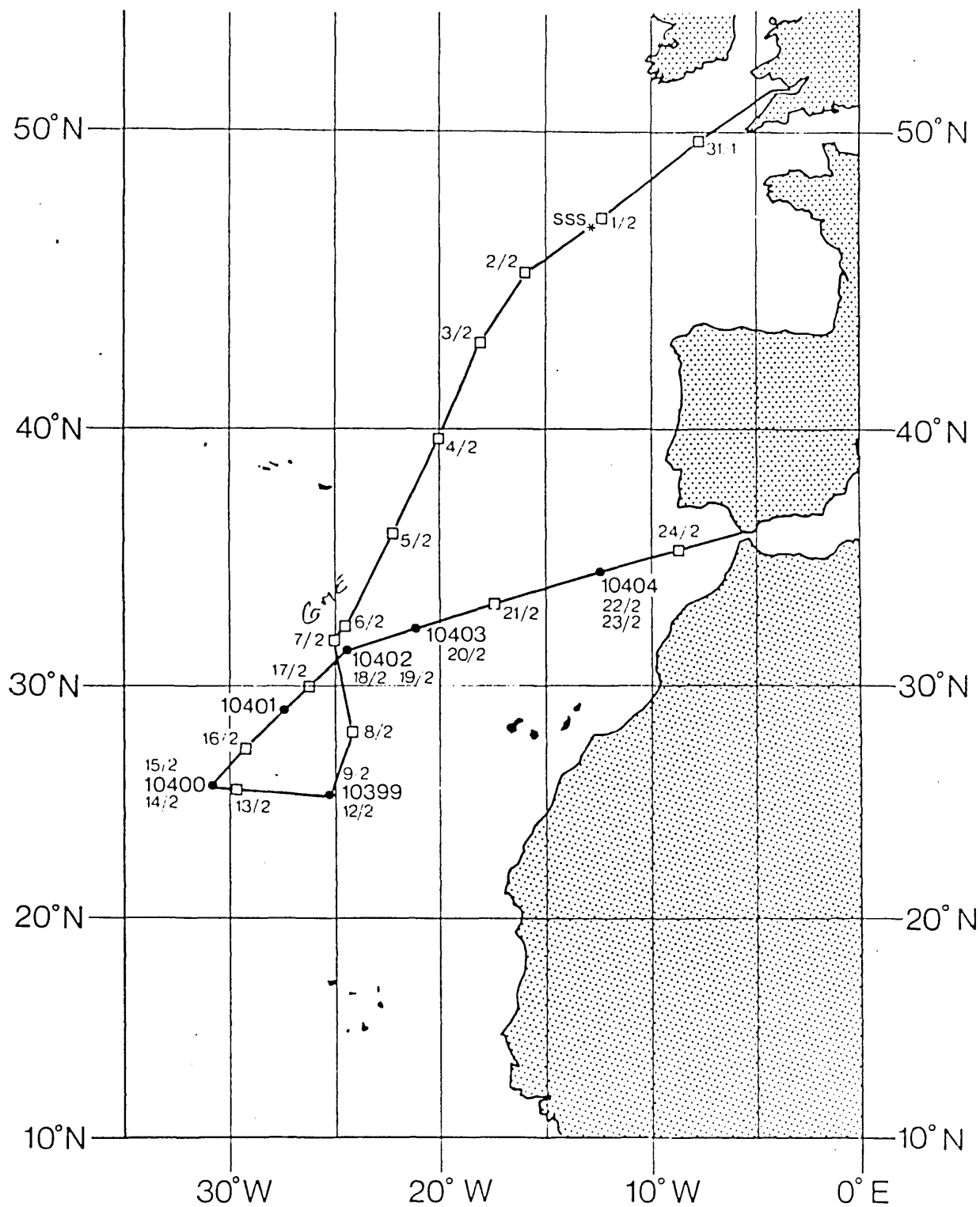


Figure 3.1 DISCOVERY CRUISE 125: ship's track.

Bold figures: station positions. Light figures: midday positions

* sss Standard Seawater Service collection

Table 3.1. Mineralogy of Sediments

Sample No.	Composition			
	Major	Minor	and	Trace
IOS-3	Calcite			Illite Kaolinite
M77-20	Calcite	Quartz		
10399 # 7K	Calcite	Kaolinite, illite Smectite, chlorite		Plagioclase feldspar
IOS-6	Calcite	Quartz, Kaolinite Illite, Montmorillonite		
IOS-4	Calcite	Montmorillonite, Illite Kaolinite		Quartz
IOS-5	Calcite	Quartz, Kaolinite Illite		
IOS-2	Calcite	Quartz, Illite Montmorillonite		Mixed layer chlorite
S 702	Calcite Quartz	Illite		
SH 1578	Smectite (30-40%) Fe Oxyhydroxides (8-10%) SiO ₂ as amorphous silica			
10400 # 8K	Illite Quartz	Kaolinite Smectite Fe oxyhydroxides		
IOS-1	Illite Kaolinite	Quartz plagioclase feldspar Fe oxyhydroxides		Calcite (< 5%)
MV 65 I	Birnessite Todorokite	Quartz		
6269 No. 2	Amorphous Mn and Fe Oxyhydroxides	δ - MnO ₂		

Table 3.2. Cation Exchange Capacity and Surface Area of Sediments.

	Measured Value		Carbonate free basis		CaCO ₃ %
	CEC mEq/100g	SA m ² /g	CEC mEq/100g	SA m ² /g	
IOS-3	7	24	55	188	89
M77-20	7	30	51	218	88
10399 # 7K	17	85	109	548	85
IOS-6	19	54	66	188	73
IOS-4	17	63	52	193	69
IOS-5	43	58	101	136	59
IOS-2	31	131	60	253	50
S 702	20	97	35	171	45
SH 1578	124	396			
10400 # 8K	43	190			4
IOS-1	45	199			< 2
MV 65 I	100	95			0
6269 No. 2	82	340			0

Table 5.3. Chemical Composition of Sediments

Sample No.	CaCO ₃ %	SiO ₂ %	Fe %	Mn %	Al %	Mg %	Na %	K %	Ni ppm	Cu ppm	Zn ppm	Ti ppm	P ppm	Pb ppm
IOS-3	89	2.3	0.6	0.05	0.85	0.18	0.55	0.31	20	68	44	150	140	10
M77-20	88	7.3	1.7	0.12	1.4		0.20	0.32	21	297	109	660	60	8
IOS-6	73	6.3	1.6	0.09	2.4	0.5	0.38	0.66	35	90	65	1200	310	< 5
IOS-4	69	8.7	1.8	0.07	3.0	0.57	0.55	0.96	32	90	75	1500	190	< 5
IOS-5	59	10.7	2.3	0.13	3.6	0.76	0.40	1.10	49	92	87	2200	330	20
IOS-2	50	11.9	2.5	0.03	4.6	1.0	0.44	1.30	50	89	101	2300	500	20
S 702	45	17.1	3.1	0.14	5.0		0.44	1.13	165	63	89	2500	430	9
SH 1578	4	39.5	14.6	4.3	2.0		0.70	0.34	555	865	435	1100	340	75
IOS-1	< 2	25.1.	5.3	0.31	6.6	1.6	0.85	2.6	109	167	137		690	30
MV 65 I	-	-	2.2	32.9	2.2				1800	1200	1340			22
6269 No.2	-	-	13.7	16.8	1.7				4680	1580	680			760
10399#7K	85	9.3	1.8	0.10	3.4	0.73	0.88	2.4	-	-	-	1800	250	-
10400#8K	3	24.6	5.0	0.32	8.8	1.68	0.63	2.5	-	-	-	5500	680	-

Table 3.4. Chemical Composition Recalculated on a Carbonate free basis.

Sample No.	CaCO ₃ %	SiO ₂ %	Fe %	Mn %	Al %	Mg %	Na %	K %	Ni ppm	Cu ppm	Zn ppm	Ti ppm	P ppm	Pb ppm
IOS-3	89	18.0	4.7	0.39	6.7	1.41	4.31	2.43	157	533	345	1176	1098	78
M77-20	88	53.1	12.4	0.87	10.2	-	1.45	2.32	153	2160	1382	793	436	58
IOS-6	73	21.9	5.6	0.31	8.3	1.74	1.32	2.30	122	313	226	4174	1078	<17
IOS-4	69	26.5	5.5	0.21	9.2	1.74	1.68	2.93	97	275	229	4580	580	<15
IOS-5	59	25.0	5.4	0.30	8.4	1.78	0.94	2.57	115	215	204	5146	772	47
IOS-2	50	23.0	4.8	0.06	8.9	1.93	0.85	2.51	97	172	195	4444	966	39
S702	45	30.1	5.5	0.25	8.8	-	0.78	1.99	291	111	157	4405	758	16

All of these variables have therefore been recalculated on a carbonate free basis and it can be seen that on this basis there is much less variation in the CEC and SA values. Also, the concentration of many of the elements in the carbonate free fraction is fairly constant.

3.2. Experimental

The batch equilibration procedure used for measuring distribution ratios was basically the same for both Np and Am although different separation and analytical techniques were used to determine the final solution concentrations. Because of the very high Am distribution coefficients γ -counting of the solution phase was not sufficiently sensitive for the determination of Am and α -spectrometry had to be used. A simple technique involving solvent extraction followed by preparation of evaporated sources was developed making the extra work involved manageable. High Am R_d values also meant that small quantities of loaded sediment in the solution could affect measured concentrations and filtering was necessary. Neptunium, on the other hand, could be counted in a well-type γ -scintillation counter. Filtering was unnecessary since the small amount of sediment remaining in solution after centrifuging (see Section 4.1.6) would not be detected even when loaded with Np. This was confirmed by counting filtered and unfiltered samples after seven days.

^{241}Am ($t_{1/2} = 458$ yr) was used in the distribution coefficient experiments and ^{243}Am was used to monitor recoveries for α -spectrometry. ^{235}Np ($t_{1/2} = 410$ days) was the neptunium isotope used. This was chosen in preference to ^{237}Np ($t_{1/2} = 2.14 \times 10^6$ yrs) because its short half life meant that it could be used at concentrations low enough to ensure that precipitation would not occur. ^{235}Np decays principally by electron capture and can be assayed by counting in the uranium x-ray region, i.e. 10-120 keV. Unfortunately the total intensity for the K x-ray region ($K\alpha + K\beta$) is only 1.9%, i.e. 4.3×10^4 dpm/ μCi . Nevertheless, the 2 μCi purchased from Harwell were sufficient for eleven determinations and was recovered for re-use.

Details of the experimental procedures used are as follows:

3.2.1. Batch equilibrations

The temperature was kept at 4°C throughout these experiments. Sea water was filtered through 0.22 μ filters and cooled in a refrigerator before use and a refrigerated centrifuge was used. In order to ensure

that representative samples were obtained sediments were mixed with sea water to form a slurry and samples weighing between 50 and 100 mg (dry weight) were then transferred, by pipetting while agitating, into 50 ml Oak-Ridge-type polycarbonate centrifuge tubes. The tubes were placed in a shaking water bath at 4°C and shaken gently at 120 strokes/min. overnight. The samples were then centrifuged for 180 mins at 7000 rpm. and the supernate discarded. The tube + solid + solution were weighed to estimate the volume of residual solution.

Spiked sea water solutions were prepared by adding 1-2 ml of the tracer in acid solution to 500 ml of sea water. The pH was readjusted to 8.2 with NaOH. These solutions were left to equilibrate at 4°C for several weeks and then filtered through 0.22 μ filters and analysed for tracer concentration before use.

Thirty millilitre portions of spiked sea water were added to each tube containing the washed sediment and the mixture sealed, returned to the water bath and shaken at 120 strokes/min. At intervals the tubes were centrifuged for 90 mins at 7000 rpm. Samples of the supernate were removed by pipetting and analysed. After counting, the Np solutions were cooled to 4°C and returned to the original centrifuge tubes. This could not be done for Am which meant that only a limited number of readings could be taken.

Np concentrations were determined by counting in a well-type NaI scintillation counter. At the end of the adsorption period oxidation state determinations were made on the solutions and the method used is described in Section 3.2.4. The analytical method used for Am was as follows.

3.2.2. Americium Determination

Approximately 5g samples were transferred to Millipore syringes and filtered through double filters, a 0.22 μ filter above a 0.10 μ filter. These filters were dried and counted on Zn sulphide scintillation counters in order to estimate how much Am was removed by filtering. Exactly 5.0g of the filtered solution was then transferred to a 50 ml separating funnel. Any excess of filtered solution was returned to the centrifuge tube which was then weighed and returned to the shaking water bath.

To the sample in the separating funnel was added

- i) 100 μ l 0.1M HCl
- ii) 50 μ l ($\sim$ 50 dpm) ^{243}Am spike
- iii) 3ml 0.18M 2-Thenoyltrifluoroacetone (TTA), 0.01M tri-n-butyl phosphate (TBP) in cyclohexane.

The samples were then shaken on a mechanical shaker for 40 minutes and the phases allowed to separate. The organic phase was transferred to a 10 ml beaker, evaporated down to about 0.3 ml and transferred to a heated stainless steel planchette (17 mm diameter). When dry the planchettes were flamed and counted on an α -spectrometer. Recoveries were generally 70% or greater. Losses were shown to be almost entirely at the source-preparation stage. Samples of the initial sea water were also analysed by γ -counting and identical results were obtained.

3.2.3. Neptunium Determination

Exactly 5.0g of supernate was transferred to a counting vial and counted in a well-type γ -scintillation counter. The short half life of ^{235}Np had to be taken into account when calculating R_d values. R_d values were calculated by dividing the concentration of Np on the sediment by the concentration in solution on the day of measurement.

3.2.4. Determination of Neptunium Oxidation States

The method developed by Foti and Freiling (1964) for determining the distribution of neptunium among its oxidation states was used with only minor changes. This method is based on the fact that TTA in benzene extracts Np(IV) but not Np(V) or Np(VI) from dilute acid solution and that lanthanum fluoride carries Np(V) and Np(IV) but not Np(VI). If therefore the total Np is also measured it is possible to determine the distribution of the Np among the three oxidation states.

Details of the procedure used are as follows:-

- i) 5.0g of supernate was transferred to a counting vial and counted to obtain the total Np.
- ii) 7.0g was transferred to a separating funnel and 0.35 ml 12M HCl and 4 ml 0.4M TTA in benzene added. The sample was shaken for 10 minutes and the phases allowed to separate. 3.5g of the organic phase (Np(IV)) and 5.0g of the aqueous phase (Np(V) + Np(VI)) were transferred to counting vials and counted.
- iii) 7.0g was transferred to a 15 ml centrifuge tube and the following reagents added: 1 ml lanthanum nitrate solution (2.5 mg lanthanum nitrate per ml), 1 ml uranium nitrate solution (2.0 mg uranium nitrate per ml), 0.3 ml 12M HCl and 1 ml HF. The tubes were

shaken for 2 minutes and centrifuged. 5.0g of the supernate (Np(VI)) was transferred to a counting vial and the rest discarded. The precipitate (Np(IV) and Np(V)) was dissolved in 0.6 ml 2M $\text{Al}(\text{NO}_3)_3$ + 2 ml 2M HNO_3 and transferred to a counting vial with 2.4 ml water.

All fractions were counted and the amount of Np in each oxidation state calculated.

3.3. Results and Discussion

3.3.1. Americium

In recent years many studies have attempted to determine the distribution coefficients for americium on a variety of rocks, minerals and sediments (Sanchez et al., 1981; Allard and Beall, 1980; Erdal, 1979; Polzer and Milner, 1980; Barney, 1981). Typically reported K_d values have been large, ranging from 100 to $>2.2 \times 10^6$ suggesting that Am is highly sorbed by all types of minerals and rocks. However, in many of the Am sorption experiments no attempt was made to either select initial Am concentrations at levels below precipitation levels or to show that precipitation was absent. The equilibration times used varied from a few hours to more than two years.

Rai et al (1981) have critically evaluated much of this data and conducted desorption experiments on contaminated Hanford sediments. They concluded that the concentration of Am in solutions contacting sediments is limited by the solubility of some solid phase rather than by the sorption reaction as long as an excess of Am solid phase is present. They deduced that the concentration in solution depends upon the pH according to the equation

$$\log \text{Am}_{(\text{mol/l})} = (-3.76 \pm 0.26) - (1.07 \pm 0.04)\text{pH} \quad (1)$$

It is generally assumed that Am in sea water will be in the III oxidation state, although Aston (1980), as a result of theoretical calculations has suggested that Am(IV) might also exist. Both $\text{Am}(\text{OH})_3$ and $\text{Am}(\text{OH})_4$ are highly insoluble but Rai et al (1981) have shown that it is unlikely that it is the solubility of $\text{Am}(\text{OH})_3$ that controls the concentration of Am in solution since the solubility of the Am solid phase associated with sediments, $\text{Am}_{(\text{soil})}$ is approximately five orders of magnitude lower than that of $\text{Am}(\text{OH})_3$.

Because distribution coefficients are meaningful only if precipitation is absent we used the lowest starting concentrations practicable in view

of the high Am distribution coefficients and alpha spectrometry rather than gamma counting was used because of its greater sensitivity. Two different initial concentrations, approximately 1.8×10^{-9} M and 2.0×10^{-10} M were used and distribution coefficients were determined after 1, 4 and 8 weeks and 1 and 4 weeks, respectively. After adsorption the supernate was removed and the sediments were placed in fresh sea water and desorption followed. The pH of the solution was measured and found to drop from its initial value of 8.2 to between 7.7 and 8.0 at two weeks to between 7.5 and 7.8 at eight weeks.

The results of these experiments are given in Tables 3.5 and 3.6 and are illustrated in Figures 3.2. to 3.5. The following observations can be made from a study of these results:

3.3.1.1. Effect of Initial Concentration

Distribution coefficients were the same for the two different initial concentrations investigated. This indicates that in this concentration range Henry's law is obeyed and that precipitation was not occurring.

3.3.1.2. Effect of Time

The distribution coefficient increased steadily with time and for all the carbonate samples the graphs of R_d against time are straight lines after the first seven days. Erdal (1979) has suggested that this type of increase with time is due to the exposure of new surfaces due to attrition during shaking. At these low concentrations, however, it is unlikely that the availability of sites is the limiting factor and it is more probable that some slow reaction is occurring. Shanbhag and Morse (1982) added ten successive spikes to samples of calcite in sea water (10^{-8} M Am) and found that after each addition the percent adsorbed after a 30 minute reaction time was 99%. This is a clear indication that the surface sites are not being saturated. We obtained similar results with europium and our sediments (see Chapter 2). It must be borne in mind that the changes in concentration are very small. More than 99% of the Am added was removed within the first seven days (probably within minutes) and it is difficult to say whether the initial rapid reaction is different to the subsequent slow reaction. Possibly the initial reaction is a hydrolysis reaction whereas the slow reaction is due to complexation with one or more of the constituents of the sediment. Diffusion into the clay lattice could also be involved.

Table 3.5. Americium Distribution Coefficients.

	Initial conc. mols/l 10^{-10}	ADSORPTION $K_d/10^5$			DESORPTION $K_d/10^5$	
		DAYS			DAYS	
		7	28	56	14	42
IOS-3	18	0.64 ± 0.04	1.24 ± 0.11	1.96 ± 0.17	10.0 ± 0.8	9.6 ± 1.1
	2	0.63 ± 0.01	0.68 ± 0.07	-	5.5 ± 0.4	
M77-20	18	0.58 ± 0.05	1.07 ± 0.10	1.91 ± 0.16	7.0 ± 0.7	8.3 ± 1.4
	2	0.70 ± 0.01	0.96 ± 0.03	-	4.1 ± 0.1	
IOS-6	18	1.05 ± 0.09	1.93 ± 0.24	3.12 ± 0.29	11.4 ± 0.6	7.7 ± 0.4
	2	1.16 ± 0.02		-	6.2 ± 0.5	
IOS-4	18	0.75 ± 0.06	0.95 ± 0.08	1.76 ± 0.15	10.2 ± 1.0	7.1 ± 0.7
	2	0.57 ± 0.02	0.71 ± 0.06	-	3.6 ± 0.3	
IOS-5	18	1.10 ± 0.09	1.43 ± 0.13	1.99 ± 0.20	10.5 ± 0.8	8.5 ± 1.1
	2	1.04 ± 0.01		-	6.6 ± 0.6	
IOS-2	18	0.72 ± 0.05	1.28 ± 0.11	1.80 ± 0.14	9.1 ± 0.2	8.0 ± 0.9
	2	0.51 ± 0.01	1.88 ± 0.18	-	4.7 ± 0.8	
S702	18	0.50 ± 0.04	0.80 ± 0.09	1.22 ± 0.10	4.8 ± 0.4	3.8 ± 0.5
	2	0.42 ± 0.03	0.83 ± 0.04	-	3.1 ± 0.4	
SH1578	18	1.36 ± 0.11	3.83 ± 0.44	4.11 ± 0.36	23.7 ± 1.8	26.0 ± 3.3
	2	1.43 ± 0.04	2.54 ± 0.12	-	8.2 ± 0.9	
IOS-1	18	1.46 ± 0.12	2.79 ± 0.23	3.31 ± 0.21	13.6 ± 1.2	20.2 ± 1.7
	2	1.42 ± 0.05	1.62 ± 0.11	-	7.6 ± 0.4	
MV 65 I	18	1.35 ± 0.14	4.64 ± 0.38	7.65 ± 0.72	32.3 ± 3.8	32.9 ± 2.7
	2	1.12 ± 0.06	3.20 ± 0.06	-	11.7 ± 1.3	
6269 No.2	18	1.71 ± 0.15	7.91 ± 0.66	11.04 ± 0.88	33.7 ± 4.2	53.7 ± 4.7
	2	2.35 ± 0.10	3.22 ± 0.05	-	12.7 ± 1.3	

Table 3.6. Americium Distribution Coefficients

Carbonate sample 10399 # 7K

Initial sea water		Kd sorption, $\frac{\text{ml/g}}{10^5}$				Kd desorption $\frac{\text{ml/g}}{10^5}$	
Vol ml	Am conc $\frac{\text{mol/l}}{10^{-10}}$	1 day	7 day	28 day	56 day	56 day	84 day
30	13.7 ± 2.7	0.32 ± 0.04	0.71 ± 0.08	0.92 ± 0.11	1.18 ± 0.14	4.19 ± 0.77	
30	"	0.28 ± 0.02	0.54 ± 0.06	0.66 ± 0.08	0.94 ± 0.11	5.38 ± 0.79	
30	"	0.29 ± 0.03	0.56 ± 0.06	0.74 ± 0.09	0.89 ± 0.10	—	
Weighted mean		0.29 ± 0.02	0.59 ± 0.05	0.75 ± 0.07	0.97 ± 0.08	4.67 ± 0.43	
30	2.6 ± 0.3	0.36 ± 0.05	0.53 ± 0.06	0.52 ± 0.07	1.01 ± 0.14	6.27 ± 0.72	
30	"	0.37 ± 0.04	0.60 ± 0.08	0.73 ± 0.09	1.37 ± 0.38	5.98 ± 0.83	
30	"	0.33 ± 0.05	0.60 ± 0.07	0.94 ± 0.13	1.38 ± 0.18	5.71 ± 0.75	
Weighted mean		0.35 ± 0.03	0.57 ± 0.04	0.69 ± 0.11	1.18 ± 0.13	6.00 ± 0.40	
3	13.7 ± 2.7			0.16 ± 0.02			3.10 ± 0.68
3	"			0.20 ± 0.02			2.72 ± 0.51
3	"			0.19 ± 0.03			3.21 ± 0.49
Weighted mean				0.18 ± 0.01			3.00 ± 0.06

Sample Dry weight 0.12g

Table 3.6(cont...)

Red Clay Sample 10400 # 8K

	Initial sea water	K_d Sorption , $\frac{ml/g}{10^5}$				K_d Desorption $\frac{ml/g}{10^5}$
Vol ml	Conc $\frac{mol/l}{10^{-10}}$	1 day	7 day	28 day	56 day	56 day 84 day
30	13.7 ± 2.7	0.49 ± 0.06	1.13 ± 0.13	1.80 ± 0.22	3.53 ± 0.05	8.69 ± 1.34
30	"	0.55 ± 0.07	1.10 ± 0.13	1.63 ± 0.21	2.18 ± 0.27	8.15 ± 1.14
30	"	0.48 ± 0.05	1.17 ± 0.13	2.01 ± 0.27	1.56 ± 0.18	8.43 ± 1.48
Weighted mean		0.50 ± 0.03	1.13 ± 0.07	1.79 ± 0.13	2.17 ± 0.08	8.39 ± 0.75
30	2.6 ± 0.3	0.37 ± 0.05	1.10 ± 0.13	1.85 ± 0.29	3.19 ± 0.36	5.72 ± 0.69
30	"	0.37 ± 0.04	0.97 ± 0.11	1.73 ± 0.38	2.02 ± 0.24	6.38 ± 0.11
30	"	0.33 ± 0.06	1.17 ± 0.13	1.62 ± 0.26	1.77 ± 0.22	5.37 ± 0.77
Weighted mean		0.35 ± 0.03	1.08 ± 0.08	1.72 ± 0.17	2.10 ± 0.35	6.04 ± 0.24
3	13.7 ± 2.7	0.30 ± 0.04				5.57 ± 0.66
3	"	0.20 ± 0.03				4.90 ± 0.57
3	"	0.19 ± 0.02				5.70 ± 0.68
Weighted mean		0.23 ± 0.04				5.34 ± 0.36

Sample wt. = 0.09 g dry wt.

Table 3.7. Concentration of Americium in solution during sorption experiments.

	Initial conc. mols/l 10^{-10}	ADSORPTION $\frac{\text{mols/l}}{10^{-12}}$			DESORPTION $\frac{\text{mols/l}}{10^{-12}}$	
		DAYS			DAYS	
		7	28	56	14	42
IOS-3	18	13.0 $\pm$ 1.0	6.7 $\pm$ 0.6	4.1 $\pm$ 0.4	0.84 $\pm$ 0.26	0.87 $\pm$ 0.87
	2	1.40 $\pm$ 0.09	1.34 $\pm$ 0.13	-	0.17 $\pm$ 0.04	-
M77-20	18	8.7 $\pm$ 0.7	4.5 $\pm$ 0.5	2.4 $\pm$ 0.2	0.65 $\pm$ 0.19	0.58 $\pm$ 0.58
	2	1.00 $\pm$ 0.06	0.73 $\pm$ 0.05	-	0.17 $\pm$ 0.04	-
IOS-6	18	5.9 $\pm$ 0.5	3.3 $\pm$ 0.3	2.6 $\pm$ 0.2	0.53 $\pm$ 0.04	0.81 $\pm$ 0.02
	2	0.63 $\pm$ 0.04	0.40 $\pm$ 0.05	-	0.16 $\pm$ 0.02	-
IOS-4	18	8.3 $\pm$ 0.8	6.6 $\pm$ 0.6	3.4 $\pm$ 0.3	0.62 $\pm$ 0.07	0.89 $\pm$ 0.10
	2	1.17 $\pm$ 0.08	0.93 $\pm$ 0.11	-	-	-
IOS-5	18	7.5 $\pm$ 0.7	5.8 $\pm$ 0.6	3.5 $\pm$ 0.2	0.79 $\pm$ 0.24	0.98 $\pm$ 0.13
	2	0.89 $\pm$ 0.05	0.55 $\pm$ 0.05	-	0.13 $\pm$ 0.01	-
IOS-2	18	11.3 $\pm$ 0.9	6.4 $\pm$ 0.6	4.4 $\pm$ 0.4	0.91 $\pm$ 0.03	1.03 $\pm$ 0.01
	2	1.76 $\pm$ 0.11	0.50 $\pm$ 0.06	-	0.20 $\pm$ 0.02	-
S702	18	9.3 $\pm$ 0.8	5.9 $\pm$ 0.6	3.7 $\pm$ 0.3	0.94 $\pm$ 0.28	1.23 $\pm$ 0.16
	2	1.49 $\pm$ 0.10	0.75 $\pm$ 0.06	-	0.20 $\pm$ 0.02	-
SH1578	18	7.9 $\pm$ 0.7	3.3 $\pm$ 0.4	2.9 $\pm$ 0.3	0.52 $\pm$ 0.05	0.47 $\pm$ 0.06
	2	0.85 $\pm$ 0.06	0.48 $\pm$ 0.04	-	0.15 $\pm$ 0.02	-
IOS-1	18	7.3 $\pm$ 0.8	3.8 $\pm$ 0.3	3.1 $\pm$ 0.1	0.78 $\pm$ 0.07	0.53 $\pm$ 0.05
	2	0.72 $\pm$ 0.05	0.63 $\pm$ 0.06	-	0.14 $\pm$ 0.01	-
MV 65 I	18	3.2 $\pm$ 0.7	2.3 $\pm$ 0.2	1.4 $\pm$ 0.1	0.33 $\pm$ 0.04	0.33 $\pm$ 0.03
	2	0.64 $\pm$ 0.05	0.22 $\pm$ 0.01	-	0.10 $\pm$ 0.01	-
6269 No.2	18	8.7 $\pm$ 0.8	1.9 $\pm$ 0.2	1.3 $\pm$ 0.1	0.47 $\pm$ 0.06	0.28 $\pm$ 0.03
	2	0.36 $\pm$ 0.03	0.27 $\pm$ 0.02	-	0.07 $\pm$ 0.01	-

Table 3.8. Am Solution Concentration

			SOLUTION CONCENTRATION				
	Sample weight g	Volume ml	Initial Sea water $\frac{\text{mol/l}}{10^{-10}}$	Sorption , 28 day	$\frac{\text{mol/l}}{10^{-12}}$ 56 day	Desorption , 56 day	$\frac{\text{mol/l}}{10^{-12}}$ 84 day
CARBONATE SEDIMENT 1039) #7K	0.12	30	13.7 ± 2.7	4.40 ± 0.36	3.37 ± 0.26	0.69 ± 0.09	0.14 ± 0.02
	0.12	30	2.6 ± 0.3	0.89 ± 0.13	0.52 ± 0.06	0.11 ± 0.01	
	0.12	3	13.7 ± 2.7	2.03 ± 0.15			
RED CLAY 10400 #8K	0.09	30	13.7 ± 2.7	2.48 ± 0.18	2.04 ± 0.52	0.53 ± 0.04	0.10 ± 0.01
	0.09	30	2.6 ± 0.3	0.49 ± 0.05	0.37 ± 0.03	0.11 ± 0.01	
	0.09	3	13.7 ± 2.7	1.72 ± 0.22			

FIGURE 3,2 AMERICIUM DISTRIBUTION COEFFICIENTS

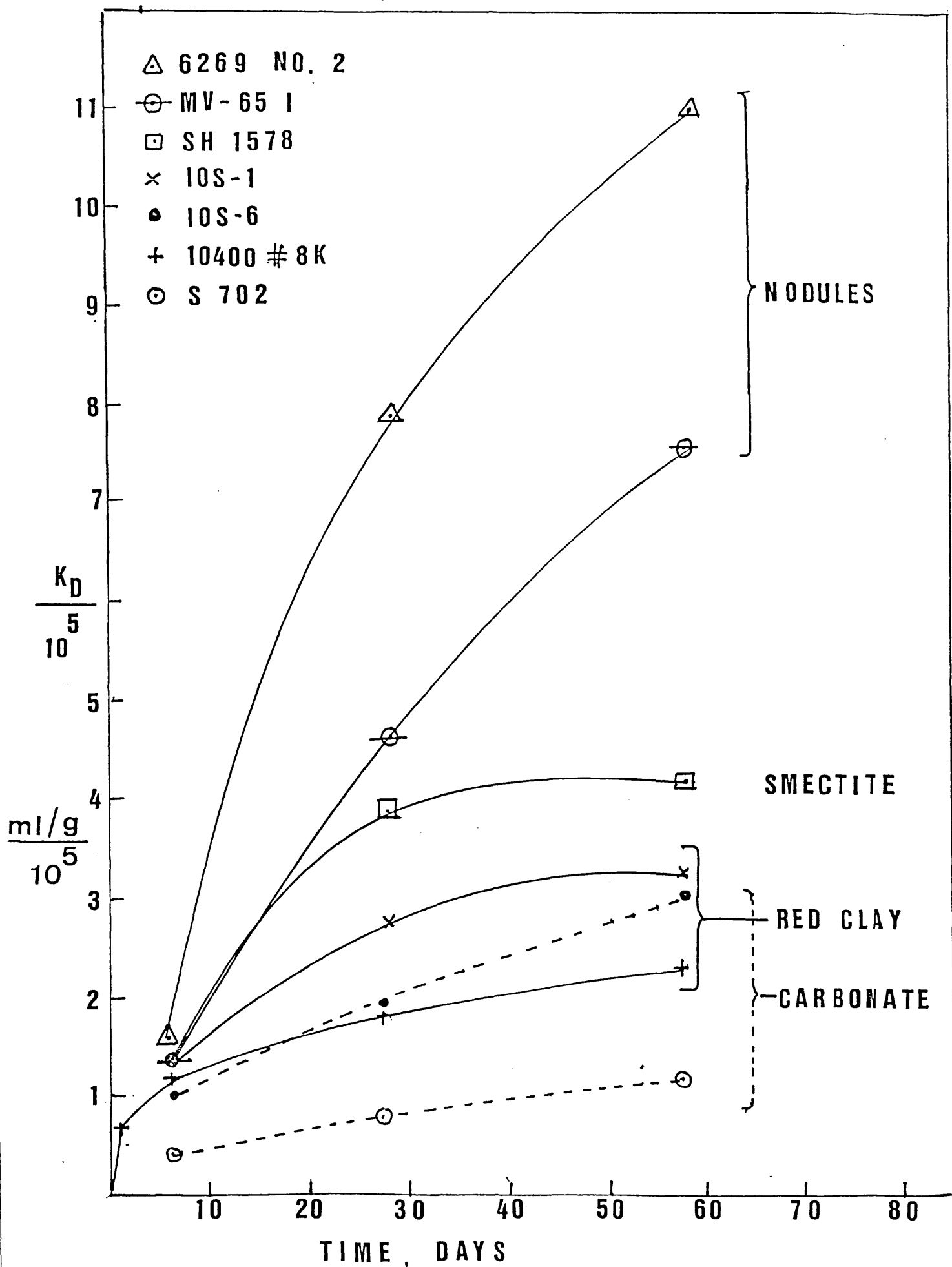


FIGURE 3.3 AMERICIUM DISTRIBUTION COEFFICIENTS
HIGH-CARBONATE SEDIMENTS

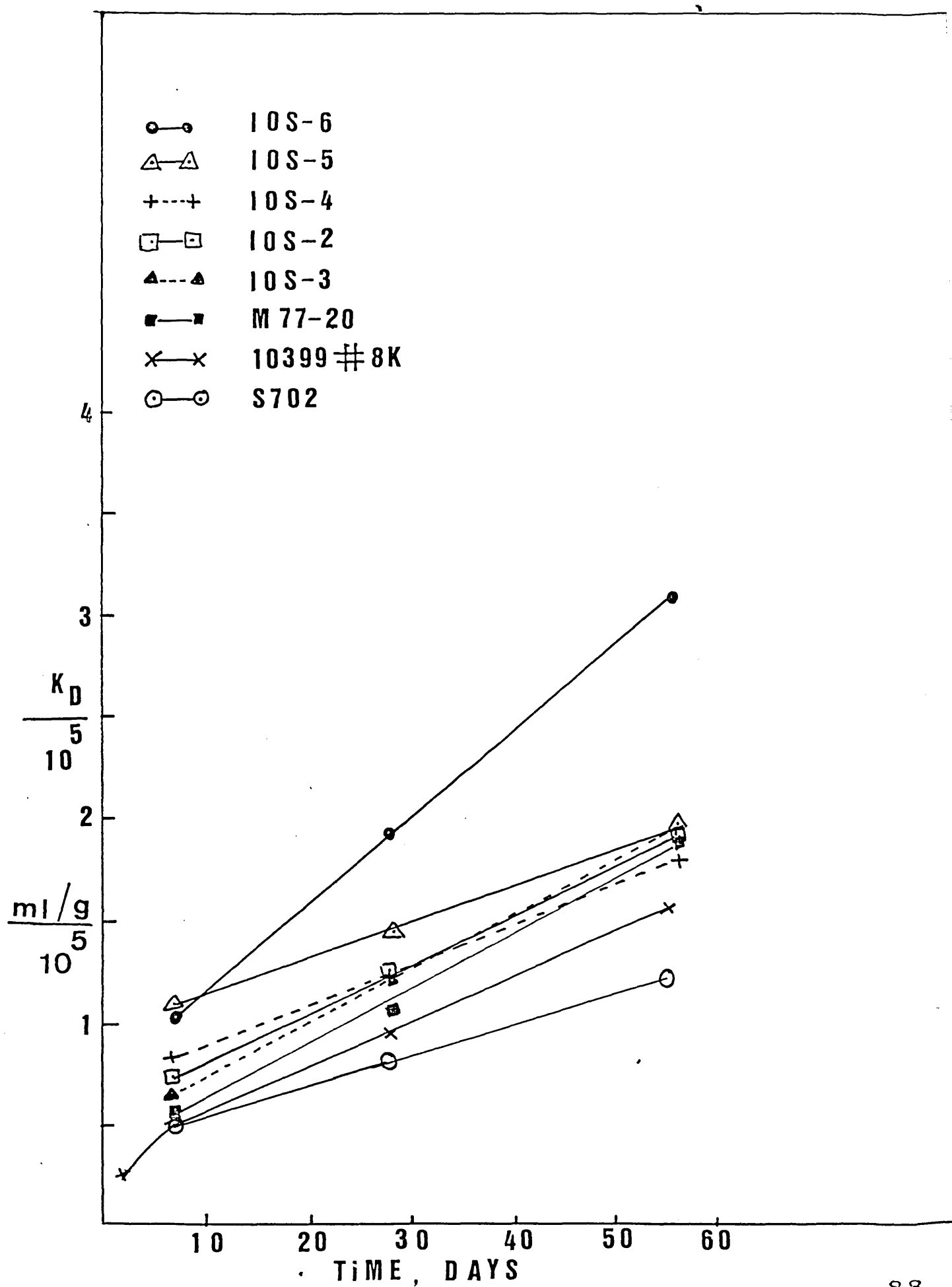


Fig 3.4 . CONCENTRATION OF Am IN SOLUTION : LOW-CARBONATE SAMPLES

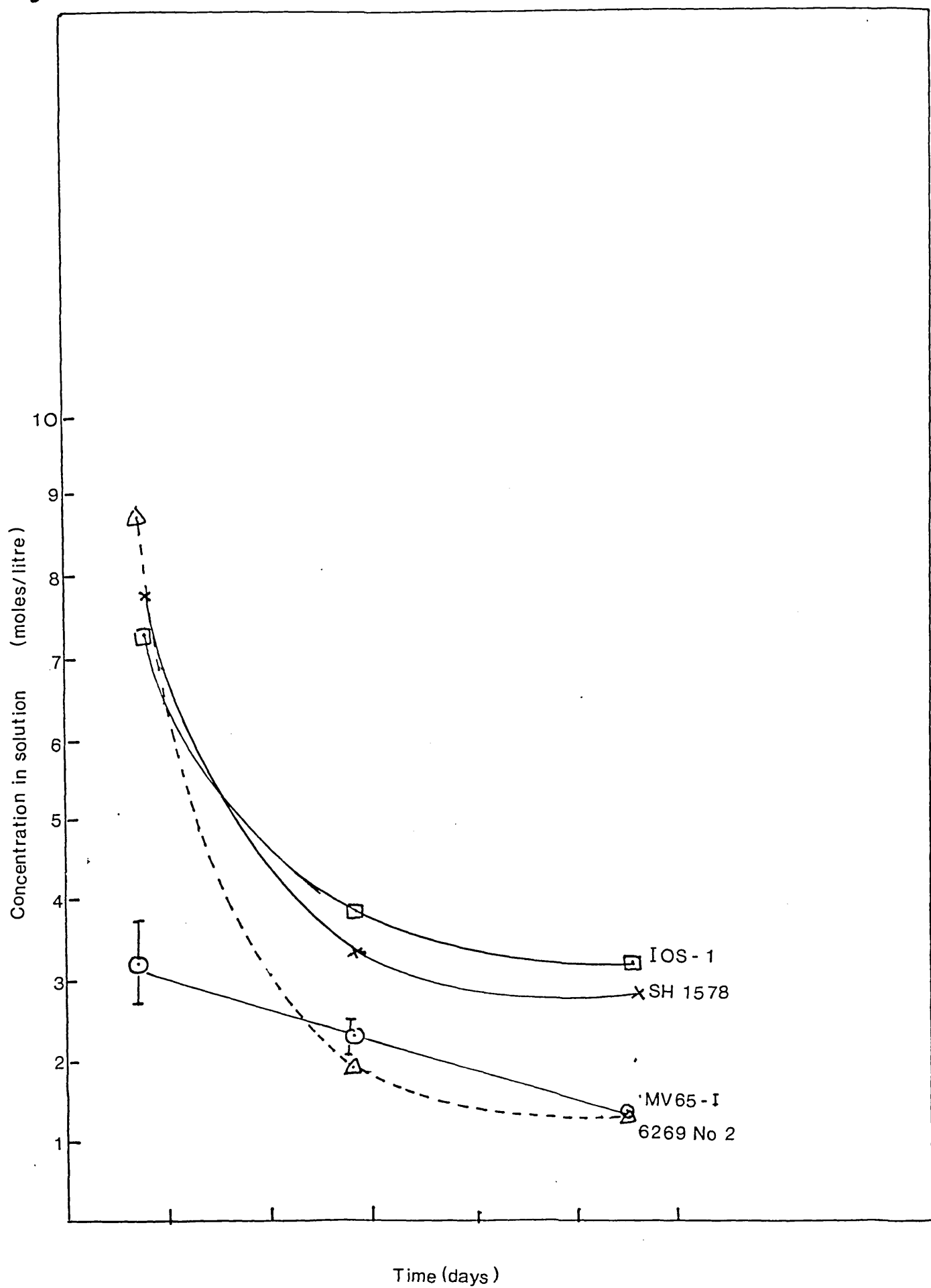
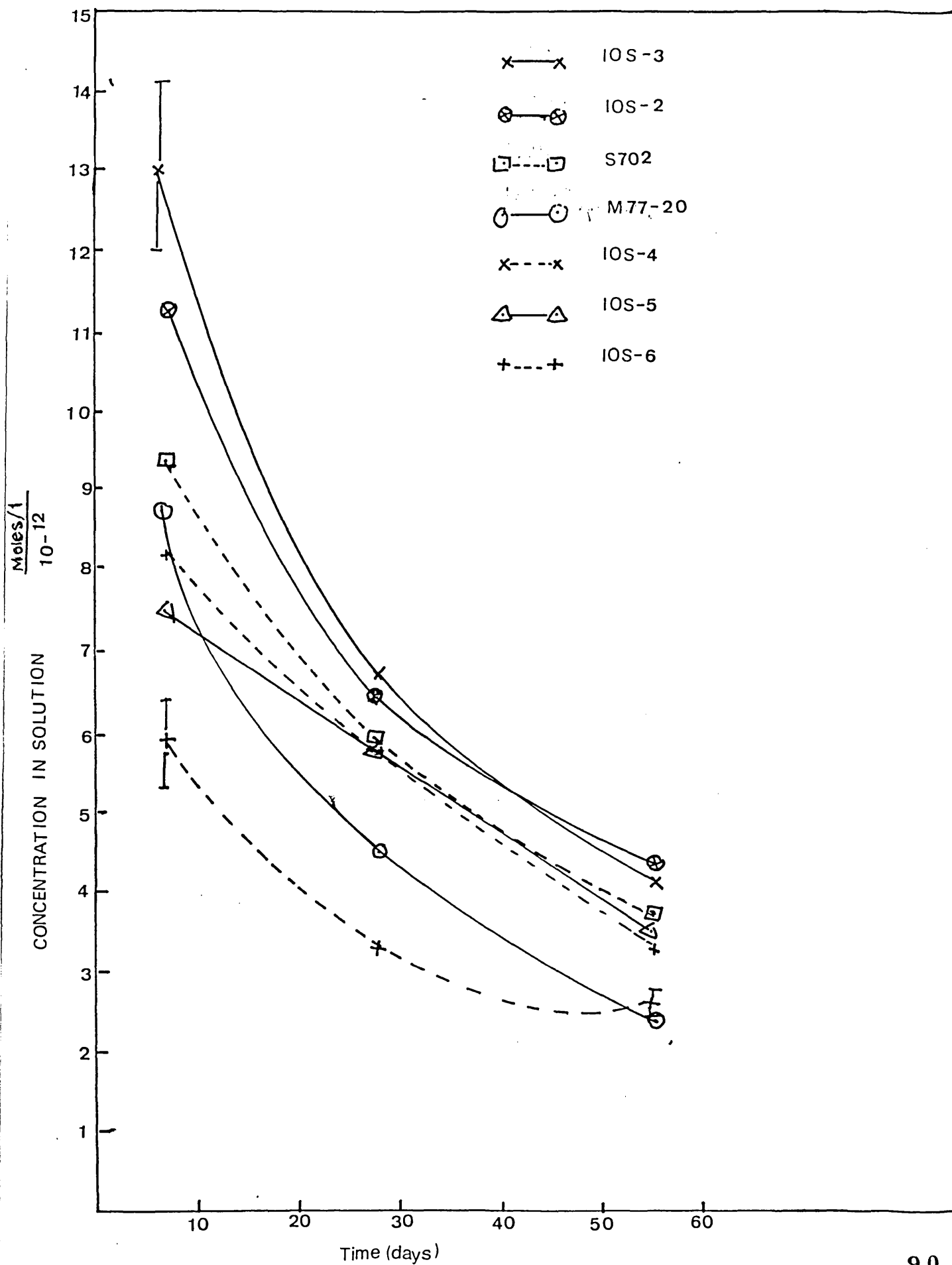


FIG 3.5 CONCENTRATION OF Am IN SOLUTION : HIGH-CARBONATE SAMPLES



3.3.1.3. Effect of Sediment Properties

Figure 3.2. shows the plot of R_d against time for the five low-carbonate samples together with two of the high-carbonate samples for comparison. In Figure 3.3. all of the high-carbonate samples are plotted on a larger scale.

It can be seen that the initial R_d values for the five mineral rich samples are all very similar and are higher than for the carbonate samples. In particular the manganese nodules have very high R_d values and their surface properties must be involved in the sorption reaction. The distribution ratio for the manganese nodules was still rising rapidly after eight weeks but the ratio for the other samples seemed to be levelling off.

All eight high-carbonate samples behaved in much the same way and it is not possible to correlate R_d values with any of their measured properties in spite of the fact that they encompassed a wide range of calcium carbonate content (45-89%), surface area (24-131 m²/g) and cation exchange capacity (35-101 mEq/100g). This is probably because, at these low Am concentrations, whatever the mechanism of adsorption, there is no shortage of available sites and the effect of these variables would not be apparent. Nevertheless, the high R_d values for the Fe/Mn rich samples do seem to indicate that these elements are involved in the sorption process. The hydrous oxides of iron and manganese occur in virtually all sediments and could well exert an influence on the sorptive properties which is out of all proportion to their concentration.

3.3.1.4. Final Solution Concentration

A study of the graphs of solution concentration against time (Figures 3.4. and 3.5.) might help to clarify the situation. It can be seen that there are wide variations in the solution concentrations after seven days but the difference between samples becomes less as the time increases and the percent adsorbed rises from between 99.3 and 99.8% at seven days to between 99.7 and 99.9% at 56 days. Possibly the concentration will eventually drop to a common value, although it will clearly be a considerable time before the desorption value of 0.5×10^{-12} moles/l (99.97% on the sediment) is reached.

Tables 3.7. and 3.8. show the Am concentrations found in solution. In order to compare these values with those predicted by Rai (equation 1, Section 3.3.1.) the predicted concentrations at the pH of these experiments was calculated. Table 3.9. shows these values for the pHs of interest.

Table 3.9. Predicted concentration of Am in solution at different pH values.

	pH	log Am	Predicted Am concentration $\frac{\text{moles/l}}{10^{-12}}$	
			Mean	range
8 week adsorption	7.5	-11.79±0.39	1.62	0.65 to 4.12
	7.8	-12.11±0.40	0.78	0.31 to 2.00
2 week desorption	7.9	-12.21±0.41	0.62	0.25 to 1.57
	8.0	-12.32±0.41	0.48	0.18 to 1.23

It can be seen that the concentrations in solution after the eight week R_d determination and after the two week desorption lie within the ranges predicted by Rai et al. However, it is also clear that there are significant differences in solution concentration at the various stages of our experiments and it appears that it is an over simplification to explain its validity just in terms of solubility effects. Once below the solubility limit other sorption/desorption reactions can be observed.

3.3.1.5. Desorption

This is one important respect in which Am differs from Np (see Section 3.3.2.). Np R_d values are similar for sorption and desorption, indicating that the reaction is reversible. Desorption distribution ratios for Am, on the other hand, are an order of magnitude higher than the 56 day adsorption distribution ratios. Other workers (e.g. Sanchez et al., 1981) have reported similar results, and this is generally taken to mean that the sorption-desorption reaction is not reversible. An alternative explanation, that is discussed in detail in Chapter 5, is that this was either due to the presence of some poorly sorbed species or was an experimental artifact resulting from poor phase separation.

Desorption distribution ratios are considerably higher for the Fe/Mn rich samples than for the carbonate samples. This is another indication that these elements are involved in the sorption process and that this reaction is not reversible.

3.3.1.6. Particle Size

When determining sorption coefficients for Am the solutions were always filtered through a pair of millipore filters (0.22 μ above 0.10 μ) before analysis. The filters were counted on a zinc sulphide scintillation counter. A comparison with the spectra obtained on the alpha spectrometer showed that the sources were reasonably thin and that this procedure gave a fair measure of the total Am retained on the filters. From these experiments it was possible to calculate the approximate weight of sediment retained by the filters assuming that the activity per gram of the fine particles on the filters was the same as the activity per gram of the bulk sediment. (This is probably not true and the calculated weights are probably too high). Estimates of the mass of sediment retained by 0.22 μ filters when five gram samples of solution that had been previously centrifuged for 180 minutes at 7000 rpm were filtered, ranged from 2 μ g for sample S702 to 20 μ g for MV 65 I.

It was found that in all cases there was no measurable Am on the 0.1 μ filter if sediment was present. In the absence of sediment a high proportion of the particulate Am passed through the 0.22 μ filter and was retained by the 0.1 μ filter. Thus, although Am readily forms colloidal particles in sea water it is clear that in the presence of sediment these particles become attached to the solid phase and are not free to move.

3.3.1.7. Sea Water/Sediment Ratio

The results obtained in this set of experiments (Table 3.6.) were very interesting and possibly throw new light on some of the reactions occurring. In theory if only one sorbable species is present and Henry's law is obeyed then the sea water/sediment ratio should not affect the value obtained for the distribution ratio. However, it can be seen from Table 3.6. that for both samples the R_d values were significantly lower when the sea water/sediment ratio was 30:1 than when it was 300:1. The most likely explanation is that a small proportion of the americium was present in a non-sorbable form and the next phase of this project was a thorough investigation into the effect of varying the solid/solution ratio. The results of this are given in Chapter 5.

3.3.2. Neptunium

Compared with americium and plutonium very few neptunium distribution ratios have been determined on geological materials. The few results that have been reported are mostly less than 100 ml/g although Allard et al. (1980) found that apatite had a R_d of 8000 ml/g. Harvey (1980a) has calculated that sediments in the Irish sea have a R_d of about 5000 ml/g under environmental conditions and Aston (1980) determined distribution ratios on three marine sediments in spiked sea water. He reports values of 390, 1950 and 3200 ml/g for a calcareous deep sea deposit, an argillaceous mud and an intertidal silt, respectively.

From the limited amount of thermodynamic data available it appears that in well oxygenated sea water neptunium should occur as the soluble pentavalent species NpO_2^+ although the possible presence of bicarbonate and hydroxyl complexes cannot be ignored. Recent work has indicated that neptunium is susceptible to changes in oxidation state under the conditions found in the environment. Bondietti and Francis (1979) investigated the sorption of Np using different basalt, granite and shale rocks in a deoxygenated ($< 1 \text{ ppm O}_2$) nitrogen purged system. After seven days of equilibration they found that both the Np remaining in solution and the Np on the rocks was 60 to 80% Np(IV). On the other hand, sorption experiments with shale and with basalt which had been pretreated with NaOCl to oxidise the iron resulted in little or no reduction, although more than 80% of the Np was rapidly removed from solution. This would seem to indicate two different mechanisms for Np sorption, one of which involves a redox $\text{Np(V)} \rightarrow \text{Np(IV)}$ reaction.

Harvey (1980) studied the reduction of Np(V) under varying E_h and pH conditions and found that reduction occurred when E_h was $< 150 \text{ mV}$ over the pH range 7.0 to 8.0. No reduction was observed when the E_h was above $+180 \text{ mV}$ to $+200 \text{ mV}$ at any pH value.

In our experiments the pH started at 8.2 and gradually dropped to about 7.5, presumably because of the dissolution of CO_2 from the air. The E_h must have been around $+300 \text{ mV}$. The two manganese nodule samples were analysed by Mossbauer spectroscopy (Figures 3.6 - 3.8) which showed that the iron was almost entirely in the ferric state ($> 99.5\%$). The likelihood was, therefore, that reduction would not occur, but in view of the very different behaviour observed for the carbonate sediment and the iron and manganese rich samples it seemed worthwhile determining

the oxidation state of the Np in solution before and after the R_d determination. The results are given in Table 3.9. and it can be seen that in all cases Np(V) was the only oxidation state present. No attempt was made to determine the oxidation state of the Np actually on the sediments and it is quite possible that reduction may have occurred during sorption. If it were not for the fact that Am behaves in a similar way (and Am (III) could not undergo reduction) it would be tempting to explain the results obtained with the iron and manganese rich sediments, as being due to a slow reduction reaction. These results are given in Tables 3.10 and 3.11 and Figures 3.9. - 3.13. The left hand side of each graph shows how the R_d (Figures 3.9. and 3.11.) or the solution concentration (Figures 3.11-3.13.) varied with time during adsorption and the right hand side shows the variation during desorption.

It can be seen that, except for the red clay, 10400 #8K, all the distribution coefficients measured were greater than 10^3 . For the high-carbonate samples there was little change in R_d with time and the desorption R_d values were very similar to the adsorption R_d values, indicating a reversible reaction. For both adsorption and desorption equilibrium was quickly established (i.e. before the first reading at seven and fourteen days, respectively, was taken). The two manganese nodule samples and SH 1578 (14.6% Fe) behaved quite differently to the high-carbonate samples. Their distribution coefficients increased steadily over the first six weeks finally levelling off and then actually beginning to drop, indicating that desorption was taking place. The maximum R_d values for these samples were considerably higher than for the carbonate samples although, except for 6269 No. 2, the desorption R_d values were similar. Sample 6269 No. 2 is mostly amorphous Fe and Mn oxy-hydroxides and has a very high surface area and cation exchange capacity. SH 1578 also contains a high proportion of Fe oxy-hydroxides and it too has a very high R_d . MV 65 I is mainly manganese and although it has a similar CEC to the other two samples its surface area is considerably lower. This would indicate that the high R_d values for 6269 No. 2 and SH 1578 are due either to the high surface area or, more probably, to some reaction with the iron. The fact that desorption R_d values were close to the final adsorption R_d values indicates that, as with the carbonate sediments, this reaction is reversible.

The sediment IOS-1 is different to the other low-carbonate samples in that it contains a high proportion of amorphous silica and only 5.3% Fe. The shape of its graphs are similar to those of the other three samples but the R_d is lower. This indicates that sorption is by the iron fraction and that the silica, in spite of its high surface area, plays little part.

