THE INFLUENCE OF TEMPERATURE ON MIGRATION OF RADIONUCLIDES IN DEEP-SEA SEDIMENTS:

SIMULATION EXPERIMENTS CONCERNING SORPTION AND HEAT FLOW RELATED TO DEEP-SEA DISPOSAL OF HIGH-LEVEL RADIOACTIVE WASTE

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RADIOACTIVE WASTE

by

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Corrigendum to the report:

The influence of temperature on migration of radionuclides in deep-sea sediments: simulation experiments concerning sorption and heat flow related to deep-sea disposal of high level radioactive waste, by L.A. van Geldermalsen and J.W. Wegereef

The following lines should read:

page 4, line 4: ...within a period of 10^5 to 10^8 years after burial.
page 9, line 13: ... (up to .54 °C in these deposits, Hollister et al. 1980)
page 22, line 6: ...the solutions were filtered and then allowed to "age" for a night. The filtrate was used to...
page 22, line 24: ...since filtering through two .15 μM
page 22, line 25: ...a large part (30%)...
page 22, line 26: ...again retained part (30%) of...
page 25, formula 4-7 becomes: (Co-Ct)*V/(Ct*M).
page 28, formula 4-11 becomes: ∂S/∂t = Kd*∂C/∂t
page 28, line 26: and (9) becomes:
page 38, distribution coefficient (*10^5 ml/g)

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7 - Migration under influence of sorption
   1 Introduction
   2 Modelling aspects of migration
   3 Diffusion influenced by sorption
   4 Effects of sorption and decay in a release model for a
     buried source

8 - Literature


OBJECTIVES, CONCLUSIONS AND RECOMMENDATIONS
Objectives, conclusions and recommendations

Objectives

Four international organizations are particularly involved in coordinating programs of research into disposal of high-level radioactive waste (Harrison, 1984). The four are the IAEA and NEA (e.g. through the SEABED working group), the Commission of the European Communities, and the Council for Mutual Economic Assistance (CMEA). The last organization coordinates research in the U.S.S.R. and most of the Eastern European countries.

In general terms, these international agencies coordinate and promote technological developments, provide safety guidelines, initiate research programs, and coordinate specific activities concerning seabed disposal and terrestrial disposal.

Apart from this, the International Council of Scientific Unions (ICSU) also draw conclusions and made some recommendations based on the work of its steering committees and working groups. These are as follows:

1) Disposal is taken to mean the sequestering of material with no intention to retrieve it (although it may be technically possible to do so), whereas storage is intended to be temporary.

2) Criteria for site selection should be determined by safety and science and not by economics and politics, although these factors will inevitably be involved for the actual selection.

3) Nuclear wastes are with us now, so safe means must be found for their disposal. Programs are already under way in different countries to investigate various methods of disposal.

4) High-level wastes are potentially hazardous for at least 10^5 years and the behavior of the nuclides contained therein must be considered over that period.

5) The system of dose limitations developed by the International Committee on Radiation Protection is rational, and the dose limits are set at a level so low that risk is comparable to other risks of everyday life.

6) Primary attention should be given to international agencies and the research they support, sponsor, or coordinate; but national programs should be reviewed where necessary.

7) The review should be limited to disposal using technology now available.

8) The working group on environmental pathways should consider migra-
tation of nuclides in the biosphere and the other two working groups should review data concerning the migration of nuclides from the repository to the biosphere. Some overlap would be inevitable and probably useful.

This study is a contribution to the NEA-SEABED programme and is initiated by the DORA, the Dutch official commission of the Ministry of Economic Affairs charged with the management of the radioactive waste disposal in the deepsea. The research was carried out in two periods. The first period (1981-1982) was financed by the Commission for the European Communities in a cost-sharing program (contract number 258-81-7 WAS NL) together with the Ministry of Economic Affairs (contract number TW-83/TA-Z/112:jfk) (Appendix I). The second period was financed by the Ministry of Economic Affairs (same contract number) alone. The research was carried out at the Delta Institute for Hydrobiological Research at Yerseke and the Technical University "Twente" at Enschede.