It would seem therefore, that as with americium, sorption of neptunium is by more than one mechanism. Samples high in iron adsorb Np more strongly than do the carbonate sediments but the reaction is slower. Where carbonate is present the reaction is rapid and an equilibrium is quickly set up. Beall et al. (1981) have suggested that calcium carbonate is a strong complexing agent for neptunium and americium and it is probable that chemisorption to calcium carbonate plays an important part in the sorption of these elements. Hydrolysis is also likely to be important since the neptunyl ion hydrolyses strongly at pHs above 7.5. Thus, the combination of sea water with its high pH and of the sediments with high carbonate content would seem to be ideal for the removal of Np from solution and the presence of iron can only improve matters. This is the case even in relatively oxidising conditions; in more reducing conditions which might well exist in the sediments (particularly near the surface where organic matters may be present) (Harvey, 1981) R_d values are likely to be even higher. Under natural conditions the pH should remain at 8.2 and this too should result in distribution ratios which are, if anything higher than the measured values.

3.4. Summary and Conclusions

In this Chapter experiments designed to study the sorption of neptunium and americium by marine sediments from sea water containing these nuclides in concentrations low enough to avoid precipitation have been described. The main points to emerge from this work are:

1. Distribution coefficients for all the sediments studied were $>10^5$ for americium. Neptunium distribution coefficients were more variable, red clays giving the lowest values and the iron and manganese rich samples the highest. Apart from one red clay, all the neptunium distribution coefficients were $>10^3$. Conditions used were relatively oxidizing and under more reducing conditions R_d values are likely to be even higher. This means, therefore, that if transport is mainly by diffusion it would take Np about 10^8 years (50^{237}Np half lives) and Am about 10^{10}

years (10^6 ^{243}Am half lives) to pass through 30m of sediment (Murray and Stanners, 1982; Nuttal et al., 1981). Americium would, therefore, certainly never reach the sediment/water interface and neptunium is unlikely to pose a significant hazard. Provided, therefore, that the other properties are satisfactory, all the sediments studied (with the possible exception of the red clays for neptunium) should form excellent barriers to the migration of both these nuclides.

2. It appears that for both elements sorption is by at least two different mechanisms one of which is associated with the manganese-oxide fraction in the sediments. The other is probably associated with the calcium-carbonate fraction and hydrolysis is also likely to be involved. The Np in solution remained in the V oxidation state throughout the experiments.

3. At these low levels, solubility does not appear to be the controlling factor in the desorption of Am.

4. The reactions for Np appear to be reversible (with the possible exception of the Fe-Np reaction) but desorption distribution ratios for Am are an order of magnitude higher than adsorption distribution ratios. This apparent difference between sorption and desorption R_d values may be due to the presence of a poorly sorbed species in the sorption experiments.

5. In the presence of sediments and under our experimental conditions particulate Am was trapped by the solid phase and was all retained by 0.22 μ filters. Colloidal Am is unlikely, therefore, to be mobile.

Finally, it must be pointed out that this study has been purely comparative. It was designed to study the effect of sediment mineralogy and composition on the sorption of neptunium and americium from sea water. Under different experimental conditions different absolute values might well be obtained, for example, it has been shown (see Chapter 5) that the solid/solution ratio used in batch distribution experiments can have a marked effect on observed distribution ratios.

Table 3.9. Activity of Np in fractions obtained during the oxidation state analysis after the adsorption experiments.

	5g untreated sample c/1000 sec.	TTA Extraction		LaF Precipitation		
		Aqueous layer Np V + Np VI c/1000 sec.	Organic layer Np IV c/1000 sec.	Precipitate Np IV + Np V c/1000 sec.	Supernate Np VI c/1000 sec.	
IOS-3	1362 ± 75	1367 ± 75	-10 ± 66	1360 ± 36	-29 ± 66	
M77-20	284 ± 67	375 ± 68	11 ± 47	206 ± 59	128 ± 92	
IOS-6	1329 ± 74	1208 ± 74	-	1193 ± 36	-53 ± 66	
IOS-4	2044 ± 79	1876 ± 77	32 ± 66	1918 ± 38	-54 ± 66	
IOS-5	1005 ± 72	1033 ± 72	-8 ± 65	1193 ± 36	-53 ± 66	
IOS-2	2906 ± 84	2560 ± 82	84 ± 66	2771 ± 41	-9 ± 66	
S 702	674 ± 70	758 ± 70	31 ± 47	570 ± 61	138 ± 92	
SH 1578	542 ± 69	498 ± 69	42 ± 47	448 ± 59	24 ± 91	
IOS-1	1838 ± 78	1905 ± 63	46 ± 47	1646 ± 68	-29 ± 91	
MV 65 I	640 ± 69	640 ± 69	74 ± 47	679 ± 61	-17 ± 91	
6269 No.2	633 ± 69	650 ± 300	64 ± 47	565 ± 61	-29 ± 91	

Note Blanks subtracted and figures adjusted to be equivalent to a 5g sample.

Table 3.10. Neptunium Distribution Coefficients

ADSORPTION $\frac{R_d}{10^3}$											DESORPTION $\frac{R_d}{10^3}$	
	7 day	14 day	21 day	28 day	40 day	45 day	47 day	63 day	87 day	105 day	14 day	32 day
IOS-3	4.3 ± 0.1	4.5 ± 0.1	4.7 ± 0.2	5.1 ± 0.2		5.4 ± 0.2			3.1 ± 0.2		3.9 ± 0.2	4.0 ± 0.2
M77-20	5.6 ± 0.4	5.6 ± 0.4	5.4 ± 0.3	6.2 ± 0.4	8.5 ± 0.8		6.1 ± 0.4	8.6 ± 0.9		8.4 ± 2.0	4.5 ± 0.3	5.3 ± 0.4
IOS-6	3.3 ± 0.1	3.7 ± 0.1	1.8 ± 0.1	2.0 ± 0.1		2.0 ± 0.1			2.6 ± 0.2		2.8 ± 0.1	2.1 ± 0.2
IOS-4	3.9 ± 0.1	4.1 ± 0.1	4.5 ± 0.2	4.3 ± 0.1		2.2 ± 0.1			2.0 ± 0.1		2.5 ± 0.1	2.4 ± 0.1
IOS-5	4.4 ± 0.1	5.1 ± 0.2	4.9 ± 0.1	4.2 ± 0.1		3.5 ± 0.1			4.5 ± 0.4		4.1 ± 0.2	2.8 ± 0.1
IOS-2	1.5 ± 0.1	1.6 ± 0.1	2.0 ± 0.1	2.3 ± 0.1		1.9 ± 0.1			1.2 ± 0.1		1.4 ± 0.1	1.5 ± 0.1
S702	2.5 ± 0.1	2.4 ± 0.1	3.3 ± 0.1	3.0 ± 0.1	3.6 ± 0.2		3.1 ± 0.1	3.2 ± 0.2		3.2 ± 0.3	2.8 ± 0.1	2.1 ± 0.1
SH1578	1.1 ± 0.1	2.9 ± 0.1	4.1 ± 0.1	5.9 ± 0.2	8.9 ± 0.5		11.9 ± 0.9	12.4 ± 1.0		7.1 ± 0.9	4.4 ± 0.2	4.8 ± 0.2
IOS-1	0.45 ± 0.03	0.95 ± 0.04	1.3 ± 0.1	1.5 ± 0.1	1.3 ± 0.1		1.2 ± 0.1	1.6 ± 0.1		1.4 ± 0.1	1.4 ± 0.1	1.4 ± 0.1
MV 65 I	0.73 ± 0.03	1.2 ± 0.1	1.7 ± 0.1	2.3 ± 0.1	3.5 ± 0.1		4.0 ± 0.2	4.9 ± 0.3		4.1 ± 0.3	2.6 ± 0.1	2.6 ± 0.1
6269 No.2	3.3 ± 0.1	6.8 ± 0.3	11.1 ± 0.5	13.1 ± 0.7	19.9 ± 1.7		14.8 ± 0.9	20.7 ± 2.3		9.5 ± 0.8	8.9 ± 0.6	9.0 ± 0.6

Table 5.11.

Neptunium Distribution Coefficients

100

		Adsorption R_d , ml/g							Desorption R_d , ml/g				
		1 day	7 day	14 day	28 day	35 day	42 day	56 day	2 day	7 day	16 day	29 day	56 day
10399 # 7K	Run 1	1607±30	2296±53	3128±95	3511±114	2986±881	3050±89	2432±60	6219±186	5805±325	6137 ±216	4247 ±216	3340 ±118
	Run 2	1392±24	1851±37	2738±73	4151±154	3022±89	4862±210	4102±151	4102±151	5428±163	4396 ±178	3007 ±102	3075 ±112
	Weighted Mean	1476±104	1997±209	2883±183	3737±306	2964±240	3326±651	2660±573	5772±392	5743±217	6840 ±160	3237 ±486	3200 ±132
1040 # 8K	Run 1	103 ± 3	190 ± 3	341 ± 5	565 ± 8	616 ± 9	598 ± 8	356 ± 5	1313±105	843± 19	845 ±19	586 ±11	555 ±10
	Run 2	113 ± 3	241 ± 4	347 ± 5	514 ± 8	505 ± 7	492 ± 7	273 ± 3	1154± 98	827± 20	695 ±15	551 ±11	540 ± 9
	Weighted Mean	108 ± 5	208 ±25	343 ± 5	536 ±25	547 ±54	538 ±53	293 ±36	1228± 80	835± 14	753 ±73	569 ±18	547 ± 8

Table 3.12. Concentration of Neptunium in Solution.

	ADSORPTION $\frac{\text{mols}}{\ell}$ 10^{-13}										DESORPTION $\frac{\text{mols}}{\ell}$ 10^{-13}	
	7 day	14 day	21 day	28 day	40 day	45 day	47 day	63 day	87 day	105 day	14 day	32 day
IOS-3	10.5 ± 0.3	10.1 ± 0.3	9.4 ± 0.3	8.9 ± 0.3		8.1 ± 0.3			12.8 ± 0.7		9.6 ± 0.4	$9.2 \pm 0.$
M77-20	4.0 ± 0.2	3.9 ± 0.3	4.6 ± 0.3	4.0 ± 0.3	2.8 ± 0.2		3.9 ± 0.3	2.6 ± 0.3		2.7 ± 0.7	4.7 ± 0.4	$3.9 \pm 0.$
IOS-6	11.4 ± 0.3	10.1 ± 0.3	18.6 ± 0.3	18.2 ± 0.4		16.8 ± 0.3			12.5 ± 0.7		11.1 ± 0.4	$14.6 \pm 0.$
IOS-4	11.6 ± 0.3	11.0 ± 0.3	9.8 ± 0.3	10.5 ± 0.4		18.0 ± 0.3			19.2 ± 0.8		13.9 ± 0.4	$14.8 \pm 0.$
IOS-5	10.5 ± 0.3	9.0 ± 0.3	9.3 ± 0.3	10.9 ± 0.4		12.4 ± 0.3			9.5 ± 0.8		9.5 ± 0.4	$14.2 \pm 0.$
IOS-2	25.4 ± 0.3	23.4 ± 0.3	19.7 ± 0.3	17.6 ± 0.4		20.3 ± 0.3			27.3 ± 0.8		21.6 ± 0.5	$20.3 \pm 0.$
S702	8.4 ± 0.2	7.2 ± 0.3	6.9 ± 0.3	7.4 ± 0.33	6.2 ± 0.2	6.8 ± 0.3	7.0 ± 0.3	6.8 ± 0.3		6.4 ± 0.7	6.9 ± 0.4	$9.0 \pm 0.$
SH1578	24.6 ± 0.3	11.7 ± 0.3	9.6 ± 0.3	6.7 ± 0.3	7.2 ± 0.2			3.2 ± 0.3		5.1 ± 0.7	7.7 ± 0.4	$6.9 \pm 0.$
IOS-1	38.4 ± 0.4	24.0 ± 0.5	21.4 ± 0.3	18.6 ± 0.3	20.2 ± 0.2		20.8 ± 0.3	17.0 ± 0.4		17.2 ± 0.7	15.9 ± 0.7	$16.8 \pm 0.$
MV 65 I	26.0 ± 0.4	17.2 ± 0.4	14.9 ± 0.3	10.9 ± 0.3	7.2 ± 0.2		6.5 ± 0.3	5.3 ± 0.3		6.0 ± 0.7	8.7 ± 0.4	$6.5 \pm 0.$
6269 No. 2	15.2 ± 0.3	8.2 ± 0.3	5.7 ± 0.3	4.8 ± 0.3	3.1 ± 0.2		4.2 ± 0.3	2.9 ± 0.4		5.9 ± 0.7	5.7 ± 0.4	$5.6 \pm 0.$

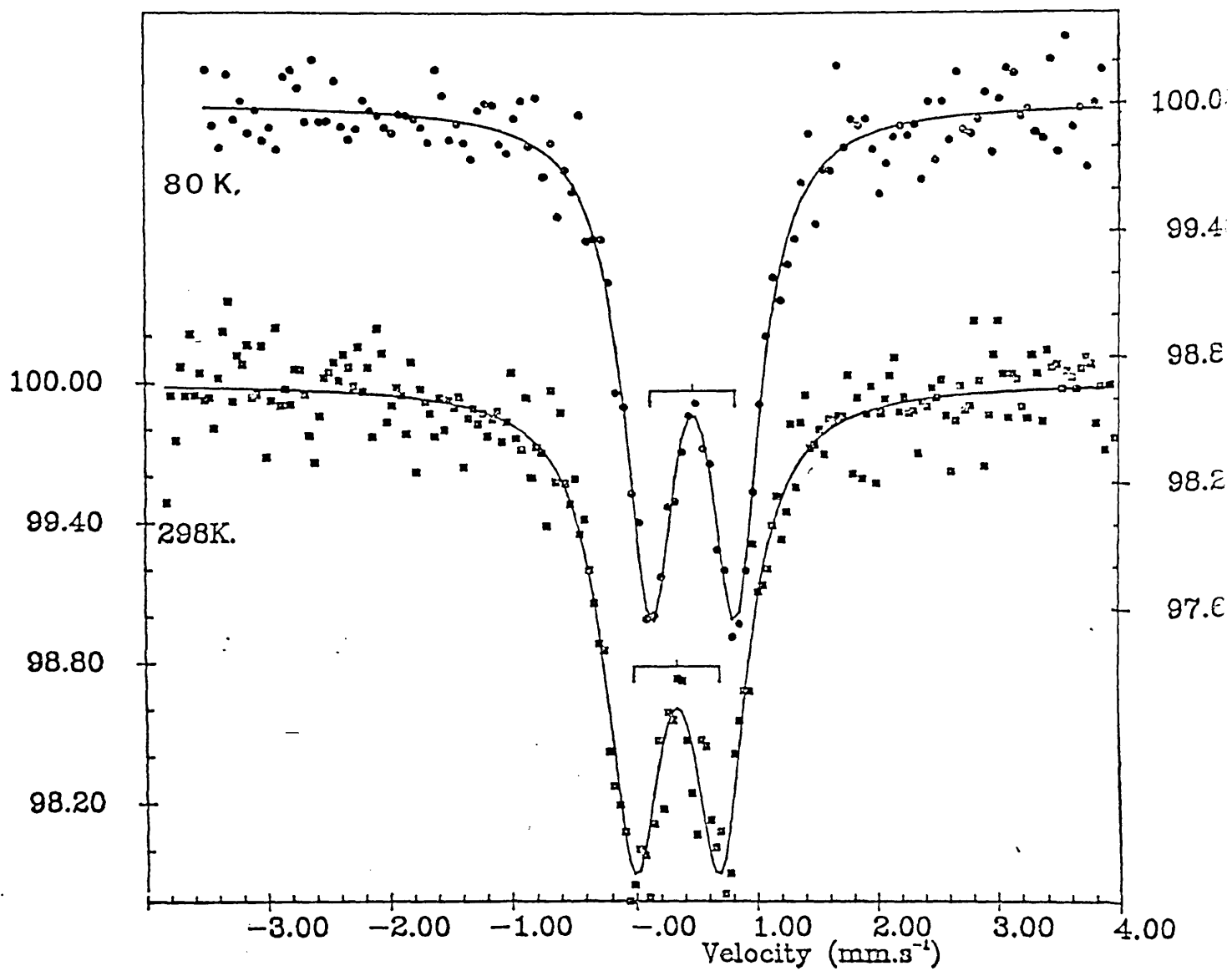


FIG 3.6 Moessbauer Spectra of manganese nodule MV65I (50mg crushed).

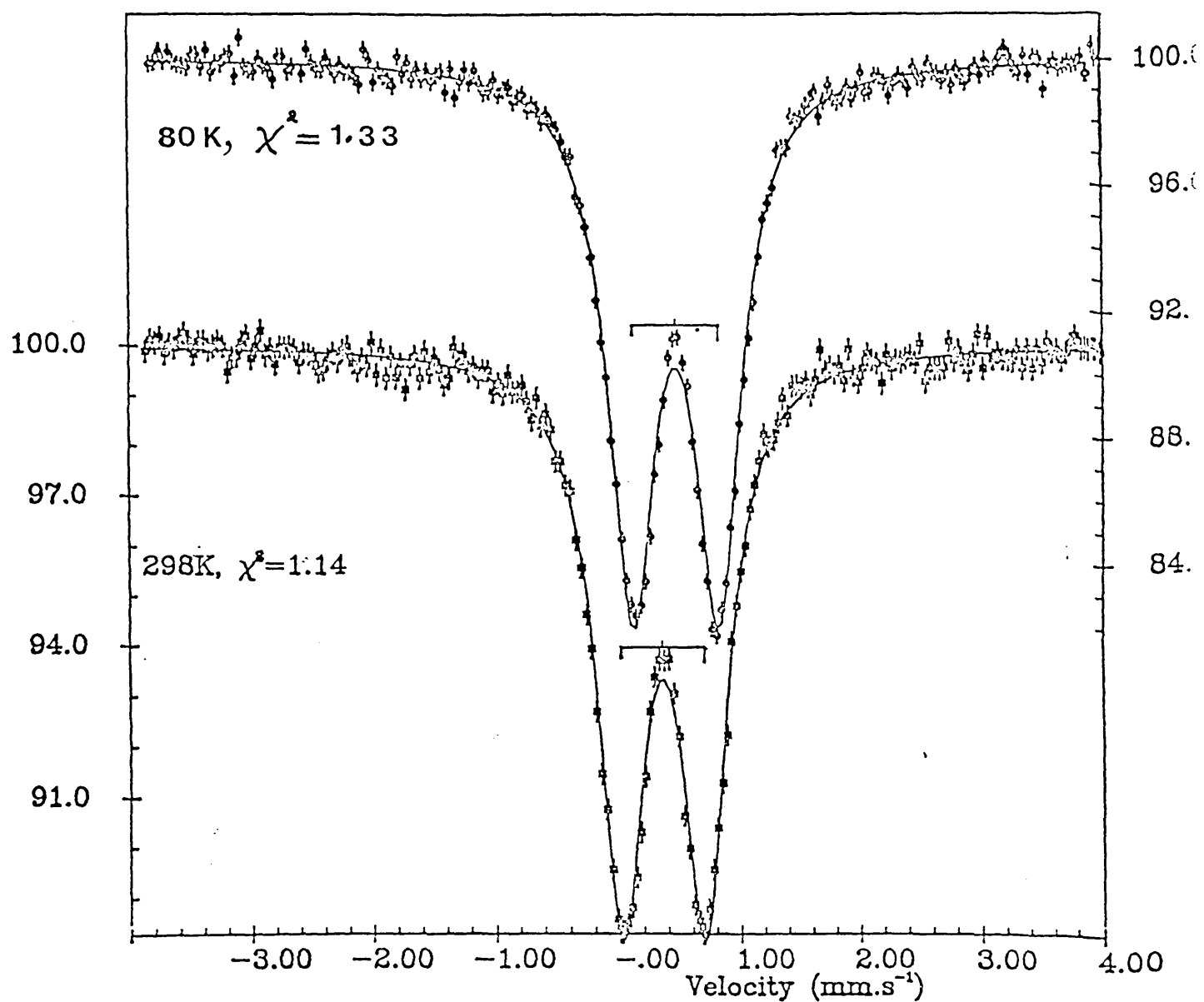


FIG 3.7 Moessbauer spectra of manganese nodule sample 6269 (50mg crushed)

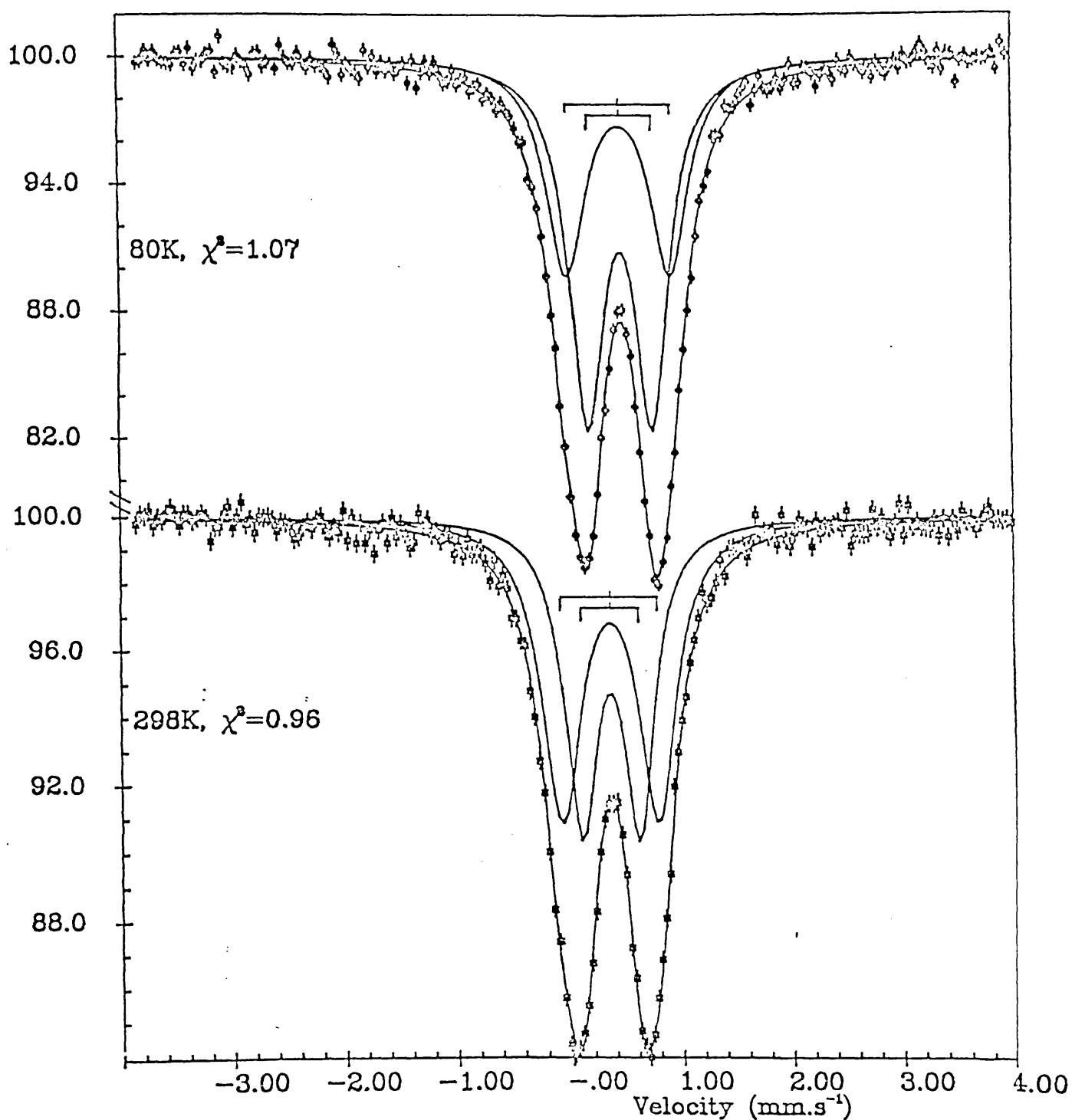


FIG 3.8 Moessbauer Spectra of manganese nodule 6269 (50mg crushed), two site

FIGURE 3.9 Np DISTRIBUTION COEFFICIENTS, : LOW-CARBONATE SEDIMENTS

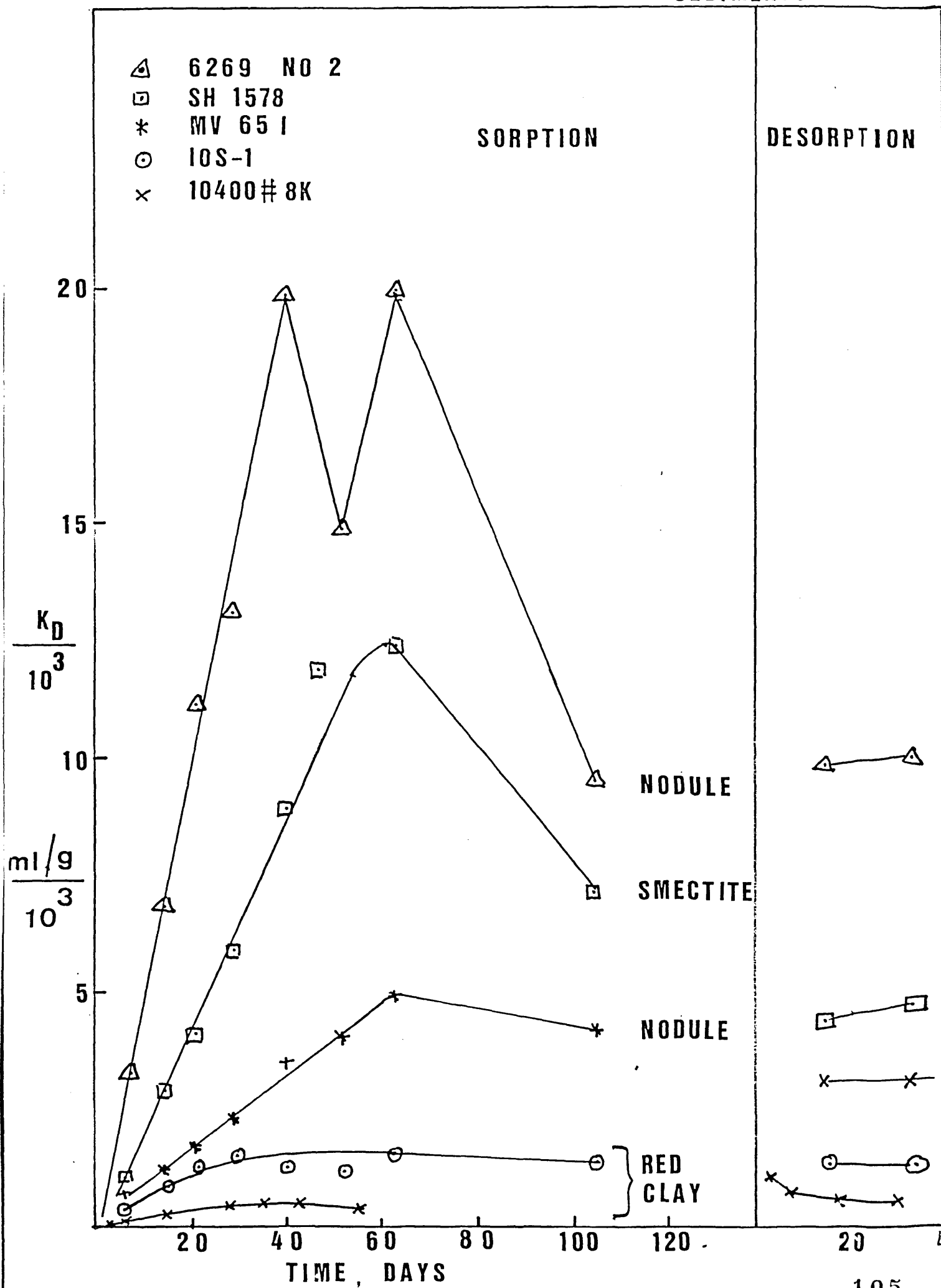


FIGURE 3.10 Np DISTRIBUTION COEFFICIENTS: HIGH-CARBONATE SEDIMENTS

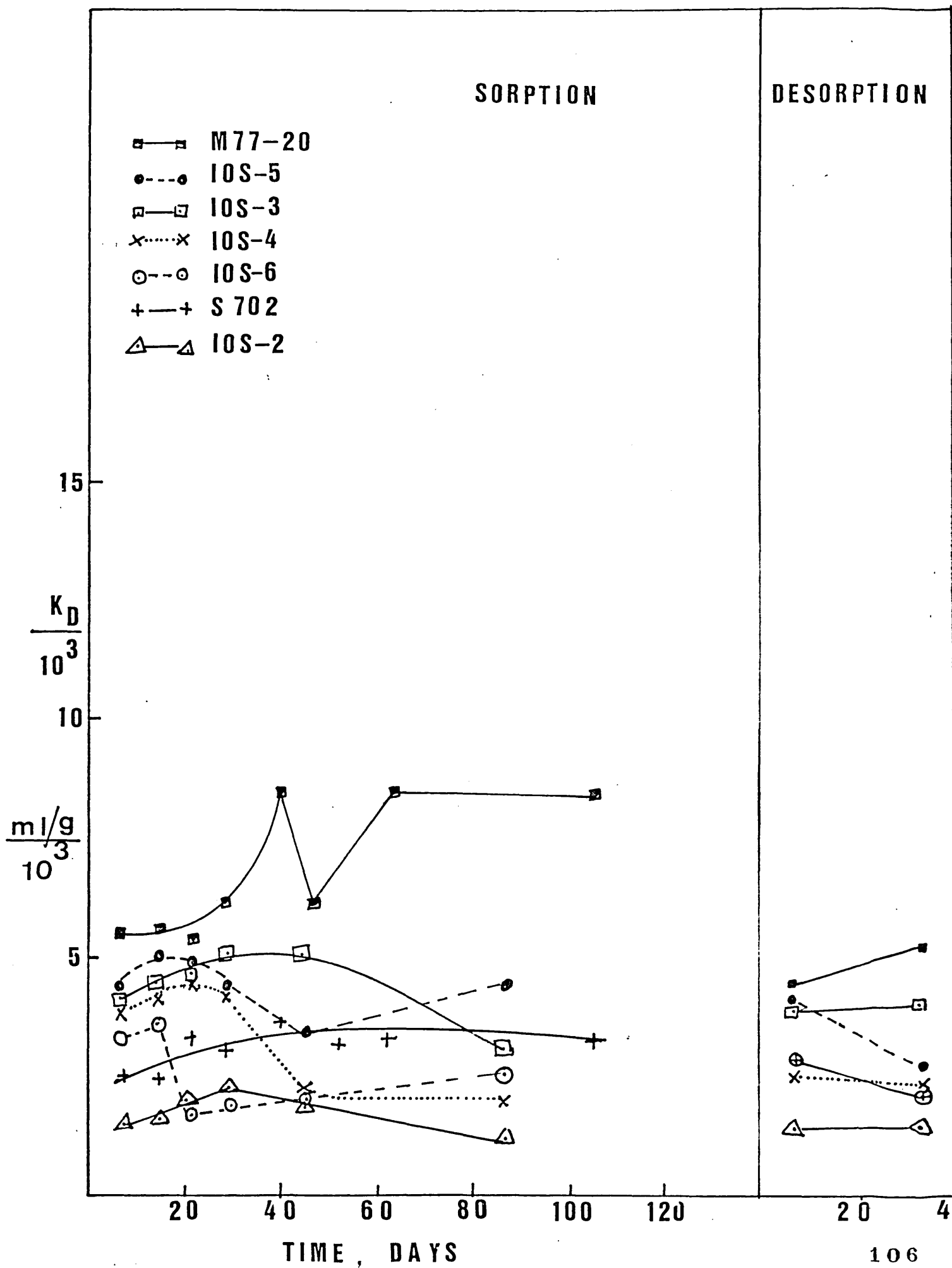


FIG 3.11 NEPTUNIUM CONCENTRATION- LOW-CARBONATE SAMPLES

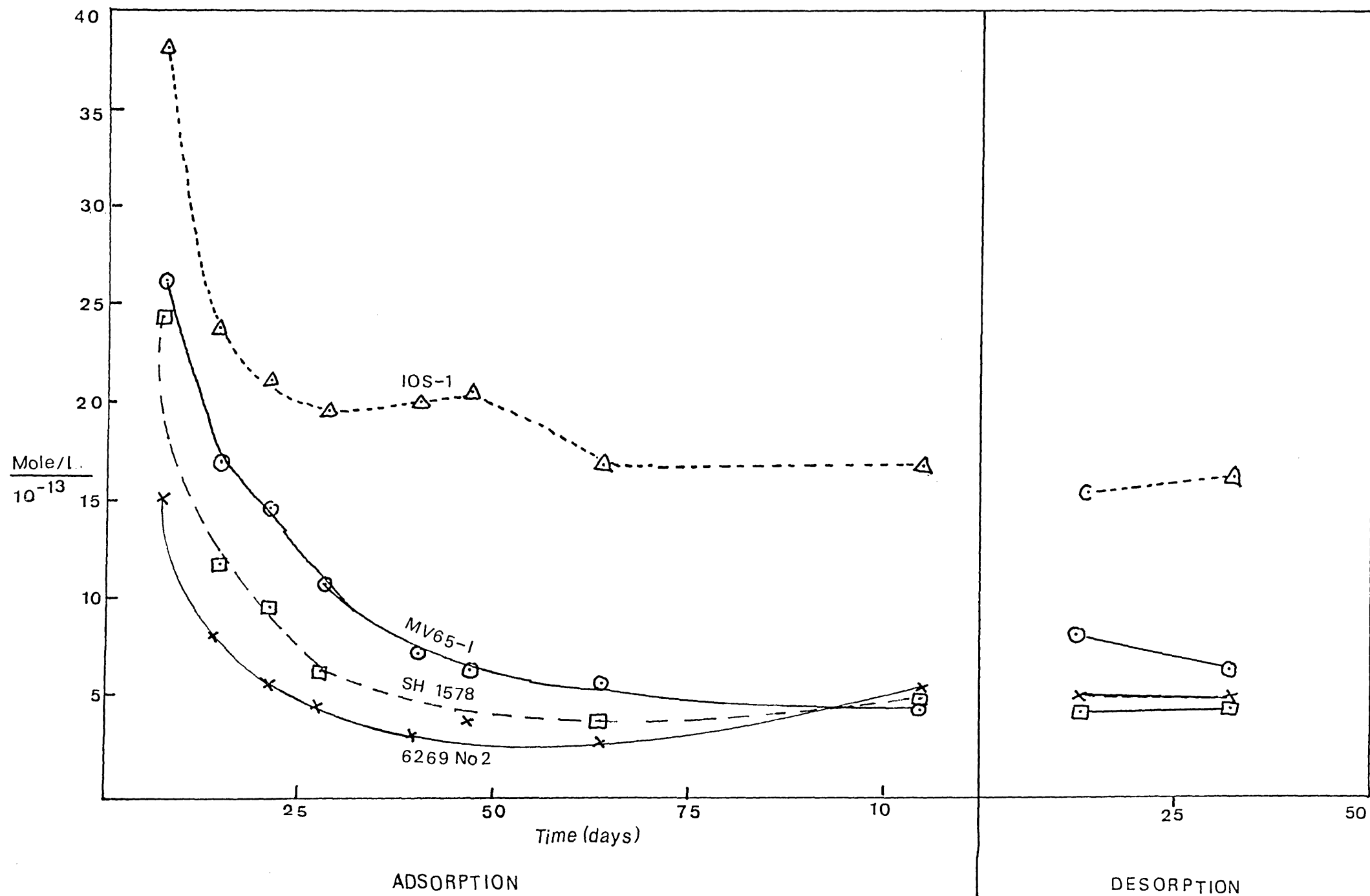


FIG 3.12 NEPTUNIUM CONCENTRATION IN SOLUTION : HIGH-CARBONATE SAMPLES

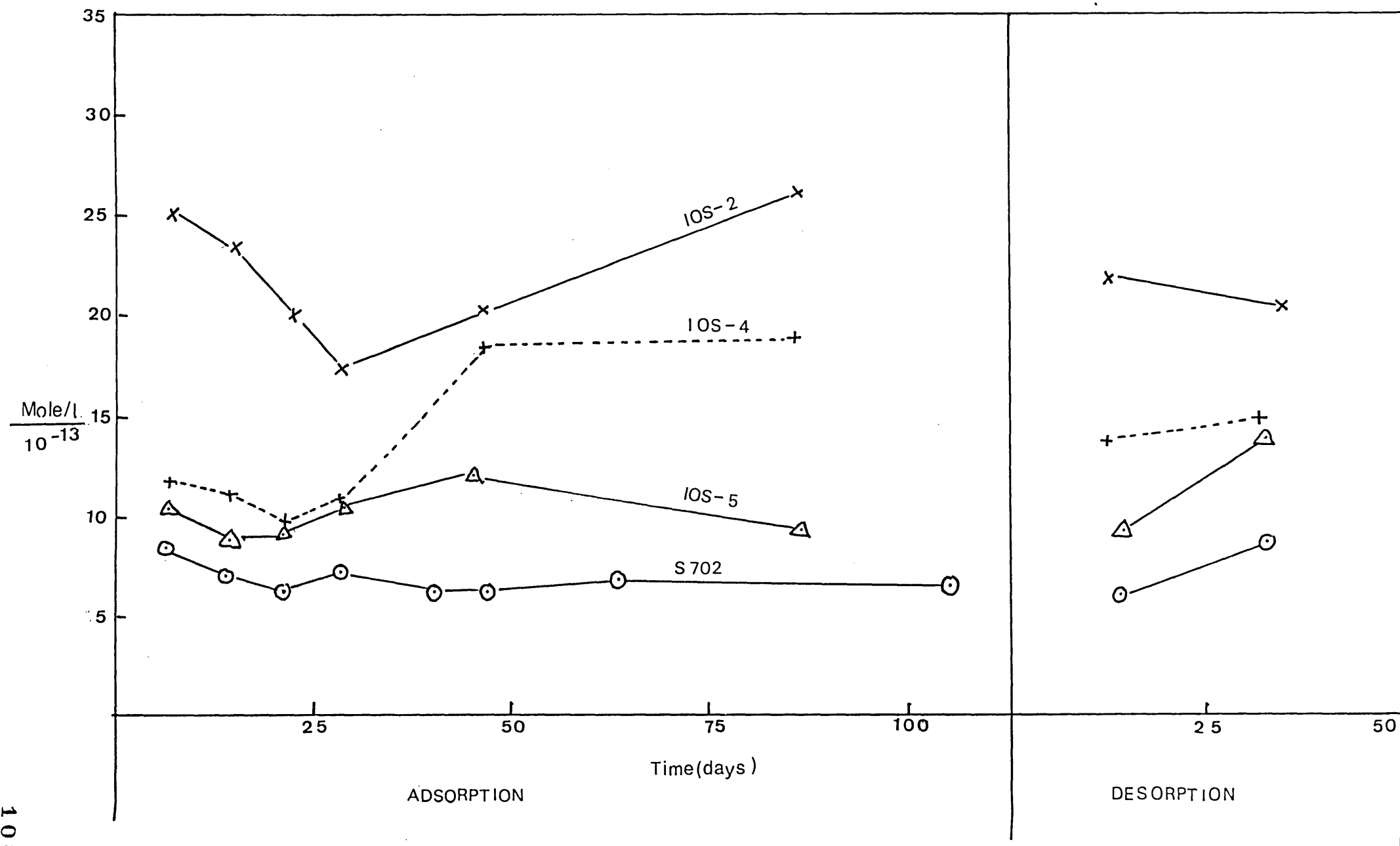
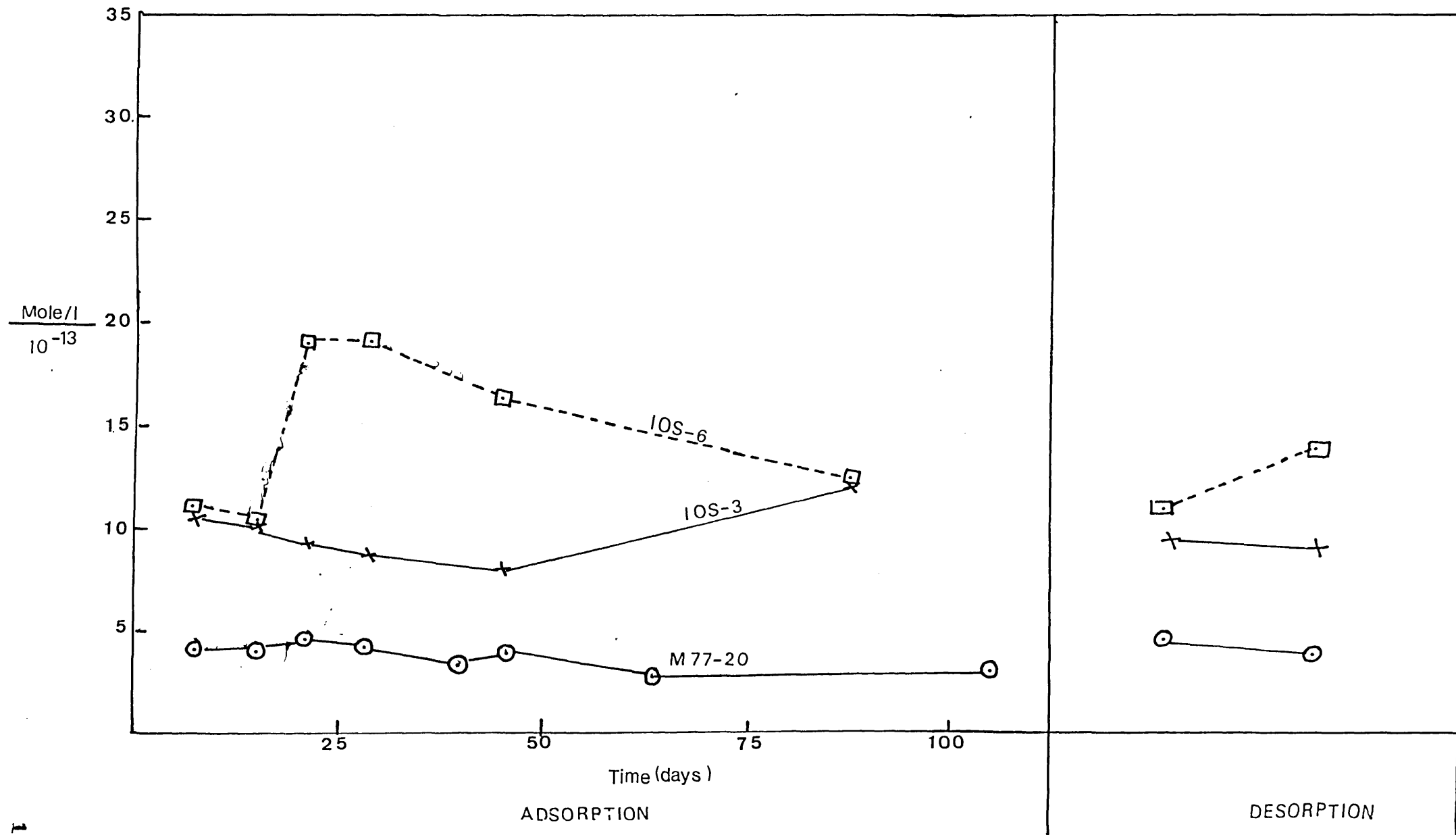


FIG 3.13 NEPTUNIUM CONCENTRATION IN SOLUTION : HIGH CARBONATE SAMPLES



CHAPTER 4

THE SORPTION OF PLUTONIUM BY MARINE SEDIMENTS

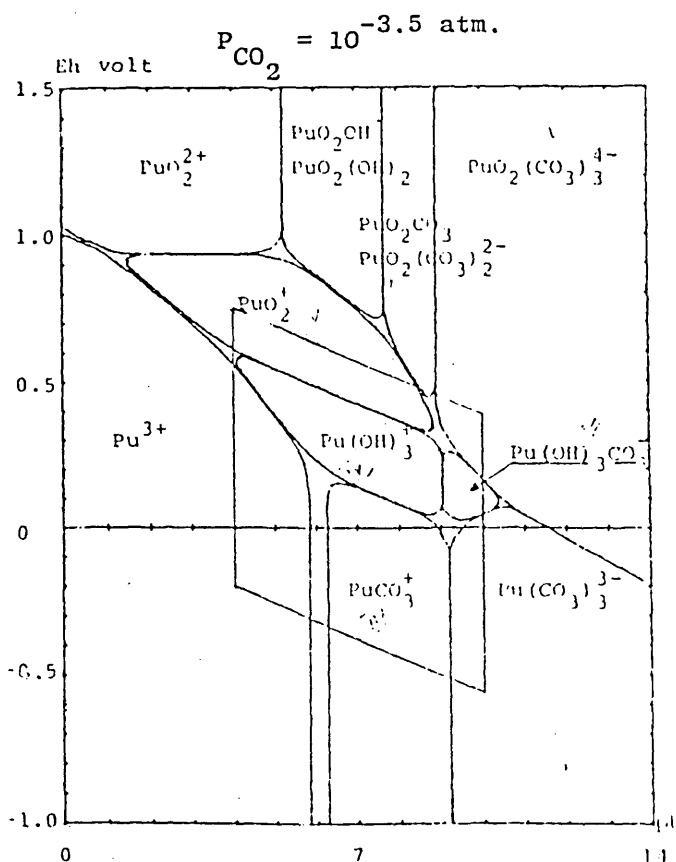
4.1. Introduction

During the past forty years artificially produced plutonium isotopes have entered the environment as the result of fall-out from nuclear explosions, the discharge of effluent from reactors and reprocessing plants and the occasional accident. For this reason it is the most extensively studied of all the actinides and a substantial amount of data have been accumulated. Plutonium can exist in solution in several oxidation states the most common of which are the oxidised Pu-V and Pu-VI forms and the reduced Pu-III and Pu-IV forms. It appears that the behaviour of Pu in the environment will be dependent upon which oxidation states are present. Furthermore, it seems that Pu-III and Pu-IV are likely to behave similarly to Am-III and Th-IV which are strongly sorbed by sediments whereas Pu-V and Pu-VI would be expected to have lower distribution coefficients and to behave like Np-V and U-VI.

Distribution ratios reported for plutonium in the sea water/sediment system are generally of the order of 10^4 whatever the oxidation state at the beginning of the experiment (Gromov and Spitzyn (1974), Schell et al., (1979), Sanchez et al., (1981), Duursma and Parsi (1976)). In addition to laboratory determinations many measurements have been made for the concentration of plutonium in surface sediments together with the overlying water. From the data, values of R_d can be calculated. The values obtained in this way are remarkably constant with a maximum range of 10^4 to 5×10^5 ml/g and appear to be independent of sediment type and biological activity (Edgington, 1980).

In recent years a great deal of effort has gone into establishing the likely oxidation state distribution of plutonium in natural waters. Rai et al (1980) using published thermodynamic data have constructed E_h -pH diagrams for the species of plutonium in equilibrium with PuO_2 in water. This diagram has been widely quoted, e.g. Edgington (1980) and represents the interaction of PuO_2 with water and OH^- ions but takes no account of the formation of other complexes such as HCO_3^- or CO_3^{--} . It predicts that in well oxygenated sea water (pH 8) the major fraction of Pu should exist as Pu-V and the remainder as Pu-III. Skytte Jensen (1982), in a more detailed analysis and taking carbonates into account

Fig. 4.1. (a) 0
E_h-pH diagrams
(a) Rai, D. and Strickert, R.G. (1980)
(b) Skytte Jensen (1982)



(b)

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that the ratio of oxidised Pu(V + VI) to reduced Pu (III + IV) was generally greater than three. Wahlgren et al. using the same technique found that the Pu(V + VI)/Pu(III + IV) ratio was four in the waters of Lake Michigan. In the Pacific Ocean, however, higher ratios were found by Nelson, Metta and Larsen (1980) and by Nelson, Carey and Bowen (1984). Here the ratio was around one through most of the water column and rose to about 9 in the deep layer near the sediment. In the interstitial waters of Irish Sea sediments Nelson and Lovett (1980) found that the ratio was very low, generally between 0.1 and 0.3. Finally, although leaching tests cannot be conclusive since the oxidation state may change during the leaching process, the experiments of Nelson and Lovett indicate that the Pu adsorbed on sediments and particulate matter is all in the reduced forms. It appears, therefore, from all this work that Pu in well oxygenated sea water is mainly in the oxidised Pu-V form but that it is reduced during sorption on to the sediments. The Pu concentration and the oxidation state distribution in the pore waters will result from a complex interaction between the redox equilibrium and sorption/desorption reactions for the various species.

Clearly it is important when studying the sorption of plutonium to know which oxidation states we are dealing with and, in the set of experiments described here, the oxidation state distribution was determined at each state. Because it was wished to simulate natural conditions as closely as possible and because interchange between the different oxidation states can occur there seemed little point in attempting to start in one specific oxidation state. Instead, sea water spiked with ^{238}Pu was left to equilibrate for several weeks after which the oxidation state distribution was determined. This sea water was then contacted with sediment and, at intervals, the liquid phase was analysed for each oxidation state. In this way it was possible to compare the rates at which each form was removed from solution. The three sediments studied were the carbonate-rich (10399 # 7K), the red clay, (10400 # 8K) and the smectite-rich (SH1578). Both sorption and desorption experiments were carried out.

4.2. Experimental

The experimental work was divided into two parts, firstly the development of an analytical method suitable for the determination of the oxidation-state distribution of plutonium in solution and secondly

sorption-desorption experiments.

4.2.1. Analytical

The method of Lovett and Nelson (1981) distinguishes between the reduced Pu(III + IV) forms and the oxidised Pu(V + VI) forms. It involves the addition of an "holding oxidant" $K_2Cr_2O_7$ to the sample. This oxidises Pu-III to Pu-IV and Pu-V to Pu-VI and prevents the reduction of Pu-V and Pu-VI to either of the reduced states. The reduced Pu is then co-precipitated with neodymium fluoride while the oxidised Pu remains in the supernate. The Pu-VI in the supernate is then reduced with ferrous iron and precipitated in the same way with neodymium fluoride. An adaptation of this method was tested and found to work well. More difficulty was found when attempting to use the method of Foti and Freiling (1964) which uses a combination of lanthanum fluoride precipitations and solvent extraction with 2-theonyltrifluoroacetone (TTA) to separate all four oxidation states. Finally a combination of the two sets of methods was used and a total of six determinations was made on each solution. These were:

- (1) III + IV + V + VI : Total Pu
- (2) III + IV + V : LaF_3 precipitation in the presence of uranyl hold-back carrier.
- (3) VI : Reduction of Pu in supernate from (2) with ferrous iron followed by another LaF_3 precipitation.
- (4) III + IV : LaF_3 precipitation in presence of $K_2Cr_2O_7$ holding oxidant.
- (5) V + VI : Reduction of Pu in supernate from (4) with ferrous iron followed by LaF_3 precipitation.
- (6) IV : TTA extraction from HCl solution at pH 0.3.

After separation from the other oxidation states the Pu was always determined by the same method as that used for total Pu. This involved adjustment of all the Pu to Pu-IV followed by extraction into 2-thenoyltrifluoroacetone (TTA) dissolved in benzene (Moore and Hudgens, 1957). Evaporated sources were prepared from the organic layer and counted on an alpha spectrometer. A ^{239}Pu -IV spike was used to monitor recoveries. Complete details of the analytical method used are given in the appendix to this Chapter.

The method was tested on a number of solutions containing pure Pu-III, Pu-IV and Pu-VI prepared by different methods. It was found that the separation between the oxidised Pu(V + VI) and reduced

Pu(III + IV) was reproducible and specific. Extraction of Pu-IV into TTA at pH 0.3 was also quantitative and very little Pu-III and no Pu-VI (whether prepared by electrolysis or dichromate reduction) was extracted under the conditions used. The results obtained when co-precipitating Pu(III + IV + V) with LaF_3 in the presence of uranium hold-back carrier were somewhat confusing. In the presence of even minute traces of potassium dichromate (as little as 10^{-7}M) < 10% of the Pu-VI was precipitated. However, in the absence of oxidising agents Pu-VI prepared by electrolysis or by fuming with perchloric acid was almost quantitatively precipitated. It would appear, therefore, that either the Pu-VI prepared by the latter two methods was actually Pu-V or was rapidly converted to Pu-V on addition to sea water prior to analysis or that in the absence of an oxidising agent Pu-VI is precipitated by the LaF_3 method used. Until this matter is resolved the Pu-V results should be treated with caution.

4.2.2. Sorption Experiments

Distribution coefficients were determined using the standard procedures developed for Am and Np and described in Part 2. Briefly, 0.1g of sediment was shaken gently with 35g of sea water which had been spiked with ^{238}Pu and allowed to equilibrate for several weeks. Immediately before use this initial sea water was filtered through 0.22 μ filters and analysed. The concentration of total Pu was $3 \times 10^{-11}\text{M}$. After the required time interval the sample was centrifuged in a cooled centrifuge at 7000 rpm for 30 minutes. The entire supernate was then filtered through double 0.22 μ filters and analysed as quickly as possible.

4.3. Results and Discussion

Table 4.1. and Figure 4.2. show how the distribution coefficients and the concentration of total Pu changed with time during sorption. Table 4.2. and Figure 4.3. show how the concentrations of the various oxidation states changed with time. The first column of Table 4.2. repeats the experimental values for the total Pu and the last column gives the $\text{Pu(V + VI)}/\text{Pu(III + IV)}$ ratio. The intermediate columns give the results of the individual oxidation state determinations, the sum of the pairs Pu(III + IV) and Pu(V + VI) and Pu(III + IV + V) and Pu-VI. It can be seen that, within experimental error, these sums are generally the same as the independently determined total Pu.

Table 4.1. Plutonium Distribution Ratios During Sorption

Sample	Sorption time	Total Pu in soln Bq/l	% Adsorption	R_d $\frac{\text{ml/g}}{10^4}$
Initial seawater $3.1 \times 10^{-11} \text{ M}$		4356 ± 1144		
SH 1578	1 h	1026 ± 171	76.4 ± 5.7	0.16 ± 0.03
	22 h	88 ± 8	98.0 ± 4.6	2.34 ± 0.22
	30 d	24 ± 2	99.4 ± 4.7	8.97 ± 0.84
	102 d	24 ± 2	99.4 ± 4.7	9.40 ± 0.67
10399 # 7K	1 h	2416 ± 98	44.5 ± 4.2	0.022 ± 0.002
	22 h	855 ± 41	80.4 ± 4.3	0.102 ± 0.007
	30 d	34 ± 3	99.2 ± 4.7	3.46 ± 0.30
	102 d	20 ± 1	99.5 ± 4.7	5.86 ± 0.40
10400 # 8K	1 h	2982 ± 895	31.5 ± 2.7	0.012 ± 0.001
	22 h	1724 ± 35	60.4 ± 3.9	0.058 ± 0.004
	30 d	122 ± 15	97.2 ± 4.6	1.44 ± 0.19
	102 d	26 ± 2	99.2 ± 4.7	4.71 ± 0.32

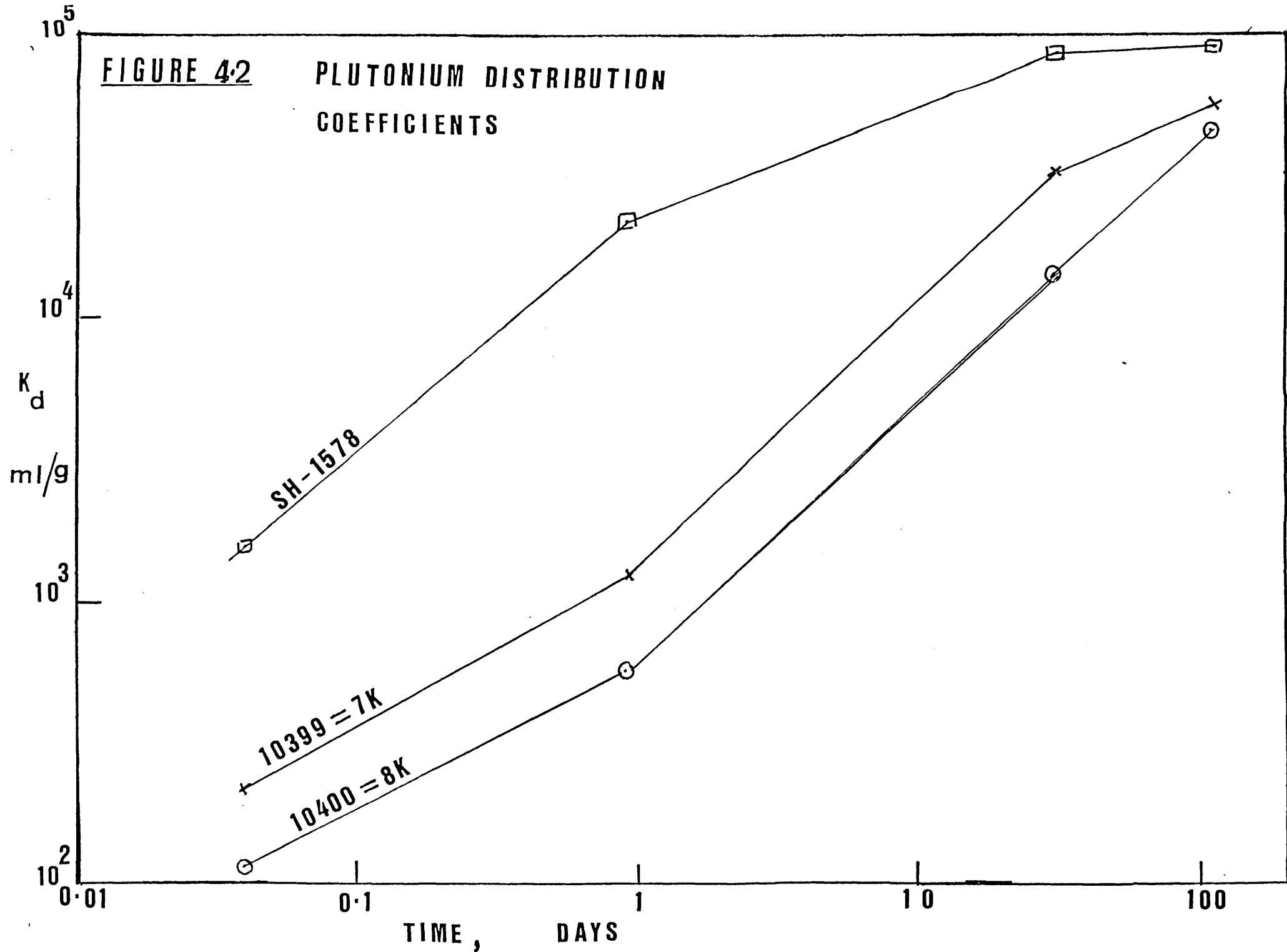
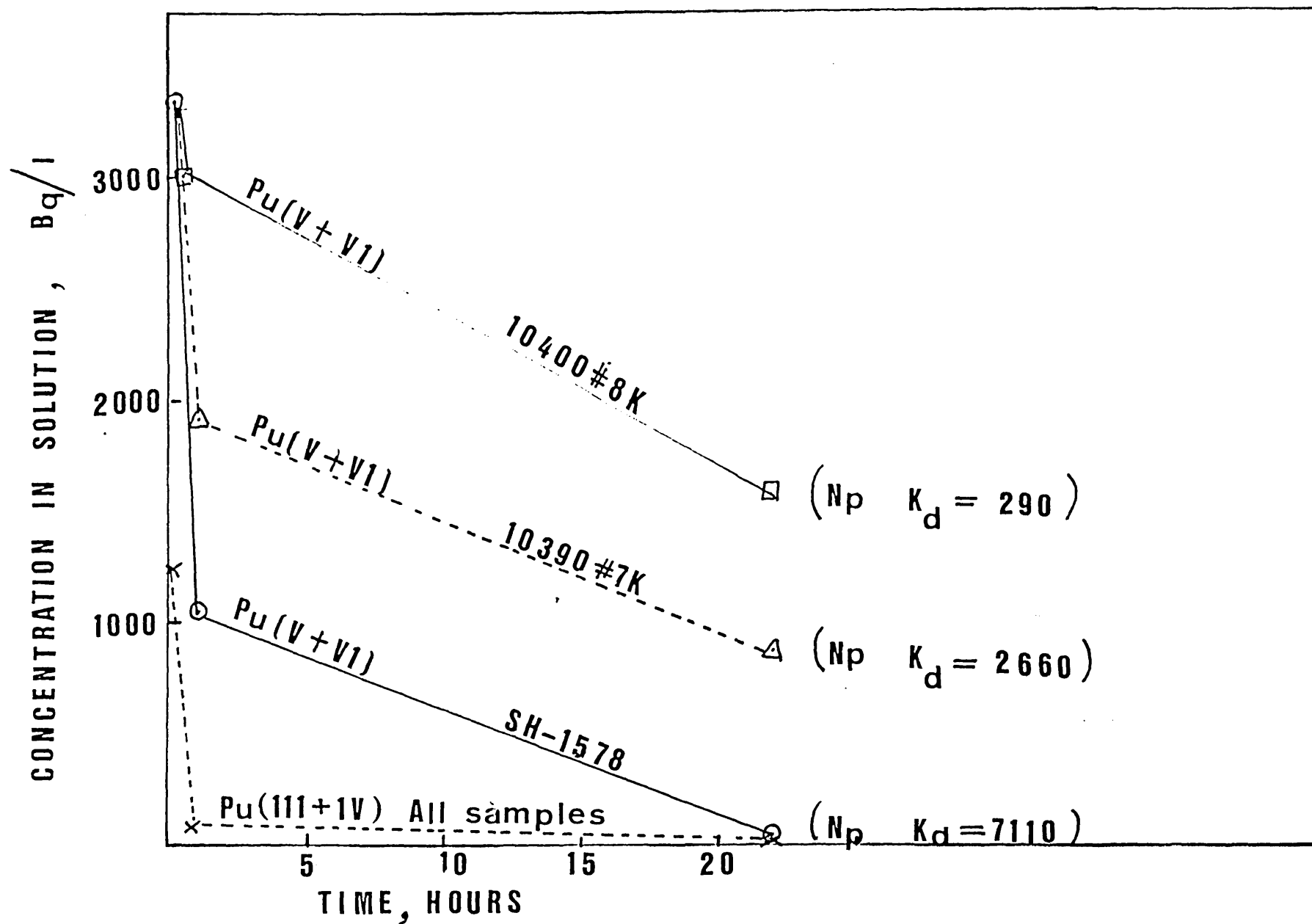


Table 4.2. Pu Oxidation State Distribution During Sorption

Sample	Time	Pu-238 Concentration. (Bq/l) during sorption								Ratio	
		Total	(III + IV)	V + VI	(III + IV) + (V + VI)	(III+IV+V)	VI	(III+IV+V) + VI	IV { III (III+IV)-IV }	V + VI III + IV	
Initial sea-water 3.1x10 ⁻¹¹ M		4356 ± 1421	1242 ± 120	3366 ± 144	4609 ± 187	4656± 186	-	-	1200 ± 138	42 ± 183	2.7 ± 0.3
SH 1578	1 h	1026 ± 171	103 ± 3	1053 ± 316	1156 ± 49	1022 ±129	-	-	90 ± 10	13 ± 11	10.2 ± 3.1
	22 h	88 ± 8	36 ± 2	44 ± 3	80 ± 4	89 ± 2	-	-	46 ± 2	-10 ± 3	1.2 ± 0.1
	30 d	24 ± 2	19 ± 2	2.4 ± 0.7	21 ± 2	21 ± .1	1.5 ± 0.6	22 ± 1	20 ± 1	- 1 ± 2	0.1 ± 0.04
	102 d	24 ± 2	17 ± 1	4.8 ± 1.4	22 ± 2	24 ± 2	0.3 ± 0.3	24 ± 2	19 ± 1	-2 ± 2	0.3 ± 0.1
10399 # 7K	1 h	2416 ± 98	107 ± 11	1983 ± 88	2090 ± 627	2364±709	-	-	80 ± 5	28 ± 12	19 ± 2
	22 h	855 ± 41	49 ± 2	897 ± 51	945 ± 51	766± 42	-	-	43 ± 2	5 ± 3	18 ± 1
	30 d	34 ± 3	19 ± 2	22 ± 2	41 ± 3	44± 25	1.4 ± 0.5	45 ± 2	18 ± 1	1 ± 2	1 ±0.2
	102 d	20 ± 1	13 ± 1	6 ± 2	19 ± 1	20± 2	0.9 ± 0.3	21 ± 2	14 ± 2	-1 ± 2	0.5 ±0.2
10400 # 8K	1 h	2982 ± 895	128 ± 6	3011 ±109	3139 ± 109	2909±146	-	-	64 ± 14	64 ± 15	24± 1
	22 h	1724 ± 35	68 ± 4	1589 ±189	1657 ± 189	1345± 61	-	-	65 ± 6	4 ± 7	23± 3
	30 d	122 ± 15	17 ± 1	126 ± 6	143 ± 6	98± 9	12 ± 2	110 ± 9	21 ± 2	-4 ± 2	7± 1
	102 d	26 ± 2	14 ± 1	8 ± 1	22 ± 1	24± 1	1 ± 1	25 ± 1	17 ± 1	-3 ± 2	0.6± 0.1

**FIGURE 43 CONCENTRATION OF OXIDISED & REDUCED PLUTONIUM-238
IN SOLUTION DURING THE FIRST 22 HOURS**



This, of course, tells us nothing about the accuracy of the individual determinations but simply shows that the reduction and precipitation method used for Pu(V + VI) and Pu-VI determination was quantitative. Each analytical figure is the weighted mean of two determinations and the errors are based on counting statistics only. The analytical method gives an over-determined system of six equations in four unknowns and these were solved by the method of Wilson (1958) to give the most consistent distribution. However, as this method gives an equal weight to each determination and does not include errors in the final figures it is more informative to look at the individual results and these are given in the Tables.

It can be seen from Table 4.2. that throughout the experiments virtually all the oxidised Pu appeared to be in the V form as was to be expected in view of the theoretical and experimental work discussed in Section 4.1. The reduced Pu was all in the IV form as predicted by Skytte Jensen. It is interesting to note that approximately 72% of the Pu in the initial spiked sea water was in the oxidised Pu(V + VI) forms. This agrees well with the values found by Nelson and Lovett for surface waters in the Irish Sea. Thus although the Pu concentration in this spiked sea water was roughly three orders of magnitude higher than in the Irish Sea (3.1×10^{-11} as compared with 6.7×10^{-14} M) the oxidation state distributions were similar.

From a study of all these results the following additional observations can be made.

4.3.1. Sorption

- i) The overall distribution ratio based on the total Pu in solution was between 10^4 and 10^5 for all three samples and continued to rise until the end of the experiment after 102 days. These values are in agreement with the published results discussed in Section 4.1.
- ii) The concentration of reduced Pu(III + IV) dropped much more rapidly than the concentration of Pu(V + VI). Thus for sample 10400 # 8K the concentration of Pu(III + IV) dropped by more than a factor of ten during the first hour whereas after that time the Pu(V + VI) was still more than two thirds of its original value. It is fairly meaningless to calculate distribution ratios for individual oxidation states because there may be interchange between them but it is interesting to compare R_d values after one hour and to note that for Pu(III + IV) the R_d was 3000 ml/g as compared with 50 ml/g for Pu(V + VI).

iii) With time the oxidised Pu(V + VI) was also very efficiently removed from solution. In fact after 102 days there was more reduced than oxidised Pu in solution for all the samples. It is impossible to tell whether the Pu-V is adsorbed as Pu-V or whether it is reduced during or before sorption but it is clear that it is the rate of sorption of Pu-V which governs the rate at which the overall R_d increases with time. It is probably significant that there is a strong correlation between the rate at which Pu-V is removed from solution and the Np distribution coefficient. This is illustrated in Figure 4.7 where the Np R_d values are written next to the corresponding graphs showing the rate at which the Pu-V concentration decreases during the first 22 hours. This figure also illustrates the dramatic difference in the rates of sorption of the reduced and oxidised forms of plutonium. If one assumes that removal from solution is accompanied by reduction then one can rank the sediments in order to reducing ability, the order being SH 1578 > 10399 # 7K > 10400 # 8K. So although the range in final distribution coefficients was not large the rate at which Pu was adsorbed by the different sediments varied significantly. Thus the smectite, SH 1578, adsorbed 98% of the total Pu within the first 22 hours, whereas the red clay and the carbonate-rich sediment adsorbed 60% and 80%, respectively, during the same period. This rate appears to be related to the ability of the sediments to reduce plutonium from the Pu-V to the Pu-IV form.

4.3. Desorption

Preliminary desorption experiments showed that, as with sorption, the reduced plutonium was all in the IV form and the oxidised plutonium was all in the V form. At this stage concentrations were very low and in order to make it possible to take larger aliquots only three determinations, viz. total Pu, Pu(III + IV) and Pu(V + VI) were carried out on each solution.

Three successive desorption steps (two lasting one day only followed by a long 127 day desorption) were carried out on the sediments which had been loaded in the 102 day sorption experiment and one 27 day desorption was carried out on the 30 day sorption sediments. The results are given in Table 4.3. It can be seen that,

i) The first one day R_d on the 102 day sediments and the only R_d on the 30 day sediments are lower than the R_d for the sediments which had a preliminary leach. Only about 10% of this difference could be explained by the presence of some Pu in the liquid entrained after sorption (see Table 4.3.). Harvey (1980b) when doing leaching tests on sediments from

the Irish Sea also found that the first leach contained more Pu than did the subsequent leaches. The indications are, therefore, that a small proportion of the Pu adsorbed on the sediment was present in a form which was more readily desorbed than the bulk of the Pu. Alternatively, it may have been sorbed on sites which hold the Pu less strongly. This readily desorbable Pu only amounts to about 0.03% of the total Pu on the sediment.

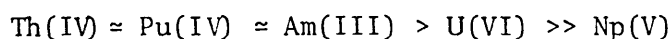
ii) The second and third desorptions after 1 day and 27 days, respectively, gave similar R_d values, indicating that desorption equilibrium was quickly established.

iii) As for americium, desorption R_d values were five to ten times higher than sorption R_d values. It is impossible to tell from the present set of experiments whether this is simply due to the fact that the reaction is not an equilibrium reaction or whether the presence of some non-sorbable species lowers the observed sorption R_d . If we assume that the sorption-desorption reaction is an equilibrium reaction and that the desorption R_d is the true R_d then the proportion of non-sorbable Pu is about 0.5% of that originally present (Table 4.3.).

iv) The percentage of reduced plutonium in solution after desorption was rather variable. Once again the smectite (SH 1578) seemed to have the most reducing properties and the proportion of reduced Pu is always higher than in the initial sea water but no firm conclusions can be drawn from these results.

4.4. Comparison with Neptunium and Americium

Edgington (1980a, 1980b) by comparing the R_d values reported in the literature has ranked the actinides in order of decreasing distribution coefficient as follows:



This ranking was based on the results from a number of different sediments studied under different conditions. As a result of the present work we now have a complete set of R_d values for Pu, Am and Np all determined under identical conditions and on the same sediments. Table 4.4. shows these values for both sorption and desorption, but if one bears in mind the fact that the sorption R_d values might be lowered by the presence of non-sorbable species it is probably best to compare desorption values. Included in Table 4.4., on the assumption that this is a measure of the ability of the sediments to reduce the actinides,

Table 4.4. Relationship between distribution coefficients and the rate at which Pu-V is removed from solution by the different sediments

Sample	"Reducing Power" as indicated by percent Pu-V remaining in solution after			DISTRIBUTION COEFFICIENT , ml/g			
				Np	Pu		Am
	1 hr	22 hr	30d	sorption and desorption	sorption 102 d	desorption	sorption 56 d desorption
SH 1578	31	1	0.1	7×10^3	9×10^4	9×10^5	4×10^5 26×10^5
10399 7K	59	27	0.7	3×10^3	6×10^4	2×10^5	2×10^5 $\sim 6 \times 10^5$
10400 8K	89	47	3.7	0.3×10^3	5×10^4	2×10^5	1×10^5 $\sim 6 \times 10^5$

TABLE 4.3. Plutonium Desorption

Sample	Sorption Time	Desorption		Pu Entrained after removal of sorption soln Bq/l	Pu-238 Concentration in solution				$\frac{(V + VI)}{(III+IV)}$	Sediment loading Bq/g	% "non-sorbable"	R_d , $\frac{ml/g}{10^4}$	
		No.	Time days		Total	III+IV	V + VI	(III+IV) + (V + VI)				Desorption	Sorption
SH 1578	102 d	1st	1	0.3±0.1	4.5±0.5					2312±77		51.4±5.4	
	102 d	2nd	1		2.3±0.4	1.6±0.2	1.0±0.2	2.6±0.3	0.6±0.1	2312±77		100.1±7.9	9.4±0.7
	102 d	3rd	27		2.6±0.1	2.1±0.2	0.9±0.1	3.0±0.2	0.4±0.06	2312±77	0.49±0.05	90.7±3.2	
	30 d	1st	125	0.7±0.2	4.4±0.1	3.4±0.1	1.2±0.1	4.6±0.2	0.4±0.03	2212±74	0.45±0.05	49.8±1.9	9.0±0.9
10399 # 7K	102 d	1st	1	0.15±0.05	8.0±0.6					1226±40		15.4±1.3	
	102 d	2nd	1		5.7±0.6	2.6±0.2	5.2±0.4	7.8±0.4	2±0.2	1226±40		21.6±2.5	5.9±0.4
	102 d	3rd	27		2.6±0.1	2.0±0.2	0.9±0.1	2.9±0.2	0.5±0.07	1226±40	0.30±0.02	24.1±0.9	
	30 d	1st	125	0.24±0.06	10.0±0.2	3.7±0.2	7.2±1.1	10.9±0.2	1.9±0.3	1212±40	0.55±0.06	12.1±0.5	3.5±0.3
10400 # 8K	102 d	1st	1	0.15±0.05	8.9±0.8					1247±41		14.1±1.3	
	102 d	2nd	1		8.1±0.4	2.8±0.2	5.6±0.4	8.4±0.4	2.0±0.2	1247±41		15.3±0.9	4.7±0.3
	102 d		27		6.1±0.2	3.3±0.3	3.8±0.3	7.1±0.4	1.4±0.2	1247±41	0.45±0.04	20.3±0.9	
	30 d		125	0.62±0.08	20.3±1.8	18.8±0.5	1.3±0.2	20.1±0.5	0.07±0.01	1811±57	2.3 ±0.4	8.9±0.9	1.4±0.2

is the percent of Pu-V remaining in solution after the different time intervals. Of course this may not be a valid assumption and these figures may simply be an indication of the relative ability of the different sediments to adsorb pentavalent actinides.

It can be seen that the distribution ratios for all three actinides decrease in the same order and that this is the order of decreasing "reducing power". It is also clear that distribution ratios decrease in the order $Am > Pu \gg Np$ although the difference between Am and Pu is not large, particularly for desorption. Desorption of Pu would be largely governed by the sorption/desorption reaction for reduced Pu-IV and Am is in the reduced Am-III form. Np, on the other hand, was shown to be entirely in the Np-V form in all the solutions. We cannot tell from these experiments whether or not it is reduced during sorption. The fact that distribution coefficients are so much lower than for Pu probably means that it is sorbed in the Np-V form although the strong correlation between the Np distribution coefficient and the rate at which Pu-V is removed from solution indicates that the same mechanism is involved in the sorption of both Pu-V and Np-V.

4.5. Summary and Conclusions

1) Oxidation state experiments showed that the $Pu(V + VI)/Pu(III + IV)$ ratio in spiked sea water which had been left to equilibrate for several weeks was approximately three. This ratio increased dramatically when the sea water was contacted with sediment as the reduced $Pu(III + IV)$ was sorbed much more rapidly than the oxidised $Pu(V + VI)$. Nevertheless with time the $Pu(V + VI)$ was effectively removed from solution and the final ratio after 102 days was less than 0.6 for all three sediments. It was shown that the reduced Pu was virtually all in the Pu-IV form and the oxidised Pu in the Pu-V form throughout the experiments.

From the waste management point of view it is clear that Pu oxidation state is not important. Both reduced and oxidised forms were strongly sorbed by all three types of sediment studied, final overall distribution coefficients being $>10^4$ in all cases.

2) Although final Pu distribution coefficients were similar for the three sediments, there were significant differences in the rate at which they removed Pu-V from solution. This is presumably related to their ability to reduce Pu-V to Pu-IV. There is a strong correlation between this rate and the Np-V distribution coefficient. The order of decreasing activity was smectite > high-carbonate sediment > red clay.

This does not appear to be related to any of the other measured properties of the sediments such as surface area, cation exchange capacity or trace element composition.

3) Desorption experiments with plutonium indicate that at least two species are sorbed onto the sediment, one (a very small percentage of the total Pu) being more readily desorbable than the other. In addition the presence of some non-sorbable Pu may explain the fact that desorption R_d values are higher than sorption R_d values.

4) For all three sediments distribution ratios decreased in the order Am > Pu > Np. For Np, distribution ratios decreased in the order smectite > high-carbonate sediment > red clay and for Am and Pu, in the order smectite > high-carbonate $\approx$ red clay.

Finally, it should be noted that in these experiments conditions had to be rigidly controlled to allow comparisons between sediments and nuclides to be made. The sediment concentration was approximately 3 g/l. Subsequent work has shown that at very high solid/solution ratios the behaviour of high-carbonate sediments is completely different. These results are given in Chapter 5.

APPENDIX TO CHAPTER 4

ANALYTICAL METHOD USED FOR THE DETERMINATION OF TOTAL PLUTONIUM AND ITS OXIDATION STATE DISTRIBUTION

Reagents

- 1) TTA in benzene - 2.5g - thenoyltrifluoroacetone dissolved in 50 ml benzene. Freshly prepared.
- 2) La carrier - 2.5 mg La/ml.
- 3) U hold-back carrier - 2.0 mg U/ml.
- 4) 2M Aluminium nitrate.
- 5) 1M Hydroxylamine hydrochloride.
- 6) 1M Sodium nitrite.
- 7) Holding oxidant solution - 0.0075 M $K_2Cr_2O_7$ in 3.75 M H_2SO_4 .
- 8) ^{239}Pu -IV tracer - prepared as follows:
Add ^{239}Pu to 16M HNO_3 and evaporate to dryness. Dissolve in 8M HNO_3 and pass through an anion exchange column (Dowex-1 X8 100-200 #, NO_3^- form, 50mm x 7mm column). Wash well with 8M HNO_3 and discard washings. Elute ^{239}Pu -IV with 20 ml 0.1M NHO_3 and immediately add 20 ml 16M HNO_3 to the eluate. Dilute with 8M HNO_3 to the required volume. Final concentration should be about 5 Bq/ml.

Method

1. Total Plutonium

- 1) To the sample add 50 μ m ^{239}Pu tracer and 3 ml 8N HNO_3 and evaporate to near dryness.
- 2) Add 3 ml 2M HNO_3 and 1 ml 1M hydroxylamine hydrochloride. Heat at 80°C for five minutes.
- 3) Transfer to a separating funnel using
 - i) enough 1M HNO_3 to make the volume 4 ml.
 - ii) 2 ml 1M sodium nitrite.
- 4) Allow to stand until gas evolution ceases, add 3 ml TTA in benzene and shake for 20 min.
- 5) Transfer organic layer to a 15 ml centrifuge tube and centrifuge for 5 mins.
- 6) Transfer organic layer to a 10 ml beaker and evaporate down to about 0.3 ml.
- 7) Using a Pasteur pipette transfer the sample onto a heated stainless steel planchette. Rinse the beaker with a few drops of benzene.
- 8) Flame the planchette and count on an alpha spectrometer.

2. Pu-IV

- 1) Transfer a 4g sample to a separating funnel containing 1g sea water and 0.35 ml 12M HCl. Add 50 μ l ^{239}Pu -IV spike.
- 2) Add 3 ml TTA in benzene and shake for 20 mins.
- 3) Prepare source as for Total Pu, steps 5-8.

3. Pu(III + IV)

- 1) Transfer a 4g sample to a 15 ml plastic centrifuge tube containing 1g sea water, 0.65ml 8M HNO_3 , 0.47 ml holding oxidant solution and 1 ml La carrier. Shake briefly and allow to stand for 30 min.
- 2) Add 1 ml 40% wt/vol HF. Shake for two minutes and allow to stand for two hours.
- 3) Centrifuge for about 10 min. at 5000 rpm.
- 4) Transfer supernate to a second centrifuge and keep it for the Pu(V + VI) determination.
- 5) To the precipitate add 50 μ l ^{239}Pu spike, 0.6 ml 2M aluminium nitrate, and 2 ml 2M HNO_3 . Shake to dissolve the precipitate.
- 6) Transfer the solution to a 50 ml beaker using 8M HNO_3 to wash out the centrifuge tube and evaporate to near dryness.
- 7) Proceed exactly as for Total Pu, steps 2-8.

4. Pu(V + VI)

- 1) To the supernate reserved after the Pu(III + IV) precipitation add 50 μ l ^{239}Pu spike and approx. 20mg ferrous ammonium sulphate. Shake well and allow to stand for 30 min.
- 2) Add 1 ml La carrier, shake for 2 min. and allow to stand for two hours.
- 3) Proceed exactly as for Pu(III + IV) steps 3-7.

5. Pu(III + IV + V)

- 1) Transfer a 4g sample to a plastic centrifuge tube containing 1g sea water, 1 ml La carrier, 1 ml U hold-back carrier and 0.3 ml 12M HCl.
- 2) Add 1 ml 40% wt/vol HF and proceed exactly as for Pu(III + IV) steps 2-7, but this time the supernate from step 4 should contain only Pu-VI.

6. Pu-VI

- 1) Take the supernate reserved after the Pu(III + IV + V) precipitation and proceed exactly as for Pu(V + VI).

THE EFFECT OF SOLID/SOLUTION RATIO ON THE MEASURED DISTRIBUTION RATIO5.1. Introduction

In Chapter 3 it was observed that the distribution ratio for americium decreased as the solid/solution ratio increased and it was suggested that the reason for this might be the presence of some "non-sorbable" species. A careful study of the literature showed that although most workers in the field seemed to choose a particular solid/solution ratio rather arbitrarily and then to investigate other variables such as concentration, solid/solution ratio effects had been frequently observed and various explanations offered (Sanchez et al., 1981; Cremers, 1983; Ames and McGarrah, 1980; Sheppard et al., 1979; Sheppard et al., 1980; O'Connor and Donnelly, 1980; Voice et al., 1983; Yuan-Hui Li et al., 1984; Serne and Relaya, 1982). Thus, Sanchez and Schell (1981) working with esturine sediments found a large decrease in the distribution ratios of Am and Pu as they increased the sediment concentration from 200 mg/l to 1000 mg/l. They suggested that their data indicated that the sorption of these nuclides onto available surface sites is considerable, and may result from the sediment particles serving as a nucleation site for precipitation of the isotopes. An increase in the sediment concentration would not therefore necessarily effect a proportionate increase in radionuclide removal.

Cremers (1983) looking at the problem from the ion exchange point of view, points out that the exchange complex is in thermodynamic equilibrium with some "interstitial in situ" solution and the total pool of exchangeable ions exceeds by far the one in solution. He suggests that the apparent variations in K_d with changing solid/solution ratio can be readily explained in terms of changing compositions of both phases. The ion exchange studies reported in Section 2 indicate that K_d should increase with increase in solid/solution ratio (see Figure A9 for example) since the loading would decrease.

While both these explanations must have some validity a more down to earth explanation comes from Ames and McGarrah (1980) who show that poor phase separation will result in this effect. They found that, not only was it very difficult to prevent colloidal sized clay particles from remaining with the solution phase, but that colloids consisting, at least partially, of hydrated ferric and manganese oxy-hydroxides were generated during the shaking period. These strongly sorbed the

radionuclides being studied, but tended to remain with the solution phase after phase separation and thus lowered the apparent K_d .

This theme is taken up by Sheppard et al., (1970, 1980) who studied the sorption of Cs, Sr and Am on solids. They concluded that the distribution ratios of radionuclides are a "function of the soils studied and the particle size resolution technique used". They found that for their set of soils three broad classes of particles determined the observed distribution ratios. These were (i) ionic ones, i.e. particles containing radionuclides, with radii less than one nm, (ii) complexes of humic matter, possibly humic acid polymers with molecular weights between 8000 and 50000 (2-3 nm radii) and, (iii) larger soil particles with radii in the 10-50 nm range.

Finally, O'Connor and Donolly (1980) reviewed the literature covering studies involving a number of organic and inorganic solutes and sorbents and reported that "linear partition coefficients are inversely dependent upon the concentration of solids in the system. Voice, Rice and Weber (1983) studied their data and initiated a study to assess the effects of solid concentration on the partitioning of hydrophobic compounds. They concluded that the observed change in partitioning behaviour could be attributed to a transfer of sorbing, or solute binding, material to the liquid phase during the course of a partitioning experiment. This material whether dissolved, macro-molecular, or microparticulate was not removed from the solution phase during the separation procedure and was capable of stabilizing the compound of interest in solution.

Clearly if distribution ratios determined by the batch method are to be of use in modelling radionuclide movement it is essential that the situation be clarified. If necessary models will have to deal separately with the movement of ions, polymer-size molecules and micro-particulates. We, therefore, decided to investigate the problem by first, undertaking a mathematical analysis to determine how sensitive the measured distribution ratio would be to the presence of some non-separable nuclide and secondly, an experimental study in which we determined distribution ratios for Am, Pu, and Np over as wide a range of sediment-sea water concentration as possible. The results of this work now follow.

5.2. Theoretical Study

The sediment-sea water system, like the soil-water system is extremely complex and the difficulties of extending physico-chemical models from simple well-defined systems to natural ones are enormous. Nevertheless, considerable progress has been made recently and both the mass action models (Harmsen, 1979; Cremers, 1983) and the double layer or surface complexation models (Davis et al., 1978; Westall et al., 1976; Relayea et al., 1980) show promise of eventually enabling us to make predictions on a sound theoretical basis. The present status of these models has been well reviewed in the report of the recent NEA work shop on "Sorption - Modelling and Measurement" (NEA, 1983).

We have made no attempt to apply these complex models but have simply calculated the effect that more than one stable species in solution would have on the measured distribution ratio. Experimentally it is difficult to distinguish between a "two-site" situation where sorption is on adsorption sites with different selectivities and a "two species" situation in which the ion in solution is present in two stable forms, e.g. one ionic and the other in liganded form. In this analysis we have concentrated on a two-species model because at these very low nuclide concentrations (at which Henry's law is obeyed) and relatively high sediment concentrations it is unlikely that there will be competition for even the more highly selective sites. Also, a two-species model is more appropriate for the situation in which the second species is simply particulate material which has not been removed during the phase separation.

For the purpose of these calculations we have considered two cases: (i) A fixed proportion of the original nuclide present in the non-separable form. This non-separable nuclide could be colloidal material or complexes already present in the solution before addition of the sediment or it could be micro-particles of sediment onto which nuclides have been sorbed. In this case increasing the sediment concentration would not increase the amount of nuclide remaining with the solution phase because although the number of particles would increase the nuclide concentration per particle would decrease, (ii) The amount of nuclide remaining with the solution phase is proportional to the sediment concentration as proposed by Voice et al (1983) in their re-solubilisation theory.

(1) A fixed proportion of the original nuclide with a low distribution ratio

In most batch-distribution experiments the nuclide in the solution phase is measured before and after sorption and the R_d calculated from the formula,

$$R_d = \left(\frac{C_o - C}{C} \right) \cdot v/m \quad (1)$$

where C_o = initial concentration of the radionuclide in solution

C = concentration of radionuclide in solution after sorption

v = volume of liquid phase

m = mass solid phase.

now let $x C_o$ = initial concentration of the species that is adsorbed with a high R_d (R_H).

then $(1-x)C_o$ = initial concentration of the species that is adsorbed with a low R_d (R_L)

let $C = C_H + C_L$ where C_H and C_L are the final concentrations of the high- and low- R_d species respectively.

Then from (1)

$$C = \frac{C_o z}{R_d + z} \quad \text{where } z = v/m$$

$$\text{So that } C_H = \frac{x C_o z}{R_H + z} \quad \text{and } C_L = \frac{(1-x) C_o z}{R_L + z}$$

$$\therefore C = C_H + C_L = \frac{C_o z x (R_L + z) + C_o z (1-x) (R_H + z)}{(R_H + z) (R_L + z)}$$

$$\text{Now } R_d \text{ (observed)} = \left(\frac{C_o}{C} - 1 \right) z$$

$$\begin{aligned} &= \left(\frac{\frac{C_o z}{\frac{C_o z x (R_L + z) + C_o z (1-x) (R_H + z)}{(R_H + z) (R_L + z)}} - 1}{1} \right) z \\ &= \left(\frac{(R_H + z) (R_L + z)}{x(R_L - R_H) + R_H + z} \right) - z \end{aligned} \quad (2)$$

$$\text{and } \frac{C_o - C}{C} = \left(\frac{(R_H + z) (R_L + z)}{z[x(R_L - R_H) + R_H + z]} \right) - 1 \quad (3)$$

(2) Amount of low R_d species proportional to sediment concentration

In this case $(1-x) \propto m$

$$\text{i.e. } (1-x) \propto \frac{1}{z}$$

$$\therefore (1-x) = \frac{k}{z}$$

$$\therefore x = \frac{z-k}{z}$$

Substituting in eqn. (2) gives

$$R_d = \left[\frac{z (R_H + z) (R_L + z)}{(z-k) (R_L - R_H) + R_H + z} \right] - z \quad (4)$$

$$\text{and } \frac{C_o - C}{C} = \left[\frac{(R_H + z) (R_L + z)}{(z-k) (R_L - R_H) + R_H + z} \right] - 1 \quad (5)$$

The effect of changing the different variables in these equations is illustrated in Figures 5.1 - 5.4. In each figure two sets of graphs are given, viz. $\log R_d$ vs. $\log m/v$ and $\log (C_o - C)/C$ vs. $\log m/v$. The latter graphs are often more informative than the former since from the definition of R_d it can be deduced that if there is only one species present and if it is all adsorbed with the same effective R_d , a plot of $\log (C_o - C)/C$ vs. $\log m/v$ should give a straight line with gradient one and intercept $\log R_d$. (Since by definition $R_d = (C_o - C)/C \cdot v/m$, i.e. $\log (C_o - C)/C = \log m/v + \log R_d$). The presence of a second species changes both the slope and intercepts as can be seen from Figures 5.1. - 5.4.

Figures 5.1. and 5.2. show these graphs for the situations where (i) there is a fixed proportion of low- R_d nuclide and (ii) the amount of low- R_d nuclide is proportional to the sediment concentration. For the purpose of illustration the distribution ratio of the high- R_d species (R_H) is taken as 10^6 and of the low R_d species as 0.1. Figure 5.3. shows the effect of lowering the value of R_d for a fixed amount of low- R_d species (in this case 0.05%).

It can be seen from Figure 5.1. that if R_H is as high as 10^6 the observed distribution ratio is extremely sensitive to the presence of even minute amounts of low- R_d species. At low solid/solution ratios the observed R_d will tend to R_H but as the solid/solution ratio increases the observed R_d will drop sharply. Figure 5.2. shows that if the amount of low- R_d species increases with increasing sediment concentration

then the distribution ratio drops more sharply with increasing solid/solution ratio than it does when there is simply a fixed amount present and the gradient of the graph of $\log (C_o - C)/C$ vs. m/v actually becomes negative.

From Figure 5.3. it can be seen that the effect of a small amount of low- R_d species decreases with decreasing R_d . Thus 0.05% of a species with $R_d = 0.1$ will have no detectable effect if R_H is 10^3 or less.

Figure 5.4. illustrates the case where R_L instead of being close to zero has a reasonably high value (100 in this example). It can be seen that now R_d is constant (and the graph of $\log (C_o - C)/C$ vs. m/v has a slope of one) at high solid/solution ratios but that at low solid/solution ratios R_d rises steeply as m/v decreases. For this situation to exist stable complexes, each with their own distribution ratio and not in equilibrium with each other would have to be formed. It could possibly arise in natural waters where minute traces of organic ligands are available for complexing. It is, however, fairly unlikely to occur in our experiments where the amount of nuclide present is also extremely small, although a graph of this shape was obtained for neptunium on red clay.

Finally, we should consider the effect that the presence of more than one species will have on desorption distribution ratios. It has become common practise, after measuring a distribution ratio, to replace the solution phase with fresh ground water and then to determine the desorption R_d . Frequently, desorption distribution ratios are an order of magnitude or more greater than sorption distribution ratios and this is generally interpreted as meaning that the sorption-desorption reaction is irreversible. Cremers (1983) says that such experiments have little value as the composition of both phases may have changed during the reversibility tests. Nevertheless, from the point of view of radionuclide migration desorption is as important as sorption and it is essential that desorption processes be understood. Serne and Relaya (1982) have speculated that the difference in R_d can be caused by some of the following mechanisms: (i) collapse of interlayers of 2:1 lattice clays such as illite, (ii) precipitation of insoluble minerals or coprecipitation and entrapment in amorphous coatings, (iii) reduction to more insoluble species by crystal lattice elements such as Fe, (iv) non-linear isotherms where R_d increases as the total mass of nuclides in the system is reduced,

(v) diffusion of nuclides deep into the rock matrix, (vi) presence of multiple sorption sites with a few with extremely high affinity for the particular nuclide (two-site model). Although one or more of the above processes are probably involved in different experimental systems it is also possible that the presence of some low- R_d species (frequently the result of poor phase separation) has often magnified this effect. These would lower the observed sorption R_d but would be removed after the sorption experiment and would not be present to lower the observed desorption R_d . How significant this effect is would depend not only on the quantity of low- R_d nuclide present but also on its nature. Most of it might be removed during the first phase separation but micro-particulates are likely to be trapped with the solid phase and continuously released through a number of desorption stages. This trapping effect would be greatest at high solid/solution ratios, with the result that the desorption R_d would approach the sorption R_H at low solid/solution ratios but would still be lowered at high solid/solution ratios. This is the type of effect that we have observed with americium.

Note: In deep sea sediments the water content ranges from 50% to 80% i.e. the solid concentration ranges from about 250 to 500 g/l (m/v between 0.25 and 1.0, i.e. $\log m/v$ between 0 and -0.6). In most of the experiments reported in Chapters 2 to 4 the sediment concentration was 3.3 g/l ($m/v = 0.0033$, $\log m/v = -2.5$).

5.3. Experimental

The effect of solid/solution ratio on the sorption behaviour of ^{241}Am , ^{238}Pu and ^{237}Np on two of the sediments previously studied was investigated. Different weights of each sediment were contacted with spiked sea water and three main sets of experiments carried out. These were (i) determination of the sorption R_d , (ii) determination of the desorption R_d and (iii) determination of a "second R_d ", i.e. the liquid phase removed after the first R_d determination was added to fresh sediment to determine whether the nuclide remaining in solution after the first sorption behaved as in (i).

The two sediments studied were the high-carbonate sediment, 10399 # 7K (85% CaCO_3) and the red clay, 10400 # 8K. Details of their mineralogy, chemical composition, etc. are given in Chapter 3.

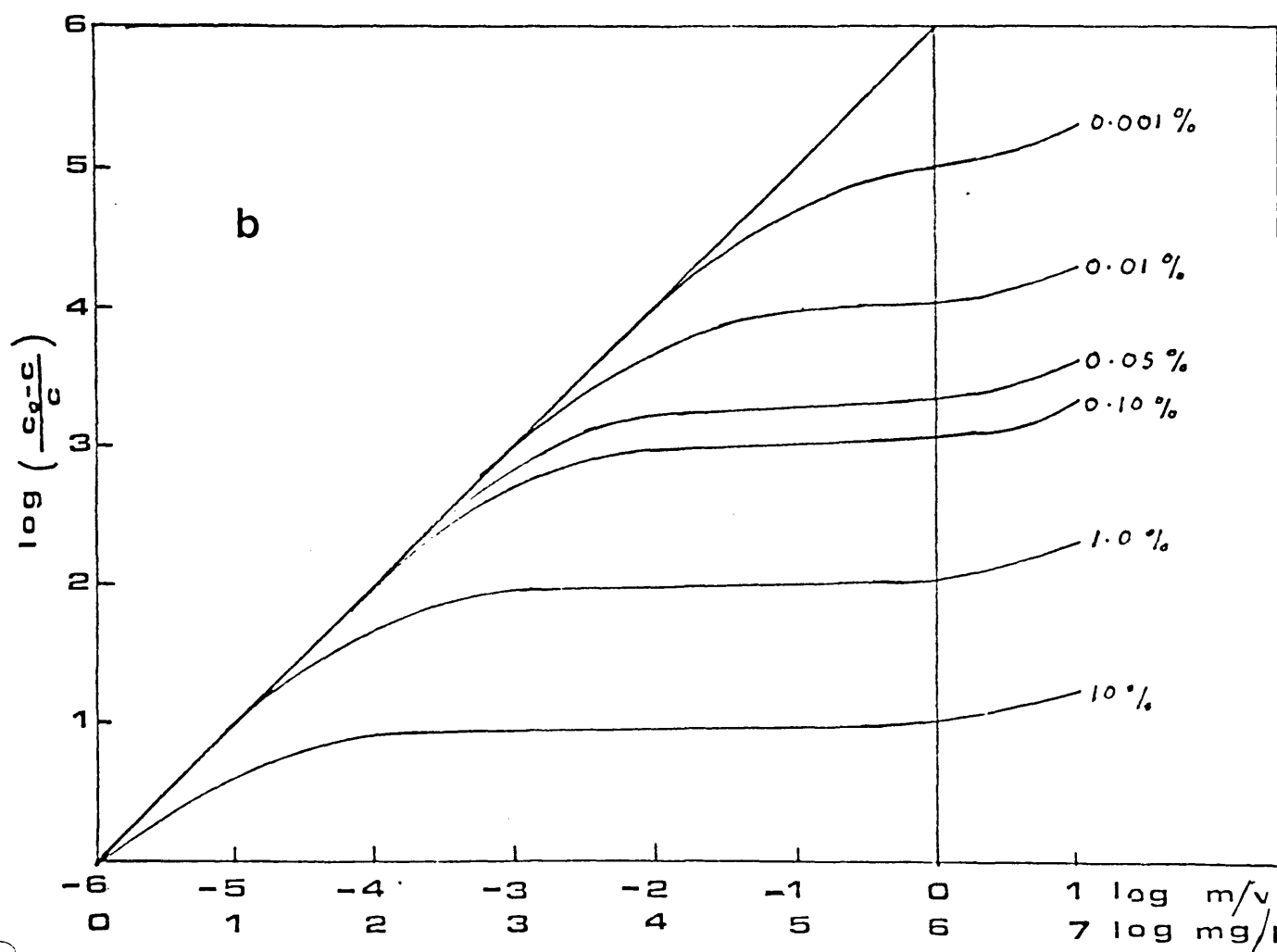
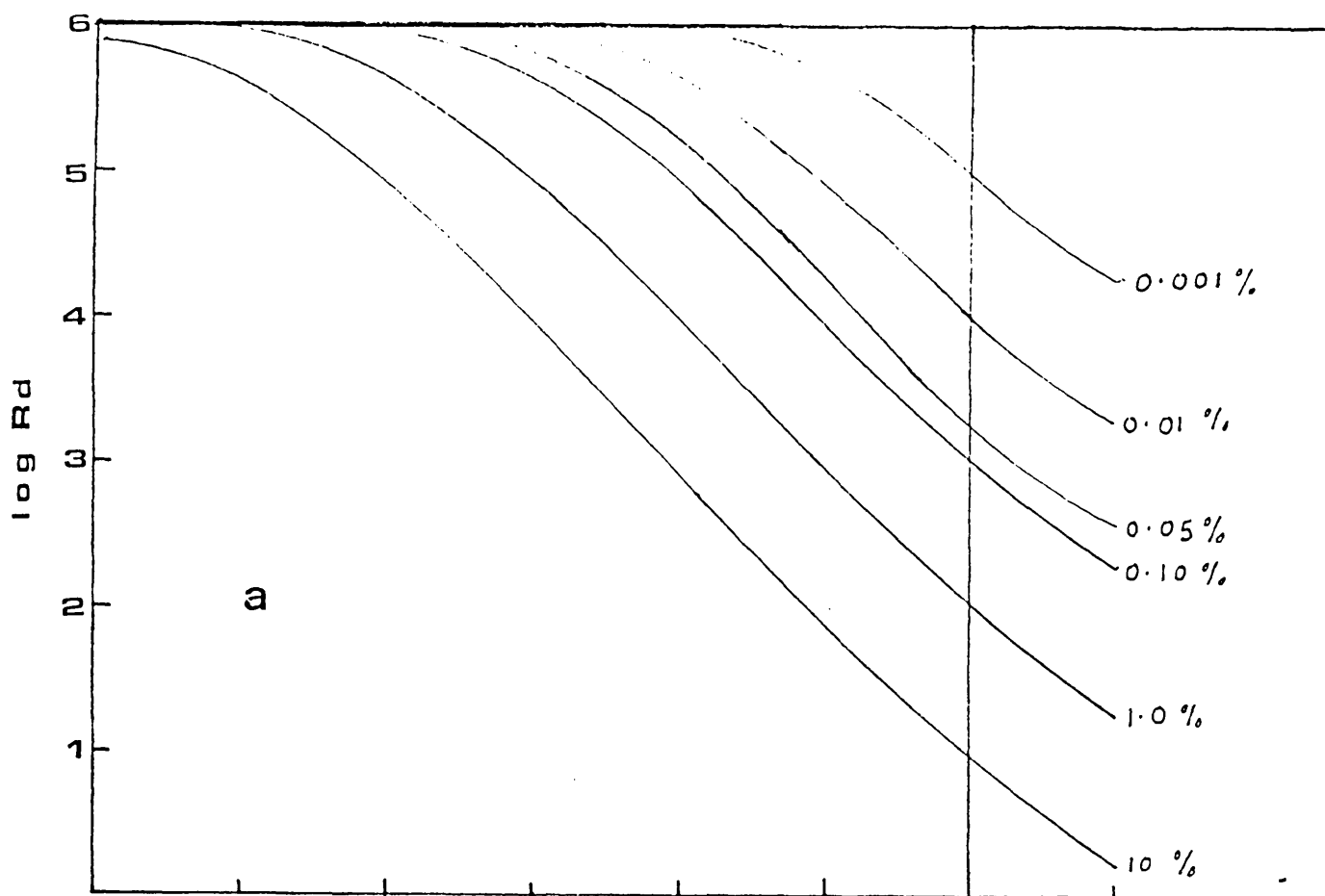


Fig.5.1 The effect of a fixed proportion of a second species which is not adsorbed by the sediment on the relationship between $\log m/v$ and (a) $\log R_d$. (b) $\log(C_0 - C)/C$ for different percentages of low R_d species ($R_H = 10^6$; $R_L = 0.1$).

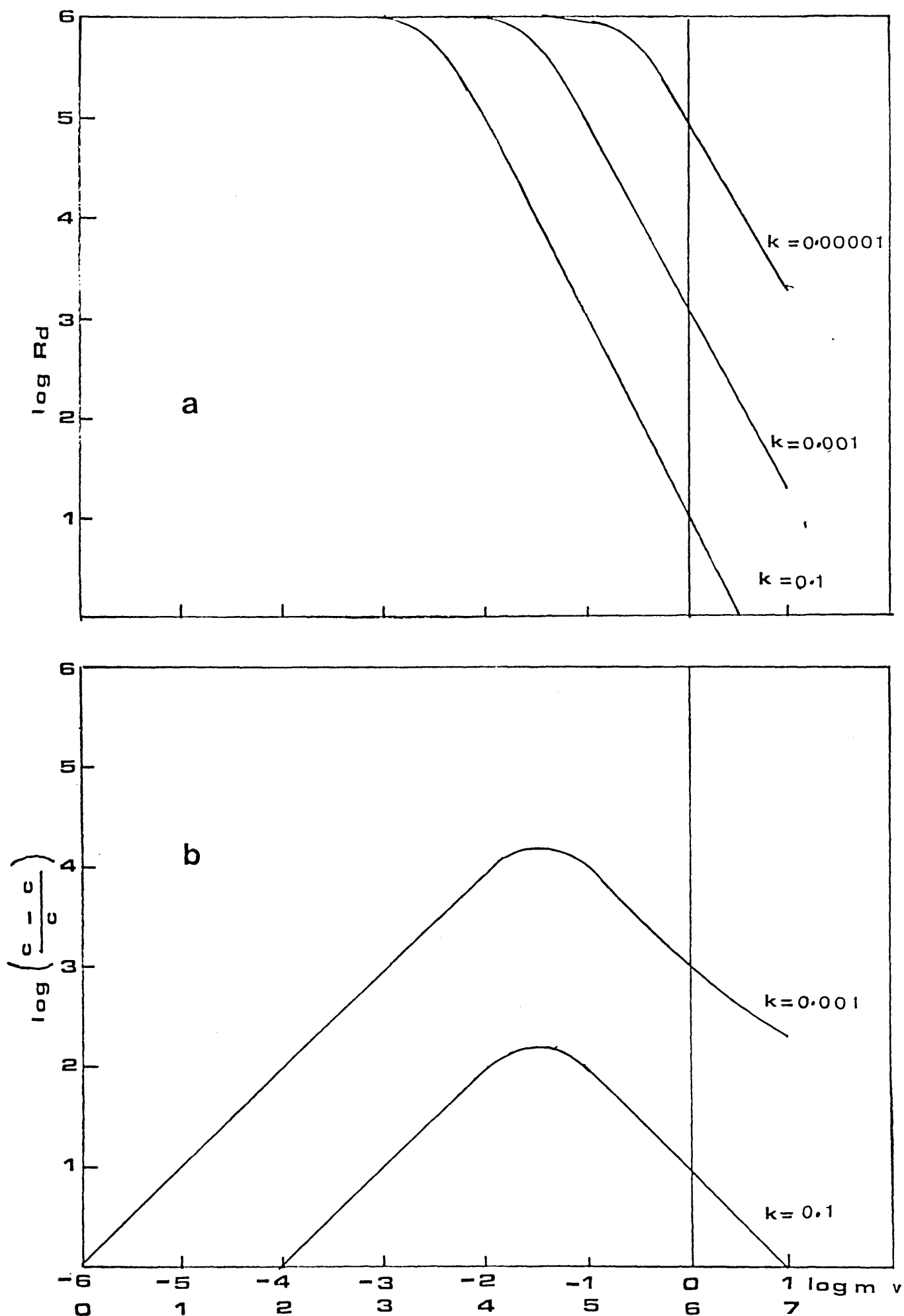


Fig 5.2 The effect of the presence of a second species which is not sorbed by the sediment and whose concentration is proportional to the sediment concentration on the relationship between $\log m/v$ and (a) $\log R_d$ (b) $\log(C_0 - c)/c$ for different proportionality constants ($R_H = 10^6$, $R_i = 0.1$). 136

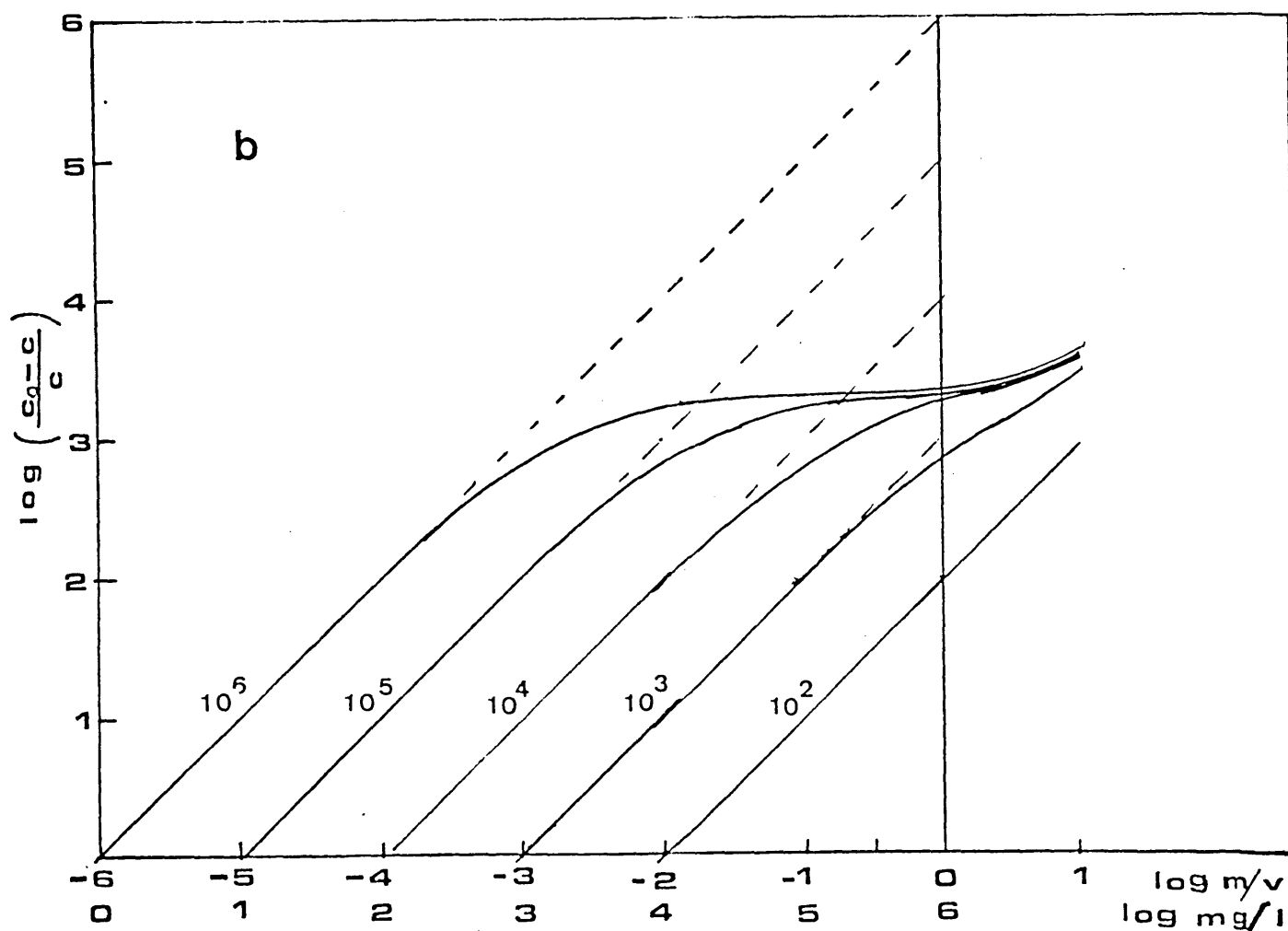
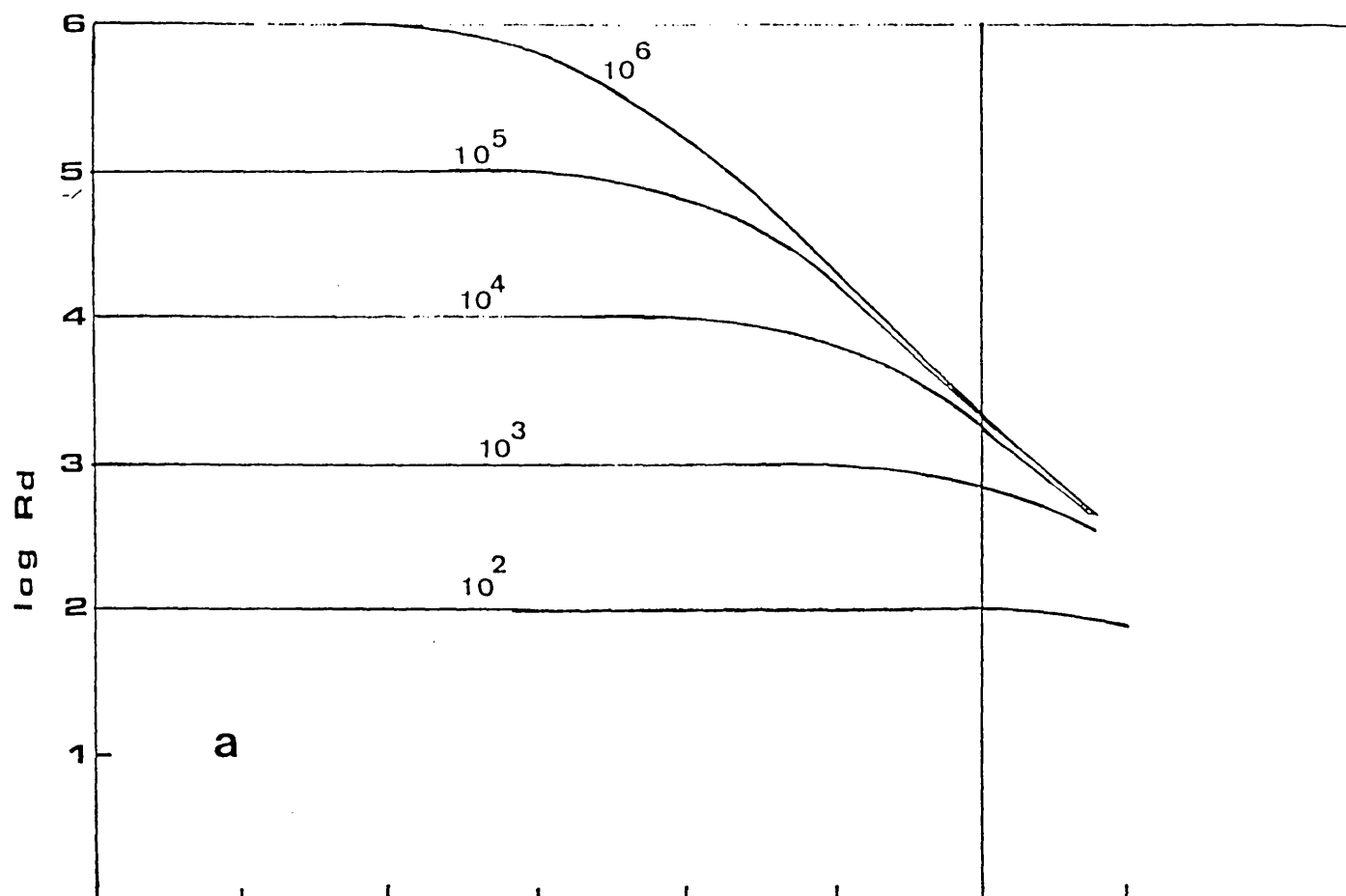