A fruitful collaboration was found with the ECN at Petten for the execution of the experiments with transuranic elements, and with the Sandia Laboratories, Albuquerque, USA, for the exchange of advanced computer codes. The RGD at Haarlem was so kind to provide proper deepsea sediments.

The main topic of the research was to study the effect of a canister with high-level radioactive waste which has not cooled down to the surrounding temperature on the migration of the radioactive transuranics through the deep sea sediment.

The research was focussed on two themes:
1) The influence of elevated temperatures on chemical processes in the seabed sediment, which includes:
   i) the influence of elevated temperatures on characteristics of the sediment and of its interstitial water,
   ii) the influence of elevated temperatures on the sorption of transuranic elements by the seabed sediments,
2) The mathematical modelling of effects induced by a heat source in the seabed sediment, which includes:
   i) the modelling of convection and heat dispersion around a heat source in the seabed sediment.
   ii) the modelling of sorption of nuclides and the effect of temperature on sorption.
iii) the development of a model of the migration of the transuranics through the seabed sediments.

iv) the calculation of the release of transuranics from the buried canisters to the overlying seawater based on the application of a migration model and obtained experimental results.

Conclusions

The effect of heat radiation from the canister on the nuclide migration is noticeable in the immediate vicinity of the canister. The effects are twofold:

1) the chemistry of the interstitial water and the sediment change due to the elevated temperatures while the adsorption coefficients can also change. It was found that the pH of the sediments was slightly decreased at increasing temperatures up to 60°C. It is generally known that adsorption of cations decreases at decreasing pH. Other parameters of interstitial water chemistry did also change, but it is not known how this might influence sorption.

- According to preceding experiments with cadmium, lower adsorption coefficients at higher temperatures were also expected for transuranic elements, but this was only demonstrated for americium. An unambiguous decrease of the adsorption coefficient was not demonstrated for plutonium and neptunium.

- Although a partial effect of temperature on the interaction of sediments and transuranic elements was found, this effect might be less important for the migration of nuclides through the sediments than the temperature effect on pore-water movement.

2) the pore water movement due to the heat convection may mix the surrounding water of the canister very quickly. This effect enlarges the initial volume of radioactive waste when we assume that the canister has no walls. The size of these mixing cells might well define the burial depth of the canister. The sizes of these convection cells are probably dependant on a threshold value for the flow of pore water: the larger the threshold values are, the smaller the convections cells get.

In order to get an idea of the release of radioactive nuclides from a
source buried 30 m in the sub seabed sediment to the overlying ocean water, a few calculations were made. A fraction of $10^{-7}$ to $10^{-8}$ of the original amount of neptunium-237 (with a half life of $2.14 \times 10^6$ yr and a Kd of 250 ml/g) was calculated to be released to the water within a period of to year after burial. For plutonium-239 (with a half life of 24390 yr and a Kd of 25000 ml/g) this was calculated to be $10^{-20}$. The fraction of americium-243 was even smaller: americium has a shorter half life (7370 yr) and a higher Kd of 40000 ml/g. So neptunium plays the major role in the safety assessment of radio active waste disposal.
Recommendations

1) The problem of the threshold values for the convection-induced pore-water flow must be studied thoroughly in order to indicate a safe burial depth of hot canisters in subseabed sediments.

2) Neptunium has a very low Kd and plays therefore a major role in the propagation of alpha emitting particles in the biosphere, it should be treated cautiously in waste disposal and can serve as the most sensitive element in safety assessment calculations for long range periods.

3) It is not known what the effects of high temperatures (up to 250°C) of canisters in the seabed sediment are, either this problem must be studied, or the disposal of high-level radioactive waste should be postponed until it is cooled down to 100°C.