Fig. 5.3 The effect of a fixed proportion (0.05%) of a second species which is not sorbed by the sediment on the relationship between $\log m/v$ and (a) $\log R_d$ (b) $\log (C_0 - c)/c$ for different values of R_H (R_H variable, $R_L = 0.1$)

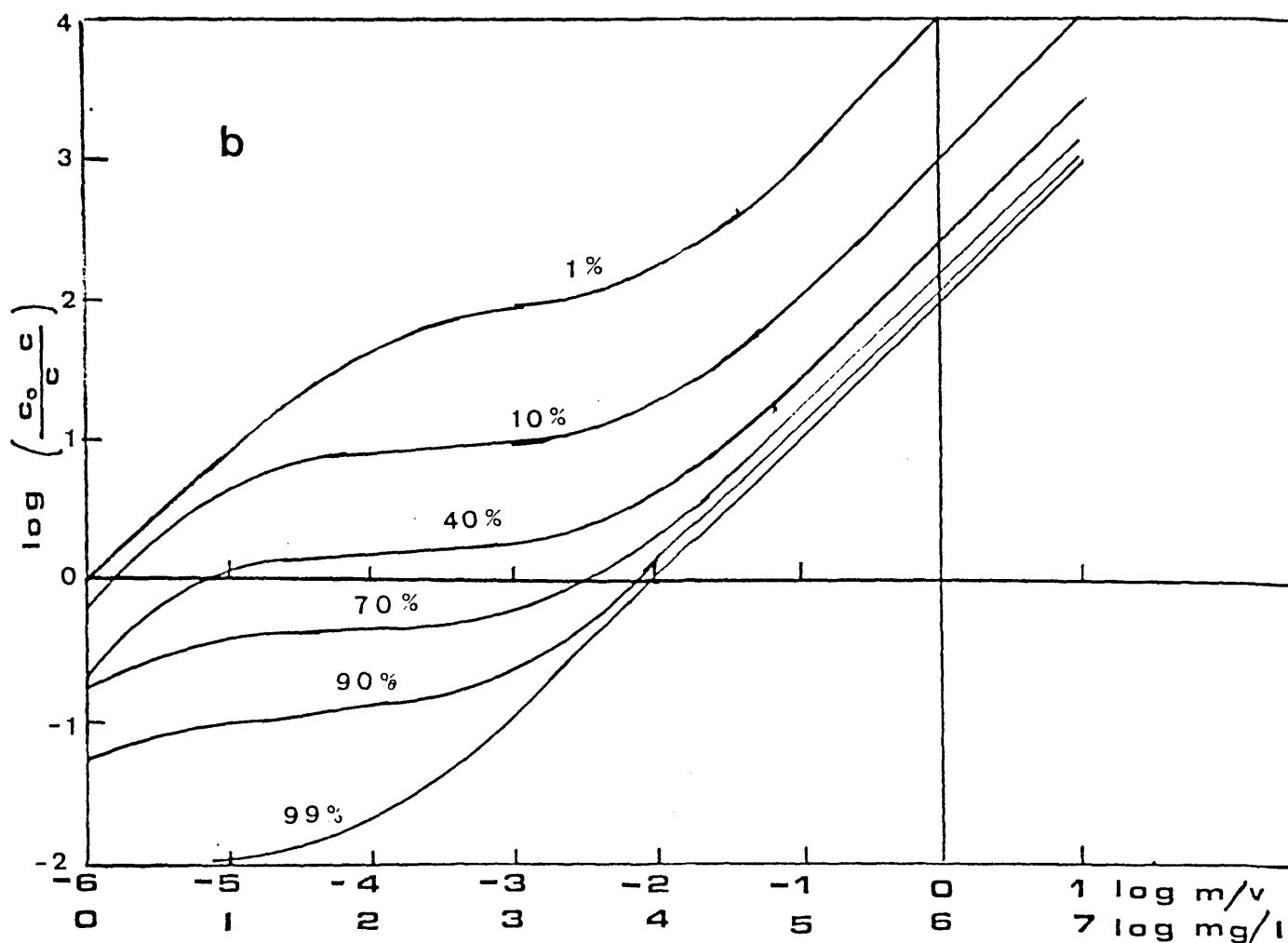
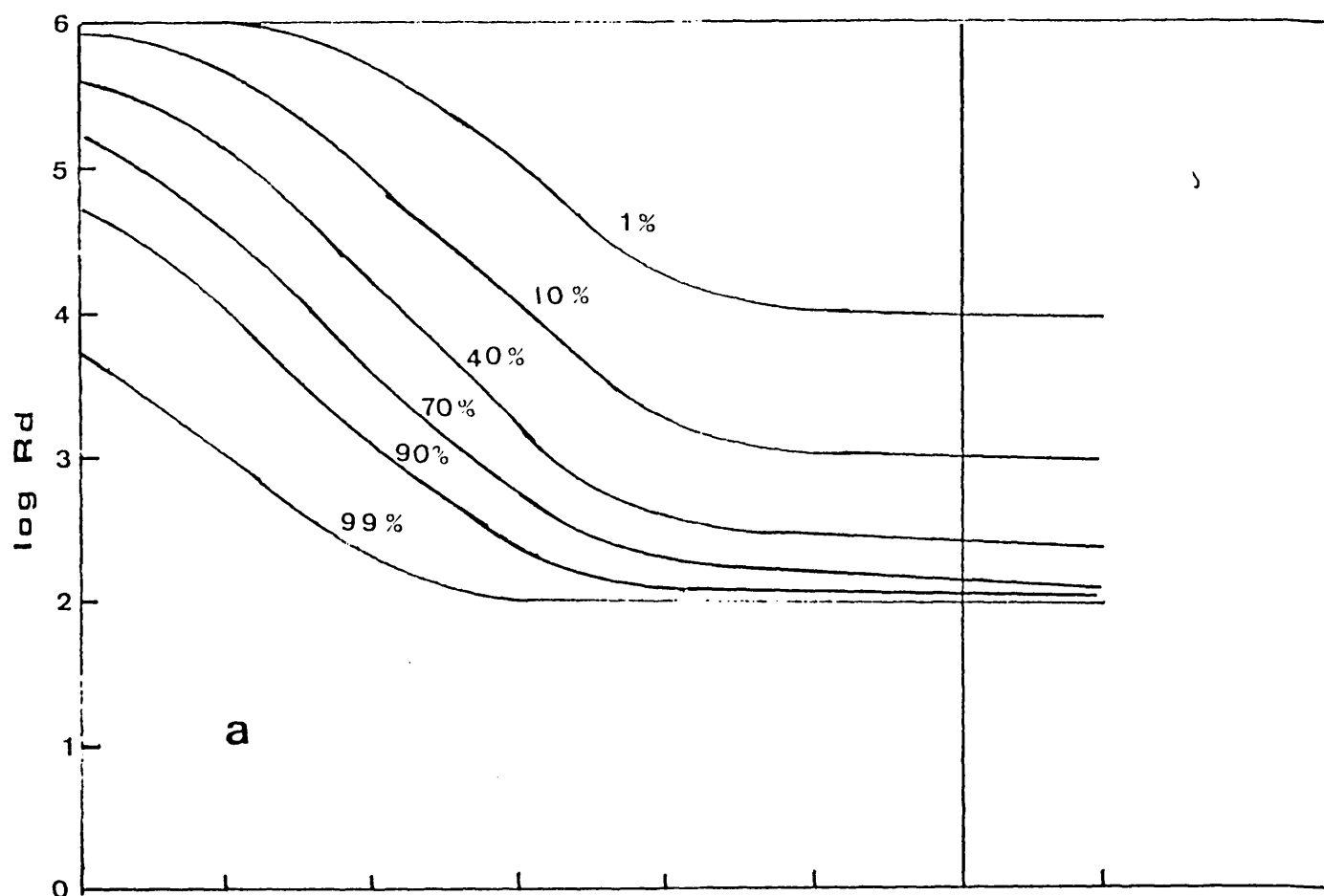


Fig 5.4 The effect of a fixed proportion of a second species with $R_d=100$ on the relationship between $\log m/v$ and (a) $\log Rd$ (b) $\log(C_0-c)/c$ for different percentages of low R_d species. ($R_H = 10^6$, $R_L = 10^2$).

The batch distribution method used for the determination of distribution ratios was the same as that used previously, i.e. a weighed amount of sediment slurry was placed in 50 ml Oakridge centrifuge tubes. Sea water which had been spiked several weeks previously (and the pH re-adjusted to 8.2 if necessary) was filtered through 0.22 μ filters immediately before use and added to the sediment. The tubes were placed horizontally in a water bath and shaken gently at 120 strokes per minute. Phases were separated by centrifuging at 7000 rpm (5280 g) for 90 min. followed by filtration either through 0.22 μ or 0.10 μ millipore filters. The temperature was kept at 4°C throughout.

The analytical methods used for the determination of americium and plutonium (and its oxidation state distribution) remained unchanged. However, because of the prohibitive cost of ^{235}Np , ^{237}Np was used in these experiments, the ^{235}Np being reserved for use as a yield monitor during the determination of ^{237}Np by alpha spectrometry. The ^{235}Np was counted on a Phillips automatic gamma scintillation counter. There were two peaks in the uranium X-ray region (the 6.9 KeV $\text{L}\beta$ + 20.7 KeV $\text{L}\gamma$ transitions and the 94.7 KeV $\text{K}\alpha_2$ + 98.4 KeV $\text{K}\alpha_1$ transition). Generally both peaks were counted and gave similar recoveries. The lower of the two peaks gave the higher count rate and the lower background. ^{237}Np also emits gamma rays at 105 and 108 KeV but the concentration of ^{237}Np was so low in samples that this could not be detected and no correction was necessary. There was, however, a small amount of ^{237}Np in the ^{235}Np spike (0.2 dpm ^{237}Np per 7 nCi portion of spike) and this had to be corrected for. Sources for alpha spectrometry were prepared by reducing all the Np to the IV state and extracting it into 2-thenoyltrifluoroacetone (TTA) in benzene (Moore, 1957). Details of the analytical method used are as follows:

5.3.1. Analytical Determination of Neptunium-237

- (1) To exactly 5g sample in a 50 ml separating funnel add
 - (i) 0.75 ml 12M HCl
 - (ii) 1.6 ml 5M hydroxylamine hydrochloride
 - (iii) 1.0 ml 2M ferrous sulphamide (freshly prepared by dissolving iron filings in sulphamic acid).
 - (iv) 50 μl ^{235}Np spike (150 nCi/ml)
- (2) Add 3 ml 0.5M TTA in benzene and shake for 10 mins.
- (3) Allow the phases to separate and wash once with 1M HCl.
- (4) Transfer the organic layer to a 15 ml centrifuge tube and centrifuge for 5 min.

- (5) Transfer the organic layer to a 10 ml beaker, evaporate down to approximately 0.3 ml and transfer to a heated stainless steel planchette.
- (6) Flame the planchette and count the ^{237}Np on an alpha spectrometer.
- (7) Determine the yield by counting the ^{235}Np on a gamma counter.

5.3.2. Results and Discussion

It was found that each nuclide and each sediment behaved differently and they will, therefore, be discussed one at a time. Comparisons are made where appropriate and the main results are summarised in Table 9. Errors quoted in the Tables and error bars in the graphs are standard deviations based on counting statistics. Where more than one determination was made weighted means are given.

5.4. Americium

Three different sets of sorption experiments were carried out. In each case the phases were separated by centrifuging at 7000 rpm, (5280g) for 90 min. before filtering through millipore filters but in the first two sets the solutions were filtered through double 0.22 μ above double 0.10 μ filters whereas in the third set filtration was simply through single 0.22 μ filters. Desorption R_d were determined after Run 2 and solutions from Runs 1 and 2 were contacted with fresh sediment to ascertain whether the americium remaining in solution after sorption behaved in the same way as that originally present in the initial solution. The results of these experiments are given in Tables 5.1 - 5.4. and in Figures 5.5 - 5.7.

5.4.1. Sorption

It can be seen from Tables 5.1. and 5.2. and from Figure 5.6. that the observed distribution ratio dropped sharply as the solid solution ratio increased. In Figures 5.5. and 5.6. $\log (C_o - C)/C$ has been plotted against $\log m/v$ and superimposed upon the experimental points are theoretical curves calculated by the method described in Section 5.2. Because americium has such a high distribution ratio the measured R_d is very sensitive to small amounts of any low R_d species present and it would have been more satisfactory if it had been possible to decrease the sediment concentration below our minimum of 200 mg/l. Nevertheless, it can be seen that the experimental and theoretical curves show remarkable agreement and it seems highly likely that the reason for the observed drop in distribution ratio with increasing

sediment concentration is that some low- R_d nuclide remained with the solution phase after separation. There is no indication that the proportion of this species increased with increasing sediment concentration and it is probable that this non-separable americium was in the form of micro-particulate material. From the graphs it can be estimated that the distribution ratio of the high- R_d americium was about 10^6 for the carbonate sediment and that when filtered through 0.22 μ filters approximately 0.05% of the original americium remained with the aqueous phase as compared with 0.02 to 0.03% when filtered through 0.1 μ filters. The difference between the two filters was not as marked for the red clay where it appears that the distribution ratio for the high- R_d species was between 1×10^6 and 2×10^6 and that the amount of non-separable americium was about 0.02% and 0.03% when filtered through 0.1 and 0.22 μ filters, respectively.

The fact that considerably more Am remained in solution when filtration was through a single 0.22 μ filter rather than a bank of two 0.22 μ above two 0.10 μ filters could mean either that more Am was being adsorbed by the bank of four filters than by the single 0.22 μ filter or that particles in the 0.10 to 0.22 μ range were contributing to the non-separable species when the single 0.22 μ filter was used. The contact time with the filters was very short and the second explanation seems more likely. The filters were counted on a zinc sulphide scintillation counter but the system was not sensitive enough to detect any difference between the top and bottom 0.10 μ filters. Frequently, however, the top 0.22 μ filter did retain a large amount of activity due to a visible film of sediment. In theory centrifuging at 5280g for 90 min. should remove all sediment particles with diameter above 0.05 μ . However, a film of sediment could often be seen on the surface of the liquid after centrifuging and it was sometimes difficult to remove the solution phase without removing some of this sediment. The maximum particle diameter of 0.06 was calculated assuming a particle density of 2.6 g/cc but colloidal particles could conceivably have much lower densities. If the density was 1.2g/cc, for example, particles with diameter 0.18 μ would remain in suspension after centrifuging and such particles could have contributed to the low- R_d species when 0.22 μ filters were used. Olsson et al. (1982, 1983) have shown that americium readily forms colloids and pseudo-colloids in the pH range 5-12. The properties of these colloids are strongly pH dependent but at pH 8 they appear to become uncharged and

Table 5.1. Americium Distribution Ratios on Red Clay - 10400 # 8K

Run	Tube No.	Sediment Concentration g/l	Concentration in Solution			Distribution Ratio	
			Initial		After Sorption Bq/l	Sorption ml/g 10 ⁵	Desorption ml/g 10 ⁵
			Bq/l 10 ⁴	moles/l 10 ¹⁰			
Run 1 - 24 days. 0.22μ above 0.10μ filters.	350	420.0	1.95±0.12	6.61±0.41	3.71±0.29	0.122±0.018	-
	354	263.7	2.57±0.16	8.75±0.53	3.97±0.49	0.240±0.043	-
	358	46.0	3.30±0.20	11.23±0.69	9.48±0.97	0.739±0.087	-
	362	3.81	3.46±0.21	11.75±0.73	22.13±1.77	4.005±0.329	-
	366	0.905	3.49±0.22	11.85±0.73	36.78±3.23	10.207±0.782	-
Run 2 - 74 days. 0.22μ above 0.10μ filters.	351	466.1	2.07±0.13	7.03±0.43	2.27±0.23	0.195±0.064	0.381±0.097
	355	271.5	2.54±0.21	8.64±0.73	2.93±0.28	0.319±0.091	0.906±0.226
	359	57.60	2.94±0.24	11.06±0.67	5.68±0.35	0.940±0.170	6.89±1.800
	363	4.186	3.46±0.21	11.74±0.73	18.96±0.89	4.459±0.366	17.430±1.75
	367	0.973	3.49±0.21	11.84±0.73	27.93±1.83	13.130±1.065	-
Run 3 - 35 days 0.22μ filters.	501	102.1	3.16±0.191	10.59±0.65	7.86±1.06	0.387±0.019	-
	502	83.5	"	"	8.45±0.35	0.441±0.131	-
	500	58.4	"	"	10.80±0.70	0.485±0.015	-
	499	28.0	"	"	12.20±0.13	0.895±0.289	-
	498	7.10	"	"	13.85±0.59	3.136±0.081	-
	497	3.47	"	"	17.48±0.94	5.021±0.129	-
	494	1.87	"	"	24.29±1.99	6.858±0.181	-
	496	0.89	"	"	24.99±1.41	13.858±0.326	-
	495	0.04	"	"	42.13±3.05	18.143±0.407	-

Table 5.2. Americium Distribution Ratios on THE CARBONATE SEDIMENT IO399 # 7K

Run	Tube No.	Sediment Concentration g/l	Concentration in Solution			Distribution Ratios	
			Before Sorption		After Sorption Bq/l	Sorption $\frac{\text{ml/g}}{10^5}$	Desorption $\frac{\text{ml/g}}{10^5}$
			$\frac{\text{Bq/l}}{10^4}$	$\frac{\text{moles/l}}{10^{10}}$			
Run 1 - 23 days 0.22u above 0.1u filters	330	592.0	1.84±0.12	6.24±0.40	2.72±0.02	0.114±0.021	
	334	260.1	2.37±0.15	8.04±0.51	5.07±0.44	0.179±0.025	
	338	51.74	3.19±0.22	10.83±0.76	7.65±0.82	0.805±0.110	
	342	4.95	3.31±0.21	11.26±0.72	30.82±2.59	2.208±0.178	
	346	1.11	3.33±0.21	11.33±0.72	61.62±4.68	4.884±0.345	
Run 2 - 53 days 0.22u above 0.10u filters	331	566.2	1.86±0.12	6.33±0.40	3.31±0.39	0.086±0.012	0.399±0.089
	335	285.1	2.50±0.16	8.52±0.54	6.17±0.49	0.216±0.039	1.929±0.249
	339	60.53	3.17±0.20	10.77±0.69	9.58±0.87	0.539±0.065	9.964±0.711
	343	4.42	3.32±0.21	11.27±0.72	28.96±2.30	3.307±0.277	17.410±3.536
	347	1.01	3.33±0.21	11.31±0.72	36.37±3.00	8.779±0.687	
Run 3 - 34 days 0.22u Filters	504	85.11	3.116±0.191	10.59±0.65	13.35±0.91	0.260±0.064	
	492	57.12	"	"	15.48±1.14	0.351±0.089	
	491	28.71	"	"	16.30±1.71	0.664±0.020	
	490	14.83	"	"	21.92±1.76	0.955±0.023	
	489	7.53	"	"	17.83±1.85	2.314±0.068	
	489	4.00	"	"	26.63±2.44	2.916±0.072	
	487	2.00	"	"	37.90±4.06	4.107±0.100	
	493	1.34	"	"	35.66±4.30	6.519±0.166	
	486	0.91	"	"	38.72±3.44	9.008±0.230	
	505	0.21	"	"	129.09±24.68	11.254±1.000	

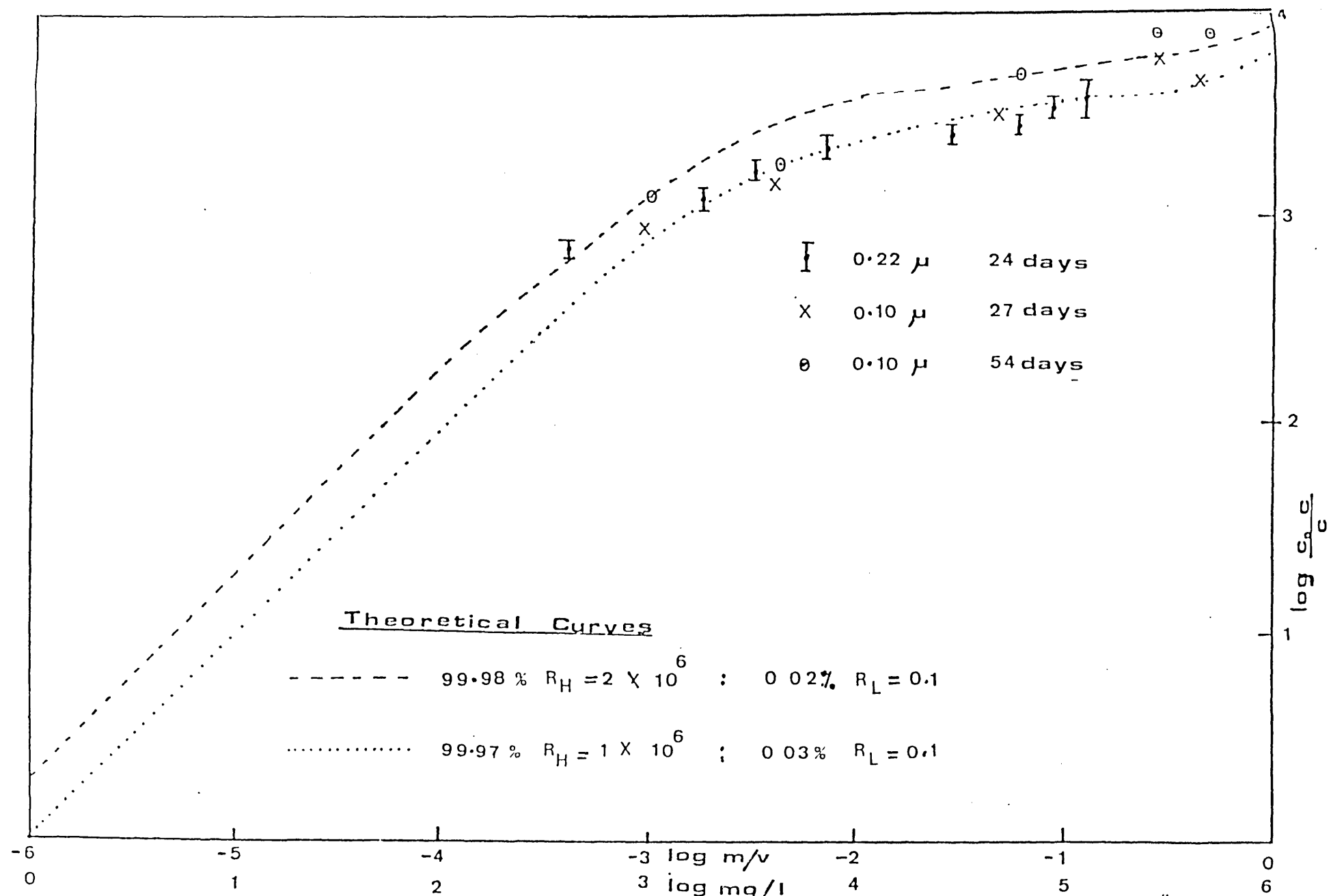


Fig 5.5 Effect of solid/soln ratio on the value of $\log (Co-c)/c$ for americium on the red clay, 10400 #8K.

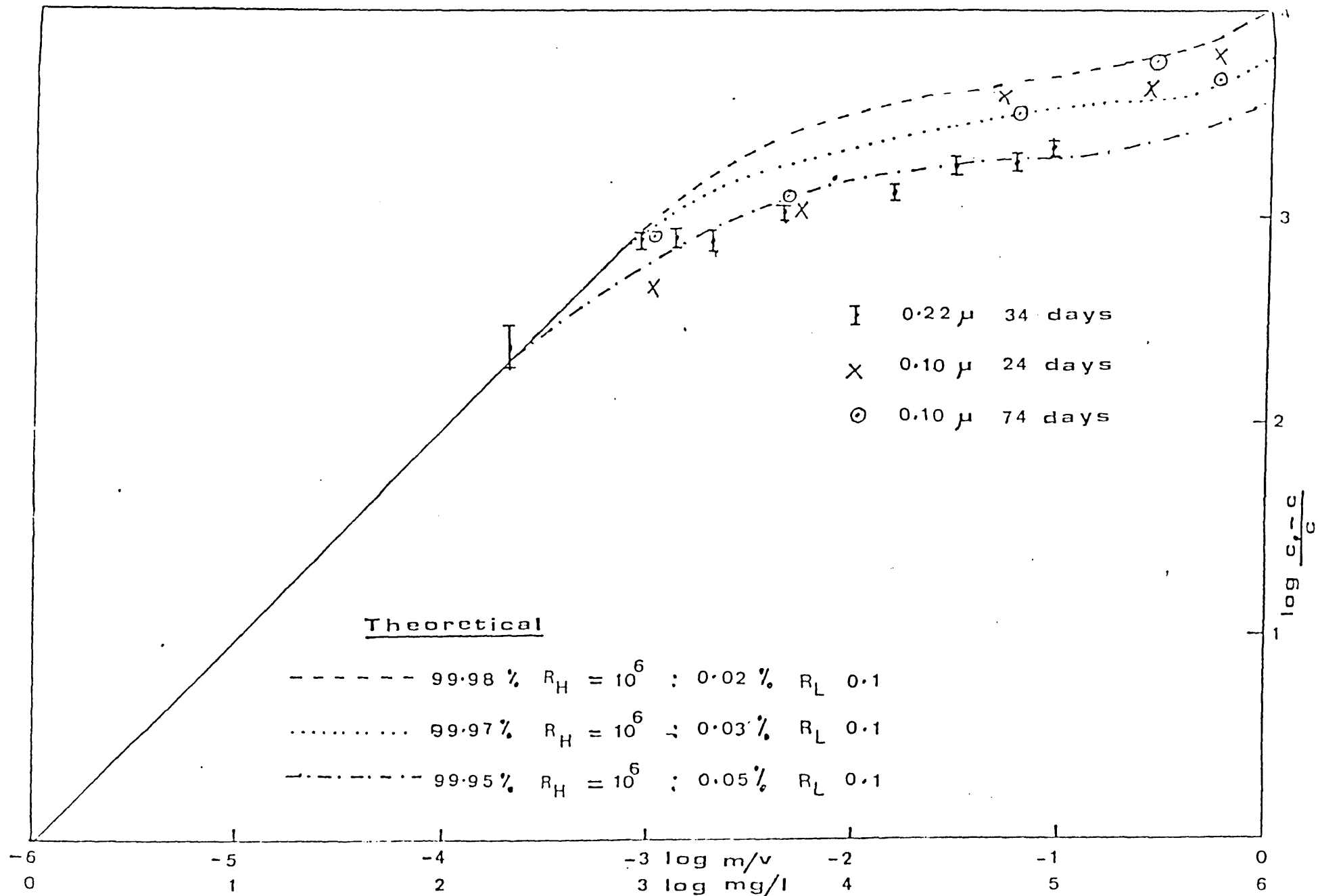


Fig. 5.6

Effect of solid/soln ratio on the value of $\log (C_0 - c)/c$ for americium on the high-carbonate sediment 10399-47K.

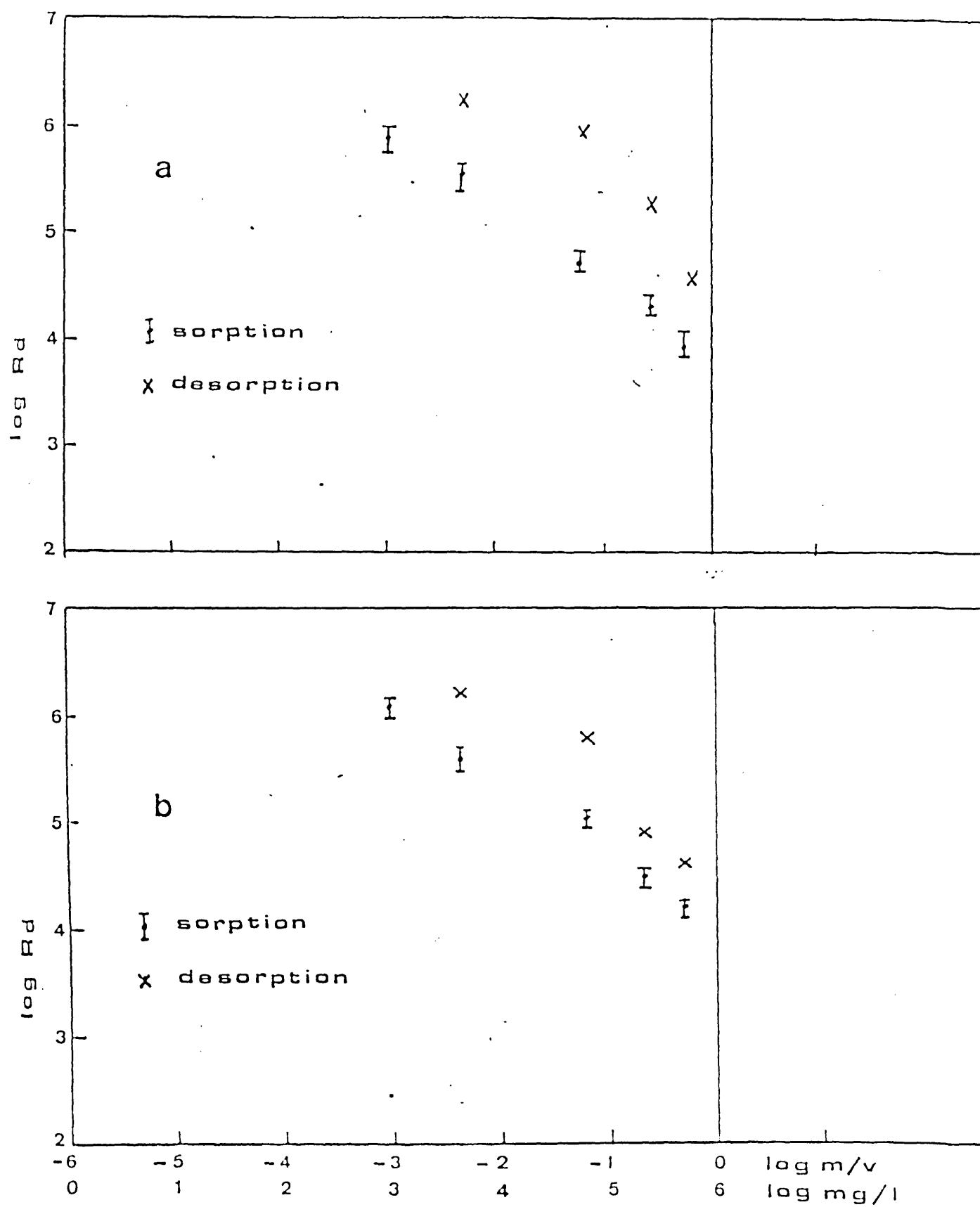


Fig 5.7 Sorption and desorption R_d at different solid/soln ratios for americium on (a) high-carbonate sediment, 10399 #7K (b) red clay, 10400 #8K.

were not entirely retained by Al_2O_3 columns. It is also possible that colloidal sized particles of iron and manganese oxy-hydroxides were generated during shaking. Our work has shown that americium is strongly adsorbed onto these minerals and the presence of even minute quantities of such material would substantially lower the observed R_d .

5.4.2. "Second Distribution Ratios"

These experiments confirmed that the americium remaining with the solution phase was different to the sorbed americium. The distribution ratios obtained when the solution removed after the first R_d determination was contacted with fresh sediment were much lower than they were in the first experiment. Distribution ratios obtained in this way are given in Table 5.3. and it can be seen that the second R_d values are several orders of magnitude lower than values obtained for the same solid/solution ratio when the fresh spiked sea water was used. It can be seen that (i) When the initial concentration was low, i.e. when almost all the high- R_d species had been removed in the first sorption then the second R_d was very low, i.e. < 100 . (ii) When the initial concentration was slightly higher, i.e. when some high- R_d species remained after the first sorption then the second R_d rose to between 200 and 400 if the solid/solution ratio was kept low in the second sorption ($< 12\text{g/l}$). At higher second solid/solution ratios the effect of the higher proportion of low- R_d species was again apparent and the second R_d dropped to 60.

5.4.3. Desorption

It can be seen from Tables 5.1. and 5.2. and from Figure 5.7. that the desorption R_d values were higher than sorption R_d values although at low solid/solution ratios the desorption R_d values were not significantly different from R_H , i.e. the value which would have been observed if no low- R_d species had been present. It seems likely, therefore, that the americium sorption/desorption reaction is not as irreversible as has been hitherto supposed and that the large difference between sorption and desorption R_d values that have been observed by ourselves and others (Nea, 1983; Sanchez et al., 1981; Higgo et al., 1983; Barney et al., 1980) can be at least partially explained by the presence of some low- R_d americium which was removed after the sorption stage. Sanchez, Schell and Sibley (1981) have reported not only very high desorption as compared with sorption distribution ratios but also found that the R_d for americium dropped even more sharply with increasing solid/solution ratio than it did in

	Tube No.		Sediment Concentration		Second R _d Experiment.				Equivalent First R _d for same solid/ soln. ratio ml/g.		
	1st R _d	2nd R _d			Am conc. in solution		R _d ml/g				
			Initial Bq/l	Final Bq/l							
Red clay 10400 8K.	362	368	381	6.49	22.7	1.3	9.72	0.50	206	25	2.6 x 10 ⁵
	366	364	0.91	3.17	37.8	2.5	11.06	0.75	372	44	4.7 x 10 ⁵
	355	405	272	11.91	2.93	.28	1.71	0.28	60	22	1.8 x 10 ⁵
	359	406	576	12.30	5.51	0.3	3.66	0.38	41	12	1.8 x 10 ⁵
	363	407	4.19	11.16	18.9	0.9	4.74	0.28	268	24	1.1 x 10 ⁴
	363	408	4.19	55.44	14.2	0.7	3.38	0.26	58	6	2.0 x 10 ⁵
	367	403	0.97	11.00	27.1	1.8	5.26	0.54	377	51	2.0 x 10 ⁵
	367	409	0.97	73.4	23.4	1.5	3.94	0.35	67	8.0	4.5 x 10 ⁴
high-carbonate sediment.	342	348	4.95	9.145	30.3	2.6	11.73	0.47	173	21	2.0 x 10 ⁵
	346		1.11	4.045	61.6	4.7	14.90	0.70	775	120	4.0 x 10 ⁵

Table 5.3. Distribution ratios obtained when the liquid phase remaining after the first R_d experiment was contacted with fresh sediment.

our experiments. They were working with estuarine sediments with high organic carbon contents and the formation of organic complexes may have led to remobilisation of the americium and a situation in which the amount of low- R_d species was proportional to the sediment concentration, i.e. to the type of behaviour shown in Figure 5.2.

5.5. Neptunium

Because ^{237}Np was used instead of ^{235}Np the concentration of neptunium was four orders of magnitude higher than in previous experiments. Nevertheless distribution coefficients were unchanged (i.e. about 500 for the red clay and about 4×10^3 for the high-carbonate sediment) showing that Henry's law is obeyed over this concentration range. This was also shown to be the case for americium and plutonium (Chapters 2-4) and is to be expected at these very low concentrations (Cerofolini, 1982).

Figure 5.8. shows the graphs of $\log R_d$ vs. $\log m/v$ for both sediments and Figures 5.9. and 5.10. are the plots of $\log (C_0 - C)/C$ against $\log m/v$. On the same axes are drawn the theoretical curves that would have been observed if different percentages of the original neptunium had been in a non-separable form. The two sediments behaved rather differently and will, therefore, be discussed separately.

(i) High-carbonate sediment:- Because the R_d for this sediment was relatively high the final concentration in solution was low and the analytical precision poor. It appears, however, that the distribution ratio did not change with increasing solid/solution ratio and was the same for both sorption and desorption. It should be pointed out, however, that with an R_d of only 10^3 , as compared with the 10^6 found for americium, the system would be far less sensitive to the presence of small amounts of a low- R_d species and it can be seen from Figure 5.9. that less than about 0.2% of a species with $R_d = 0.1$ would not have been detectable. The second distribution ratios obtained with the solution remaining, after the first R_d determination were not significantly different from the first distribution ratios, so in none of the three sets of experiments is there any indication that more than one species is present.

(ii) Red-clay:- The graph of $\log R_d$ vs. $\log m/v$ was horizontal for solid/solution ratios greater than about 0.016 but shows a rather surprising upward turn at the two lowest points and this is reflected in the shape of the plot of $\log (C_0 - C)/C$. It can be explained by

Table 5.4. Neptunium Distribution Ratios

Sediment	Tube No.	Sediment Concentration g/l	Concentration in solution after			Distribution Ratio		
			Sorption Bq/l	Desorption Bq/l	Contacting Sorption Soln. with fresh sediment	Sorption ml/g	Desorption ml/g	Second Sorption on fresh sediment
Red Clay, 10400 //8K	449	163.86	2.92±0.26	1.60±0.10	-	507±48	765±60	-
	450	68.56	6.45±0.16	5.09±0.23	-	466±26	561±38	-
	451	31.60	12.77±0.95	8.08±0.37	-	487±30	752±51	-
	452	16.40	26.20±3.15	12.75±0.30	-	430±27	856±51	-
	453	5.72	48.63±3.51	22.83±0.85	12.51±1.09	579±38	1204±89	462±7
	454	1.77	90.36±1.95	23.21±0.68	51.35±2.04	749±62	2293±243	458±18
Carbonate Sediment, 10399 // 7K	431	162.55	0.40±0.12	0.0±0.1	-	3229±1350	-	-
	432	61.96	0.61±0.35	0.54±0.13	-	5533±2619	-	6046±1464
	433	30.42	2.37±0.19	1.61±0.14	-	2878±288	-	4112±408
	434	15.92	2.72±0.38	2.95±0.36	-	5780±566	-	4245±554
	435	6.36	10.37±0.33	7.57±0.59	0.33±0.18	3035±301	5822±75	3883±215
	436	1.74	25.70±0.56	17.34±0.80	2.93±0.13	4125±229	930±33	5399±399

²³⁷Np concentration in solution before sorption 209.8±9.6 Bq/l, i.e. $(3.37±0.15) \times 10^{-8}$ Moles/l.

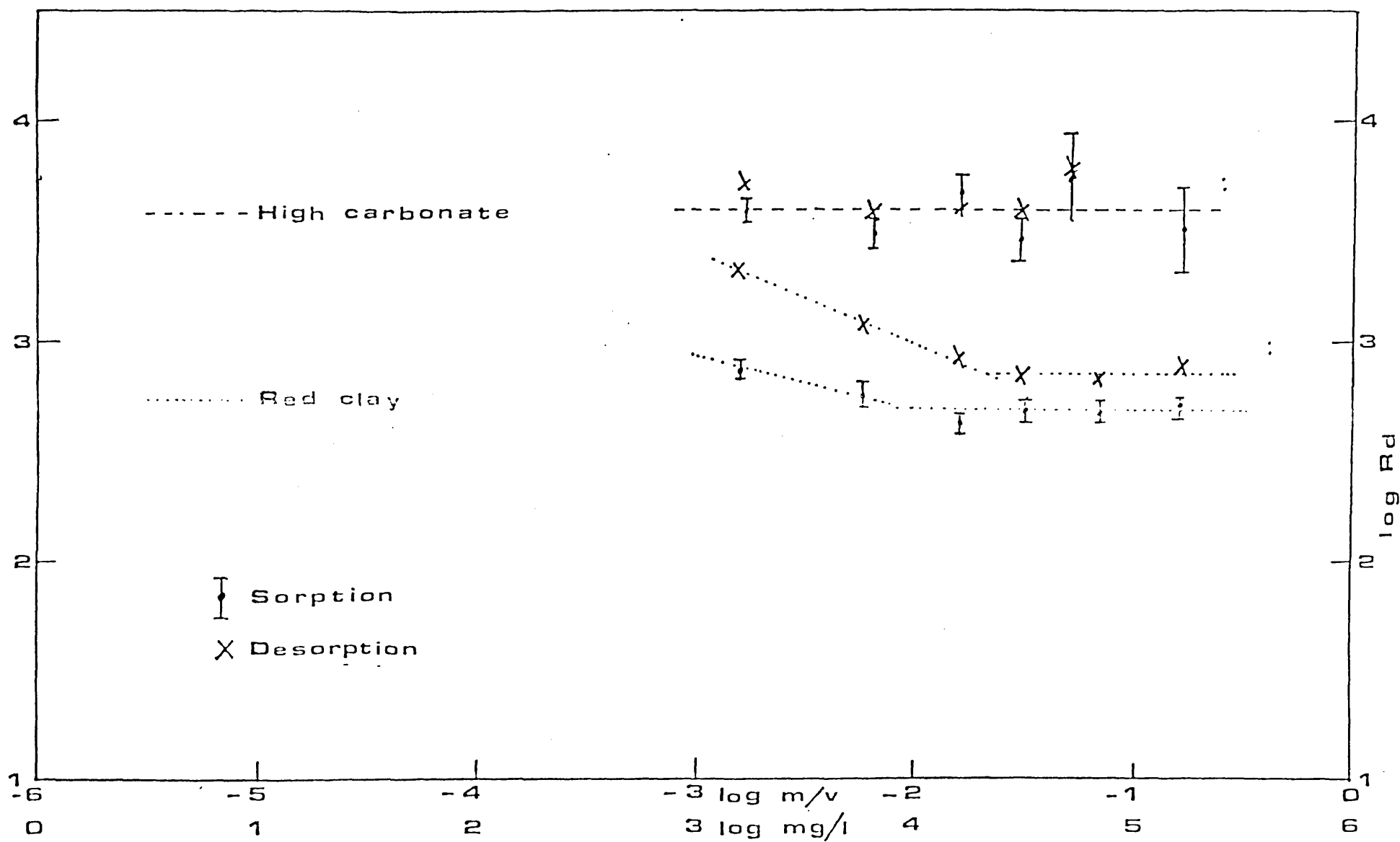


Figure 5.8. Sorption and desorption R_d 's at different solid/soln ratios for neptunium on (a) the high-carbonate, 10399 #7K (b) the red clay 10400 #8K.

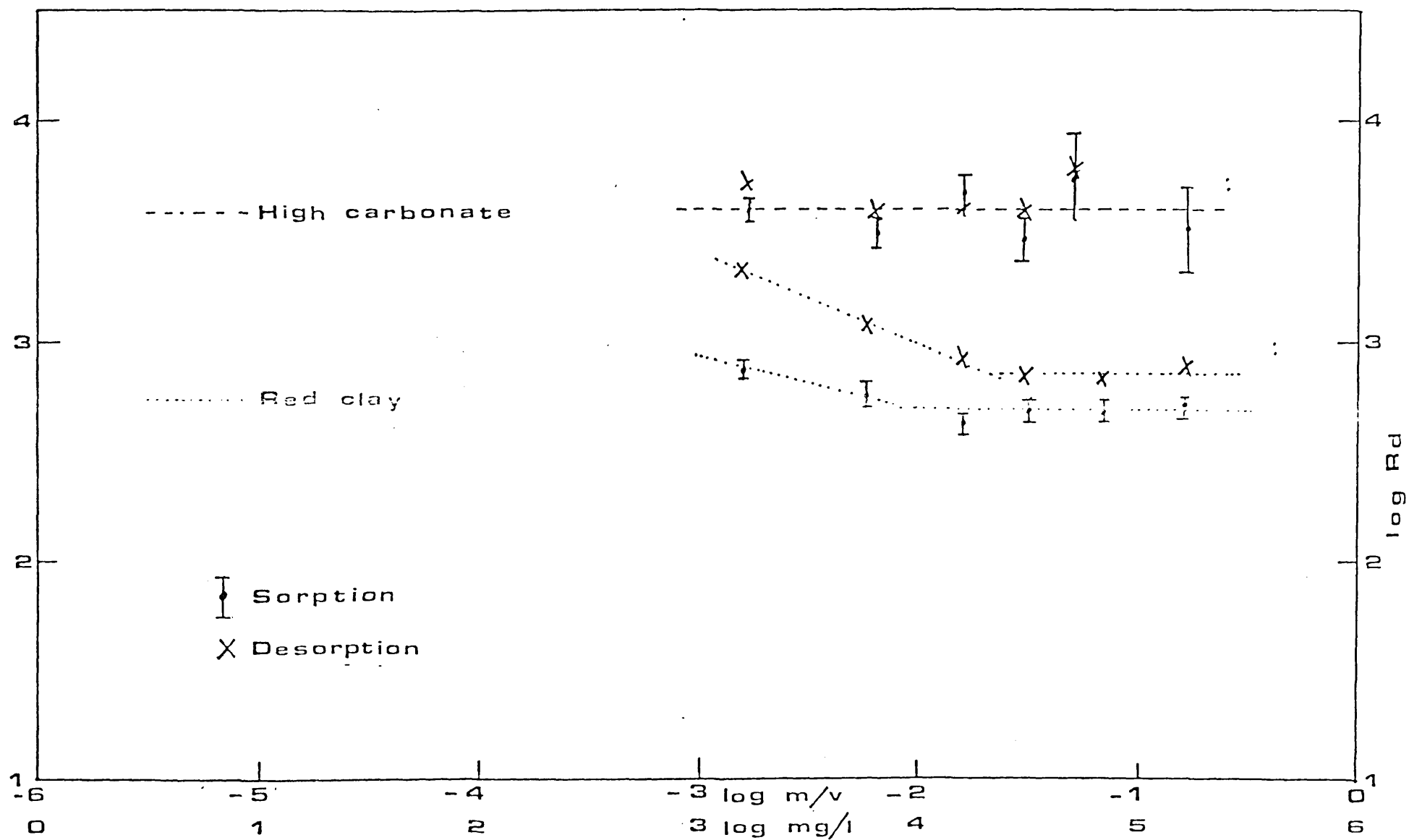


Fig. 5.8 Sorption and desorption R_d 's at different solid/soln ratios for neptunium on (a) the high-carbonate, 10399 #7K (b) the red clay 10400 #8K.

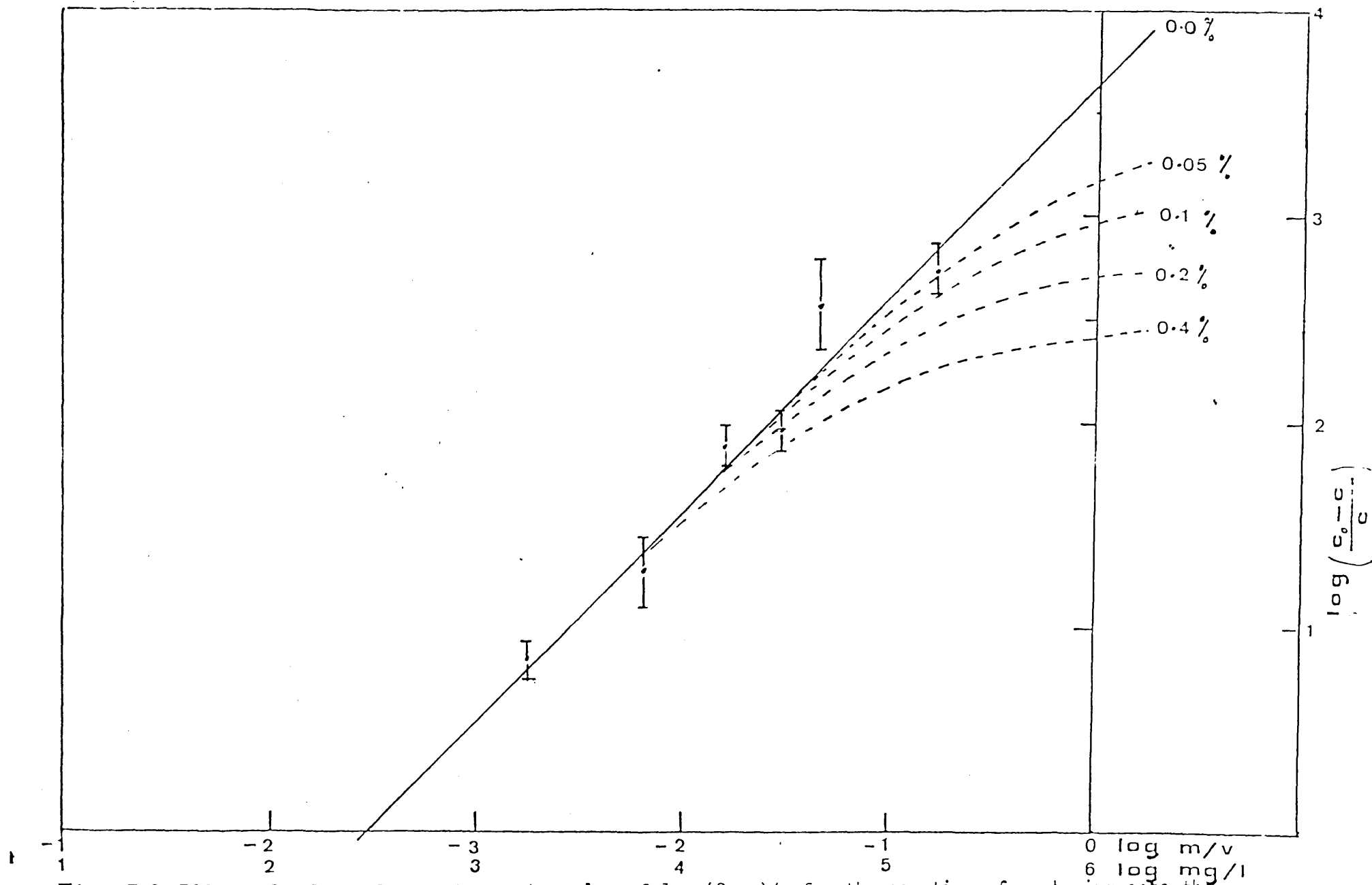


Fig. 5.9 Effect of solid/soln. ratio on the value of $\log (C_0 - c)/c$ for the sorption of neptunium onto the hig-carbonate sediment 10399 #7K. Dotted lines represent theoretical curves for different percentages of a non-separable species. ($R_H = 3980$, $R_L = 0.1$)

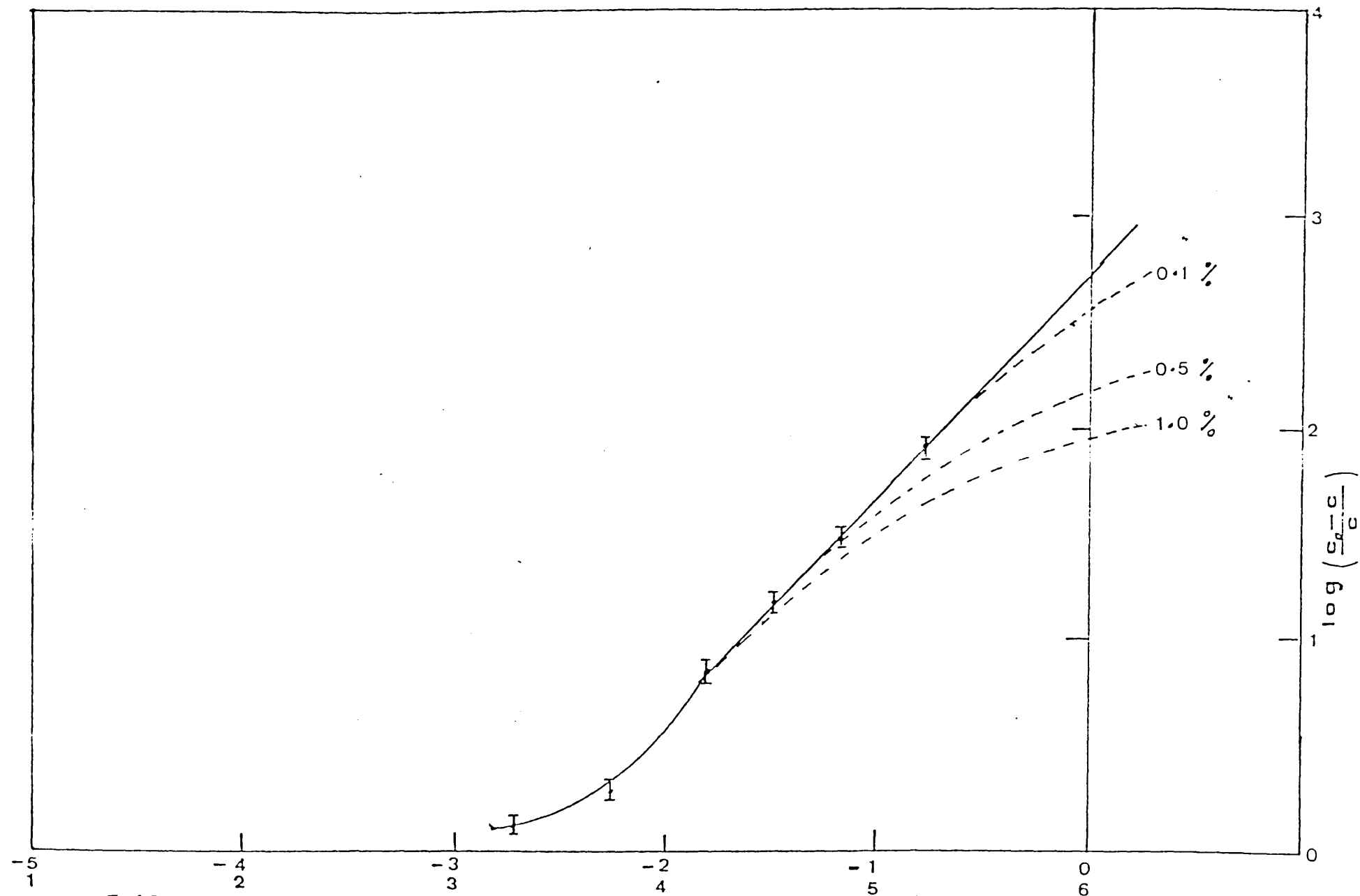


Fig. 5.10 Effect of solid/soln ratio on the value of $\log (C_0 - c)/c$ for sorption of neptunium on red clay, $10400 \pm 8K$. Dotted lines represent theoretical curves for different percentages of a non-separable species ($R_H = 500$, $R_L = 0.1$).

assuming that most of the neptunium was adsorbed with a low R_d (approximately 400) but that some (approximately 20%) was sorbed with a high R_d , i.e. a situation similar to that shown in Figure 5.4.(b) has been encountered. This would also explain the fact that the difference between the sorption and desorption distribution ratios increased as the sediment concentration decreased (since at low solid/solution ratios the ratio of high- R_d to low- R_d species would be greater on the sediment than in the solution after sorption). It would also explain the fact that when the liquid phase remaining after the first R_d determination was contacted with fresh sediment the second R_d was lower than the first R_d at high solid/solution ratios (since most of the high- R_d species would have been removed during the first sorption). It is difficult however to make any suggestions as to what these two species might be and too much should not be read into two experimental points. From Figure 5.10. it can be seen that, because the R_d of the main species is so low, less than about 0.5% of a non-separable species would not have been detectable.

5.6. Plutonium

The sorption behaviour of plutonium was very different for the red clay and the carbonate sediment and the two sets of experiments will be considered separately.

5.6.1. Red Clay

The results obtained with the red clay, 10400 # 8K are given in Table 5.6. and Figures 5.11 and 5.12.

5.6.1.1. Sorption

It can be seen from Figure 5.11. that the graph of $\log (C_0 - C)/C$ vs. m/v is very similar in shape to that obtained for americium and that the distribution ratio tends to 7.9×10^4 as m/v becomes very small. The experimental curve fits very closely the theoretical one calculated for 99.95% Pu with $R_d = 7.9 \times 10^4$ and 0.05% with $R_d = 0.1$. It is interesting to note that the percentage of low R_d species appears to be higher than for americium on the same sediment (and using 0.22 μ filters). This could mean that whereas for americium all the low- R_d nuclide was particulate, some of the plutonium was complexed in other ways. Selective leaching experiments, both ours and others (Cole, 1984; Edgington, 1980) show that whereas americium appears to be adsorbed non-selectively to all phases plutonium is preferentially adsorbed to

organic matter and to iron and manganese phases. Complexes with these phases may be formed and then re-solubilised thus contributing to the low- R_d fraction. From the shape of the $\log (C_0 - C)/C$ vs. $\log m/v$ graph and from the slope of the $\log R_d$ vs. $\log m/v$ graph it appears that the amount of low- R_d species is not proportional to the amount of sediment present. The low- R_d species is clearly in the reduced form since at high solid/solution ratios (when most of the Pu in solution would be the low- R_d species) all the plutonium was in the reduced form. This would be expected if the low- R_d species was the result of sorption to the sediment since all the evidence to date indicates that reduction occurs during sorption.

At lower solid/solution ratios, when final solution concentrations are higher and a higher proportion of the plutonium remaining in solution is the high- R_d species there is still some Pu(V + VI) in solution after sorption. The effect of this increasing proportion of high- R_d species was very clear in the experiments in which the solution remaining after the first sorption was contacted with fresh sediment, i.e. when second distribution ratios were determined.

5.6.1.2. "Second Distribution Ratio"

These "second" distribution ratios are plotted together with the first distribution ratios in Figure 5.12. It can be seen when the solid/solution ratio was high in the first sorption (and very little high- R_d species was therefore present in the initial solution used in the second sorption) that the second R_d was very low. As the solid/solution ratio used in the first sorption decreased and the proportion of high- R_d species in solution phase increased so did the second R_d . These results confirm, therefore, the conclusion reached in the previous section that two different plutonium species were present in the solution phase during these experiments.

5.6.1.3. Desorption

The desorption distribution ratios are also plotted in Figure 5.12. They are all higher than the corresponding sorption ratios. When only a small amount of sediment is present during sorption the proportion of high- to low- R_d species sorbed onto the sediment will be higher than in the original solution and the desorption R_d will therefore be higher than the sorption R_d . From our results it appears that only in the very highest solid/solution ratio experiment was enough low- R_d species

Table 5.5. Plutonium Sorption and Desorption on Red Clay.

Tube No.	Sediment Concent. g/l	Concentration in Solution (Bq/l) after					Distribution Ratio			Second Sorption on fresh sediment $\frac{\text{ml/g}}{10^4}$	% in Reduced III + IV) Form after Sorption
		Sorption	First Desorption 1 hour	Second Desorption 19 hours	Third Desorption 36 day	Contacting Sorption Solution with fresh	Sorption $\frac{\text{ml/g}}{10^4}$	19 hour Desorption $\frac{\text{ml/g}}{10^4}$	36 day Desorption $\frac{\text{ml/g}}{10^4}$		
390	163.16	20.4±1.6	17.0±1.2	6.0±0.4	5.2±0.5	3.51±0.25	0.97±0.08	3.43±0.27	3.90±0.39	0.0023±0.0003	102±2
391	65.57	26.5±1.4	13.3±1.0	15.7±0.2	5.0±0.9	6.40±0.38	1.87±0.12	3.24±0.16	10.07±1.93	0.0017±0.0002	105±7
392	33.45	35.1±2.2	10.0±0.9	8.3±0.7	8.5±0.8	9.25±0.81	2.76±0.18	12.07±1.14	11.78±1.25	0.0079±0.0010	94±7
393	17.79	39.6±2.0	19.9±1.4	11.0±1.1	13.9±0.9	13.41±1.02	4.61±0.27	16.98±1.85	13.49±1.10	0.0053±0.0008	108±8
394	68.97	83.9±3.3	44.0±2.8	34.8±2.0	34.4±1.9	22.02±2.08	5.60±0.28	13.83±1.03	13.99±0.99	0.0081±0.0009	68±6
395	19.02	260.4±13.8	116.3±5.4	176.3±12.7	96.8±4.1	44.45±2.03	6.51±0.31	9.82±0.84	17.98±1.13	0.0143±0.0011	37±2

Note ^{238}Pu concentration before sorption (34133±1502) Bq/l i.e. $(2.337\pm0.104) \times 10^{-10}$ mol/l

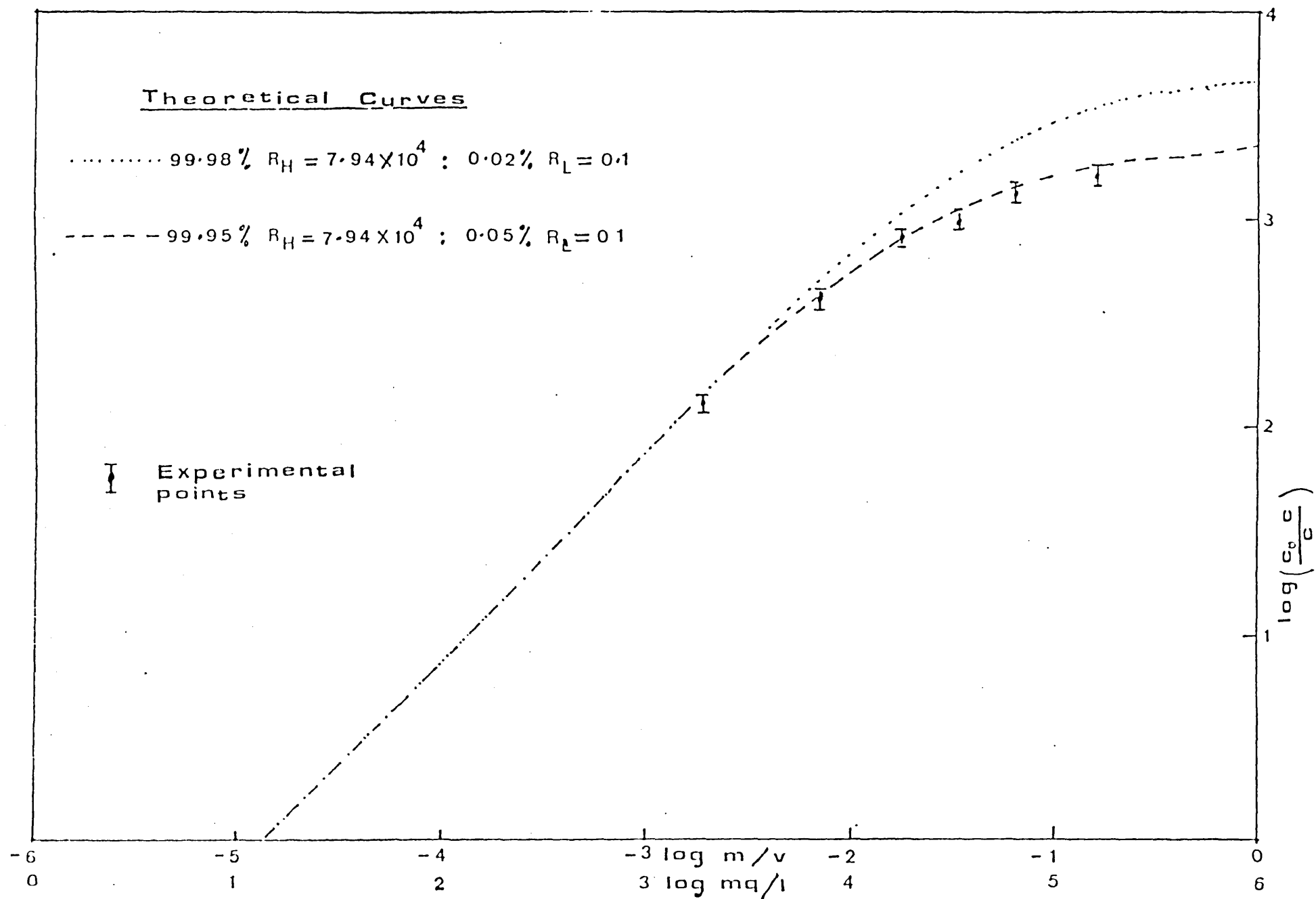


Fig 5.11 Effect of solid/soln ratio on the value of $\log(C_o - c)/c$ for the sorption of plutonium on red clay, 10400 #8K.

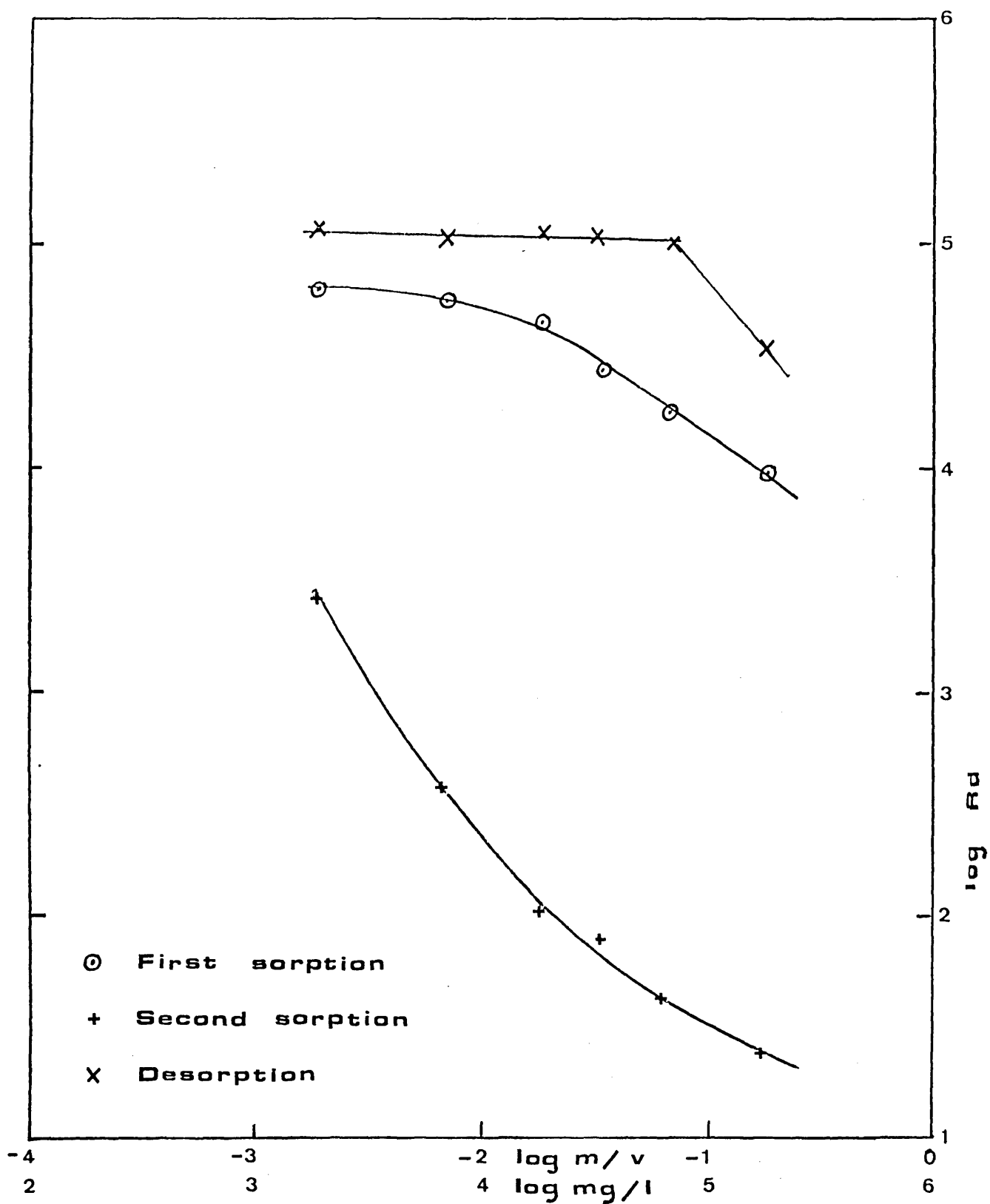


Fig. 5.12 Sorption, "second sorption" and desorption R_d as a function of m/v for the red clay, 10400, 8K.

adsorbed to significantly lower the desorption R_d . For the others the desorption distribution ratios were all between 1×10^5 and 2×10^5 . Only about 10% of the observed difference between sorption and desorption distribution ratios can be explained by the presence of some low- R_d species and we must therefore conclude that the sorption/desorption reaction is to some extent irreversible. Desorption distribution ratios were very similar after 19 hours and 36 days confirming our previous results which indicated that it will be a very long time (if ever) before the desorption R_d drops to the sorption value.

5.6.2. Carbonate Sediment

Two sets of samples of the high-carbonate sediment, 10399# 7K were shaken with sea water which had an initial concentration of 35000 Bq/l ($2.33 \times 10^{-10} M$) ^{238}Pu . The solid/solution ratio ranged from about 0.002 to 0.2 (2g/l - 200g/l) and a series of experiments were carried out on them. Phase separation was always carried out by centrifuging for 90 minutes at 7000 rpm. (5280g) followed by filtration through 0.22 μ millipore filters.

The first set of sediments (Tubes 370-375) was i) analysed after 24 days and the distribution ratios calculated. ii) the supernate remaining after the first sorption was transferred to tubes containing 0.1g quantities of fresh sediment and a second distribution ratio determined. iii) Fresh unspiked sea water was added to the loaded sediment and the desorption distribution ratio was measured.

The second set of sediments was (i) analysed after 29 days (exactly 5g of the solution phase removed) for reduced Pu(III + IV) and oxidised Pu(V + VI) as well as total Pu, (ii) after 128 days the solution phase was again analysed but this time the excess solution was added to fresh sediment keeping the solid/solution ratio the same as in the original sorption experiments.

The results of these experiments are given in Tables 5.6. - 5.8. and will now be discussed in detail.

5.6.2.1. Sorption

Table 5.6. shows the three sets of distribution ratios together with the percent reduced Pu in solution after phase separation. It can be seen that for solid/solution ratios greater than about 0.04 (40g/l) the distribution ratios were remarkably low (100 to 200 ml/g instead of the usual $>10^4$ ml/g) and there was no significant increase

in R_d as the contact time increased from 24 to 128 days. Furthermore, at these high solid/solution ratios the plutonium in solution was virtually all in the oxidised (V + VI) forms. At low solid/solution ratios, on the other hand, the plutonium was mostly in the reduced (III + IV) forms and distribution ratios were greater than 10^4 . For the two samples containing the least sediment the distribution ratio after 129 days did seem to be significantly greater than after 29 days.

We thus have the situation that in carbonate sediments plutonium behaves quite differently at high and low solid/solution ratios. The obvious explanation is that at high solid/solution ratios carbonate complexes are formed which are sorbed less strongly than are PuO_2^+ and Pu(OH)_3^+ which are the forms in which plutonium exists in sea water in the absence of sediment. (this thesis Chapter 4; Cleveland et al., 1983; Rees and Nash, 1983; Edgington, 1980). No attempt was made to determine whether the plutonium was in the V or the VI form but the fact that neptunium did not behave in the same way indicates that we were probably dealing with Pu(VI) complexes, since neptunium has been shown to be in the V form in sea water and in our laboratory experiments. This is in agreement with the predictions of Skytte Jensen which give $\text{Pu}_2(\text{CO}_3)_2^{2-}$ and $\text{PuO}_2(\text{CO}_3)$ as the most likely carbonate species at pH 8.2 and Eh about 400 mv. The bicarbonate $\text{Pu(O}_2)(\text{OH})_2(\text{HCO}_3)^{-1}$ may also be present. Sullivan and Woods (1982) have studied the interaction of Pu(VI) with bicarbonate and concluded that in sea water soluble Pu(VI) would exist in roughly equal amounts as $\text{PuO}_2(\text{OH})_2$ and $\text{Pu(OH)}_2(\text{HCO}_3)^{-1}$ with about 15% as $\text{PuO}_2(\text{CO}_3)_2^{2-}$.

At this point it is worth discussing the behaviour of plutonium in Lake Mono. This is a saline, alkaline (pH 10) lake in Eastern California in which the dominant anions are CO_3^{2-} and HCO_3^- rather than Cl^- . The total (CO_3^{2-}) in Lake Mono (0.3M) is about three orders of magnitude greater than in sea water (10^{-6}M). In this lake the concentration of plutonium in the water column is about two orders of magnitude greater than is usual for surface waters and the R_d observed between sediment and water is about 10^3 , i.e. one to two orders of magnitude lower than generally observed for surface waters. Simpson et al. (1980, 1982) suggested that complexing by carbonates was probably responsible for this behaviour and this view is supported by the later work of Anderson et al (1982) and Cleveland et al. (1983a).

Table 5.6. Plutonium Distribution Ratios on Carbonate Sediment 10399//7K. SORPTION.

Tube No.	Shaking time days	Sediment Concentration g/l	Solution Concentration after sorption Bq/l	Distribution Ratio ml/g	% in Reduced III & IV form after sorption	pH after sorption
370	24	205.5	1175±62	133±9	-	7.84
376	29	171.6	1257±89	148±7	4.1±1.2	
376	128	206.0	969±75	166±8	2.7±0.3	
371	24	89.14	1503±161	237±28	-	8.07
377	29	80.81	2041±298	190±9	3.1±0.5	
377	128	96.97	1578±83	212±7	3.0±0.2	
372	24	41.57	2022±142	372±31	-	8.07
378	29	40.02	2120±88	368±17	4.1±0.3	
378	128	48.02	2441±124	270±13	3.0±0.2	
373	24	15.64	1863±59	406±24	-	8.09
379	29	19.77	115±8	14,596±795	69±6	
379	128	23.73	73±4	19,731±1030	45±5	
374	24	7.71	1103±73	3,788±303	-	8.11
380	29	7.67	1615±115	2,562±120	21±2	
380	128	9.20	142±8	26,016±1282	43±4	
375	24	1.85	233±18	76,489±600	-	8.18
381	29	1.81	314±26	57,920±2765	49±5	
381	128	2.17	140±7	107,208±5218	71±5	

Note Before Sorption

Pu-238 concentration = (34133±1502) Bq/l, i.e. $(2.337 \pm .104) \times 10^{-10}$ moles/l

pH = 8.2.

% in reduced form = 29%.

Although the situation in Lake Mono is clearly very different from that in our experiments, there are parallels and it is interesting to note that there is evidence of significant carbonate complexation in natural systems.

5.6.2.2. Desorption

Sediments from Run 1 were taken through four desorption steps. After each stage the desorption solution was completely replaced with fresh unspiked sea water. The first three desorptions were short, i.e. a one hour wash followed by two one day desorptions, but the final desorption was continued for 61 days. Only one (128 day) desorption was carried out on the sediments from Run 2. The results are given in Table 5.7. and plotted in Figure 5.12. It can be seen that they were rather erratic for the short desorption stages, probably because equilibrium had not been reached and there is no clear indication that there is a readily desorbable fraction. Three out of the four highest solid/solution ratio R_d are not very different from the desorption R_d and, as for sorption, virtually all the plutonium in solution was in the oxidised (V + VI) forms. It may be, therefore, that the plutonium-carbonate sorption-desorption reaction is reversible. At low solid/solution ratios the plutonium behaved in much the same way as it does with the red clay. Desorption R_d values were significantly higher than sorption R_d values but it is impossible to estimate to what extent this was due to the presence of small amounts of a non-separable species (which may have lowered the sorption R_d) and to what extent it was due to an irreversible sorption reaction.

5.6.2.3. "Second" Distribution Ratios

The results of the experiments in which the solution remaining after the first distribution ratio experiment were contacted with fresh sediment are given in Table 5.8. They confirmed that different species were present at different solid/solution ratios and threw some further light on their behaviour. The two extreme cases will be considered separately.

(i) Solid/solution ratio low in the first R_d experiment: Here behaviour was similar to that observed with the red clay, i.e. second R_d values were very much lower than first R_d values indicating that most of the high- R_d species had been removed in the first sorption. The plutonium remaining in the solution phase after the first sorption was mostly the low- R_d species. (Possibly completely non-sorbable particulate material) and

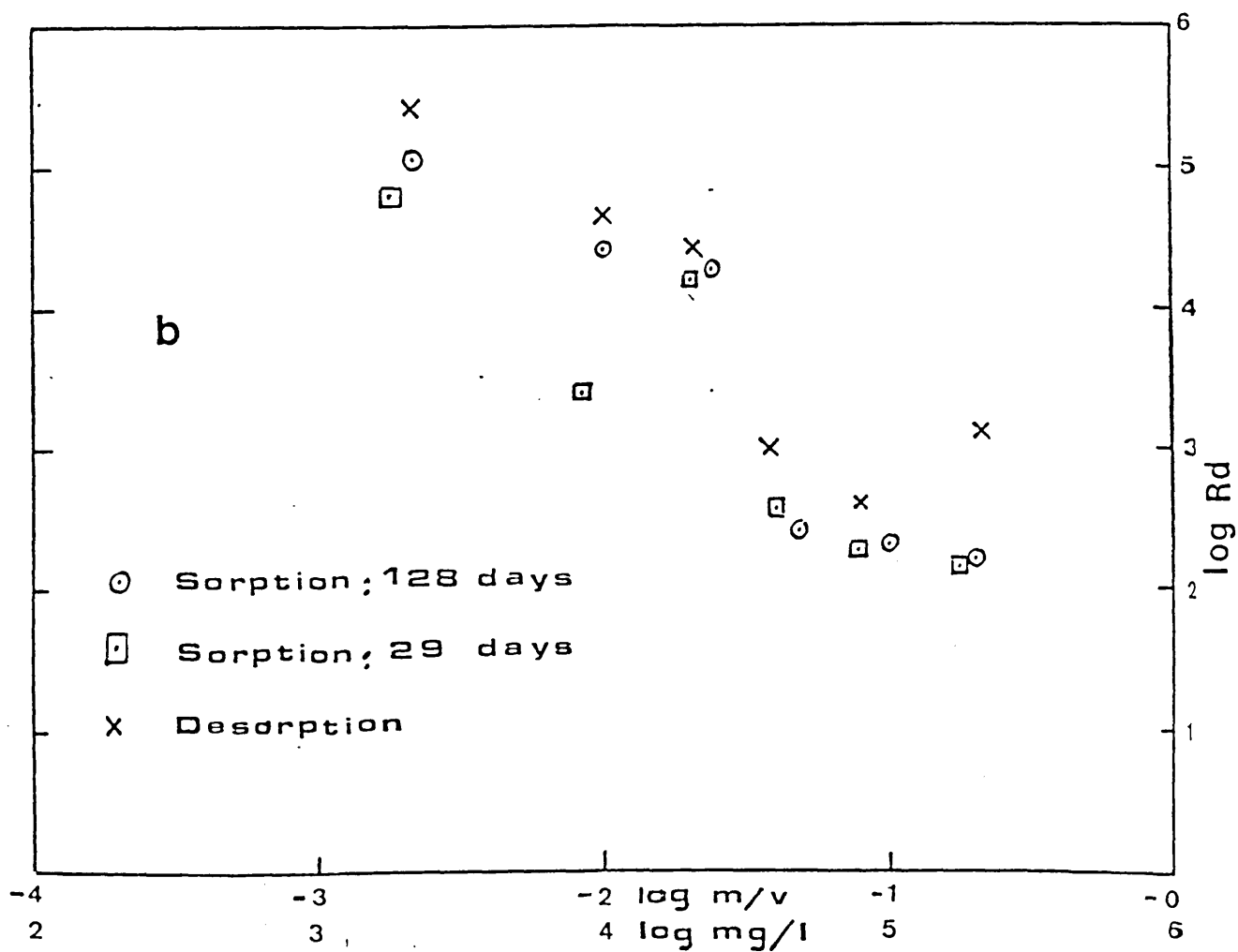
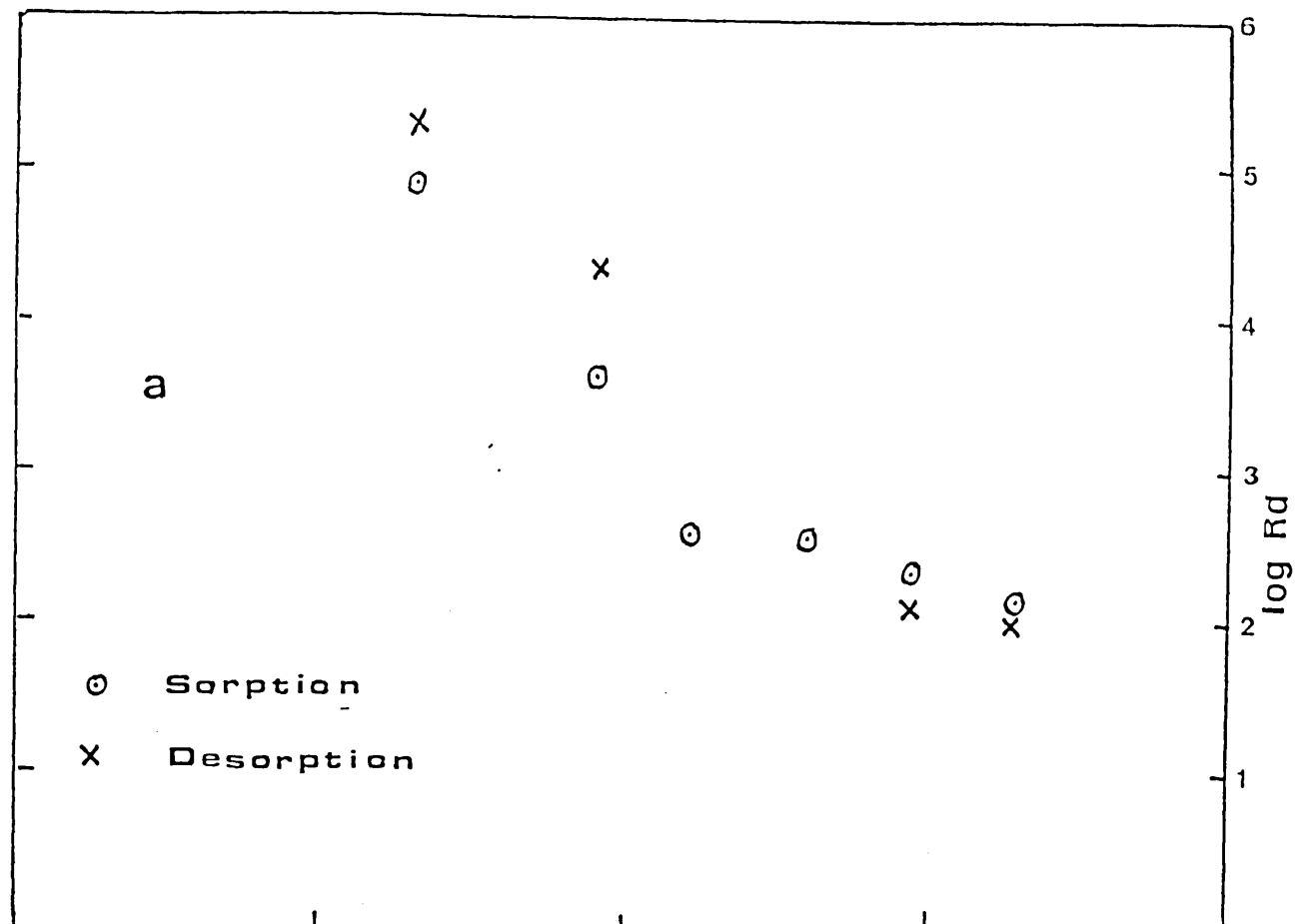


Fig. 5-13 Sorption and desorption Rd for plutonium on (a) high-carbonate sediment, 10399 #7K (b) red clay, 10400 #8K

Table 5.7a. Plutonium Desorption from Carbonate Sediments. - Run 1.

Tube No.	Sediment Concentration g/l	Solution Concentration (Bq/l) after					Distribution Ratio		% in Reduced (III + IV) form after 61 day desorption
		Sorption	1st Desorption 1 h.	2nd Desorption 1 day	3rd Desorption 1 day	4th Desorption 61 day	Sorption ml/g	61 day Desorption ml/g	
370	205.5	1175±62	850±57	532±26	563±35	1453±150	133±9	96±11	2.4±0.3
371	89.14	1503±161	1222±69	-	975±76	2491±98	237±28	119±8	2.4±0.3
374	7.71	1103±73	696±57	378±42	483±29	58±2	3,788±303	68,100±4,200	31.0±2.4
375	1.85	233±18	79±5	81±8	86±4	78±3	76,489±600	223,600±12,600	84.7±6.0

Table 5.7b. Plutonium Desorption from Carbonate Sediment -Run 2.

Tube No.	Sediment Concentration g/l	Solution Concentration after		Distribution Coefficient after	
		Sorption Bq/l	Desorption Bq/l	Sorption ml/g	Desorption ml/g
376	206.0	969 $\pm$ 75	158 $\pm$.8	166 $\pm$ 8	1256 $\pm$ 84
377	96.97	1578 $\pm$ 83	1218 $\pm$ 33	212 $\pm$ 7	394 $\pm$ 11
370	48.02	2441 $\pm$ 124	960 $\pm$ 47	270 $\pm$ 13	982 $\pm$ 48
379	23.73	73 $\pm$ 4	76 $\pm$ 5	19731 $\pm$ 1030	25675 $\pm$ 1626
380	9.20	142 $\pm$ 8	94 $\pm$ 8	26016 $\pm$ 1282	43051 $\pm$ 4167
381	2.17	140 $\pm$ 7	75 $\pm$ 4	107208 $\pm$ 5218	262120 $\pm$ 16971

the effect of this was to lower the observed distribution ratio by two to three orders of magnitude.

(ii) Solid/solution ratio high in the first R_d experiment: When the solid/solution ratio was high for both the first and second sorptions the distribution ratio was the same both times and virtually all the plutonium was in the oxidised (V + VI) forms after both sorptions. This must mean either that only one plutonium species was present in solution or that equilibrium between different species was rapidly re-established as one species was removed from solution. Because the R_d values were low, the presence of the usual small amount of non-separable species would not have been detectable.

When the solid/solution ratio in the second sorption was low the distribution ratio rose to $>10^3$ and the percentage of oxidised Pu(V + VI) dropped. Clearly, therefore, in the absence of large quantities of sediment some of the plutonium carbonates have reverted to more readily sorbable species. The fact that the second R_d values are intermediate between the values of 10^2 and $>10^4$ that are normally obtained for first R_d at high and low solid/solution ratios, respectively, indicates that both high- and low- R_d species were now present. These results also show that the presence of high concentrations of sediment were necessary to keep the plutonium in the low R_d carbonate form. The carbonate and bicarbonate contents of the solution phases were obviously the same at the end of the first sorption and the beginning of the second, so unless they decreased during the second sorption period the presence of the low- R_d complexes cannot be entirely a function of carbonate and bicarbonate concentration. Possibly complexes are formed at the surface of the sediment and re-solubilised. Once in solution they could revert to other forms which could either be adsorbed or once again react with the sediment to form low- R_d species.

5.7. Summary and Conclusions

Table 5.9. summarises the results of this investigation. It has been shown that the batch method for determining distribution ratios is sensitive to the solid/solution ratio used in the experiments, particularly if the R_d of the nuclide being studied is high. The magnitude of this effect is, to a large extent, dependent on the experimental system used. A critical parameter is the efficiency of phase separation after equilibrium, but it will also depend on whether or not complexes are formed with trace constituents of the sediments or sea water and on the size and charge of any micro-particulate

Table 5.8. Plutonium distribution ratios : Solution removed after first sorption contacted with fresh sediment - carbonate sediment 10399 # 7K.

Tube No.		Sediment Conc		Solution Concentration		Distribution Ratio		% in reduced (III + IV) forms	
Original Fresh Sediment		First Sorption g/l	Second Sorption g/l	Before starting 2nd sorption Bq/l	After 2nd sorption Bq/l	First ml/g	Second ml/g	After First sorption	After Second Sorption
376	480	171.63		797±62	28±1	148±7	134±14	4.1±1.2	2.7±0.3
377	481	80.81		1436±76	75±1	190±9	189±16	3.1±0.5	3.0±0.2
378	482	40.02		2161±110	168±12	368±17	253±23	4.1±0.3	3.0±0.3
379	483	19.77		69±6	28±2	14596±795	64±9	69±6	45±5
380	484	7.67		138±8	60±4	2562±120	142±18	21±2	43±4
381	485	1.81		140±7	77±2	57920±2765	353±44	49±5	71±5
370	410	205.5	6.11	1173±63	60±3	133±9	3053±190	-	43±2
371	411	89.14	5.76	1502±164	169±6	237±28	1384±168	-	23±2
372	412	41.57	6.22	2018±141	245±9	372±31	1104±95	-	22±2
373	413	15.64	4.86	1860±70	212±12	406±24	1604±73	-	37±3
374	414	7.71	5.26	1103±82	165±7	3788±304	1076±92	-	53±4
375	415	1.85	4.67	234±23	127±6	76484±600	180±32	-	101±1

material present in the system. If more than one stable species occurs in solution then the observed R_d will be close to that of the species with the highest R_d but will decrease as the solid/solution ratio increases. Because of this environmentalists, determining distribution ratios in natural waters at very low solid/solution ratios are likely to observe higher and more reproducible values than those obtained in the laboratory but the effect of a small amount of a low- R_d species is likely to pass unnoticed.

In general environmentalists tend to use very low sediment concentrations when determining distribution ratios and to use rather different experimental methods (Voice et al., 1983; Duursma, 1970; Yuan-Hui Li, 1984) to those used by workers in the field of waste management. Nevertheless, the theoretical conclusions described in Section 5.2. should apply. Yuan-Hui Li et al (1984) investigated the sorption of a number of nuclides to red clays and found that although the distribution ratio remained roughly constant as the sediment ratio decreased from 1.7 to 0.1 g/l (as predicted in Section 5.2.) there was a sharp increase at even lower sediment concentrations. It seems probable that at the very low sediment concentrations another effect such as sorption to container walls is coming into play.

In addition to the above effects which are probably fairly general, the behaviour of plutonium when contacted with high-carbonate sediments is particularly noteworthy and could have a significant effect on radio-nuclide migration models. Here the R_d values dropped from the generally accepted value of $>10^4$ to around 100 as the solid/solution ratio increased. It was shown that at high solid/solution ratios the plutonium in solution was all in the oxidised (V + VI) forms and it seems probable that Pu(V) + Pu(VI) carbonates were formed which, like U(VI) carbonates are less strongly sorbed.

Table 5.9. Effect of Solid/Solution Ratio. Summary of Results

	RED CLAY - 10040#8K			CARBONATE SEDIMENT 10399#7K		
	Sorption	Desorption R_d	Second Sorption R_d	Sorption	Desorption R_d	Second Sorption R_d
Am	R_d increased with decreasing solid/soln. ratio. Levelled off at 10^6 ml/g. % non-separable $\sim 0.03\%$ (0.22μ filters) $\sim 0.02\%$ (0.10μ filters).	$> \text{Sorption } R_d$	$<< \text{1st } R_d$	R_d increased with decreasing solid/soln. ratio. Levelled off at $1 \times 10^6 - 2 \times 10^6$ % non-separable $\sim 0.05\%$ (0.22μ filters). $0.02 - 0.03\%$ (0.10μ filters).	$> \text{Sorption } R_d$	$<< \text{1st } R_d$
Np	R_d constant at about 480 ml/g for solid/soln. ratio > 0.016 . Increase for two lowest solid/soln. ratios (580 + 750 ml/g) % non-separable $< 0.2\%$ (0.10μ filters).	$> \text{Sorption } R_d$ Difference greater for lower solid/soln. ratios.	Same as first R_d for high solid/soln. ratios.	R_d constant for all solid/soln. ratios. % non-separable $< 0.5\%$ (0.10μ filters).	$\approx \text{Sorption } R_d$	$\approx \text{1st } R_d$
Pu	R_d increased with decreasing solid/soln. ratios. Levelled off at 7.9×10^4 ml/g. % non-separable $\sim 0.05\%$ (0.22μ filters)	$> \text{Sorption } R_d$	$<< \text{1st } R_d$ Difference greatest at high solid/soln. ratios.	High Solid/Solution Ratios.		
				R_d low i.e. 100-300 ml/g. All in Pu(V+VI) form.	$\approx \text{Sorption } R_d$ All in Pu(V+VI) form.	$\approx \text{1st } R_d$
				Low Solid/Solution Ratios.		
				$R_d > 10^4$ ml/g. Mostly in Pu(III + IV) form.	$> \text{Sorption } R_d$ Mostly in Pu(III + IV) form.	$<< \text{1st } R_d$

CHAPTER 6

FINAL ASSESSMENT

6.1. Adsorption Mechanisms

Throughout this work attempts have been made to obtain a greater understanding of the mechanisms by which the elements studied were adsorbed from sea water by the sediments. This has been made extremely difficult by the complex nature of both the solid and the liquid phases. Nevertheless the following conclusions can be drawn:

(i) The sorption of caesium was mainly by ion exchange although a small amount may have been by a different mechanism with a high sorption capacity which was quickly exhausted.

(ii) Probably the most important factors influencing the sorption of the actinides and europium is the fact that at the pH of sea water they readily form hydrolysis products which deposit upon the solid phases. In general hydrolysable metal ions show increased adsorption when bulk solution conditions are suitable for hydrolysis. James and Healy (1972) have presented a model for the adsorption of hydrolysable metal ions in terms of simple electrostatic ion-solid and ion-solvent interactions. The physical representation of the model is that the ion-solvent interactions present a barrier to close approach of highly charged ions to the interface between a low dielectric constant solid and water. When the ionic charge is lowered by hydrolysis or ligand complex formation, the ion solvent interaction is decreased thus lowering the energy barrier. The ions may then approach closer to the interface which results in greater coulombic and short range interaction energies, which are more favourable to adsorption.

(iii) Beall et al., (1981) have shown that minerals such as apatite (calcium hydroxy fluorophosphate) fluorites and carbonates are all strong complexing agents for americium. It appears that in the case of apatite, a phosphate group complexes the cations onto the surface of the mineral. Chemisorption of this type is likely to have occurred to a certain extent with all the minerals.

(iv) Reduction by the Fe(II) - Fe(III) redox couple probably plays an important part in the sorption of the higher valence cations, Np(V), Pu(V) and Pu(VI). Beall et al. (1981) have shown that sorption is high along pyrite (Fe(II) sulphide) grains in minerals such as biotite and there is evidence (Bondietti and Francis (1979); Nelson and Lovett (1978)) that reduction occurs during sorption. It is clear from the experiments

described in Chapter 4 that different sediments adsorb plutonium at different rates and that the rate of adsorption is proportional to the ability of the sediment to catalyse the reduction of Pu(V) and Pu(VI) to Pu(IV). The sediment with the highest reducing ability was also the sediment with the highest iron content.

(v) At high carbonate concentrations pentavalent carbonate species such as $\text{PuO}_2(\text{CO})_3^{5-}$ and possibly hexavalent species are probably occurring. These are relatively poorly sorbed and only slowly (if at all) converted to the reduced positively charged species.

6.2. Waste Disposal

We are now in a position to assess much more accurately the likely mobility of the elements studied and to estimate the burial depth necessary to contain HLW. Sandia (1983) have developed computer codes for use in sensitivity studies of radionuclide migration in deep-sea sediments and, using risk methodologies developed for the US Environmental Protection Agency, have calculated the minimum permissible K_d as a function of burial depth for a number of radionuclides. Listed in the tables which they have drawn up are several radionuclides that, even if they were not sorbed at all by the sediment, would not adversely affect the performance of a subseabed repository. This is because of factors such as short half life, small inventory, inhibition of migration by ocean waters, low concentration factors in the food chain, type of radiation emitted and permissible dose. The critical K_d values for isotopes of the elements studied in this work have been extracted from these tables and are given in Table 6.1.

Table 6.1. Critical K_d in ml/g (from Sandia, 1983 Status Report)

	Burial Depth (m)				
	2	5	10	20	30
Am - 241	10^3	10^3	10^2	10	10
Am - 243	10^4	10^3	10^2	10^2	10
Pu - 238	10^2	10	0	0	0
Pu - 239	10^3	10^2	10^2	10	1
Pu - 240	10^3	10^2	10^2	10	10
Pu - 242	0	0	0	0	0
Np - 237	10^3	10^3	10^2	10	10
Cs - 137	10^2	1	0	0	0
Cs - 135	0	0	0	0	0
Eu - 145	10	0	0	0	0

Looking at each element individually and with this table in mind we can conclude that:

(i) Neither caesium isotope is likely to pose any hazard to man even if the burial depth is as shallow as five metres.

(ii) Europium has never been considered a hazard and was studied because of its similarity to actinides in the III oxidation state. Clearly a burial depth of two metres will be adequate to contain this nuclide.

(iii) Americium is the least likely of the three actinides studied to escape from the sediments. On all the sediments studied more than 99.95% of the Am was sorbed with a R_d of 10^6 , i.e. with a K_d two to three orders of magnitude greater than that for a burial depth of only 2m. The small amount of nuclide that did not appear to be sorbed was almost certainly colloidal. There is evidence (Murray and Avogadro, 1980; Avogadro et al., 1980) that carbonate complexes of americium are present in natural waters. However, these are likely to be in equilibrium with the main positively charged trivalent species and will therefore be sorbed soon after the bulk of the americium is removed from solution. It is recommended therefore that investigations into the behaviour of americium be given a low priority in future research except where its tendency to remain in the III oxidation state makes comparison with other actinides of interest. The readiness with which it forms colloids could also be exploited in colloidal studies.

(iv) Plutonium, because of its complex chemistry is always likely to provide surprises and investigations into its behaviour should continue. The fact that the R_d for high-carbonate sediments dropped so dramatically with increasing solid/solution ratio emphasises the fact that site-specific studies are necessary, that experimental results cannot be extrapolated from one sediment type to another and that it is not possible to predict the behaviour of one actinide from that of the others (or from chemical analogues such as the rare earths). Although at first sight this low R_d is disconcerting, it is not necessarily disastrous. The main plutonium isotopes have reasonably short half lives and it can be seen from Table 10 that the critical K_d for a burial depth of 20m is only 10 ml/g which means that a K_d of 100 ml/g gives a satisfactory safety margin provided that the waste is placed 20m or more below the sediment surface.

(v) Neptunium distribution ratios did not decrease with increasing solid/solution ratio probably because it has relatively low R_d values and small amounts of a low- R_d species would not have been detected. Because ^{237}Np has such a long half-life and because it is poorly sorbed to many geological materials it is generally considered to be the actinide most likely to find its way back into the environment. However, on all the carbonate sediments tested the R_d was found to be $>10^3$ ml/g. This means that even a 2m burial depth would be satisfactory in this sediment type (Table 5.10). The R_d for the red clay was only 600 and even lower values have been reported by others, e.g. Fowler et al. (1981), a burial depth of at least 20m would be necessary in this type of sediment.

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SORPTION OF AMERICIUM AND NEPTUNIUM BY DEEP-SEA SEDIMENTS

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The sorption and desorption of americium and neptunium by a wide range of deep-sea sediments from natural sea water at 4°C has been studied using a carefully controlled batch technique. All the sediments studied should form an excellent barrier to the migration of americium since distribution coefficients were uniformly greater than 10^5 and the sorption-desorption reaction may not be reversible. The sorption of neptunium was reversible and, except for one red clay, the distribution coefficients were greater than 10^3 for all the sediments investigated. Nevertheless the migration of neptunium should also be effectively retarded by most deep-sea sediments even under relatively oxidizing conditions. The neptunium in solution remained in the V oxidation state throughout the experiments. Under the experimental conditions used colloidal americium was trapped by the sediment and solubility did not seem to be the controlling factor in the desorption of americium.

1. INTRODUCTION

The disposal of high-level nuclear waste in subseafloor sediments is under investigation in several countries as an alternative to disposal on land. If canisters containing the vitrified waste are buried in the sediments the main barrier to the final emergence of the radioactive nuclides to the marine ecosystem will be the near-surface sediments. How effective the sediments will be as a barrier will depend upon the extent to which they interact with any nuclides that escape from the waste packages.

In the immediate vicinity of the canister (the near field) the effect of radiation and high temperatures could significantly alter the properties of the sediments and the pore waters. However, these effects are not expected to extend more than a few meters, after which temperature and pressure conditions should be essentially those of the natural sediments.

The choice of possible sites for the emplacement of nuclear waste will depend upon a number of geological, geographical, physical and other factors, but clearly the properties of the sediments themselves must be one of the main concerns. Pelagic sediments far from the continental margins are composed mainly of calcareous or siliceous remains provided that the water depth is not so great that the calcium carbonate goes into solution and at greater depths the so called red clays prevail. Thus, the deeper Pacific is dominated by the red clays whereas the Atlantic is dominated by calcareous oozes. There are areas in both oceans that appear to be promising as potential disposal sites for radioactive waste, and the final choice may well depend upon which sediments are shown to be chemically and physically most suitable as a barrier.

The sea water/sediment system is extremely complex and in order to assess the suitability of marine sediments as a barrier to radionuclide migration it was decided to adopt an empirical approach. Thus, a set of thirteen carefully selected sediments was contacted with sea water which had been spiked with the nuclide of interest under conditions as close as possible to natural conditions and their sorption behavior studied. The sediments were never allowed to dry out after recovery from the seabed, the temperature was maintained at 4°C throughout the experiments and natural sea water was used. No attempt was made, however, to control the E_H and it was assumed that the effect of pressure would be small.

The samples were chosen to represent a wide variety of sediments occurring in the deep sea. The calcium carbonate content varied from less than 2% to 89% and X-ray diffraction was used to identify the other components present. In addition to the sediments containing calcium carbonate and various types of clays, two manganese nodules were crushed and studied in the same way as the other samples. The reason for including these nodules in the study is that hydrous oxides of manganese and iron occur in virtually all sediments, both as discrete oxide particles and as partial coatings on other minerals and it is likely that they exert an influence on the sorptive properties of the sediments which is out of all proportion to their concentration. The ion exchange capacities of these oxides is large, but possibly more important is the fact that they are themselves participants in oxidation reduction cycles, and evidence is accumulating that retention of actinides in sediments is frequently the result of precipitation during redox reactions rather than by ion exchange.¹ All the samples were characterized as fully as possible to assess whether any particular property had an effect on the sorptive properties. Thus in addition to the mineralogical analysis, chemical composition, surface areas and cation exchange capacities were determined.

The results of the sorption experiments are given in terms of the distribution coefficient, K_d , defined as

$$K_d = \frac{\text{Concentration of a species on the solid at time of measurement}}{\text{Concentration of the species in the liquid at time of measurement}}$$

the unit used being ml/g.

The values of K_d reported here are not necessarily the slopes of linear sorption isotherms. Rather, as is the case for most of the radionuclide-sorption literature, they are empirical ratios of concentrations for the conditions of the particular experiments that yielded the data. In safety evaluations of a waste repository the distribution coefficient is widely used to predict the migration velocity of a radionuclide through geological materials. The K_d used in this mathematical modelling assumes that the reaction is reversible, that equilibrium has been established and that the K_d measured is constant over the concentration range of interest. If any of these criteria are not satisfied, predictions based on K_d s will be incorrect. Another reason for the failure of a prediction of migration velocity from a distribution coefficient is that the laboratory batch-sorption method gives only an average K_d for all chemical forms of the nuclide. Most of the actinides exist in several oxidation states and in a complex medium such as sea water, polymers, carbonates and other complexes may exist. These may have positive or negative charges and may all react differently with the sediments and have different migration rates. Thus a high overall K_d might disguise the fact that a small fraction of the element in question is mobile. It is desirable, therefore, when using the batch technique to learn as much as possible about the speciation of the element being studied. Column studies should be able to differentiate between species of different mobilities but are more difficult and time consuming than batch experiments. Furthermore, column experiments, like batch experiments do not simulate the conditions that will exist when wastes are buried in the seabed since migration will be by diffusion and not as the result of ground-water flow. Diffusion experiments have been conducted by Duursma,² Erikson³ and Schreiner⁴ but are too slow to be practical if the distribution coefficients are high. It was decided, therefore, to use the batch method for the screening of a number of sediments, to determine the oxidation states of the nuclides involved wherever possible, and hence to make as many deductions as possible about the chemical processes occurring during sorption and desorption.

High-level wastes contain a large number of different radionuclides which must be isolated from the biosphere until they decay to innocuous radiation levels. Of these the actinides together with long-lived fission products such as ⁹⁹Tc and ¹³⁵Cs would appear to pose the greatest hazard to man⁵ although the exact order of ranking according to hazard measures will depend upon the particular disposal system used. Clearly

it is desirable to study the interaction of the sediments with all these elements, but in the first instance this investigation has been confined to the actinides, americium and neptunium.

2. EXPERIMENTAL

2.1 Sample Characterization

The mineralogy of the sediments was determined by X-ray diffraction and the elemental composition by inductively coupled plasma spectroscopy after fusing with LiBO_2 (major elements) and by atomic absorption spectroscopy after digestion in $\text{HF}/\text{HNO}_3/\text{HClO}_4$ (Minor elements).

It is recognized that both surface area (SA) and cation exchange capacity (CEC) values will depend to some extent on the method used to determine them. However, it is relative rather than absolute values that are important in this work and the methods used were chosen for their speed and reproducibility. Thus, surface areas were determined by the simplified ethylene glycol monoethyl ether (EGME) procedure^{6,7} and cation exchange capacities were determined by the caesium exchange procedure described by Beeton.⁸ The sodium acetate method⁹ was also used on some samples and agreement between the two methods was found to be good.

2.2 Determination of Distribution Coefficients

The batch partitioning experiments were carried out as far as possible according to the method prescribed by Relaya in his 'Task 4' Status Report.¹⁰ K_d values reported by different laboratories for similar or even the same materials tend to differ widely and Relaya has emphasized the need for standardization. The procedure used was basically the same for americium and neptunium although different separation and analytical techniques were used to determine the final solution concentration.

The temperature was kept at 4°C at all times and the sea water was filtered through 0.22μ filters before use. In order to ensure that representative samples were obtained sediments were mixed with sea water to form a slurry and samples weighing between 50 and 100 mg (dry weight) were transferred by pipetting while agitating into 50 ml Oakridge-type polycarbonate centrifuge tubes. After an initial prewash in sea

water they were centrifuged for 180 minutes at 7000 rpm and the supernate discarded.

Spiked sea water solutions were prepared by adding 1-2 ml of the tracer in acid solution to 500 ml sea water. The pH was readjusted to 8.2 with NaOH and the solutions left to equilibrate for several weeks. Immediately before use they were filtered through 0.22μ filters and analyzed for tracer concentration. The final concentrations in these spiked solutions were $1.8 \times 10^{-9}\text{M}$ and $1.8 \times 10^{-10}\text{M}$ for Am and $1 \times 10^{-12}\text{M}$ for Np. Even at these low concentrations the Am was not in true solution. Thus, filtration of the more concentrated solution through successive pairs of millipore filter papers showed that about 1% of the total activity was in the size range 0.1μ to 0.22μ and another 1% was in the size range 0.025μ - 0.1μ . ^{241}Am ($t_{1/2} = 458\text{y}$) and ^{235}Np ($t_{1/2} = 410$ days) were the isotopes used. ^{235}Np was chosen in preference to ^{237}Np because its short half life meant that it could be used at concentrations low enough to ensure that precipitation would not occur. ^{235}Np decays principally by electron capture and can be assayed by counting in the uranium X-ray region, 10-120 keV. Unfortunately the total intensity for the K X-ray region ($K\alpha + K\beta$) is only 1.9% i.e. 4.3×10^4 dpm/ μCi .

Thirty milliliter portions of spiked sea water were then added to each tube containing the washed sediment and the mixture sealed, placed horizontally in the water bath and shaken at 120 strokes/min. At intervals the tubes were centrifuged for 180 mins at 7000 rpm. Samples of the supernate were removed by pipetting, analyzed for the nuclide of interest and the pH determined. After counting, the Np solutions were cooled to 4°C and returned to the original centrifuge tubes. This could not be done for Am which meant that only a limited number of readings could be taken. After adsorption the supernate was removed, unspiked sea water added and desorption followed.

Np concentrations were determined by counting 5g portions in a NaI well-type scintillation counter. At the end of the adsorption and desorption periods oxidation state determinations were made on the solutions using the method of Foti and Freiling.¹¹ This method is based on the fact that TTA in benzene extracts Np(IV) but not Np(V) or Np(VI) from dilute acid solution and that lanthanum fluoride carries Np(V) and Np(IV) but not Np(VI). If therefore the total Np is also measured it is possible to determine the distribution of the Np among the three oxidation states.

Because it was considered essential to work below precipitation levels,

and because americium is very insoluble in sea water, and distribution coefficients were high, gamma counting was not sufficiently sensitive for the determination of americium. It was therefore determined by alpha spectrometry after extraction into TTA (2-thenoyl trifluoroacetone) dissolved in cyclohexane at a pH of 2.0. ^{243}Am was used as a yield monitor.

3. RESULTS AND DISCUSSION

3.1 Sediment Characterization

The results of the mineralogical and chemical analyses are given in Tables I and II, respectively, and of the surface area and cation exchange determinations in Table III. It can be seen that the samples fall into several categories, viz:

1. Those high in calcium carbonate and containing minor amounts of montmorillonite, quartz, and clay minerals. The calcium carbonate content of these samples ranges from 45% to 89% and, as many of the other variables show a direct relationship to this value, the samples have been arranged in order of decreasing CaCO_3 content. It can be seen from Table III that both cation exchange capacity, and surface area tend to vary inversely with CaCO_3 content. (The anomalously high values for 10399=7K can be explained by the presence of smectite.) Furthermore several of the major and minor constituents eg. SiO_2 , Fe, Al, K, Ni, and Mg all increase steadily as the CaCO_3 content decreases. If these variables are recalculated on a carbonate free basis there is much less variation in the CEC and SA values. Also, the concentration of many of the elements in the carbonate free fraction is fairly constant.

2. Red clays. These were obtained from the mid-Atlantic at a depth of about 6000m. They are almost completely carbonate free and contain quartz and various clay minerals. Although not detected by X-ray diffraction, the chemical analysis suggests the presence of 5%-10% amorphous iron oxy-hydroxides. Although the surface area of these sediments is high the cation exchange capacity is low.

3. Manganese nodules. 6269 No. 2 is high in amorphous iron and manganese hydroxides whereas MV 651 is composed mainly of the minerals birnessite and todorokite.

4. SH 1578, a smectite rich sediment containing amorphous silica and iron oxy-hydroxides.

TABLE I
Mineralogy of Sediments

Sample No.	Composition		
	Major	Minor	Trace
IOS-3	Calcite		Illite, Kaolinite
M77-20	Calcite	Quartz	
10399-7K	Calcite	Kaolinite, illite Smectite, chlorite	Plagioclase feldspar
IOS-6	Calcite	Quartz, Kaolinite Illite, Montmorillonite	
IOS-4	Calcite	Montmorillonite Illite Kaolinite	Quartz
IOS-5	Calcite	Quartz, Kaolinite Illite	
IOS-2	Calcite	Quartz, Illite Montmorillonite	Mixed layer chlorite
S 702	Calcite, Quartz	Illite	
SH 1578	Smectite (30-40%) Fe Oxyhydroxides (8-10%) SiO ₂ as amorphous silica		

10400#5K	Illite Quartz	Kaolinite Smectite Fe oxyhydroxides	
IOS-1	Illite Kaolinite	Quartz plagioclase feldspar Fe oxyhydroxides	Calcite (< 5%)
MV 65 1	Birnessite Todorokite	Quartz	
6269 No. 2	Amorphous Mn and Fe Oxyhydroxides	δ - MnO ₂	

TABLE II

Chemical Composition of Sediments

Sample No.	CaCO ₃ %	Si %	Fe %	Mn %	Al %	Mg %
IOS-3	89	0.7	0.6	0.05	0.85	0.18
M77-20	88	2.2	1.7	0.12	1.4	—
10399=7K	85	9.3	1.8	0.10	3.4	0.73
IOS-6	73	1.9	1.6	0.09	2.4	0.5
IOS-4	69	2.7	1.8	0.07	3.0	0.57
IOS-5	59	3.3	2.3	0.13	3.6	0.76
IOS-2	50	3.6	2.5	0.03	4.6	1.0
S 702	45	5.2	3.1	0.14	5.0	—
SH 1578	4	12.0	14.6	4.3	2.0	—
10400=8K	3	24.6	5.0	0.32	8.8	1.68
IOS-1	<2	7.7	5.3	0.31	6.6	1.6
MV 651	—	—	2.2	32.9	2.2	—
6269 No. 2	—	—	13.7	16.8	1.7	—

4. SH 1578, a smectite rich sediment containing amorphous silica and iron oxy-hydroxides.

3.2 Americium Sorption and Desorption

In recent years many studies have attempted to determine the distribution coefficients for americium on a variety of rocks, minerals and sediments.¹²⁻¹⁶ Typically reported K_d values have been large, ranging from 100 to $> 2.2 \times 10^6$ suggesting that Am is highly sorbed by most geological materials. However, in many of the Am sorption experiments no attempt was made to either select initial Am concentrations at levels below precipitation levels or to show that precipitation was absent. The equilibration times used varied from a few hours to more than two years.

Rai *et al.*¹⁵ have critically evaluated much of this data and conducted desorption experiments on contaminated Hanford sediments. They concluded that the concentration of Am in solutions contacting sediments is limited by the solubility of some solid phase, rather than by the

Na %	K %	Ni ppm	Cu ppm	Zn ppm	Ti ppm	P ppm	Pb ppm
0.55	0.31	20	68	44	150	140	10
0.20	0.32	21	297	109	660	60	8
0.88	2.4	--	--	--	1800	250	--
0.38	0.66	35	90	65	1200	310	<5
0.55	0.96	32	90	75	1500	190	<5
0.40	1.10	49	92	87	2200	330	20
0.44	1.30	50	89	101	2300	500	20
0.44	1.13	165	63	89	2500	430	9
0.70	0.34	555	865	435	1100	340	75
0.63	2.5	--	--	--	5500	680	--
0.85	2.6	109	167	137	--	690	30
--	--	1800	1200	1340	--	--	22
--	--	4680	1580	680	--	--	760

sorption reaction, as long as an excess of Am solid phase is present. They deduced that the concentration in solution depends upon the pH according to the equation

$$\log \text{Am}_{(\text{mol/l})} = (-3.76 \pm 0.26) - (1.07 \pm 0.04)\text{pH} \quad (1)$$

It is generally assumed that Am in sea water will be in the III oxidation state, although Aston (1980), as a result of theoretical calculations has suggested that Am(IV) might also exist. Both $\text{Am}(\text{OH})_3$ and $\text{Am}(\text{OH})_4$ are highly insoluble but Rai *et al.*¹⁷ have shown that it is unlikely that it is the solubility of $\text{Am}(\text{OH})_3$ that controls the concentration of Am in solution since the solubility of the Am solid phase associated with sediments, $\text{Am}_{(\text{soil})}$ is approximately five orders of magnitude lower than that of $\text{Am}(\text{OH})_3$.

In our experiments two different initial concentrations, approximately $1.8 \times 10^{-9}\text{M}$ and $2.0 \times 10^{-10}\text{M}$ were used and distribution coefficients were determined after 1, 4 and 8 weeks and 1 and 4 weeks, respectively.

TABLE III

Cation Exchange Capacity and Surface Area of Sediment

	Measured Value		Carbonate free basis		CaCO ₃ %
	CEC MEq/100g	SA m ² /g	CEC MEq/100g	SA m ² /g	
IOS-3	7	24	55	188	89
M77-20	7	30	51	218	88
10399=7K	17	85	109	548	85
IOS-6	19	54	66	188	73
IOS-4	17	63	52	193	69
IOS-5	43	58	101	136	59
IOS-2	31	131	60	253	50
S 702	20	97	35	171	45
SH 1578	124	396			
10400=8K	43	190			4
IOS-1	45	199			<2
MV 65 I	100	95			-
6269 No. 2	82	340			-

Desorption was followed for up to fifteen weeks. It was found that the pH of the solution dropped from its initial value of 8.2 to between 7.7 and 8.0 at two weeks to between 7.5 and 7.8 at eight weeks.

Distribution coefficients were found to be high ($> 10^4$) for all the sediments studied but they did differ by more than an order of magnitude and the following observations can be made from a study of the results which are given in Tables IV and V and are illustrated in Figures 1 and 2.

Effect of initial concentration: Distribution coefficients were the same for the two different initial concentrations investigated. Thus at these concentrations Henry's law is obeyed and precipitation was probably not occurring.

Effect of time: After the initial rapid sorption the distribution coefficient increased steadily with time and for all the carbonate samples the graphs of K_d against time are straight lines after the first seven days.

Erdal¹⁴ has suggested that this type of increase with time is due to the exposure of new surfaces due to attrition during shaking. At these low concentrations, however, it is unlikely that the availability of sites is the limiting factor and it is more probable that some slow reaction is occurring. Shanbhag and Morse¹⁵ added ten successive spikes to samples of calcite in sea water (10^{-8} M Am) and found that after each addition the percent adsorbed after a 30 minute reaction time was 99%. This is a clear indication that the surface sites are not being saturated. We obtained similar results with europium and our sediments. It must be borne in mind that the changes in concentration are very small. More than 99% of the Am added was removed within the first seven days (probably within hours) and it is difficult to say whether the initial rapid reaction is different to the subsequent slow reaction. Both hydrolysis and complexation with one or more constituents of the sediments probably occur. Diffusion into the clay lattice or micropores could also be involved.

Effect of sediment properties: Figure 1 shows the plot of K_d against time for the five low-carbonate samples together with two of the high-carbonate samples for comparison. In Figure 2 all the high-carbonate samples are plotted on a larger scale.

It can be seen that the initial K_d s for the five low-carbonate samples are all very similar and are higher than for the carbonate-rich samples. In particular the manganese nodules have very high K_d s and their surface properties must be involved in the sorption reaction. The distribution coefficient for the two manganese modules was still rising rapidly after eight weeks, although for the other samples they seemed to be levelling off.

All eight high-carbonate samples behaved in much the same way, and it is not possible to correlate K_d with any of their measured properties in spite of the fact that they encompassed a wide range of calcium carbonate contents (45-89%), surface areas (24-131 m²/g) and cation exchange capacities (35-101 mEq/100g). This is probably because, at the low Am concentrations used, whatever the mechanism of adsorption, there is no shortage of available sites and the effect of these variables would not be apparent.

Desorption: Desorption is one important respect in which Am differs from Np (see Section 4). Np K_d s are similar for sorption and desorption, indicating that the reaction is reversible. Desorption K_d s for Am, on the

TABLE IV

Americium Distribution Coefficients

	Initial conc. $\frac{\text{mols}}{\ell}$ 10 ⁻¹⁰	ADSORPTION $K_d/10^5$				$\frac{\text{ml/g}}{10^5}$
		DAYS				
		1	7	28	56	
IOS-3	18		0.64 ± 0.04	1.24 ± 0.11	1.96 ± 0.88	
	2		0.63 ± 0.01	0.68 ± 0.07	—	
M77-20	18		0.58 ± 0.05	1.07 ± 0.10	1.91 ± 0.16	
	2		0.70 ± 0.01	0.96 ± 0.03	—	
10399 $\approx$ 7K	14	0.29 ± 0.02	0.59 ± 0.05	0.74 ± 0.07	0.97 ± 0.08	
	3	0.35 ± 0.03	0.57 ± 0.04	0.65 ± 0.11	1.18 ± 0.13	
IOS-6	18		1.05 ± 0.09	1.93 ± 0.24	3.12 ± 0.29	
	2		1.16 ± 0.02		—	
IOS-4	18		0.75 ± 0.06	0.95 ± 0.08	1.76 ± 0.15	
	2		0.57 ± 0.02	0.71 ± 0.06	—	
IOS-5	18		1.10 ± 0.09	1.43 ± 0.13	1.99 ± 0.20	
	2		1.04 ± 0.01		—	
IOS-2	18		0.72 ± 0.05	1.28 ± 0.11	1.80 ± 0.14	
	2		0.51 ± 0.01	1.88 ± 0.18	—	
S702	18		0.50 ± 0.04	0.80 ± 0.09	1.22 ± 0.10	
	2		0.42 ± 0.03	0.83 ± 0.04	—	
SH1578	18		1.36 ± 0.11	3.83 ± 0.44	4.11 ± 0.36	
	2		1.43 ± 0.04	2.54 ± 0.12	—	
10410 $\approx$ K	14	0.50 ± 0.03	1.13 ± 0.07	1.79 ± 0.13	2.17 ± 0.08	
	3	0.69 ± 0.05	1.08 ± 0.08	1.72 ± 0.17	2.10 ± 0.35	
IOS-1	18		1.46 ± 0.12	2.79 ± 0.23	3.31 ± 0.21	
	2		1.42 ± 0.05	1.62 ± 0.11	—	
MV65 I	18		1.35 ± 0.14	4.64 ± 0.38	7.65 ± 0.72	
	2		1.12 ± 0.06	3.20 ± 0.06	—	
6269 No. 2	18		1.71 ± 0.15	7.91 ± 0.66	11.04 ± 0.88	
	2		2.35 ± 0.10	3.22 ± 0.05	—	

Note: Errors are the result of counting statistics. Where more than one determination was carried out weighted means are given.

DESORPTION $K_d/10^5$			$\frac{\text{ml/g}}{10^5}$	
DAYS				
14	42	70	84	105
10.0 $\pm$ 0.8	9.6 $\pm$ 1.1			9.3 $\pm$ 0.4
5.5 $\pm$ 0.4		4.8 $\pm$ 0.3		
7.0 $\pm$ 0.7	8.3 $\pm$ 1.4			
4.1 $\pm$ 0.1		1.2 $\pm$ 0.07		
			4.67 $\pm$ 0.43	
			6.00 $\pm$ 0.44	
11.4 $\pm$ 0.6	7.7 $\pm$ 0.4			6.1 $\pm$ 0.2
6.2 $\pm$ 0.5		4.4 $\pm$ 0.2		
10.2 $\pm$ 1.0	7.1 $\pm$ 0.7			6.7 $\pm$ 0.3
3.6 $\pm$ 0.3		3.5 $\pm$ 0.2		
10.5 $\pm$ 0.8	8.5 $\pm$ 1.1			10.1 $\pm$ 0.4
6.6 $\pm$ 0.6		6.5 $\pm$ 0.4		
9.1 $\pm$ 0.2	8.0 $\pm$ 0.9			9.9 $\pm$ 0.5
4.7 $\pm$ 0.8		4.2 $\pm$ 0.2		
4.8 $\pm$ 0.4	3.8 $\pm$ 0.5			6.7 $\pm$ 0.3
3.1 $\pm$ 0.4		2.3 $\pm$ 0.2		
23.7 $\pm$ 1.8	26.0 $\pm$ 3.3			24.5 $\pm$ 0.9
8.2 $\pm$ 0.9		7.8 $\pm$ 0.5		
			8.39 $\pm$ 0.75	
			6.04 $\pm$ 0.24	
13.6 $\pm$ 1.2	20.2 $\pm$ 1.7			11.8 $\pm$ 0.5
7.6 $\pm$ 0.41		5.1 $\pm$ 0.1		
32.3 $\pm$ 3.8	32.9 $\pm$ 2.7			35.5 $\pm$ 2.5
11.7 $\pm$ 1.3		5.9 $\pm$ 0.5		
33.7 $\pm$ 4.2	53.7 $\pm$ 4.7			53.5 $\pm$ 4.2
12.7 $\pm$ 1.3		10.9 $\pm$ 0.9		

TABLE V

Concentration of Americium in Solution During Sorption Experiments

	Initial conc. $\frac{\text{mols}}{\text{g}}$ 10^{-10}	ADSORPTION			
		$\frac{\text{mols/g}}{10^{-10}}$			
		DAYS			
		1	7	28	56
IOS-3	18		13.0 ± 1.0	6.7 ± 0.6	4.1 ± 0.4
	2		1.40 ± 0.09	1.34 ± 0.13	-
M77-20	18		8.7 ± 0.7	4.5 ± 0.5	2.4 ± 0.2
	2		1.00 ± 0.06	0.73 ± 0.05	-
10399#7K	14	11.4 ± 0.7	5.3 ± 0.4	4.4 ± 0.4	3.4 ± 0.3
	3	1.8 ± 0.1	1.1 ± 0.1	0.89 ± 0.13	0.52 ± 0.06
IOS-6	18		5.9 ± 0.5	3.3 ± 0.3	2.6 ± 0.2
	2		0.63 ± 0.04	0.40 ± 0.05	-
IOS-4	18		8.3 ± 0.8	6.6 ± 0.6	3.4 ± 0.3
	2		1.17 ± 0.08	0.93 ± 0.11	-
IOS-5	18		7.5 ± 0.7	5.8 ± 0.6	3.5 ± 0.2
	2		0.89 ± 0.05	0.55 ± 0.05	-
IOS-2	18		11.3 ± 0.9	6.4 ± 0.6	4.4 ± 0.4
	2		1.76 ± 0.11	0.50 ± 0.06	-
S702	18		9.3 ± 0.8	5.9 ± 0.6	3.7 ± 0.3
	2		1.49 ± 0.10	0.75 ± 0.06	-
SH1578	18		7.9 ± 0.7	3.3 ± 0.4	2.9 ± 0.3
	2		0.85 ± 0.06	0.48 ± 0.04	-
10400#8K	14	9.0 ± 0.5	3.8 ± 0.3	2.5 ± 0.2	2.0 ± 0.5
	3	1.2 ± 0.1	0.74 ± 0.05	0.49 ± 0.05	0.37 ± 0.03
IOS-1	18		7.3 ± 0.8	3.8 ± 0.3	3.1 ± 0.1
	2		0.72 ± 0.05	0.63 ± 0.06	-
MV 651	18		3.2 ± 0.7	2.3 ± 0.2	1.4 ± 0.1
	2		0.64 ± 0.05	0.22 ± 0.01	-
6269 No. 2	18		8.7 ± 0.8	1.9 ± 0.2	1.3 ± 0.1
	2		0.36 ± 0.03	0.27 ± 0.02	-

DESORPTION					Approx final sediment loading moles/g 10-10
$\frac{\text{mols/g}}{10^{-12}}$					
DAYS					
14	42	70	84	105	
0.84 $\pm$ 0.26	0.87 $\pm$ 0.87			0.90 $\pm$ 0.06	5.4
0.17 $\pm$ 0.04		0.19 $\pm$ 0.02			0.6
0.65 $\pm$ 0.19	0.58 $\pm$ 0.58			0.48 $\pm$ 0.04	5.4
0.17 $\pm$ 0.04	--	0.07 $\pm$ 0.05			0.6
			0.69 $\pm$ 0.09		4.1
			0.11 $\pm$ 0.01		0.8
0.53 $\pm$ 0.04	0.81 $\pm$ 0.02			1.03 $\pm$ 0.07	5.4
0.16 $\pm$ 0.02		0.17 $\pm$ 0.01			0.6
0.62 $\pm$ 0.07	0.89 $\pm$ 0.10			0.94 $\pm$ 0.07	5.4
		0.19 $\pm$ 0.02			0.6
0.79 $\pm$ 0.24	0.98 $\pm$ 0.13			0.83 $\pm$ 0.06	5.4
0.13 $\pm$ 0.01	--	0.14 $\pm$ 0.01			0.6
0.91 $\pm$ 0.03	1.03 $\pm$ 0.01			0.84 $\pm$ 0.06	5.4
0.20 $\pm$ 0.02	--	0.22 $\pm$ 0.02			0.6
0.94 $\pm$ 0.28	1.23 $\pm$ 0.16			0.70 $\pm$ 0.05	5.4
0.20 $\pm$ 0.02	--	0.27 $\pm$ 0.03			0.6
0.52 $\pm$ 0.05	0.47 $\pm$ 0.06			0.50 $\pm$ 0.04	5.4
0.15 $\pm$ 0.02	--	0.15 $\pm$ 0.01			0.6
			0.53 $\pm$ 0.04		4.1
			0.11 $\pm$ 0.01		0.8
0.78 $\pm$ 0.07	0.53 $\pm$ 0.05			0.91 $\pm$ 0.07	5.4
0.14 $\pm$ 0.01	--	0.20 $\pm$ 0.01			0.6
0.33 $\pm$ 0.04	0.33 $\pm$ 0.03			0.30 $\pm$ 0.03	5.4
0.10 $\pm$ 0.01	--	0.12 $\pm$ 0.01			0.6
0.47 $\pm$ 0.06	0.28 $\pm$ 0.03			0.28 $\pm$ 0.03	5.4
0.07 $\pm$ 0.01	--	0.08 $\pm$ 0.01			0.6

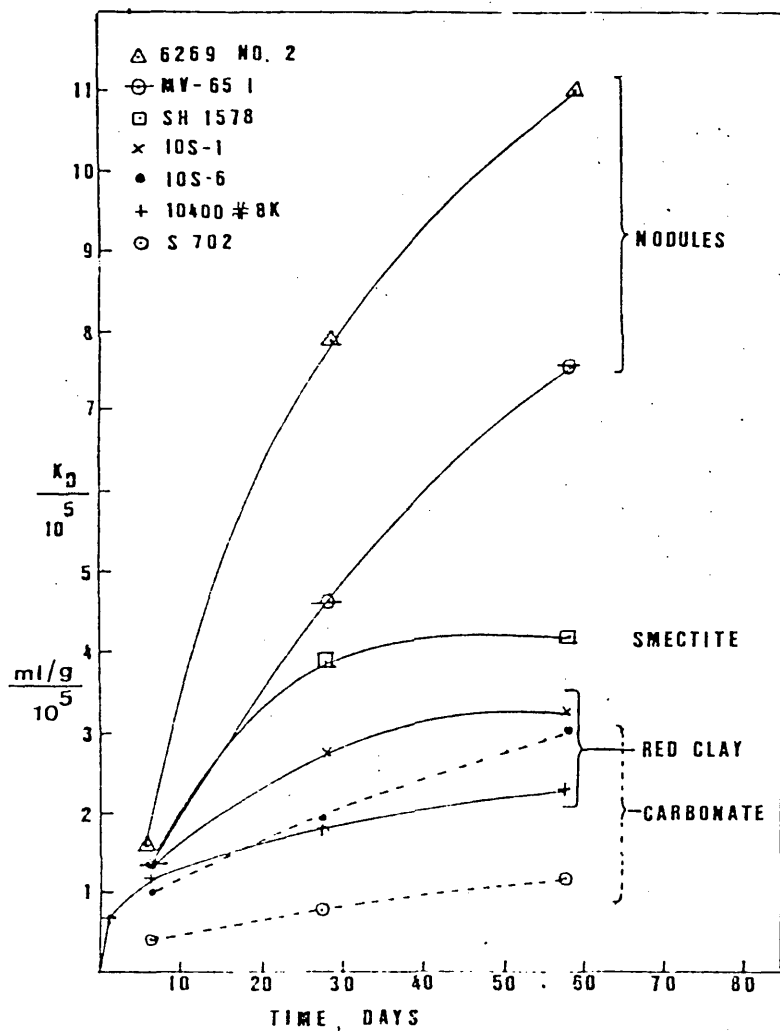


FIGURE 1. Americium Distribution Coefficients

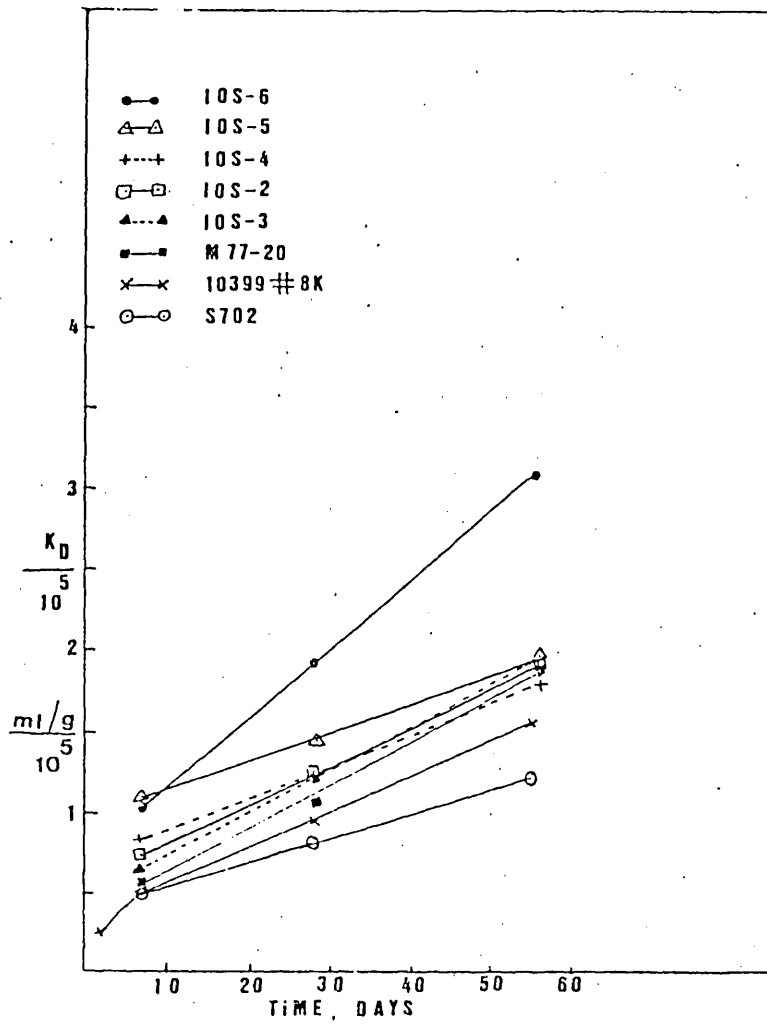


FIGURE 2. Americium Distribution Coefficients. High-Carbonate Sediments.

other hand, are five to ten times higher than the 56 day adsorption K_d s. Other workers (e.g. Sanchez¹²) have found the same thing but it may simply be that it takes a long time for the adsorption reaction to reach completion whereas the desorption equilibrium appears to be quickly established. Thus, there was little change in the desorption K_d over the time period 14 to 105 days.

Solution concentration: Table V shows the Am concentration found in solution during the sorption and desorption experiment. It can be seen that there is a wide variation in the solution concentration after seven days but the difference between samples becomes less as the time increases and the percent adsorbed rises from between 99.3% and 99.8% at seven days to between 99.7% and 99.9% at 56 days. Possibly the concentration will eventually drop to a common value, although it will clearly be a considerable time before the desorption value of 0.5×10^{-12} moles/l (99.97% on the sediment) is reached.

In order to compare these values with those predicted by Rai (eqn. 1, Section 3.2) the predicted concentrations at the pH of these experiments was calculated. Table VI shows these values for the pHs of interest.

It can be seen from Table V that the concentrations in solution after the eight week K_d determination and after desorption lie within the ranges predicted by Rai *et al.* However, it is also clear that there are significant differences in solution concentration at the various stages of

TABLE VI

Predicted Concentration of Am in Solution at Different pH s

	pH	log Am(mol/l)	Predicted Am concentration moles/l 10 ⁻¹²	
			Mean	Range
8 week adsorption	7.5	-11.79 ± 0.39	1.62	0.65 to 4.12
	7.8	-12.11 ± 0.40	0.78	0.31 to 2.00
2 week desorption	7.9	-12.21 ± 0.41	0.62	0.25 to 1.57
	8.0	-12.32 ± 0.41	0.48	0.18 to 1.23

our experiments and it appears that it is an over simplification to explain its validity just in terms of solubility effects. For example the solution concentration after desorption does depend upon the amount of americium on the sediment indicating that the desorption mechanism cannot be one of simple solubility. Some equilibrium sorption-desorption reaction must be occurring.

Desorption K_d are considerably higher for the manganese modules and the smectite than for the carbonate samples and red clays. An irreversible reaction with the iron and manganese minerals could be occurring here.

It may be that more than one species is present in solution, one of which is not sorbed by the sediment (e.g. an anionic or neutral complex). The effect of this would be to lower the observed sorption K_d . The desorption K_d would then be the "true" equilibrium K_d for the strongly sorbed species. This possibility is currently being looked into.

Particle size: When determining sorption coefficients for Am the solutions were always filtered through a pair of millipore filters (0.22μ above 0.10μ) before analysis. The filters were counted on a zinc sulphide scintillation counter. A comparison with the spectra obtained on the alpha spectrometer showed that the sources were reasonably thin and that this procedure gave a fair measure of the total Am retained on the filters. From these experiments it was possible to calculate the approximate weight of sediment retained by the filters assuming that the activity per gram of the fine particles on the filters was the same as the activity per gram of the bulk sediment. (This is probably not true and the calculated weights are probably too high). Estimates of the mass of sediment retained by 0.22μ filters when five gram samples of solution that had been previously centrifuged for 180 minutes at 7000 rpm were filtered, ranged from $2 \mu\text{g}$ for sample S702 to $20 \mu\text{g}$ for MV 65 I.

It was found that in all cases the 0.22μ filter retained all the particulate Am. Thus, although about 1% of the activity in the initial $1.8 \times 10^{-9}\text{M}$ solution was in the size range 0.01μ - 0.022μ no activity in this size range could be detected after the solution had been contacted with sediment. If this happens under natural conditions it would mean that colloidal Am is unlikely to migrate through the sediments.

Container-wall adsorption: In preliminary experiments both solid and liquid phases were counted after adsorption. These confirmed the con-

clusions of other workers, e.g. Erdal¹⁴ that in the absence of sediment significant quantities of Am are adsorbed by the container walls but that when sediment is present this drops to negligible proportions because of the scavenging action of the sediment.

3.3 Neptunium Adsorption and Desorption

Compared with americium and plutonium very few neptunium distribution coefficients have been determined on geological materials. The few results that have been reported are mostly less than 100 ml/g although Allard³ found that apatite had a K_d of 8000 ml/g. Harvey¹⁹ has calculated that sediments in the Irish sea have a K_d of about 5000 ml/g under natural conditions and Aston²⁰ determined K_{ds} on three marine sediments in spiked sea water. He reports values of 3200, 1950 and 390 ml/g for a calcareous deep sea deposit, an argillaceous mud and an intertidal silt, respectively.

From the limited amount of thermodynamic data available it appears that in well oxygenated sea water neptunium should occur as the soluble pentavalent species NpO_2^+ although the possible presence of bicarbonate and hydroxyl complexes cannot be ignored. However, recent work has indicated that neptunium is susceptible to changes in oxidation state under the conditions found in the environment. Bondietti and Francis²¹ investigated the sorption of Np using different basalt, granite and shale rocks in a deoxygenated (< 1 ppm O_2) nitrogen purged system. After seven days of equilibration they found that both the Np remaining in solution and the Np on the rocks was 60% to 80% Np(IV). On the other hand, sorption experiments with shale and with basalt, which had been pretreated with NaOCl to oxidize the iron, resulted in little or no reduction, although more than 80% of the Np was rapidly removed from solution. This would seem to indicate two different mechanisms for Np sorption, one of which involves a redox $\text{Np(V)} \rightarrow \text{Np(IV)}$ reaction.

Harvey¹⁹ studied the reduction of Np(V) under varying E_h and pH conditions and found that reduction occurred at E_h 's below 150 mV over the pH range 7.0 to 8.0. No reduction was observed above +180 mV to +200 mV at any pH value.

In our experiments the pH started at 8.2 and gradually dropped to about 7.5, presumably because of the dissolution of CO_2 from the air. The E_h must have been around +300 mV. The two manganese nodule samples were analyzed by Mossbauer spectroscopy which showed that

the iron was almost entirely in the ferric state ($> 99.5\%$). The likelihood was, therefore, that reduction would not occur, but in view of the very different behavior observed for the carbonate sediment and the iron and manganese rich samples it seemed worthwhile determining the oxidation state of the Np in solution before and after the K_d determination. These experiments showed that in all cases Np(V) was the only oxidation state present. No attempt was made to determine the oxidation state of the Np actually on the sediments and it is quite possible that reduction may have occurred during sorption. In fact if it were not for the fact that Am behaves in a similar way (and Am(III) could not undergo reduction) it would be tempting to explain the results obtained with the iron and manganese rich sediments as being due to a slow reduction reaction.

The results of the distribution coefficient determinations are given in Table VII and Figures 3 and 4. The left-hand side of each graph shows how the K_d varied with time during sorption and the right-hand side the variation during desorption. It can be seen that the red clays had the lowest distribution coefficients and the manganese nodules and smectite the highest. Desorption K_{ds} tended to be similar to the final sorption K_{ds} indicating that the reaction is reversible. Barney,²² when studying the sorption of Np from synthetic groundwaters onto various rocks, also found that the sorption-desorption reaction was reversible.

Distribution coefficients for all the carbonate samples are greater than 10^3 and there was little change with time i.e. for both sorption and desorption equilibrium was quickly established. There is possibly a tendency for the distribution coefficient to increase with the CaCO_3 content but the relationship is not clear cut. It is not unlikely that reactions with CaCO_3 are involved in the sorption process but there is such an excess of CaCO_3 in all the samples that differences, even between 45% and 90% CaCO_3 would not be expected to have a significant effect on the distribution coefficient.

The two manganese nodule samples and SH 1578 (14.6% Fe) behaved quite differently to the high-carbonate samples. Their distribution coefficients increased steadily over the first six weeks finally levelling off and then actually beginning to drop, indicating that the desorption was taking place. The maximum K_{ds} for these samples were considerably higher than for the carbonate samples although, except for 6269 No. 2, the desorption K_{ds} are similar. Sample 6269 No. 2 is mostly amorphous Fe and Mn oxy-hydroxides and has a very high surface area and cation exchange capacity. SH 1578 also contains a high proportion of Fe oxy-

TABLE VII

Neptunium Distribution Coefficients

	ADSORPTION $\frac{K_d}{10^3} \frac{\text{ml/g}}{10^3}$				
	7 day	14 day	21 day	28 day	40 day
IOS-3	4.3 $\pm$ 0.1	4.5 $\pm$ 0.1	4.7 $\pm$ 0.2	5.1 $\pm$ 0.2	
M77-20	5.6 $\pm$ 0.4	5.6 $\pm$ 0.4	5.4 $\pm$ 0.3	6.2 $\pm$ 0.4	8.5 $\pm$ 0.8
IOS-6	3.3 $\pm$ 0.1	3.7 $\pm$ 0.1	1.8 $\pm$ 0.1	2.0 $\pm$ 0.1	
IOS-4	3.9 $\pm$ 0.1	4.1 $\pm$ 0.1	4.5 $\pm$ 0.2	4.3 $\pm$ 0.1	
IOS-5	4.4 $\pm$ 0.1	5.1 $\pm$ 0.2	4.9 $\pm$ 0.1	4.2 $\pm$ 0.1	
IOS-2	1.5 $\pm$ 0.1	1.6 $\pm$ 0.1	2.0 $\pm$ 0.1	2.3 $\pm$ 0.1	
S702	2.5 $\pm$ 0.1	2.4 $\pm$ 0.1	3.3 $\pm$ 0.1	3.6 $\pm$ 0.2	3.6 $\pm$ 0.2
SH1578	1.1 $\pm$ 0.1	2.9 $\pm$ 0.1	4.1 $\pm$ 0.1	5.9 $\pm$ 0.2	8.9 $\pm$ 0.5
10400=8K			See Figure		
IOS-1	0.45 $\pm$ 0.03	0.95 $\pm$ 0.04	1.3 $\pm$ 0.1	1.5 $\pm$ 0.1	1.3 $\pm$ 0.1
MV 65 I	0.73 $\pm$ 0.03	1.2 $\pm$ 0.1	1.7 $\pm$ 0.1	2.3 $\pm$ 0.1	3.5 $\pm$ 0.1
6269 No. 2	3.3 $\pm$ 0.1	6.8 $\pm$ 0.3	11.1 $\pm$ 0.5	13.1 $\pm$ 0.7	19.9 $\pm$ 1.7

Note: (i) The initial Np concentration was either 1.0×10^{-12} M or 1.4×10^{-12} M

(ii) Errors quoted are based on counting statistics only.

hydroxides and it too has a very high K_d . MV 65 I is mainly manganese dioxide and although it has a similar CEC to the other two samples its surface area is considerably lower. This would indicate that the high K_d s for 6269 No. 2 and SH 1578 are due either to the high surface area or to some reaction with the iron.

In spite of their high surface areas and relatively high iron content the two red clays have the lowest distribution coefficients. The shape of the graphs is similar to that of the other low-carbonate samples i.e. the K_d increases slowly with time for the first few weeks. This is in contrast to the carbonate samples where the reaction is rapid and equilibrium is quickly set up and may indicate that sorption is to the amorphous iron in these samples rather than to the silica or clays.

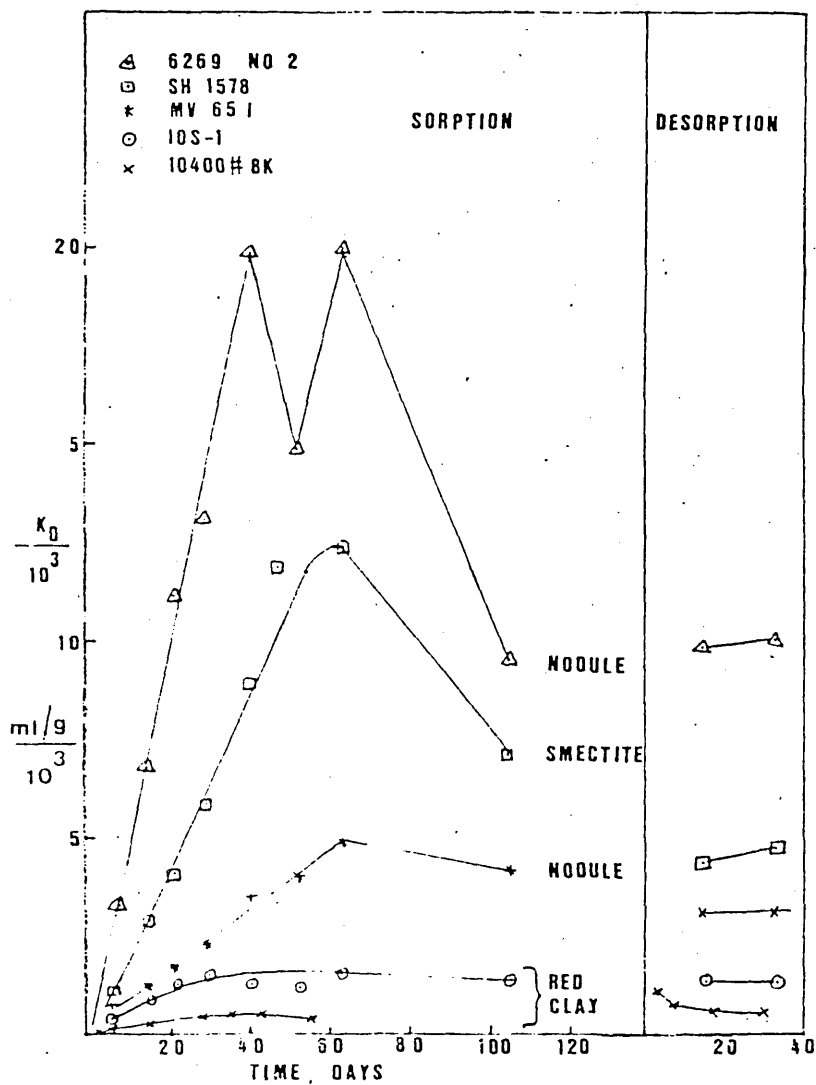
It would seem therefore, that as with americium, sorption of neptunium is by more than one mechanism. Beall¹ has suggested that calcium carbonate is a strong complexing agent for neptunium and americium and it is probable that chemisorption to calcium carbonate plays an important part in the sorption of these elements. Hydrolysis is also

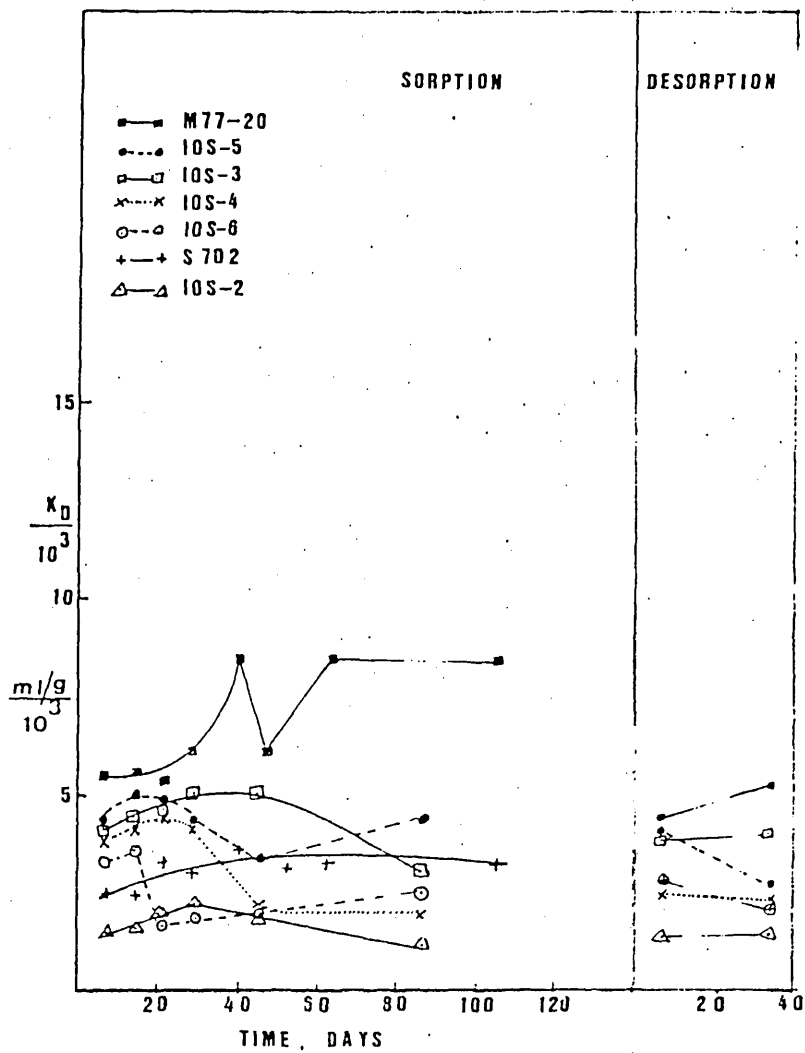
					DESORPTION	
					$\frac{K_d}{10^3}, \frac{\text{ml/g}}{10^3}$	
45 day	47 day	63 day	87 day	105 day	14 day	32 day
5.4 ± 0.2			3.1 ± 0.2		3.9 ± 0.2	4.0 ± 0.2
	6.1 ± 0.4	8.6 ± 0.9		8.4 ± 2.0	4.5 ± 0.3	5.3 ± 0.4
2.0 ± 0.1			2.6 ± 0.2		2.8 ± 0.1	2.1 ± 0.2
2.2 ± 0.1			2.0 ± 0.1		2.5 ± 0.1	2.4 ± 0.1
3.5 ± 0.1			4.5 ± 0.4		4.1 ± 0.2	2.8 ± 0.1
1.9 ± 0.1			1.2 ± 0.1		1.4 ± 0.1	1.5 ± 0.1
	3.1 ± 0.1	3.2 ± 0.2		3.2 ± 0.3	2.8 ± 0.1	2.1 ± 0.1
	11.9 ± 0.9	12.4 ± 1.0		7.1 ± 0.9	4.4 ± 0.2	4.8 ± 0.2
(Readings taken at different time intervals)						
	1.2 ± 0.1	1.6 ± 0.1		1.4 ± 0.1	1.4 ± 0.1	1.4 ± 0.1
	4.0 ± 0.2	4.9 ± 0.3		4.1 ± 0.3	2.6 ± 0.1	2.6 ± 0.1
	14.8 ± 0.9	20.7 ± 2.3		9.5 ± 0.8	8.9 ± 0.6	9.0 ± 0.6

likely to be important since the neptunyl ion hydrolyses strongly at pHs above 7.5. Thus the combination of sea water with its high pH and of the sediments with high carbonate content would seem to be ideal for the removal of Np from solution and the presence of iron can only improve matters. This is the case even in relatively oxidizing conditions; in more reducing conditions K_d s are likely to be even higher. Under natural conditions the pH should remain at 8.2 and this too should result in K_d s which are, if anything, higher than the measured values.

4. SUMMARY AND CONCLUSIONS

Sorption of neptunium and americium by marine sediments from sea water containing these nuclides in concentrations low enough to avoid precipitation has been studied. The main points to emerge from this work are:

FIGURE 3. N_p Distribution Coefficients: Low-Carbonate Sediments.

FIGURE 4. N_p Distribution Coefficients: High-Carbonate Sediments.

1. Distribution coefficients for all the sediments studied were $> 10^5$ for americium. Neptunium distribution coefficients were more variable, red clays giving the lowest values and the iron and manganese rich samples the highest. Apart from one red clay, all the neptunium distribution coefficients were $> 10^3$. Conditions used were relatively oxidizing and under more reducing conditions K_{ds} are likely to be even higher. This means therefore that if transport is mainly by diffusion it would take Np about 10^8 years (50 Np-237 half lives) and Am about 10^{10} years (10^6 Am-243 half lives) to pass through 30m of sediment.²³⁻²⁶ Americium would, therefore, certainly never reach the sediment/water interface and neptunium is unlikely to pose a significant hazard. Provided, therefore, that the other properties are satisfactory, all the sediments studied (with the possible exception of the red clays for neptunium) should form excellent barriers to the migration of both these nuclides.

2. It appears that for both elements sorption is by at least two different mechanisms one of which is associated with the manganese-oxide fraction in the sediments. The other is probably associated with the calcium-carbonate fraction and hydrolysis is also likely to be involved. The Np in solution remained in the V oxidation state throughout the experiments.

3. At these low levels, solubility does not appear to be the controlling factor in the desorption of Am.

4. The reactions for Np appear to be reversible (with the possible exception of the Fe-Np reaction) but desorption K_{ds} for Am are an order of magnitude higher than adsorption K_{ds} . This apparent difference between sorption and desorption K_{ds} may be due to the presence of a poorly sorbed species in the sorption experiments.

5. In the presence of sediments and under our experimental conditions particulate Am was trapped by the solid phase and was all retained by 0.22μ filters. Colloidal Am is unlikely, therefore, to be mobile.

Finally, it must be pointed out that this study has been purely comparative. It was designed to study the effect of sediment mineralogy and composition on the sorption of neptunium and americium from sea water. Under different experimental conditions different absolute values might well be obtained and it remains now to investigate the effect of changing variables such as E_h , solid/solution ratio, pressure and the presence of canister corrosion products on a smaller number of samples.

ACKNOWLEDGMENT

The work described in this report has been carried out for the Department of the Environment as part of its radioactive waste management research program. The results will be used in the formulation of Government policy but at this stage do not necessarily represent that policy.

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SORPTION OF PLUTONIUM BY DEEP-SEA SEDIMENTS

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The rate at which the different oxidation states of plutonium were sorbed from sea water by three different deep-sea sediments was followed. Pu-IV was sorbed much more rapidly than Pu-V and the rate at which the sediments removed Pu from solution decreased in the order smectite > high-carbonate sediment $\cong$ red clay. There was a strong correlation between these rates and the neptunium distribution ratios for the same sediments. This is presumably because neptunium is present in the Np-V oxidation state and the rate controlling step for the sorption of Pu is either the sorption of Pu-V or the reduction of Pu-V to Pu-IV. Distribution ratios for all three sediments decreased in the order Am > Pu > Np.

1. INTRODUCTION

During the past forty years artificially produced plutonium isotopes have entered the environment as the result of fallout from nuclear explosions, and the discharge of effluent from reactors and reprocessing plants. Much of this material has ended up in the sea and it is therefore extremely important that we should have a detailed understanding of its behaviour in the marine environment and the way in which it is distributed among water, sediments and biota. Furthermore, plutonium is an important constituent of high-level waste and one of the long-term options for the disposal of high-level waste presently being researched is the possible disposal of vitrified blocks in the ocean floor. Reliable data is therefore required for the distribution ratio* between sea water and marine sediments in order to make predictions about the rate of migration from canister (which might be placed under about 30m of sediment) to the sediment-water interface.

Plutonium can exist in solution in several oxidation states, the most common of which are the oxidised Pu-V and Pu-VI forms and the reduced Pu-III and Pu-IV forms and its behaviour in the environment will depend on which oxidation states are present. Furthermore, it seems that Pu-III and Pu-IV are likely to behave in a similar fashion to Am-III and Th-IV, respectively, which are strongly

*Note: It has been decided to follow the recommendations of the NEA co-ordinating group on the geological disposal of radioactive waste¹ and to use the term distribution ratio (R_d) rather than distribution coefficient (K_d) since all the results quoted are purely empirical. The two terms are defined as follows:-
 R_d = Distribution ratio of an element. This is an empirical value that is measured by laboratory experiment. R_d is the amount (either mass or activity) of the radio-element which is bound to the solid(s) present divided by the amount remaining in solution. Since this is strictly an empirical value, it does not imply reversibility or equilibrium and no attempt is made to relate it to a specific adsorption mechanism. R_d has units of $L^3 M^{-1}$, such as

$$\frac{\text{g nuclide} / \text{g nuclide}}{\text{g solid} / \text{cm}^3 \text{ liquid}}$$

K_d = distribution coefficient of an element. This parameter is similar to R_d but implies that the value represents equilibrium conditions. Such a parameter is appropriate to describe ideal ion exchange, for example. The units of K_d are the same as those of R_d .

sorbed by the sediments whereas Pu-V and Pu-VI would be expected to be sorbed with lower distribution ratios and to behave like Np-V and U-VI respectively. Recently, much effort both theoretical²⁻⁵ and experimental⁶⁻¹³ has gone into establishing the likely oxidation states of plutonium in natural waters. On balance it seems probable that the oxidised Pu is mainly in the Pu-V form and that the reduced Pu is mainly Pu-IV.

Nelson and Lovett⁶ analysed waters from the Irish Sea and found that the ratio of oxidised Pu(V + VI) to reduced Pu(III + IV) was generally greater than three. Wahlgren et al. using the same technique found that the Pu(V + VI)/Pu(III + IV) ratio was four in the waters of Lake Michigan. In the Pacific ocean, however, higher ratios were found by Nelson, Metta and Larsen⁹ and by Nelson, Carey and Bowen¹⁴. Here the ratio was around one through most of the water column and rose to ~ 9 in the deep layer near the sediment. In the interstitial waters of Irish Sea sediments Nelson and Lovett⁸ found that the ratio was very low, generally between 0.1 and 0.4. Finally, although leaching tests cannot be conclusive since the oxidation state may change during the leaching process, the experiments of Nelson and Lovett indicate that the Pu adsorbed on sediments and particulate matter is all in the reduced forms. It appears, therefore, from all this work that Pu in well oxygenated sea water is mainly in the oxidised Pu-V form but that it is reduced during sorption on to the sediments. The Pu concentration and the oxidation state distribution in the pore waters will result from a complex interaction between the redox equilibrium and sorption/desorption reactions for the various species.

In this investigation the sorption behaviour of each of the four main oxidation states of plutonium when contacted with three different types of deep-sea sediment was studied. Distribution ratios for americium and neptunium had already been determined under identical conditions and on the same sediments which had been carefully characterised¹⁵ and it was therefore possible to make comparisons among the three elements. The three sediments studied were a red clay, a carbonate-rich sediment and a smectite-rich sediment. Their mineralogy, chemical composition, surface areas and cation-exchange capacities are given in Tables 1 and 2.

Because it is desirable to simulate natural conditions as closely as possible and because interchange between the different oxidation states can occur, there seemed little point in attempting to start the experiments in one specific oxidation state. Instead, sea water spiked with Pu-238 was left to equilibrate for several weeks after which time the oxidation state distribution was determined.

Table 1. Mineralogy of Sediment

Composition			
	Major	Minor	Trace
10399 # 7K	Calcite	Kaolinite, illite, smectite	plagioclase feldspar (<2%) chlorite
10400 # 8K	Quartz, Illite	Kaolinite, smectite, Chlorite	plagioclase, feldspar (3-5%)
	Amorphous Fe oxyhydroxides (5-10%)		
SH1578	Smectite (30-40%) Fe oxyhydroxides (8-10%)		

Table 2 Chemical composition, surface area and cation exchange capacities of the sediments.

Sample No.	CaCO ₃ %	Si %	Fe %	Mn %	Al %	Mg %	Na %	K %	Ti ppm	P ppm	SA m ² /g	CEC mEq/100g
10399 # 7K	85	9.3	1.8	0.10	3.4	0.73	0.88	2.4	1800	250	85	17
10400 # 8K	3	24.6	5.0	0.32	8.8	1.68	0.63	2.5	5500	680	190	43
SH1578	4	12.0	14.6	4.3	2.0	-	0.7	0.34	1100	340	396	124

This sea water was then contacted with sediment and, at intervals the liquid phase was analysed for each oxidation state. In this way it was possible to compare the rates at which each form was removed from solution.

2. EXPERIMENTAL

2.1. Sorption Experiments

Distribution ratios were determined using a standardised procedure based on the method prescribed by Relya³. Briefly, 0.1g sediment was placed in a 50ml Oakridge centrifuge tube together with 35g of spiked sea water. The tubes were placed horizontally in a water bath at 4°C and shaken gently at 120 strokes/minute. After the required time interval the samples were centrifuged at 7000 rpm (5230g) for 30 min. The solution phase was rapidly filtered through 0.22 μ filters and analysed immediately. Fresh, unspiked sea water was added to the solid phase and after two preliminary washes desorption experiments begun.

On collection from the ocean bed the sediments were sealed and stored at 4°C. Samples were taken by mixing portions of sediment with sea water to form a slurry and then pipetting off representative portions. The spiked sea water was prepared by adding 200 μ l of a Pu-238 stock solution in dilute acid to 1 l filtered (0.22 μ) sea water. The pH was readjusted to 8.2 with a few drops of 0.1 M sodium hydroxide and the solution allowed to stand for six to eight weeks. Immediately before use it was filtered through 0.22 μ filters and analysed for total plutonium and each of its four oxidation states.

2.2. Analytical

The method of Lovett and Nelson¹³ distinguishes between the reduced Pu(III + IV) forms and the oxidised Pu(V + VI) forms. It involves the additions of an "holding oxidant" $K_2Cr_2O_7$ to the sample. This oxidises Pu-III to Pu-IV and Pu-V to Pu-VI and prevents the reduction of Pu-V and Pu-VI to either of the reduced states. The reduced Pu is then co-precipitated with neodymium fluoride while the oxidised Pu remains in the supernate. The Pu-VI in the supernate is then reduced with ferrous iron and precipitated in the same way with neodymium fluoride. An adaptation of this method using lanthanum fluoride instead of neodymium fluoride, was tested and found to work well. More difficulty was found when attempting to use the method of Foti and Freiling¹⁶ which uses a combination of lanthanum fluoride precipitations and

solvent extraction with 2-theonyltrifluoroacetone (TTA) to separate all four oxidation states. Finally, a combination of the two sets of methods was used and a total of six determinations was made on each solution. These were:

- (1) III + IV + V + VI: Total Pu
- (2) III + IV + V : LaF_3 precipitation in the presence of uranyl hold-back carrier.
- (3) VI : Reduction of Pu in supernate from (2) with ferrous iron followed by another LaF_3 precipitation.
- (4) III + IV : LaF_3 precipitation in presence of $\text{K}_2\text{Cr}_2\text{O}_7$ holding oxidant.
- (5) V + VI : Reduction of Pu in supernate from (4) with ferrous iron followed by LaF_3 precipitation.
- (6) IV : TTA extraction from HCl solution at pH 0.3.

After separation from the other oxidation states the Pu was always determined by the same method as that used for total Pu. This was based on the method of Moore and Hudgens¹⁷ and involved adjustment of all the Pu to Pu-IV followed by extraction into 2-theonyltrifluoroacetone (TTA) dissolved in benzene. Evaporated sources were prepared from the organic layer and counted on an alpha spectrometer. A ^{239}Pu -IV spike was used to monitor recoveries.

The method was tested on a number of solutions containing pure Pu-III, Pu-IV and Pu-VI prepared by different methods. It was found that the separation between the oxidised Pu(V + VI) and reduced Pu (III + IV) was reproducible and specific. Extraction of Pu-IV into TTA at pH 0.3 was also quantitative and very little Pu-III and no Pu-VI (whether prepared by electrolysis or dichromate reduction) was extracted under the conditions used. The results obtained when co-precipitating Pu(III + IV + V) with LaF_3 in the presence of U holdback carrier were unreliable. In the presence of even minute traces of potassium dichromate (as little as 10^{-7}M) < 10% of the Pu-VI was precipitated. However, in the absence of oxidising agents Pu-VI prepared by electrolysis or by fuming with perchloric acid was almost quantitatively precipitated. It would appear, therefore, that either the Pu-VI prepared by the latter two methods was actually Pu-V or was rapidly converted to Pu-V on addition to sea water prior to analysis or that, in the absence of an oxidising agent, Pu-VI is precipitated by the LaF_3 method used. Until this matter is resolved the differentiation between Pu-V and Pu-VI should be treated with caution.

3. RESULTS AND DISCUSSION

Table 3 and Figure 1 show how the distribution ratios and the concentration of total Pu in the solution phase changed with time during sorption. Table 4 and Figure 2 show how the concentrations of the various oxidation states changed with time. Adjacent to each graph in Figure 2 are the neptunium distribution ratios. These are discussed in Section 3.1.

It can be seen from Table 4 that throughout the experiments virtually all the oxidised Pu appeared to be in the V form as was to be expected in view of the theoretical and experimental work discussed in Section 3.1. The reduced Pu was all in the IV form as predicted by Skytte Jensen³. It is interesting to note that approximately 72% of the Pu in the initial spiked sea water was in the oxidised Pu(V + VI) forms. This agrees well with the values found by Nelson and Lovett for surface waters in the Irish Sea. Thus although the Pu concentration in this spiked sea water was roughly three orders of magnitude higher than in the Irish Sea ($3.1 \times 10^{-11} \text{ M}$ as compared with $6.7 \times 10^{-13} \text{ M}$) the oxidation state distributions were similar.

From a study of all these results the following additional observations can be made.

- i) The overall distribution coefficient based on the total Pu in solution was between 10^4 and 10^5 for all three samples and continued to rise until the end of the experiment after 102 days. These values are in agreement with the published results¹⁷⁻²⁴.
- ii) The concentration of reduced Pu(III + IV) dropped much more rapidly than the concentration of Pu(V + VI). Thus for sample (10400 # 8K) the concentration of Pu (III + IV) dropped by more than a factor of ten during the first hour, whereas after that time the Pu(V + VI) was still more than two thirds of its original value. It is fairly meaningless to calculate distribution coefficients for individual oxidation states because there may be interchange between them but it is interesting to compare R_d after one hour and to note that for Pu(III + IV) it was 3000 as compared with 50 for Pu (V + VI).
- iii) With time the oxidised Pu(V + VI) was also very efficiently removed from solution. In fact after 102 days there was more reduced than oxidised Pu in solution for all the samples. It is impossible to tell whether the Pu-V is adsorbed as Pu-V or whether it is reduced during or before sorption but it is clear that it is the rate of sorption of Pu-V which governs the rate at which the overall R_d increases with time. It is probably significant that there is a strong correlation

Table 3. Plutonium Distribution Ratios During Sorption and Desorption

Sample	Sorption time	Total Pu in soln Bq/l	% Adsorbed	Adsorption R_d $\frac{\text{ml/g}}{10^4}$	Desorption Time days	Desorption R_d $\frac{\text{ml/g}}{10^4}$
Initial seawater						
$3.1 \times 10^{-11} \text{ M}$		4356 ± 1144				
SH 1578	1 h	1026 ± 171	76.4 ± 5.7	0.16 ± 0.03		
	22 h	88 ± 8	98.0 ± 4.6	2.34 ± 0.22		
	30 d	24 ± 2	99.4 ± 4.7	8.97 ± 0.84	125	49.8 ± 1.9
	120 d	24 ± 2	99.4 ± 4.7	9.40 ± 0.67	27	90.7 ± 3.2
10399 7K	1 h	2416 ± 98	44.5 ± 4.2	0.022 ± 0.002		
	22 h	855 ± 41	80.4 ± 4.3	0.102 ± 0.007		
	30 d	34 ± 3	99.2 ± 4.7	3.46 ± 0.30	125	12.1 ± 0.5
	102 d	20 ± 1	99.5 ± 4.7	5.86 ± 0.40	27	24.1 ± 0.9
10400 8K	1 h	2982 ± 895	31.5 ± 2.7	0.012 ± 0.001		
	22 h	1724 ± 35	60.4 ± 3.9	0.058 ± 0.004		
	30 d	122 ± 15	97.2 ± 4.6	1.44 ± 0.19	125	8.9 ± 0.9
	102 d	26 ± 2	99.2 ± 4.7	4.71 ± 0.32	27	20.3 ± 0.9

Table 4 Pu Oxidation State Distribution During Sorption

Sample	Time	Pu-238 Concentration (Bq/l) during sorption							Ratio	
		Total	(III + IV)	V + VI	(III+IV+V)	IV	III	VI	$\frac{V + VI}{III + IV}$	
Initial Sea-water $3.1 \times 10^{-11} M$		4356 $\pm$ 1421	1242 $\pm$ 120	3366 $\pm$ 144	4656 $\pm$ 186	1200 $\pm$ 138	42 $\pm$ 183	-	2.7 $\pm$ 0.3	
SH 1578	1 h	1026 $\pm$ 171	103 $\pm$ 3	1053 $\pm$ 316	1022 $\pm$ 129	90 $\pm$ 10	13 $\pm$ 11	-	10.2 $\pm$ 3.1	
	22 h	88 $\pm$ 8	36 $\pm$ 2	44 $\pm$ 3	89 $\pm$ 2	46 $\pm$ 2	-10 $\pm$ 3	-	1.2 $\pm$ 0.1	
	30 d	24 $\pm$ 2	19 $\pm$ 2	2.4 $\pm$ 0.7	21 $\pm$.1	20 $\pm$ 1	- 1 $\pm$ 2	1.5 $\pm$ 0.6	0.1 $\pm$ 0.04	
	102 d	24 $\pm$ 2	17 $\pm$ 1	4.8 $\pm$ 1.4	24 $\pm$ 2	19 $\pm$ 1	- 2 $\pm$ 2	0.3 $\pm$ 0.3	0.3 $\pm$ 0.1	
7K 10399	1 h	2416 $\pm$ 98	107 $\pm$ 11	1983 $\pm$ 88	2364 $\pm$ 709	80 $\pm$ 5	28 $\pm$ 12	-	19 $\pm$ 2	
	22 h	855 $\pm$ 41	49 $\pm$ 2	897 $\pm$ 51	766 $\pm$ 42	43 $\pm$ 2	5 $\pm$ 3	-	18 $\pm$ 1	
	30 d	34 $\pm$ 3	19 $\pm$ 2	22 $\pm$ 2	44 $\pm$ 25	18 $\pm$ 1	1 $\pm$ 2	1.4 $\pm$ 0.5	1 $\pm$ 0.2	
	102 d	20 $\pm$ 1	13 $\pm$ 1	6 $\pm$ 2	20 $\pm$ 2	14 $\pm$ 2	-1 $\pm$ 2	0.9 $\pm$ 0.3	0.5 $\pm$ 0.2	
8K 10400	1 h	2982 $\pm$ 895	128 $\pm$ 6	3011 $\pm$ 109	2909 $\pm$ 146	64 $\pm$ 14	64 $\pm$ 15	-	24 $\pm$ 1	
	22 h	1724 $\pm$ 35	68 $\pm$ 4	1589 $\pm$ 180	1345 $\pm$ 61	65 $\pm$ 6	4 $\pm$ 7	-	23 $\pm$ 3	
	30 d	122 $\pm$ 15	17 $\pm$ 1	126 $\pm$ 6	98 $\pm$ 9	21 $\pm$ 2	-4 $\pm$ 2	12 $\pm$ 2	7 $\pm$ 1	
	102 d	26 $\pm$ 2	14 $\pm$ 1	8 $\pm$ 1	24 $\pm$ 1	17 $\pm$ 1	-3 $\pm$ 2	1 $\pm$ 1	0.6 $\pm$ 0.1	

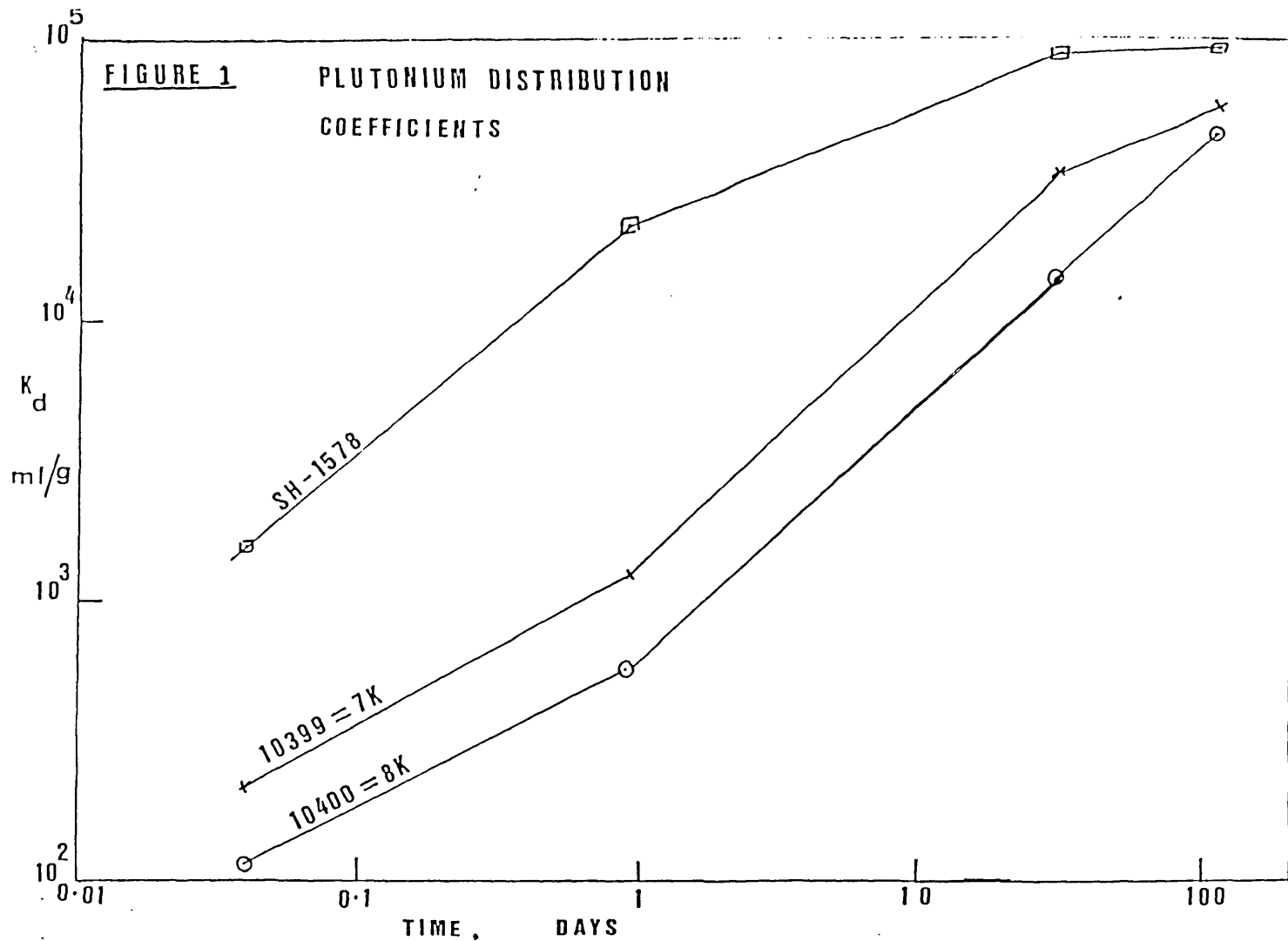
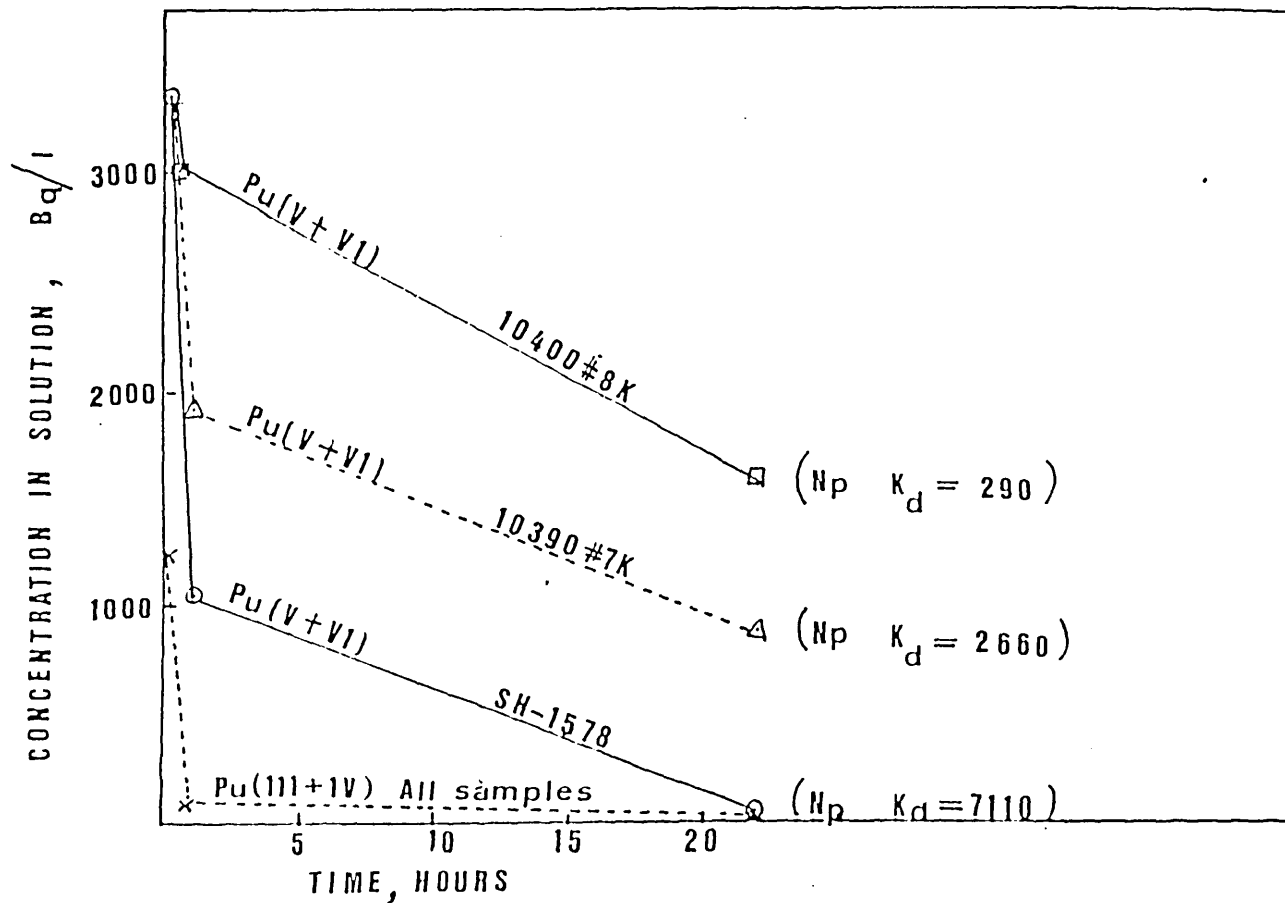


FIGURE 2. CONCENTRATION OF OXIDISED & REDUCED PLUTONIUM-238
IN SOLUTION DURING THE FIRST 22 HOURS



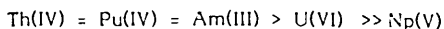
between the rate at which Pu-V is removed from solution and the Np distribution coefficient. This is illustrated in Figure 2 where the Np R_d ¹⁵ are written next to the corresponding graphs showing the rate at which the Pu-V concentration decreases during the first 22 hours. This figure also illustrates the dramatic difference in the rates of sorption.

If one assumes that removal from solution is accompanied by reduction then one can rank the sediments in order of reducing ability, the order being SH 1578 > 10399 # 7K > 10400 # 8K. So although the range in final distribution coefficients was not large the rate at which Pu was adsorbed by the different sediments varied significantly. Thus the smectite, SH 1578, adsorbed 98% of the total Pu within the first 22 hours whereas the red clay and the carbonate-rich sediment adsorbed 60% and 80%, respectively, during the same period. This rate appears to be related to the ability of the sediments to reduce plutonium from the Pu-V to the Pu-IV form.

iv) Desorption distribution ratios were five to ten times greater than sorption distribution ratios and the proportion of reduced plutonium in solution was much the same as at the end of the sorption period. To a certain extent the high desorption distribution ratios may be explained by the presence of some non-sorbable species (e.g. organic complexes or micro-particulates that were not removed during phase separation) which lowers the observed sorption R_d more than the desorption R_d . However, differences of this magnitude probably indicate that the sorption-desorption reaction is, at least to some extent, irreversible.

3.1. Comparison with neptunium and americium:

Edgington^{19,20}, by comparing the K_d values reported in the literature has ranked the actinides in order of decreasing distribution coefficient as follows:



This ranking was based on the results from a number of different sediments studied under different conditions. As a result of the present work we now have a complete set of R_d values for Pu, Am and Np all determined under identical conditions and on the same sediments and these values for both sorption and desorption are given in Table 5. Included in Table 5, on the assumption that this is a measure of the ability of the sediments to reduce the actinides, is the percent of Pu-V remaining in solution after the different time intervals. Of course, this may not be a valid assumption and these figures may simply be an indication of the relative ability of the different sediments to adsorb pentavalent actinides.

Table 5 Relationship between distribution ratios and the rate at which Pu-V is removed from solution by the different sediments

Sample	"Reducing Power" as indicated by percent Pu-V remaining in solution after			DISTRIBUTION RATIO , ml/g			
				Np	Pu		Am
	1 hr	22 hr	30d	sorption and desorption	sorption 102 d	desorption	sorption 56 d desorption
SH 1578	31	1	0.1	7×10^3	9×10^4	9×10^5	4×10^5 26×10^5
10399 7K	59	27	0.7	3×10^3	6×10^4	2×10^5	2×10^5 $\sim 6 \times 10^5$
10400 8K	89	47	3.7	0.3×10^3	5×10^4	2×10^5	1×10^5 $\sim 6 \times 10^5$

It can be seen that the R_d for all three actinides decrease in the same order and that this is the order of decreasing "reducing power". It is also clear that R_d decrease in the order $Am > Pu \gg Np$ although the difference between Am and Pu is not large, particularly for desorption. Desorption of Pu would be largely governed by the sorption/desorption reaction for reduced Pu-IV and Am is in the reduced Am-III form. Np, on the other hand, was shown to be entirely in the Np-V form in all the solutions. We cannot tell from these experiments whether or not it is reduced during sorption. The fact that distribution coefficients are so much lower than for Pu probably indicates that it is sorbed in the Np-V form although the strong correlation between the Np distribution coefficient and the rate at which Pu-V is removed from solution suggests that the same mechanism is involved in the sorption of both Pu-V and Np-V.

4. SUMMARY AND CONCLUSIONS

In this work we have studied the way in which the various oxidation states of plutonium are sorbed from sea water by three different deep-sea sediments. It was found that the $Pu(V + VI)/Pu(III + IV)$ ratio in spiked sea water which had been left to equilibrate for several weeks was approximately three. This ratio increased dramatically when the sea water was contacted with sediment as the reduced $Pu(III + IV)$ was sorbed much more rapidly than the oxidised $Pu(V + VI)$. Nevertheless, with time the $Pu(V + VI)$ was effectively removed from solution and the final ratio after 102 days was less than 0.6 for all three sediments. It was shown that the reduced Pu was virtually all in the Pu-IV form and the oxidised Pu in the Pu-V form throughout the experiments.

From the waste management point of view it is clear that Pu oxidation state is not important. Plutonium, whether originally present in reduced or oxidised form was strongly sorbed by all three types of sediment studied, final overall distribution coefficients being $> 10^4$ in all cases.

Although final Pu distribution coefficients were similar for the three sediments there were significant differences in the rate at which they removed Pu-V from solution. This is presumably related to their ability to reduce Pu-V to Pu-IV. There is a strong correlation between this rate and the Np-V distribution coefficient. The order of decreasing activity was smectite > high-carbonate sediment > red clay. This does not appear to be related to any of the other measured properties of the sediments such as surface area, cation exchange capacity or trace element composition.

For all three sediments distribution ratios decreased in the order Am > Pu > Np. For Np, distribution ratios decreased in the order smectite > high-carbonate sediment > red clay and for Am and Pu, in the order smectite > high-carbonate $\approx$ red clay.

Finally, it should be noted that in these experiments conditions had to be rigidly controlled to allow comparisons between sediments and nuclides to be made. The sediment concentration was approximately 3 g/l. Subsequent work has shown that at very high solid/solution ratios the behaviour of high-carbonate sediments is completely different. These results will be reported in a later paper.

ACKNOWLEDGEMENT

The work described in this report has been carried out for the Department of the Environment as part of its waste management research program. The results will be used in the formulation of Government Policy but at this stage do not necessarily represent that policy.

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ADSORPTION OF ACTINIDES BY MARINE SEDIMENTS : THE EFFECT OF THE
SEDIMENT/SEA WATER RATIO ON THE MEASURED DISTRIBUTION RATIO

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Abstract

The effect of the solid/solution ratio on distribution ratios measured using a standard batch technique has been investigated. Two different deep-sea sediments and the actinides americium, neptunium and plutonium have been studied. It is shown that the apparent drop in distribution ratio with increasing sediment concentration can frequently be explained by the presence of a small amount of non-separable or "low- R_d " species and that by measuring the R_d at different solid/solution ratios it is possible to estimate the proportion of low- R_d species present. These may be colloidal or stable complexes. Plutonium exhibited anomalous behaviour with the high-carbonate sediment and the distribution ratio dropped from $> 10^4$ to 10^2 ml/g as the solid/solution ratio increased from 2 g/l to 20 g/l. At high sediment concentrations the plutonium in solution was mainly in the oxidised Pu(V + VI) form and it is postulated that Pu-V or Pu-VI carbonates were the main species present.

1. INTRODUCTION

In experimental studies concerned with the fate of radionuclides in the environment major efforts have been devoted to the determination of the distribution coefficient, K_d , or more frequently the distribution ratio, R_d , between a solid adsorbent and natural waters. (R_d is numerically equal to K_d but is an empirical measured value. It does not imply equilibrium or reversibility and no attempt is made to relate it to any specific sorption mechanism¹). The values obtained are then used in two types of model:- (i) those designed to assess the suitability of various waste repositories either in geological formations on land or beneath the sea bed and (ii) models describing the movement of nuclides which have entered the environment from fall-out, nuclear reprocessing facilities or the occasional accident. This pragmatic approach is defended on the grounds that natural systems are so complicated that no other procedure is capable of providing the figures needed by the modellers. It has, however, met with limited success as the actual values obtained in the laboratory have been shown to be highly dependent upon the experimental procedure used.²

In theory the solid/solution ratio should have no effect on the distribution ratio. Many workers have, therefore, chosen a solid/solution ratio that suits their experimental system and investigated the effect of other variables such as temperature, nuclide concentration, pH etc. on the R_d . Others, however, have noted that the distribution ratio changed as the solid/solution ratio increased and various explanations have been offered. Thus, Sanchez and Schell⁶ suggested that some surface sites serve

as "nucleation sites" for precipitation of actinides and that an increase in the number of such sites would not necessarily increase the radionuclide removal from solution. Cremers⁷, discussing sorption by ion exchange, points out that the exchange complex is in thermodynamic equilibrium with some "interstitial in situ" solution and the total pool of exchangeable ions exceeds the bulk solution. He suggests that the apparent variation in K_d with changing solid, solution ratio can be explained in terms of changing composition of both phases.

A more practical explanation comes from Ames and McGarrah.⁸ They found that, not only was it very difficult to prevent colloidal clay particles from remaining suspended in the solution phase, but that colloids consisting, at least partially, of hydrated ferric and manganese oxy-hydroxides were generated during the shaking period. These strongly sorbed the radionuclides being studied but remained in the solution phase after phase separation and lowered the apparent K_d .

This theme is taken up by Sheppard et al.,^{9,10} who studied the sorption of Cs, Sr and Am on solids. They concluded that the distribution ratios of radionuclides are a "function of the soils studied and the particle size resolution technique used". They found that for their set of soils three broad classes of particles determined the observed distribution ratios. These were (i) ionic ones i.e. particles containing radionuclides with radii less than one nm (ii) complexes of humic matter, possibly humic acid polymers with molecular weights between 8000 and 50000 (2-3 nm radii) and (iii) larger soil particles with radii in the 10-50 nm range.

Finally O'Connor and Conolly¹¹ reviewed the literature covering studies involving a number of organic and inorganic solutes and sorbents and reported that "linear partition coefficients are inversely dependent upon the concentration of solids in the system". Voice, Rice and Weber¹² studied their data and initiated a study to assess the effects of solids concentration on the partitioning of hydrophobic compounds. They concluded that the observed change in partitioning behaviour could be attributed to a transfer of sorbing, or solute binding, material to the liquid phase during the course of a partitioning experiment. This material whether dissolved, macromolecular, or microparticulate was not removed from the solution phase during the separation procedure and was capable of stabilizing the compound of interest in solution.

Voice et. al. considered the effect of microparticulate matter in general. Nelson, Larson and Penrose¹³ studied the effect of colloidal organic carbon (COC). They showed conclusively that plutonium associates with any COC that may be present in the water. The COC-Pu complex is poorly sorbed by the particulate matter and remains with the solution during phase separation resulting in a lowered R_d .

Clearly if distribution ratios determined by the batch method are to be of use in modelling radionuclide movement it is essential that the situation be clarified. If necessary, models will have to deal separately with the movement of ions, polymer-size molecules and micro-particulates. We, therefore, decided to investigate the problem by first, undertaking a mathematical analysis to determine how sensitive the measured distribution

ratio would be to the presence of some non-separable nuclide and secondly, an experimental study in which we determine distribution ratios for Am, Pu, and Np over as wide a range of sediment-sea water concentrations as possible. The results of this work now follow.

2. THEORETICAL

Experimentally it is difficult to distinguish between a "two-site" situation in which sorption occurs on sorption sites with different selectivities and a "two-species" situation in which the ion in solution is present in two stable forms e.g. one ionic and another liganded. In this analysis we have concentrated on a two species model because we are working at very low nuclide concentrations (at which Henry's law is obeyed) and high sediment concentrations. It is unlikely, therefore, that there will be competition for even the more highly selective sites.

Furthermore a two species model is more appropriate for the situation in which the second species is simply particulate material which has not been removed during phase separation.

2.1 Calculations showing the effect that the presence of two stable species has on the measured distribution ratio.

(i) A fixed proportion of the original nuclide with a low distribution ratio

In most batch-distribution experiments the nuclide in the solution phase is measured before and after sorption and the R_d calculated from the formula,

$$R_d = \frac{C_o - C}{C} \cdot v/m \quad (1)$$

where C_0 = Initial concentration of the radionuclide in solution

C = Concentration of radionuclide in solution after sorption

v = Volume of liquid phase

m = Mass solid phase

now let $x C_0$ = initial concentration of the species that is adsorbed with a high R_d (R_H).

then $(1-x)C_0$ = initial concentration of the species that is adsorbed with a low R_d (R_L)

let $C = C_H + C_L$ where C_H and C_L are the final concentrations of the high- and low- R_d species, respectively.

$$\text{Then from (1) } C = \frac{C_0 z}{R_d + z}$$

$$\text{So that } C_H = \frac{x C_0 z}{R_H + z} \text{ and } C_L = \frac{(1-x) C_0 z}{R_L + z}$$

$$C = C_H + C_L = \frac{C_0 z \times (R_L + z) + C_0 z (1-x)(R_H + z)}{(R_H + z)(R_L + z)}$$

$$\text{Now } R_d (\text{observed}) = \left(\frac{C_0}{C} - 1 \right) z$$

$$\frac{C_0 z}{\frac{C_0 [zx(R_L + z) + z(1-x)(R_H + z)]}{(R_H + z)(R_L + z)}} - z$$

$$= \frac{(R_H + z)(R_L + z)}{x(R_L - R_H) + R_H + z} - z \quad (2)$$

$$\text{and } \frac{C_o - C}{C} = \frac{(R_H + z)(R_L + z)}{z[x(R_L - R_H) + R_H + z]} - 1 \quad (3)$$

(ii) Amount of low- R_d species proportional to sediment concentration

In this case $(1-x) \propto m$

$$\text{i.e. } (1-x) \propto \frac{1}{z}$$

$$(1-x) = \frac{k}{z}$$

$$x = \frac{z-k}{z}$$

Substituting in eqn. (2) gives

$$R_d = \frac{z(R_H + z)(R_L + z)}{(z-k)(R_L - R_H) + R_H + z} - z \quad (4)$$

$$\text{and } \frac{C_o - C}{C} = \frac{(R_H + z)(R_L + z)}{(z - k)(R_L - R_H) + z} - 1 \quad (5)$$

The effect of changing the different variables in these equations is illustrated in Figs. 1 - 4. In each figure two sets of graphs are given viz. $\log R_d$ vs. $\log m/v$ and $\log (C_o - C)/C$ vs. $\log m/v$. The latter graphs are often more informative than the former since from the definition of R_d it can be deduced that if there is only one species present and if it is all adsorbed with the same effective R_d , a plot of $\log (C_o - C)/C = \log m/v$ should give a straight line with gradient one and intercept $\log R_d$. (Since by definition $R_d = [(C_o - C)/C](v/m)$ i.e. $\log(C_o - C)/C = \log m/v + \log R_d$). The presence of a second species changes both the slope and intercepts as can be seen from Figs. 1 - 4.

Figs. 1 and 2 show these graphs for the situations where (i) there is a fixed proportion of low- R_d nuclide and (ii) the amount of low- R_d nuclide is proportional to the sediment concentration.

For the purpose of illustration the distribution ratio of the high- R_d species (R_H) is taken as 10^6 and of the low R_d (R_L) species as 0.1. Fig. 3 shows the effect of lowering the value of R_d for a fixed amount of low- R_d species (in this case 0.05%).

It can be seen from Fig. 1 that if R_H is as high as 10^6 the observed distribution ratio is extremely sensitive to the presence of even minute amounts of low- R_d species. At low solid/solution ratios the observed R_d will tend to R_H but as the solid/solution ratio increases the observed R_d will drop sharply. Fig. 2 shows that if the amount of low- R_d species increases with increasing sediment concentration then the distribution ratio drops more sharply with increasing solid/solution ratio than it does when there is simply a fixed amount present and the gradient of the graph of $\log (C_o - C)/C$ vs. m/v actually becomes negative.

From Fig. 3 it can be seen that the effect of a small amount of low- R_d species decreases with decreasing R_d . Thus 0.05% of a species with $R_d = 0.1$ will have no detectable effect if R_H is 10^3 or less.

Fig. 4 illustrates the case where R_L instead of being close to zero has a reasonably high value (100 in this example). It can be seen that now R_d is constant (and the graph of $\log (C_o - C)/C$ vs. m/v has a slope of one) at high solid/solution ratios but that at low solid/solution ratios R_d rises steeply as m/v decreases. For this situation to exist stable complexes, each with its own distribution ratio and not in equilibrium with each other, would have to be formed. It could possibly arise in natural waters where minute traces of organic ligands are available for complexing. It is, however, fairly unlikely to occur in our

experiments where the amount of nuclide present is also extremely small (although a graph of this shape was obtained for neptunium on red clay).

Finally we should consider the effect that more than one species will have on the desorption distribution ratio. It has become common practice after measuring a distribution ratio to replace the solution phase with fresh ground water and then to determine the desorption R_d . Frequently desorption R_d values are an order of magnitude, or more, greater than sorption R_d values and this is generally interpreted as demonstrating that the sorption-desorption reaction is irreversible. Cremers⁷ suggested that such experiments have little value because the composition of both phases may have changed during the reversibility tests.

Nevertheless, from the point of view of radionuclide migration desorption is as important as sorption and it is essential that desorption processes be understood. Serne and Relaya² have speculated that the difference in R_d values can be caused by some of the following mechanisms: (i) collapse of interlayers of 2:1 lattice clays such as illite (ii) precipitation of insoluble minerals or coprecipitation and entrapment in amorphous coatings (iii) reduction to more insoluble species by crystal lattice elements such as Fe (iv) non-linear isotherms where R_d increases as the total mass of nuclides in the system is reduced (v) diffusion of nuclides deep into the rock matrix (vi) presence of multiple sorption sites with a few with extremely high affinity for the particular nuclide (two-site model). Although one or more of the above processes are probably involved in different experimental systems it is also possible that the presence of

some low- R_d species (frequently the result of poor phase separation) has often magnified this effect. These would lower the observed sorption R_d values but would be removed after the sorption experiment and would not be present to lower the observed desorption R_d . How significant this effect is would depend not only the quantity of low- R_d nuclide present but also on its nature. Most of it might be removed during the first phase separation but micro-particulates are likely to be trapped with the solid phase and continuously released through a number of desorption stages. This trapping effect would be greatest at high solid/solution ratios, with the result that the desorption R_d would approach the sorption R_H at low solid/solution ratios but would still be lowered at high solid/solution ratios. This is the type of effect that we have observed with americium.

Note In deep sea sediments the water content ranges from 65% to 85% i.e. the solid concentration ranges from about 150 to 350 g/l (m/v between 0.25 and 1.0 i.e. $\log m/v$ between 0 and -0.6).

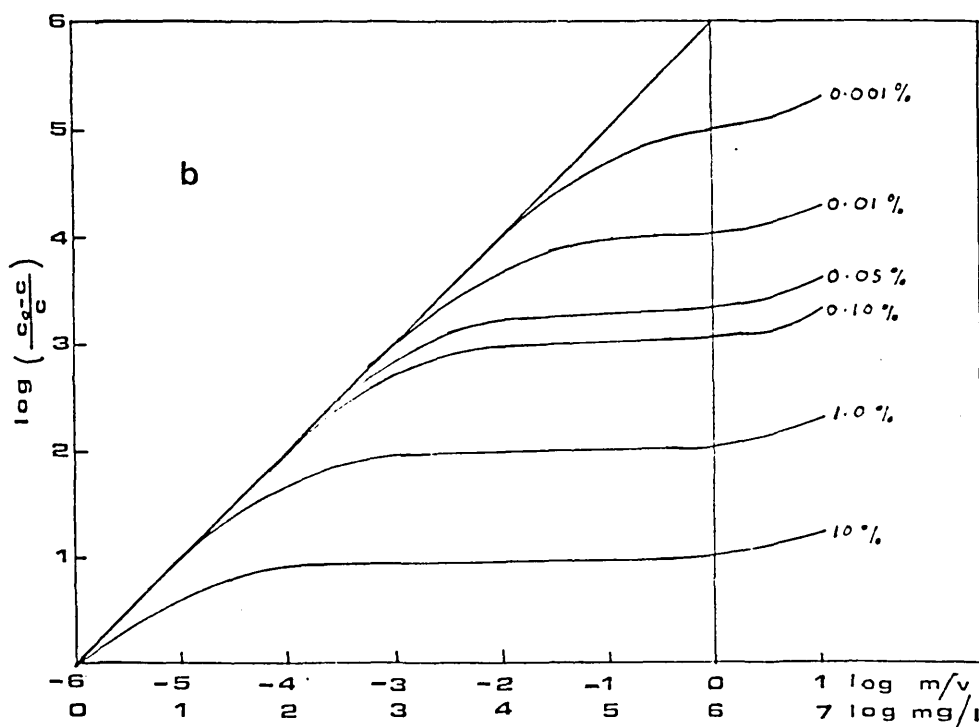
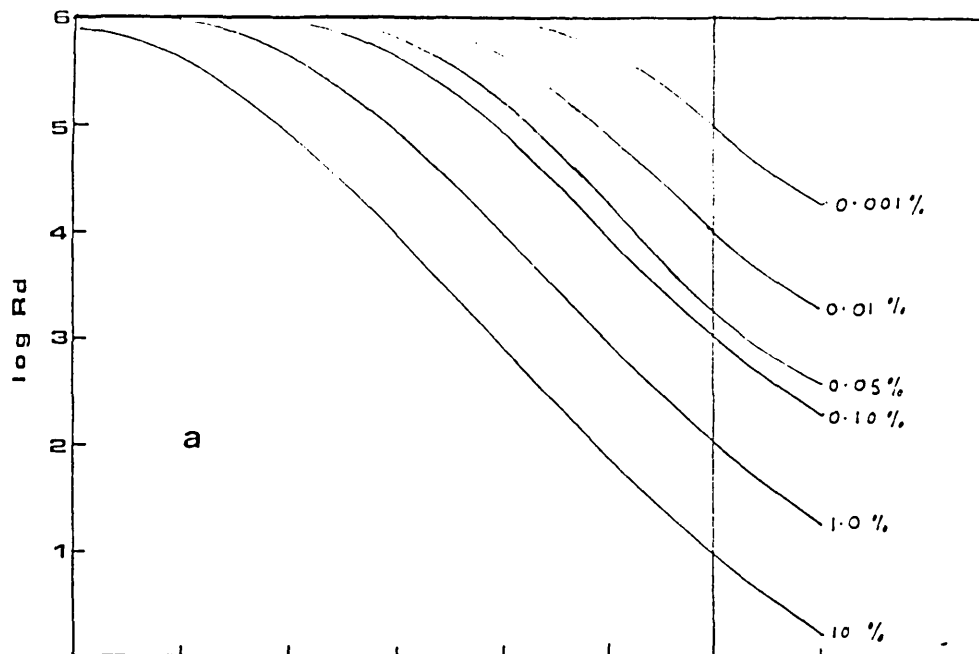


Fig. 1 The effect of a fixed proportion of a second species which is not adsorbed by the sediment on the relationship between $\log m/v$ and (a) $\log R_d$, (b) $\log(C_0 - C)/C$ for different percentages of low R_d species ($R_H = 10^6$, $R_L = 0.1$).

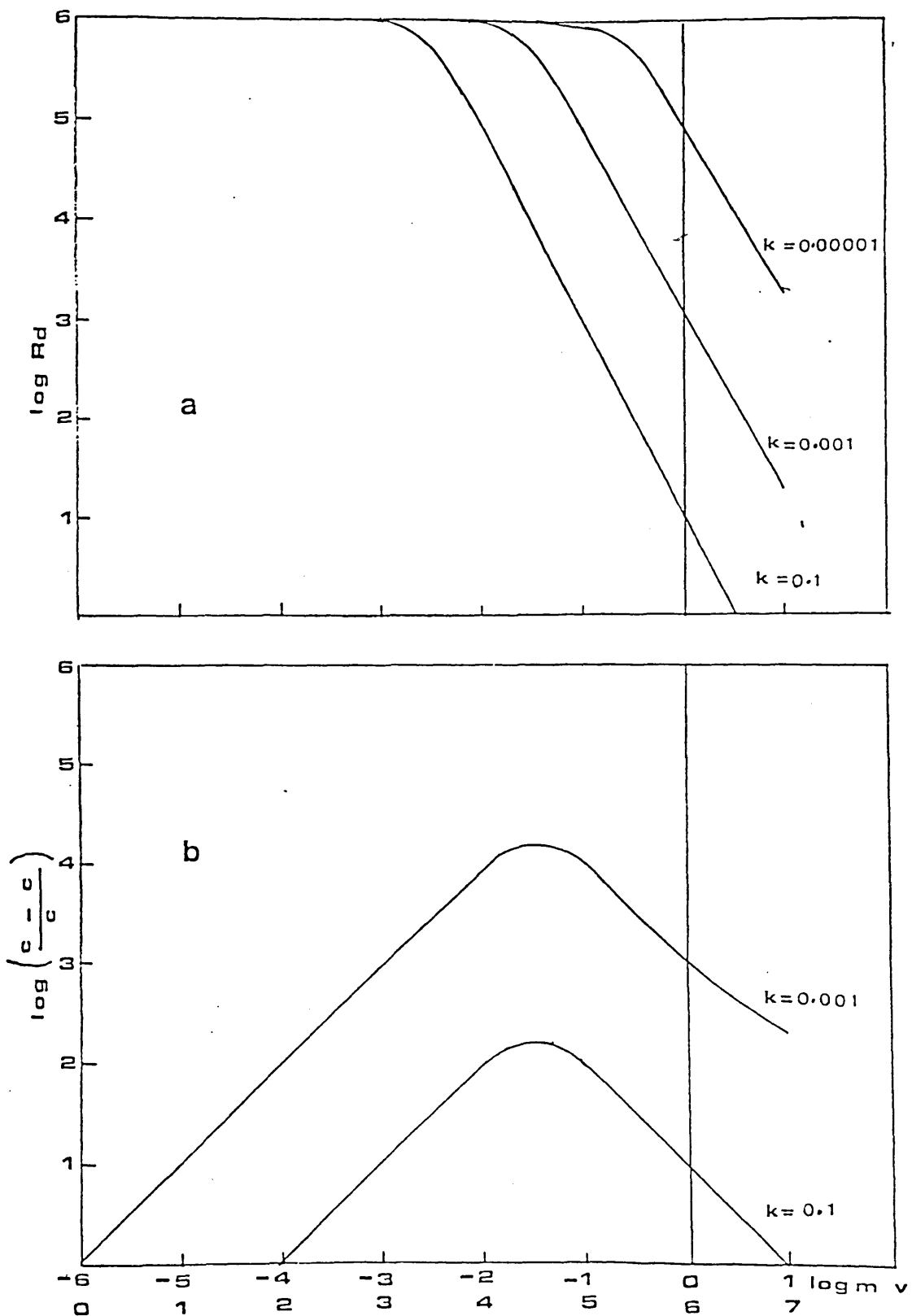


Fig 2 The effect of the presence of a second species which is not sorbed by the sediment and whose concentration is proportional to the sediment concentration on the relationship between $\log m/v$ and (a) $\log R_d$ (b) $\log(C_0 - c)/c$ for different proportionality constants ($R_H = 10^6$, $P_s = 0.1$).

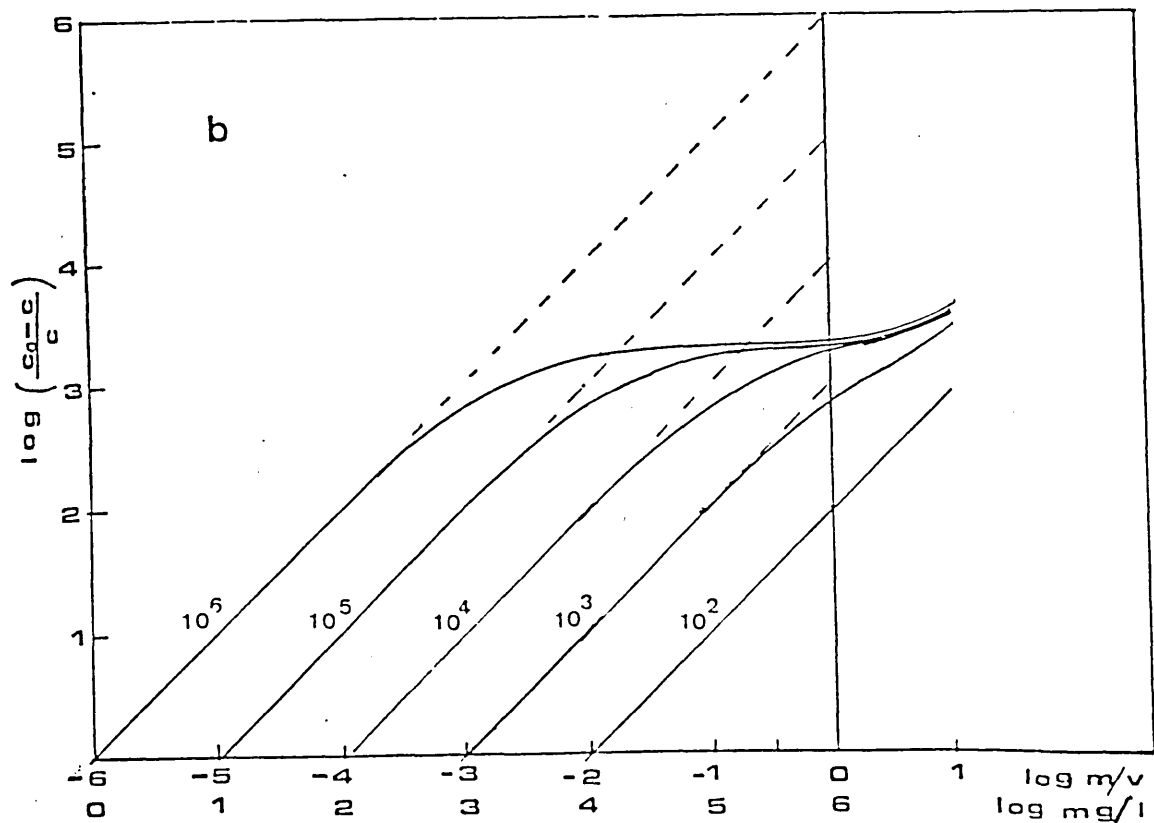
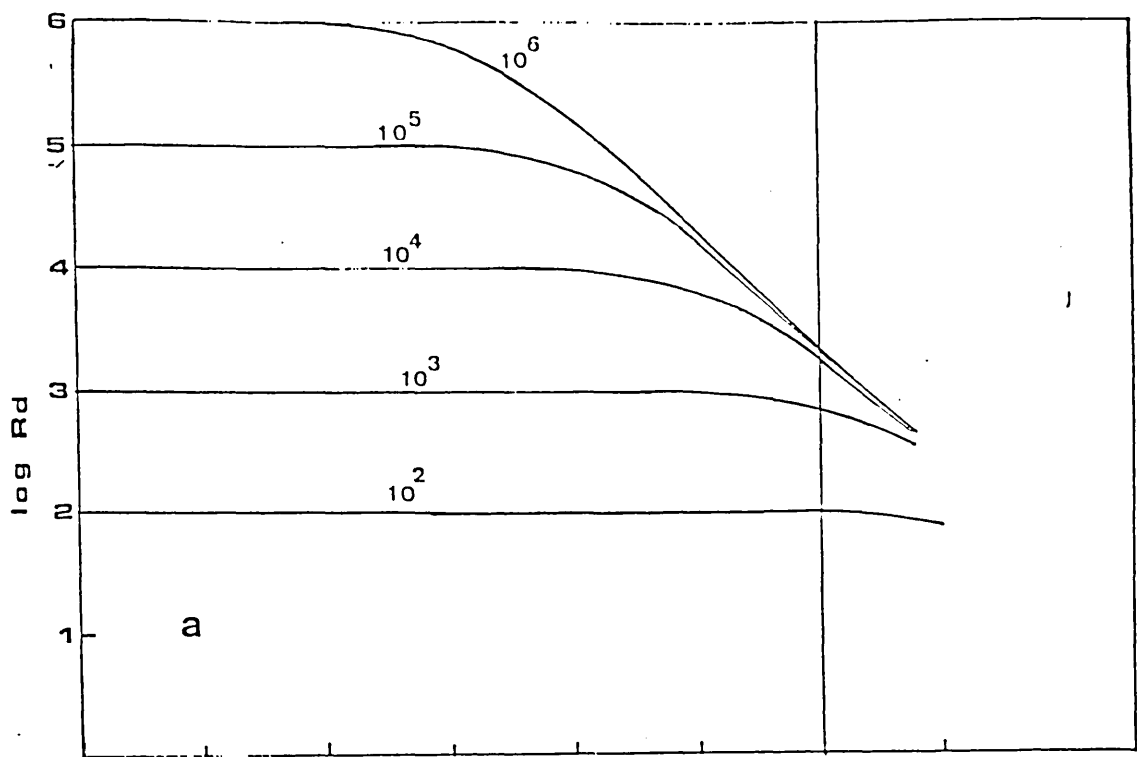


Fig. 3 The effect of a fixed proportion (0.05%) of a second species which is not sorbed by the sediment on the relationship between $\log m/v$ and (a) $\log R_d$ (b) $\log (C_0 - c)/c$ for different values of R_H (R_H variable, $R_L = 0.1$)

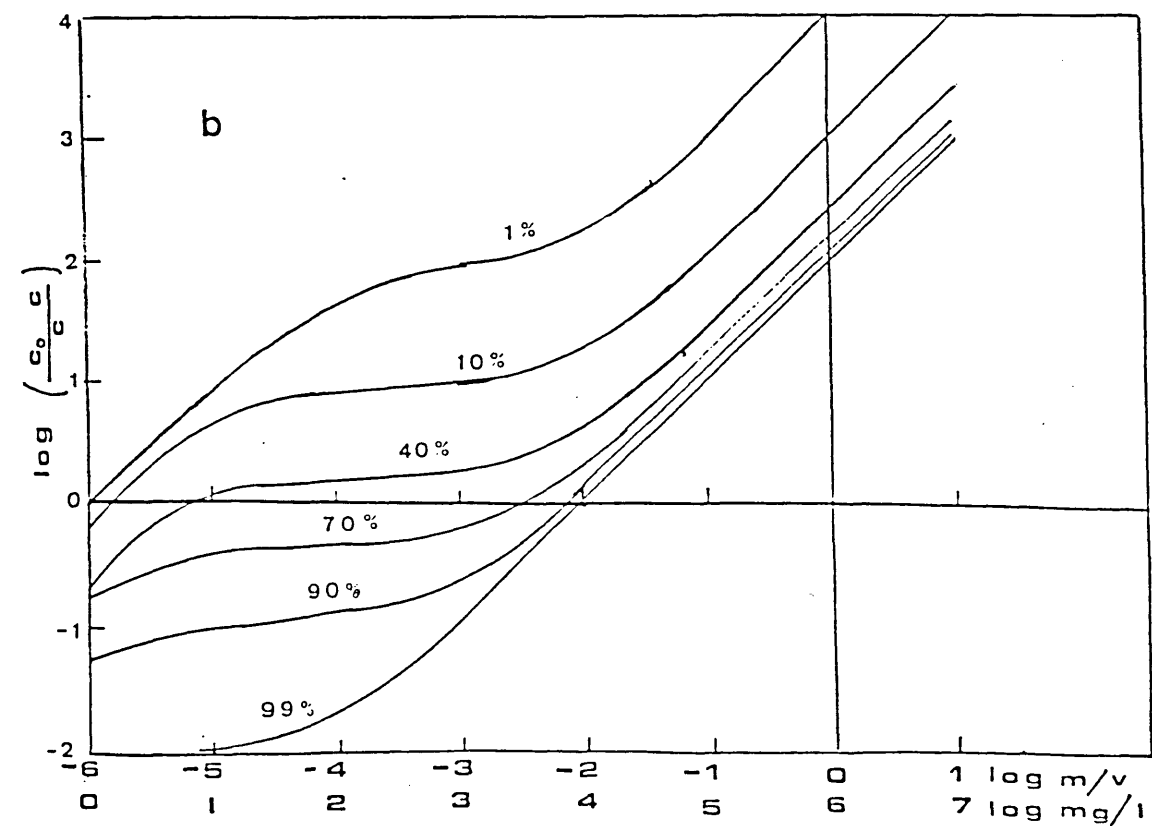
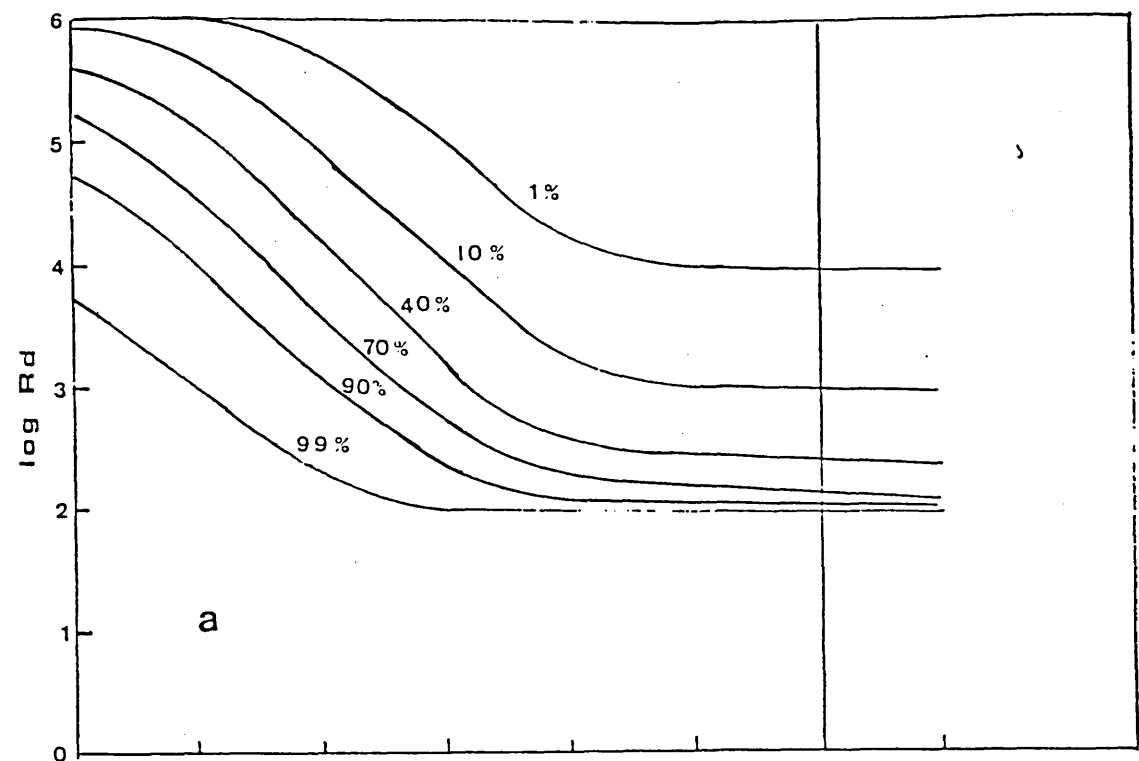


Fig 4 The effect of a fixed proportion of a second species with $R_d=100$ on the relationship between $\log m/v$ and (a) $\log R_d$ (b) $\log(C_o - c)/c$ for different percentages of low R_d species. ($R_H = 10^0$, $R_L = 10^2$).

3. EXPERIMENTAL

The effect of the solid/solution ratio on the sorption behaviour of Am-242, Pu-238 and Np-237 on two sediments taken from possible waste-disposal sites in the mid-Atlantic was investigated. These sediments were (i) No. 10400 8K, a red clay and (ii) No. 10399 7K, a high-carbonate (85% CaCO_3) sediment. Details of their mineralogy, chemical composition, surface areas and cation-exchange capacities are given in Tables 1 and 2.

Distribution ratios were determined using a standardised procedure based on the method of Relaya et. al.¹⁴ Briefly a known weight of sediment was placed in a 50 ml Oakridge centrifuge tube together with 30 g spiked sea water. The tubes were placed horizontally in a water bath at 4°C and shaken gently at 120 strokes/min. After the required time interval the tubes were centrifuged at 7000 rpm (5280 g) for 90 min. The solution phase was then filtered rapidly through 0.22 μ or 0.10 μ filters. Aliquots were removed for analysis, the remainder was added to fresh sediment and a "second Rd" determination begun. Fresh unspiked sea water was added to the solid phase and after one or two preliminary washes desorption experiments were carried out. The aim of the "second Rd" determination was to determine whether the nuclide remaining in solution after the first sorption behaved in the same way as that originally present in the spiked sea water.

In general sediment concentrations ranged from 1 g/l to 600 g/l. At these concentrations sorption to the container walls is negligible. Lower concentrations were not used because, in the absence of sediment, the actinides sorb strongly to the container

walls. It is difficult to make blank corrections for this sorption because it is much lower in the presence of sediment, which provides competing surfaces, than when sediment is absent.

From the time of collection the sediments were sealed and stored at 4°C. Samples were taken by mixing portions of sediment with slurry and then pipetting off representative portions. The spiked sea water was prepared by adding 100-200 µl portions of stock solution to 1 l filtered (0.22 µ) sea water. The pH was readjusted to 8.2 with a few drops of 0.1 N sodium hydroxide and the solution allowed to stand for six to eight weeks. Immediately before use it was filtered through 0.22 µ filters and analysed for the nuclide of interest.

Table 1. Mineralogy of Sediments

Composition			
10399 # 7K	Calcite	Kaolinite, illite, smectite	plagioclase feldspar (<2%) chlorite
10400 # 8K	Quartz, illite	Kaolinite, smectite, plagioclase, feldspar (3-5%) chlorite	
	Amorphous Fe oxyhydroxides (5-10%)		
SH1570	Smectite (30-40%) Fe oxyhydroxides (8-10%)		

Table 2. Chemical Composition, Surface Area (SA) and Cation-exchange capacity (CEC) of the Sediment

Sample No.	CaCO ₃	Si	Fe	Mn	Al	Mg	Na	K	Ti	P	SA	CEC
	1	1	1	1	1	1	1	1	ppm	ppm	m ² /g	mEq/100g
10399#7K	85	9.3	1.8	0.10	3.4	0.73	0.88	2.4	1800	250	85	17
10400#8K	3	24.6	5.0	0.32	0.8	1.60	0.63	2.5	5500	680	190	43
SH 1570	4	12.0	14.6	4.3	2.0	-	0.7	0.34	1100	340	396	124

In order to simulate conditions likely to occur in the far field after waste disposal and because the actinides have very low solubilities in sea water, initial concentrations were kept as low as possible. It was therefore necessary to analyse the solutions by alpha specrometry and a simple technique involving solvent extraction into 0.2 M 2-thenoyl trifluoroacetone (TTA) in benzene or cyclohexane and the preparation of evaporated sources from the organic layer was developed. About thirty sources could be prepared per day and recoveries were generally >90%. Table 3 shows the isotopes and experimental conditions used.

Table 3. Experimental Conditions

SORPTION	EXPERIMENTS	ANALYTICAL		
Nuclide	Initial Conc M	Spike	TTA Extration	
			pH	Solvent
^{241}Am	1×10^{-10}	^{243}Am	3.5	Cyclohexane
^{238}Pu	2.3×10^{-10}	^{239}Pu	0	benzene
^{237}Np	3.4×10^{-8}	^{235}Np	2.0	benzene

It was assumed that americium would be in the III oxidation state and we had shown earlier¹⁵ that all the neptunium in solution was in the V state both before and after sorption. Plutonium, on the other hand, can exist in solution in several

oxidation states the most common of which are the reduced Pu-III and Pu-IV forms and the oxidised Pu-V and Pu-VI forms. In order to distinguish between the reduced and oxidised forms a "holding oxidant", $K_2Cr_2O_7$ was added to each solution. This oxidises the Pu-III to Pu-IV and the Pu-V to Pu-VI and prevents the reduction of the Pu-V and Pu-VI to either of the reduced states. The reduced Pu was then co-precipitated with lanthanum flouride while the oxidised Pu remained in the supernate. This oxidised Pu could then be reduced with ferrous iron and precipitated in the same way. Details of all the analytical methods have been given in earlier papers.^{15,16}

4. RESULTS AND DISCUSSION

Each nuclide and each sediment behaved differently. They are therefore discussed one at a time and the main results are summarised in Table 9. Errors quoted in the Tables and error bars in the graphs are standard deviations based on counting statistics. Where more than one determination was made weighted means are given.

4.1 Americium

The effect of increasing the sediment concentration on the americium distribution ratio is shown in Figs. 5 and 6 where $\log(C_0 - C)/C$ has been plotted against $\log m/v$. Superimposed on the experimental points are theoretical curves calculated by the method described in Section 2. It can be seen that the theoretical and experimental curves are very similar in shape and it seems highly likely that the reason for the observed drop in distribution ratio is that some low-Rd species remained with the

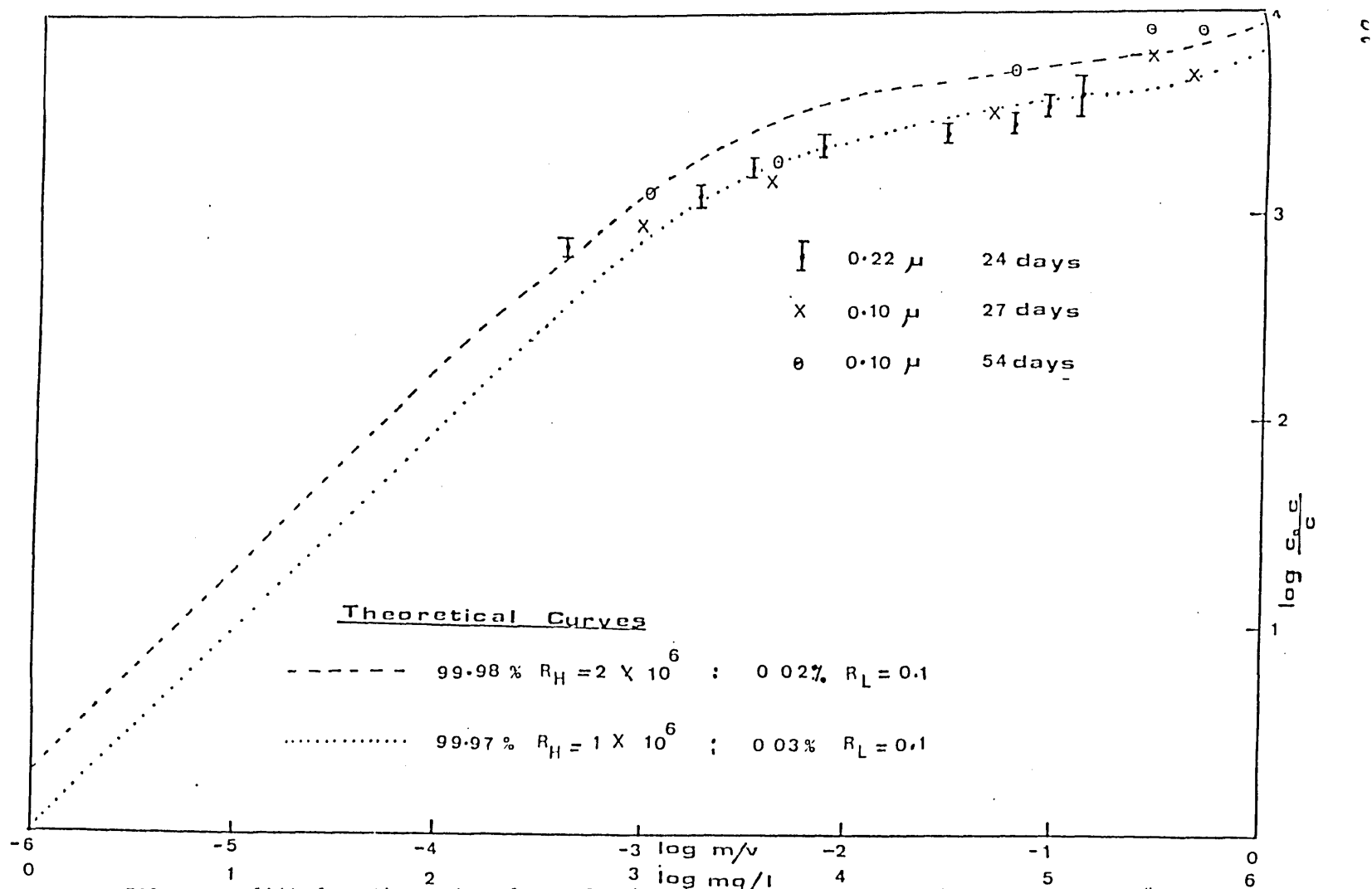


Fig 5 Effect of solid/soln ratio on the value of $\log (Co-c)/c$ for americium on the red clay, 10400 #8K.

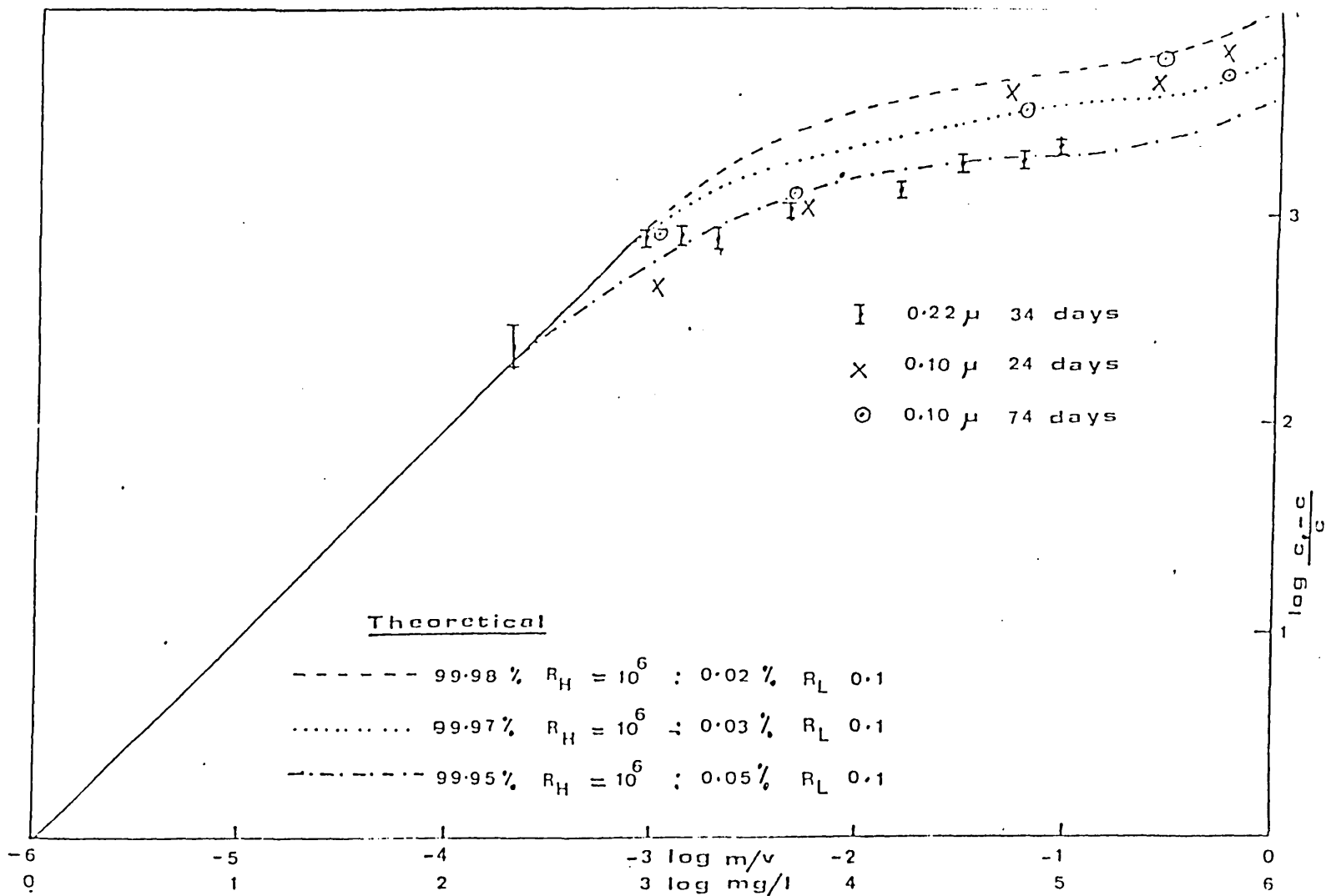


Fig. 6

Effect of solid/soln ratio on the value of $\log (C_o - c)/c$ for americium on the high-carbonate sediment 10399 $\frac{11}{77}$ 7K.

solution after phase separation. There is no indication that the proportion of this species increased with increasing sediment concentration and it is probable that this non-separable americium was attached to micro-particulates. From the graphs it can be estimated that the distribution ratio of the high- R_d americium was about 10^6 for the carbonate sediment and that when filtered through 0.22 μ filters approximately 0.05% of the original americium remained with the aqueous phase as compared with 0.02 to 0.03% when filtered through 0.1 μ filters. The difference between the filters was not as marked for the red clay where it appears that the distribution ratio for the high- R_d species was between 1×10^6 and 2×10^6 and the amount of non-separable americium was about 0.02% and 0.03% when filtered through 0.22 μ and 0.10 μ filters, respectively.

In Fig. 7 sorption and desorption R_d values are plotted on the same axes. It can be seen that the desorption distribution ratios were higher than the sorption distribution ratios although at low solid/solution ratios the desorption R_d values were not significantly different from R_H , i.e. the value which would have been observed if no low- R_d species had been present. It seems likely, therefore, that the americium sorption-desorption reaction is not as irreversible as has hitherto been supposed and that the large difference between sorption and desorption distribution ratios that has been observed by ourselves and others^{15,6,8,17} can be at least partially explained by the presence of some low- R_d americium which was removed after the sorption stage.

The presence of some low- R_d species was confirmed when the

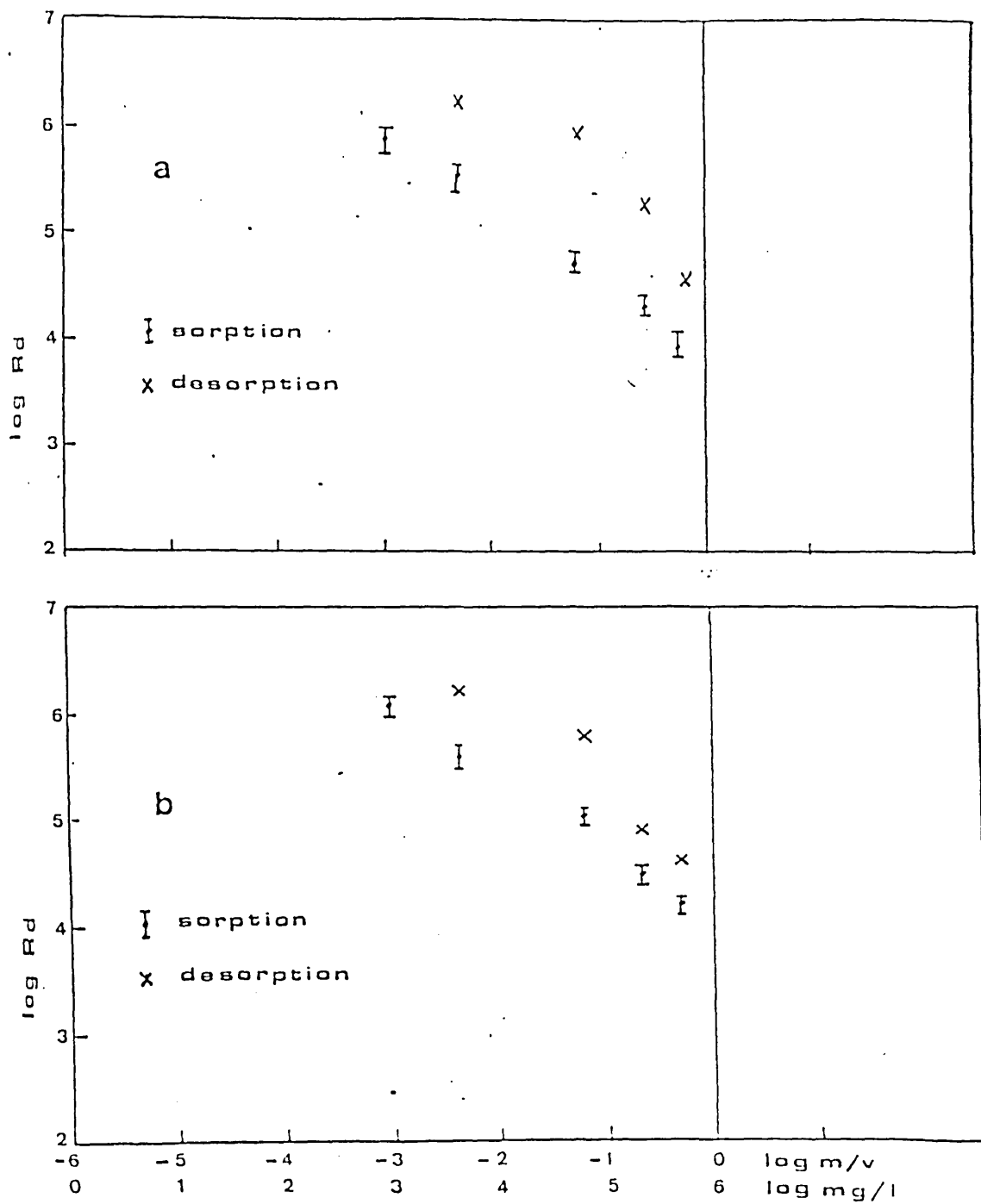


Fig 7 Sorption and desorption R_d at different solid/soln ratios for americium on (a) high-carbonate sediment, 10399 #7K (b) red clay, 10400 #8K.

solution remaining after the first sorption was contacted with fresh sediment. The results of these experiments are given in Table 4 and it can be seen that, (i) the second R_d are several orders of magnitude lower than the first, (ii) when the initial Am concentration was low i.e. when almost all the high- R_d species remained after the first sorption then the second R_d rose to between 200 and 400 if the solid/solution ratio was kept low in the second sorption. At high solid/solution ratios the effect of the high proportion of low- R_d species was again apparent and the second R_d dropped to 60.

Table 4. Distribution ratios obtained for americium when the liquid phase remaining after the first R_d experiment was contacted with fresh sediment.

Sediment	Sediment Concentration		Second R _d Experiment			Equivalent first R _d for same solid/soln. ratio ml/g
			Am conc. in soln.		R _d	
	1st R _d g/l	2nd R _d g/l	Initial Bq/l	Final Bq/l	ml/g	
Red Clay 10400 #8K	381	6.49	22.7 ±1.3	9.72 ±0.5	206 ±25	2.6 × 10 ⁵
	0.91	3.17	37.8 ±2.5	11.06 ±0.7	372 ±44	4.7 × 10 ⁵
	272	11.91	2.93 ±0.28	1.71 ±0.28	60 ±22	1.8 × 10 ⁵
	576	12.30	5.51 ±0.30	3.66 ±0.38	41 ±12	1.8 × 10 ⁵
	4.19	11.16	18.9 ±0.9	4.74 ±0.28	268 ±24	1.1 × 10 ⁴
	4.19	55.44	14.2 ±0.7	3.38 ±0.26	58 ±6	2.0 × 10 ⁵
	0.97	11.00	27.1 ±1.8	5.26 ±0.54	377 ±51	2.0 × 10 ⁵
	0.97	73.40	23.4 ±1.5	3.94 ±0.35	67 ±8	4.5 × 10 ⁴
Carbonate 10399 #7K	4.95	9.15	30.3 ±2.6	11.73 ±0.47	173 ±21	2.0 × 10 ⁵
	1.11	4.05	61.6 ±4.7	14.90 ±0.70	775 ±120	4.0 × 10 ⁵

4.2 Neptunium

Because Np-237 was used instead of Np-235 the concentration of neptunium was four orders of magnitude higher than in previous experiments.¹⁵ Nevertheless distribution coefficients were unchanged (i.e. about 500 for the red clay and about 4×10^3 for the high-carbonate sediment) showing that Henry's law is still being obeyed at this much higher loading level. Henry's law was also found to be obeyed with americium and plutonium^{15,16} which is not unexpected considering the very low concentrations used in these experiments.

Fig. 8 shows the graphs of $\log R_d$ vs. $\log m/v$ for both sediments and in Figs. 9 and 10 the plots of $\log(C_0 - C)/C$ against $\log m/v$ are presented along with the theoretical curves for different percentages of the original neptunium existing in a non-separable form. The two sediments behaved rather differently and will, therefore, be discussed separately.

4.2.1 High-carbonate sediment:- Because the R_d for this sediment was relatively high the final concentration in solution was low and the analytical precision poor. It appears, however, that the distribution ratio did not change with increasing solid/solution ratio and was the same for both sorption and desorption. It should be pointed out, however, that with an R_d of only 10^3 , as compared with the 10^6 found for americium, the system would be far less sensitive to the presence of small amounts of a low- R_d nuclide and it can be seen from Fig. 9 that less than about 0.2% of a species with $R_d = 0.1$ would not have been detectable. The second distribution ratios obtained with the solution remaining after the first R_d determination were not significantly different from the

first distribution ratios, so in none of the three sets of experiments is there any convincing evidence that more than one species is present.

4.2.2 Red-clay:- The graph of $\log R_d$ vs. $\log m/v$ was horizontal for solid/solution ratios greater than about 0.016 but shows a rather surprising upward turn at the two lowest points and this is reflected in the shape of the plot of $\log(C_o - C)/C$. It can best be explained by assuming that most of the neptunium was adsorbed with a low R_d (approx. 400) but that some (approx. 20%) was sorbed with a high R_d (i.e. the graph is of the type shown in Fig. 4b). This would also explain the facts that (i) the difference between the sorption and desorption R_d increased as the sediment concentration decreased (since at low solid/solution ratios the ratio of high- R_d to low- R_d species would be greater on the sediment than in the solution after sorption) and (ii) when the liquid phase remaining after the first R_d was contacted with fresh sediment the second R_d was lower than the first R_d at high/solid solution ratios (since most of the high- R_d species would have been removed during the first sorption). It is difficult however to make any suggestions as to what these two species might be and too much should not be read into two experimental points. Fig. 10 shows that, because the R_d of the main species is so low, less than 0.5% of a non-separable species would not have been detectable.

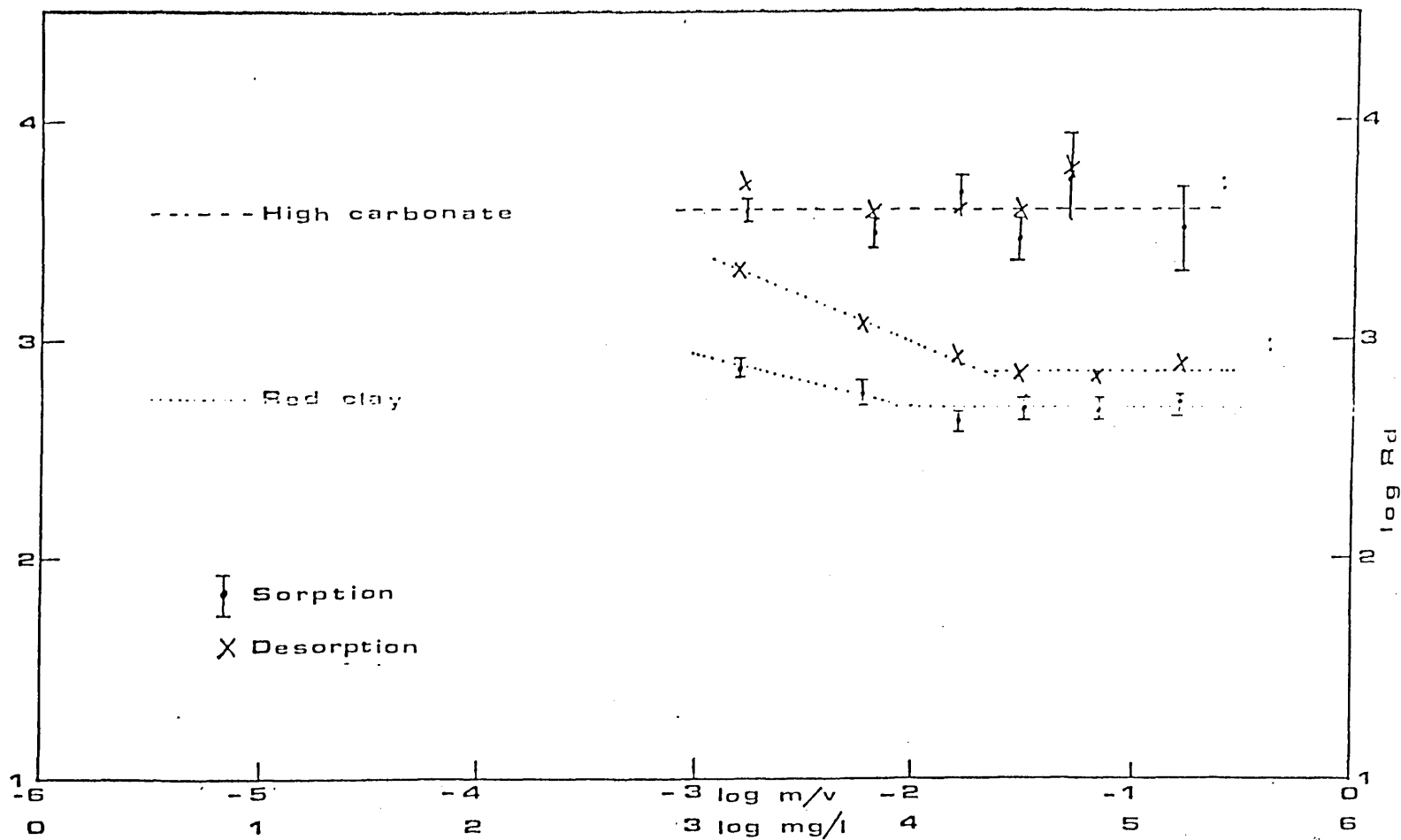


Fig. 8 Sorption and desorption R_d 's at different solid/soln ratios for neptunium on (a) the high-carbonate, 10399#7K (b) the red clay 10400 #8K.

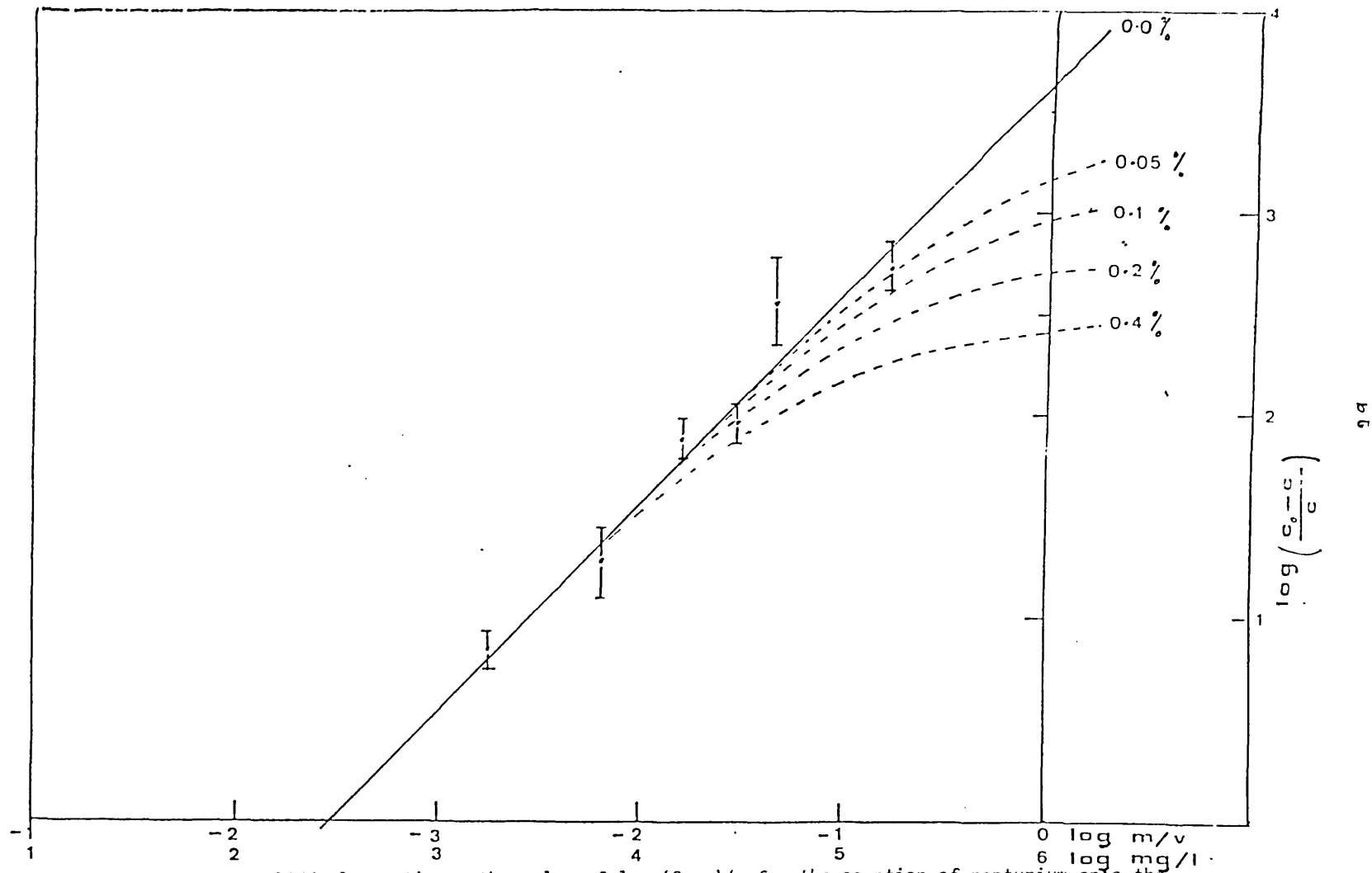


Fig. 9 Effect of solid/soln. ratio on the value of $\log (C_0 - c)/c$ for the sorption of neptunium onto the high-carbonate sediment 10399 #7K. Dotted lines represent theoretical curves for different percentages of a non-separable species. ($R_H = 3980$, $R_L = 0.1$)

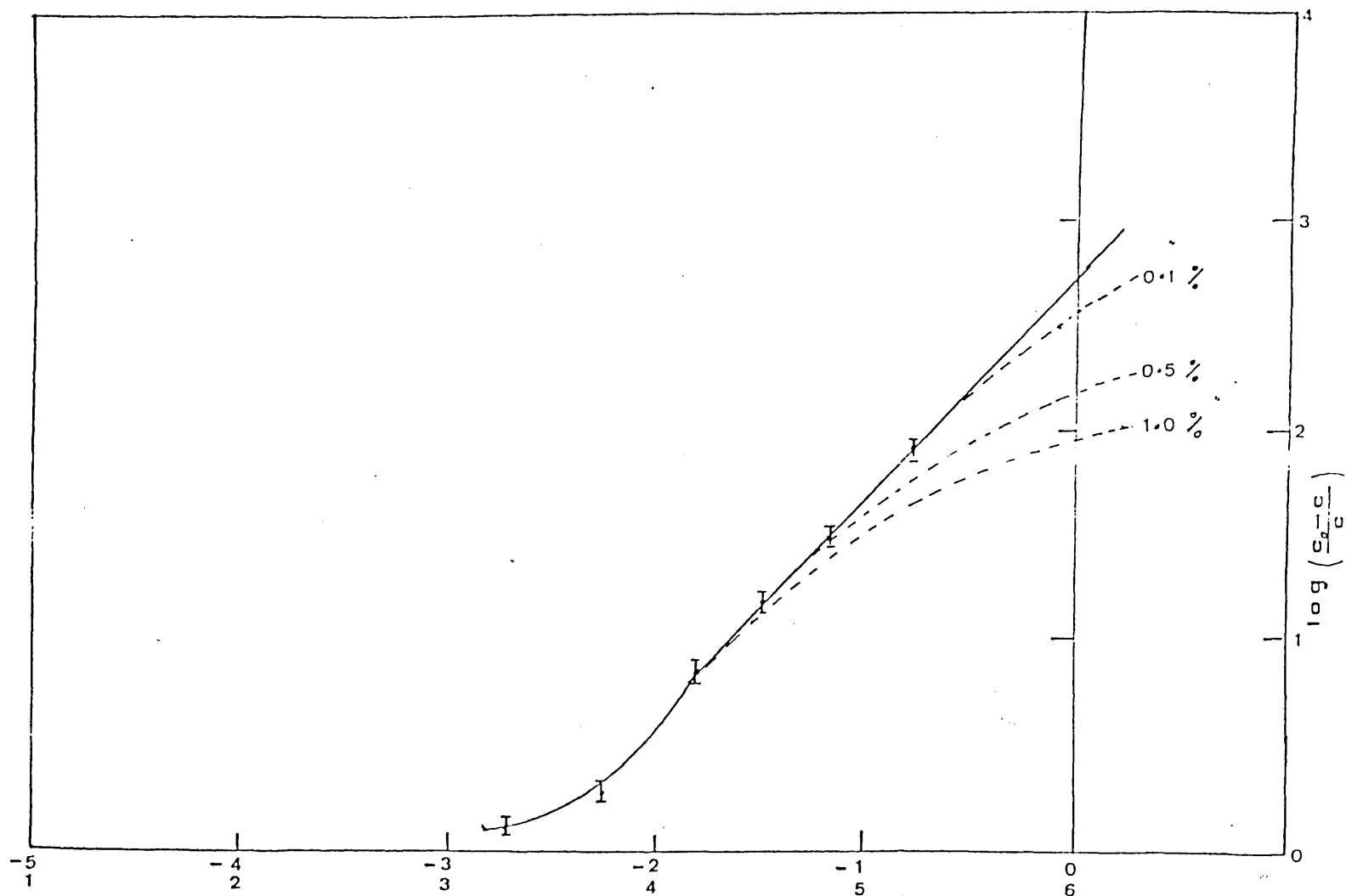


Fig. 10 Effect of solid/soln ratio on the value of $\log (C_o - c)/c$ for sorption of neptunium on red clay, $10400 \pm 8K$. Dotted lines represent theoretical curves for different percentages of a non-separable species ($R_H = 500$, $R_L = 0.1$).

4.3 Plutonium

The sorption behaviour of plutonium was very different for the two sediments and they will therefore be considered separately.

5.3.1 Red Clay:- Fig. 11 shows that the graph of $(C_0 - C)/C$ vs. m/v is very similar in shape to plots obtained for americium and that the distribution ratio tends to 7.9×10^4 as m/v becomes very small. The experimental curve fits very closely the theoretical one calculated for 99.95% Pu with an $R_d = 7.9 \times 10^4$ and 0.05% with an R_d 0.1. It is interesting to note that the percentage of low- R_d species appears to be higher than for americium under the same experimental conditions. This could mean that whereas for americium all the low- R_d species was particulate, some of the plutonium was complexed in other ways.

Selective leaching experiments have shown that whereas americium appears to be adsorbed non-selectively to all phases, plutonium is preferentially adsorbed to organic matter and to iron and manganese phases.^{3,19,1} Complexes with these phases may be formed and then resolubilised thus contributing to the low- R_d fraction.

Table 5 indicates that the low- R_d species must be in the reduced (III+IV) forms since the proportion of reduced plutonium increases as the solid/solution ratio increases. This result would be expected if the low- R_d species was formed as a result of sorption to the sediment since sorption on sediments appears to be accompanied by reduction.^{13,15,20}

The effect of changing the proportion of reduced to oxidised and high- R_d to low- R_d species is made very clear in the experiments in which the solution remaining after the first

Table 5. Plutonium Sorption and Desorption on Red Clay.

Tube No.	Sediment Concent. g/l	Concentration in Solution (Bq/l) after					Distribution Ratio			Second Sorption on fresh sediment $\frac{\text{ml/g}}{10^4}$	% in Reduced III + IV) Form after Sorption
		Sorption	First Desorption 1 hour	Second Desorption 19 hours	Third Desorption 36 day	Contacting Sorption Solution with fresh	Sorption $\frac{\text{ml/g}}{10^4}$	19 hour Desorption $\frac{\text{ml/g}}{10^4}$	36 day Desorption $\frac{\text{ml/g}}{10^4}$		
390	163.16	20.4 $\pm$ 1.6	17.0 $\pm$ 1.2	6.0 $\pm$ 0.4	5.2 $\pm$ 0.5	3.51 $\pm$ 0.25	0.97 $\pm$ 0.08	3.43 $\pm$ 0.27	3.90 $\pm$ 0.39	0.0023 $\pm$ 0.0003	102 $\pm$ 2
391	65.57	26.5 $\pm$ 1.4	13.3 $\pm$ 1.0	15.7 $\pm$ 0.2	5.0 $\pm$ 0.9	6.40 $\pm$ 0.38	1.87 $\pm$ 0.12	3.24 $\pm$ 0.16	10.07 $\pm$ 1.93	0.0017 $\pm$ 0.0002	105 $\pm$ 7
392	33.45	35.1 $\pm$ 2.2	10.0 $\pm$ 0.9	8.3 $\pm$ 0.7	8.5 $\pm$ 0.8	9.25 $\pm$ 0.81	2.76 $\pm$ 0.18	12.07 $\pm$ 1.14	11.78 $\pm$ 1.25	0.0079 $\pm$ 0.0010	94 $\pm$ 7
393	17.79	39.6 $\pm$ 2.0	19.9 $\pm$ 1.4	11.0 $\pm$ 1.1	13.9 $\pm$ 0.9	13.41 $\pm$ 1.02	4.61 $\pm$ 0.27	16.98 $\pm$ 1.85	13.49 $\pm$ 1.10	0.0053 $\pm$ 0.0008	108 $\pm$ 8
394	68.97	83.9 $\pm$ 3.3	44.0 $\pm$ 2.8	34.8 $\pm$ 2.0	34.4 $\pm$ 1.9	22.02 $\pm$ 2.08	5.60 $\pm$ 0.28	13.83 $\pm$ 1.03	13.99 $\pm$ 0.99	0.0081 $\pm$ 0.0009	68 $\pm$ 6
395	19.02	260.4 $\pm$ 13.8	116.3 $\pm$ 5.4	176.3 $\pm$ 12.7	96.8 $\pm$ 4.1	44.45 $\pm$ 2.03	6.51 $\pm$ 0.31	9.82 $\pm$ 0.84	17.98 $\pm$ 1.13	0.0143 $\pm$ 0.0011	37 $\pm$ 2

Note ^{238}Pu concentration before sorption (34133 $\pm$ 1502) Bq/l i.e. (2.337 $\pm$ 0.104) $\times 10^{-10}$ mol/l

sorption was contacted with fresh sediment. These "second" distribution ratios are plotted together with the first distribution ratios in Fig. 12 and it can be seen that when the solid/solution ratio was high in the first sorption (and very little high- R_d species was present in the initial solution for the second sorption) then the second R_d was very low. Also as the solid/solution ratio used in the first sorption increased so did the second R_d .

The desorption distribution ratios are also included in Fig. 12. These ratios are all higher than the corresponding sorption ratios and it appears that only at the very highest solid/solution ratio was there enough low- R_d species present to significantly lower the desorption R_d . Apart from this one case desorption distribution ratios were all between 1×10^4 and 2×10^4 ml/g. Roughly 10% of the difference between sorption and desorption distribution ratios can be explained by the presence of some low- R_d species and we must therefore conclude that the sorption-desorption reaction is to a large extent irreversible.

4.3.2:- High-carbonate Sediment. Table 6 shows sorption distribution ratios together with the percent reduced plutonium in solution after phase separation (90 min. centrifugation at 5280 g followed by filtration through 0.22 μ filters). It can be seen that for solid/solution ratios greater than about 0.04 (40 g/l) the distribution ratios are surprisingly low (100 - 200 ml/g) and there was no significant increase as the contact time increased from 24 to 128 days. Furthermore, at these high solid/solution ratios the plutonium in solution was virtually all in the oxidised (V + VI) forms. At low solid/solution ratios, on the other hand, the plutonium in solution was

Table 6 Plutonium Distribution Ratios on Carbonate Sediment 10399/7K. SORPTION.

Tube No.	Shaking time days	Sediment Concentration g/l	Solution Concentration after sorption Bq/l	Distribution Ratio ml/g	% in Reduced III & IV form after sorption	pH after sorption
370	24	205.5	1175±62	133±9	-	
376	29	171.6	1257±89	148±7	4.1±1.2	
376	128	206.0	969±75	166±8	2.7±0.3	7.84
371	24	89.14	1503±161	237±28		
377	29	80.81	2041±298	190±9	3.1±0.5	
377	128	96.97	1578±83	212±7	3.0±0.2	8.07
372	24	41.57	2022±142	372±31	-	
378	29	40.02	2120±88	368±17	4.1±0.3	
378	128	48.02	2441±124	270±13	3.0±0.2	8.07
373	24	15.64	1863±59	406±24	-	
379	29	19.77	115±8	14,596±795	69±6	
379	128	23.73	73±4	19,731±1030	45±5	8.09
374	24	7.71	1103±73	3,788±303	-	
380	29	7.67	1615±115	2,562±120	21±2	
380	128	9.20	142±8	26,016±1282	43±4	8.11
375	24	1.85	233±18	76,489±600	-	
381	29	1.81	314±26	57,920±2765	49±5	
381	128	2.17	140±7	107,208±5218	71±5	8.18

Note Before Sorption

Pu-238 concentration = (34133±1502) Bq/l, i.e. $(2.337 \pm .104) \times 10^{-10}$ moles/l

pH = 8.2.

% in reduced form = 29%.

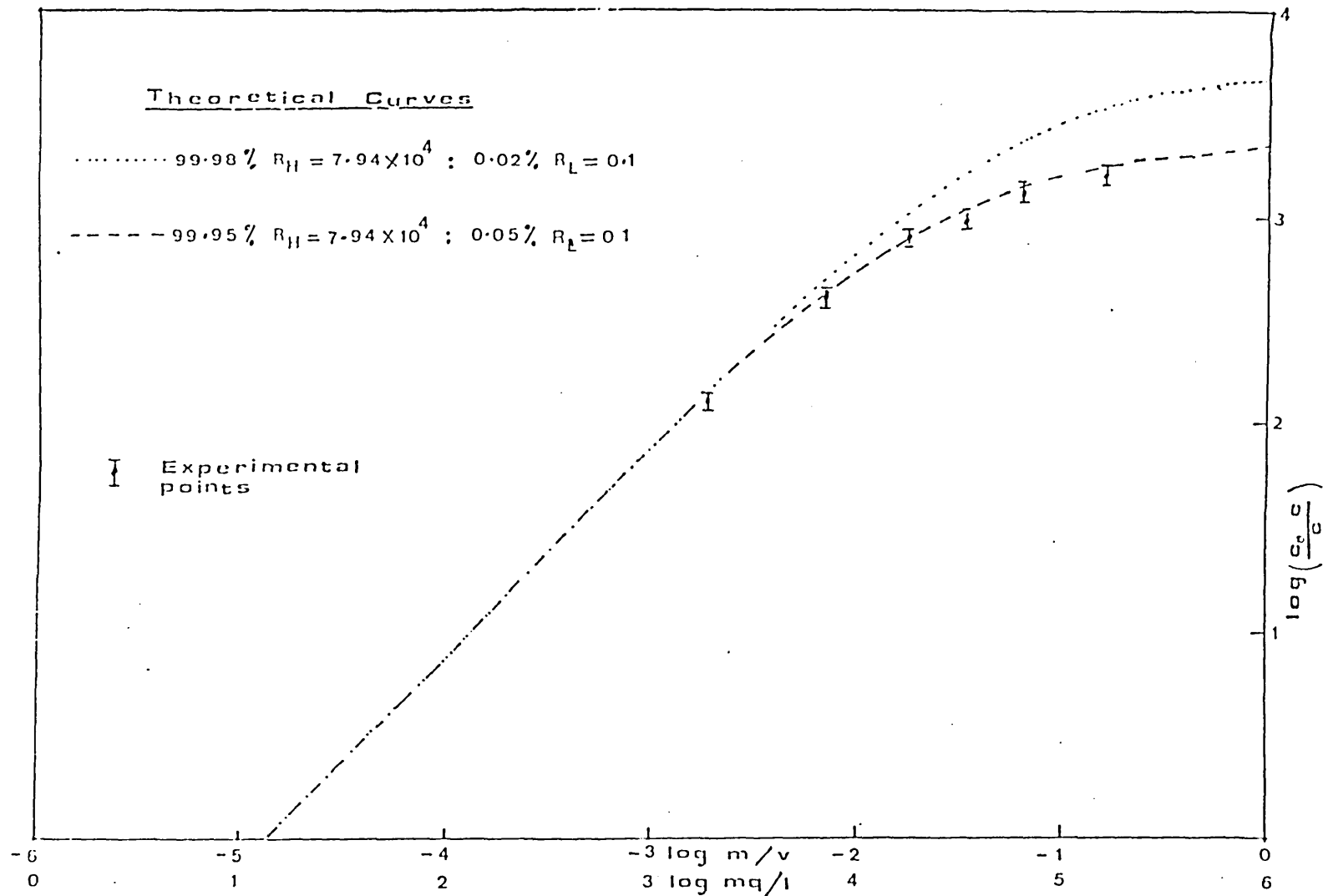


Fig 11 Effect of solid/soln ratio on the value of $\log(C_o - c)/c$ for the sorption of plutonium on red clay, 10400 #8K.

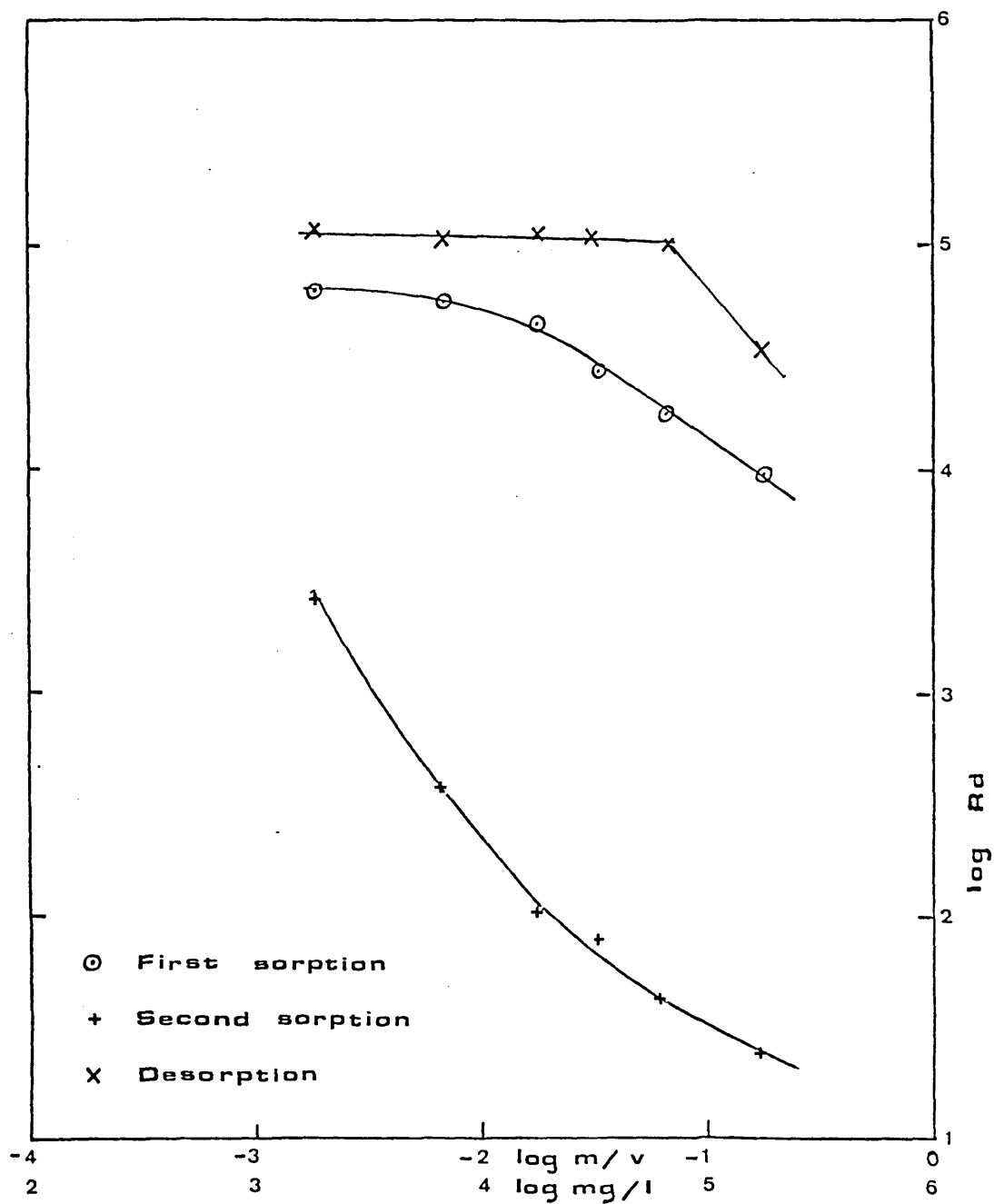


Fig. 12 Sorption, "second sorption" and desorption R_d as a function of m/v for the red clay, 10400, 8K.

mostly in the reduced (III + IV) forms and the distribution ratios were greater than 10^4 .

The obvious explanation for the low distribution ratios in the presence of large quantities of high-carbonate sediment is that carbonate complexes are being formed. These would be sorbed less strongly than are the PuO_2^+ and $\text{Pu}(\text{OH})_3^+$ ions which are probably present in sea water in the absence of sediment. No attempt was made to distinguish between the V and VI forms but the fact that neptunium did not behave in the same way indicates that we were probably dealing with Pu-VI complexes since neptunium has been shown to be in the V form in sea water and in our laboratory experiments.¹⁵ This is in agreement with the predictions of Skytte-Jensen⁴ whose Eh-pH diagrams indicate that $\text{PuO}_2(\text{CO}_3)_2^{2-}$ and $\text{PuO}_2(\text{CO}_3)_2$ are the most probably carbonate species at pH 8 and relatively high Eh.

Desorption distribution ratios are given in Table 7. At high solid/solution ratios the sorption R_d values were not very different from the desorption R_d values and the plutonium in solution was also in the oxidised (V + VI) forms. The plutonium carbonate sorption-desorption reaction appears, therefore, to be reversible. At low solid/solution ratios behaviour was similar to that with red-clays and desorption R_d values were significantly higher than sorption R_d values.

The results of the experiments in which the solution remaining after the first distribution ratio determination were contacted with fresh sediment are given in Table 8. They confirmed that different species were present at different solid/solution ratios and threw some further light on their behaviour. The two extreme cases will be considered separately:-

Table 7. Plutonium desorption from carbonate sediments

Sediment Concentration g/l	Desorption time d	Solution Concentration (Bq/l) after		Distribution Ratio		Z in Reduced (111 + 1V) after desorption
		Sorption	Desorption	Sorption ml/g	Desorption ml/g	
205.5	61	1175 ±62	1453 ±150	133 ±9	96 ±11	2.9 ±0.3
89.14	61	1503 ±161	2491 ±98	237 ±28	119 ±8	2.9 ±0.3
7.71	61	1103 ±73	58 ±2	3,788 ±303	68,100 ±4,200	31.0 ±2.4
1.85	61	233 ±18	78 ±3	76,489 ±600	223,600 ±12,600	84.7 ±6.0
206.0		969 ±75	158 ±8	166 ±8	1,256 ±84	--
96.97		1578 ±83	1218 ±33	212 ±7	394 ±11	--
48.02		2441 ±124	960 ±47	270 ±13	982 ±48	--
23.73		73 ±4	76 ±5	19,730 ±1030	25,675 ±1626	--
9.20		142 ±8	94 ±8	26,016 ±1280	43,051 ±4,167	--
2.17		140 ±7	75 ±4	107,208 ±5220	262,120 ±16,971	--

Table 8. Plutonium distribution ratios : Solution removed after first sorption contacted with fresh sediment - carbonate sediment 10399 # 7K.

Tube No.		Sediment Conc		Solution Concentration		Distribution Ratio		% in reduced (III + IV) forms	
Original Fresh Sediment		First Sorption g/l	Second Sorption g/l	Before starting 2nd sorption Bq/l	After 2nd sorption Bq/l	First ml/g	Second ml/g	After First sorption	After Second Sorption
376	480	171.63		797±62	28±1	148±7	134±14	4.1±1.2	2.7±0.3
377	481	80.81		1436±76	75±1	190±9	189±16	3.1±0.5	3.0±0.2
378	482	40.02		2161±110	168±12	368±17	253±23	4.1±0.3	3.0±0.3
379	483	19.77		69±6	28±2	14596±795	64±9	69±6	45±5
380	484	7.67		138±8	60±4	2562±120	142±18	21±2	43±4
381	485	1.81		140±7	77±2	57920±2765	353±44	49±5	71±5
370	410	205.5	6.11	1173±63	60±3	133±9	3053±190	-	43±2
371	411	89.14	5.76	1502±164	169±6	237±28	1384±168	-	23±2
372	412	41.57	6.22	2018±141	245±9	372±31	1104±95	-	22±2
373	413	15.64	4.86	1860±70	212±12	406±24	1604±73	-	37±3
374	414	7.71	5.26	1103±82	165±7	3788±304	1076±92	-	53±4
375	415	1.85	4.67	234±23	127±6	76484±600	180±32	-	101±1

(i) low solid solution ratio in the first R_d experiment: here the behaviour was similar to that observed with the red clay, i.e. second R_d values were very much lower than first R_d values indicating that most of the high-Rd species had been removed in the first sorption. The Pu remaining in solution after the first sorption was mostly the low- R_d species, possibly completely non-sorbed particulate material and the effect of this was to lower the observed R_d by two orders of magnitude.

(ii) High solid/solution ratio in the first R_d experiment. When the solid/solution ratio was high for both first and second sorptions the distribution ratio was the same both times and virtually all the Pu was in the (V+VI) forms after both sorptions. This must mean that either only one plutonium species was present in solution or that equilibrium between different species was rapidly re-established as one species was removed from solution. Because R_d values were low the presence of a small amount of non-separable species would not have been detectable.

When the solid solution ratio in the second sorption was low the R_d rose to $>10^3$ and the percentage of oxidised Pu(V+VI) dropped. Clearly, in the absence of large quantities of sediment some of the plutonium carbonates have reverted to more readily sorbable species. The fact that the second R_d values are intermediate between 10^2 and 10^4 ml/g indicates that both high- and low-Rd species were now present. It appears that the presence of high concentrations of sediment were necessary to keep the plutonium in the low- R_d form. The carbonate and bicarbonate contents of the solution phases were obviously the

same at the end of the first sorption experiment and the beginning of the second, so unless they decreased during the second sorption period the presence of the low- R_d species cannot be entirely a function of carbonate and bicarbonate concentration. Possibly, complexes are formed at the surface of the sediment and resolubilised. Once in solution they could revert to other forms which could either be adsorbed or once again form low- R_d complexes.

5. SUMMARY AND CONCLUSIONS

It has been shown that when determining distribution ratios by the batch method, it is possible to detect the presence of more than one species in solution and to make an estimate of the proportions in which they occur by measuring the distribution ratios over a wide range of solid/solution ratios. Very often the low- R_d species are probably simply micro-particulate material which has remained with the solution after phase separation but complexes may be formed with constituents of either the liquid or the solid phase. If more than one stable species is present then, at low solid/solution ratios, the observed R_d will be close to that of the species with the highest R_d and it will decrease as the solid/solution ratio increases.

Table 9 summarises the results of these investigations and it can be seen that each actinide behaved differently with each sediment. The behaviour of plutonium when contacted with high-carbonate sediments is particularly noteworthy. At high solid/solution ratios Pu-VI or Pu-V carbonate complexes were probably formed and as a result the distribution ratio dropped to 100 ml/g.

Table 9. Effect of Solid/Solution Ratio. Summary of Results

	RED CLAY - 10040#-8K			CARBONATE SEDIMENT 10399#-7K		
	Sorption	Desorption R_d	Second Sorption R_d	Sorption	Desorption R_d	Second Sorption R_d
Am	R_d increased with decreasing solid/soln ratio. Levelled off at 10^6 ml/g. % non-separable $\sim 0.03\%$ (0.22μ filters) $\sim 0.02\%$ (0.10μ filters).	$> \text{Sorption } R_d$	$\ll 1st R_d$	R_d increased with decreasing solid/soln. ratio. Levelled off at $1 \times 10^6 - 2 \times 10^6$ % non-separable $\sim 0.05\%$ (0.22μ filters). $0.02 - 0.03\%$ (0.10μ filters).	$> \text{Sorption } R_d$	$\ll 1st R_d$
Np	R_d constant at about 480 ml/g for solid/soln. ratio > 0.016 . Increase for two lowest solid/soln. ratios (580 + 750 ml/g) % non-separable $< 0.2\%$ (0.10μ filters).	$> \text{Sorption } R_d$ Difference greater for lower solid/soln. ratios.	Same as first R_d for high solid/soln. ratios.	R_d constant for all solid/soln. ratios. % non-separable $< 0.5\%$ (0.10μ filters).	$\approx \text{Sorption } R_d$	$\approx 1st R_d$
Pu	R_d increased with decreasing solid/soln. ratios. Levelled off at 7.9×10^4 ml/g. % non-separable $\sim 0.05\%$ (0.22μ filters)	$> \text{Sorption } R_d$	$\ll 1st R_d$ Difference greatest at high solid/soln. ratios.	High Solid/Solution Ratios.		
				R_d low i.e. 100-300 ml/g. All in Pu(V+VI) form.	$\approx \text{Sorption } R_d$ All in Pu(V+VI) form.	$\approx 1st R_d$
				Low Solid/Solution Ratios.		
				$R_d > 10^4$ ml/g. Mostly in Pu(III + IV) form.	$> \text{Sorption } R_d$ Mostly in Pu(III + IV) form.	$\ll 1st R_d$

From the waste disposal point of view it is clear that modellers cannot base their assessments on distribution ratios determined at an arbitrarily chosen solid/solution ratio. They must bear in mind the possibility that distribution ratios determined using the batch method might have been affected by the presence of micro-particulates or complexed material. In general the effect of such material will be to lower the observed R_d of the main species and predictions based on such results will be conservative. However, the mobilities of the micro-particulates and complexes themselves must be considered (assuming that they are not simply generated during shaking). They are likely to be neutral or negatively charged and could travel a considerable distance before being converted to a more readily sorbable form. The size of such particles could be of critical importance particularly if diffusion is the main transport mechanism.²¹

For the sediments studied in this work 0.05%, or less, of the nuclide originally present in solution appeared to be in a non-sorbable form. It now remains to assess how significant this is likely to be in terms of affecting repository performance.

Finally, it should be emphasised that although much useful information can be gained from batch-distribution experiments the actual R_d values obtained should be used with caution by modellers. Ideally they should be considered in conjunction with measurements made under conditions as close to in situ conditions as possible. In the case of the subseabed disposal where transport through the far field is likely to be by diffusion and nuclide concentrations at the leading boundary will be very low, diffusion experiments could provide useful back up information.

For land-based repositories, where transport may be by ground-water flow, once-through-flow column experiments used in conjunction with batch sorption experiments should produce credible bounding values for nuclide retardation and this is the approach recommended by the Waste/Rock Interactions Technology Program. (2)

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