4) Both the chemical results and mathematical modelling are partially applicable to studies of terrestrial disposal of HLRW.
1 - Summary

This report presents the results of a study on the effects of temperatures up to 90°C on the migration of the radionuclides plutonium, neptunium and americium through marine sediments in the near field of a canister with radioactive waste. Topics entered were: (i) the influence of temperature on the distribution coefficients of the transuranics plutonium, americium and neptunium, (ii) the effect of temperature on the composition and characteristics of interstitial water and (iii) the effects of a point heat source on the temperature distributions and flow velocities in interstitial water of sediments.

The influence of temperature on Kd's of the transuranics plutonium, americium and neptunium was studied using batch and column experiments. Two sediments originating from the Madeira Abyssal Plain, a SEABED selected waste disposal site in the North West Atlantic Ocean, were used in the batch experiments. The characteristics of the sediment clearly influence the adsorption. At 4°C the Kd of americium was $\sim 40 \times 10^3$ ml/g or $\sim 100 \times 10^3$ ml/g, depending of the sediment, while plutonium showed Kd's $\sim 20 \times 10^3$ and $\sim 25 \times 10^3$ ml/g respectively. The Kd of neptunium at 4°C was about the same for both sediments: $\sim 250$ m$^3$/g.

The Kd values of americium were found to be 2 to 4 times higher at 4°C and 35°C then at 60°C and 90°C. Plutonium and neptunium were not found to be affected unambiguously by temperatures up to 90°C.

Desorption experiments revealed higher adsorption than desorption values. This indicates that the distribution is not completely reversible. The method to detect the neptunium did not allow us to calculate accurate desorption Kd's.

Column experiments with plutonium indicated a slightly higher adsorption at 4°C than at 60°C, but we found higher Kd's compared to those derived from batch experiments.

The temperature was found to have an effect on interstitial water characteristics: pH decreased with temperature, while ammonia and silica showed higher concentrations. Microbial activity had hardly any effect on the interstitial water characteristics.

Model calculations showed that heat flow is not influenced by the convection of pore water. Experiments with fine sand and with Atlantic sediment confirmed this. A tracer study revealed that the migration was controlled
by diffusion alone.

The migration model also showed that velocities below 0.1 mm/year hardly affect the diffusion process. The hypothesis of a threshold value for the pressure gradient in the model was evaluated. It appeared that at increasing threshold values, the maximally occurring flow velocities decrease.

An accurate description was derived for the distribution coefficient in case of covalent sorption. This was applied to cadmium adsorption data and several temperatures.

A model for the migration of radionuclides in the subseabed was developed and applied to the transuranics plutonium, americium, and neptunium. Results of batch experiments were used as adsorption coefficients. The release of transuranics from the seabed to the overlying water was calculated, assuming a canister embedded 30 m below the sediment surface. A fraction of $10^{-7}$ to $10^{-8}$ of the original amount of neptunium-237 ($T_1/2 = 2.14 \times 10^6$ year) in the canister, is released to the overlying water. A fraction of $10^{-20}$ of the original amount of plutonium-239 ($T_1/2 = 24290$ yr) in the canister is released to the overlying water, for americium this is even smaller. These results are valid in a homogeneous sediment with no pore water flow.
2 - Introduction

The final solution for the disposal of high-level radioactive wastes originating from nuclear power plants is the complete isolation of this wastes from the biosphere for several half life times of its slowest decaying radionuclide, i.e. a containment for millions of years. This isolation is considered to be essential in order to protect mankind from the hazards of unintended exposure to radioactivity. A sufficient isolation of radionuclides for such a long time depends on an effective retardation of the migration of radionuclides through the geological barriers towards man. One of the options for the disposal of these wastes is the emplacement of canisters containing the waste in the seabed sediments of especially selected sites in the Atlantic Ocean. This option is based on the concept that several barriers will prevent the contamination of man and biosphere by radioactive substances released from the waste package. These barriers are the wall of the canister, the seabed sediment and the water of the ocean. Although much effort has already been expended on the evaluation of this option—see for instance Hollister et al (1980)—much research is still needed in the evaluation of the site-specific consequences of the burial of hot high-level radioactive waste and the interactions with the specific sediment.

We can divide the site specific properties that effect the migration of radionuclides through the sediment in a far-field and in a near-field situation. The properties of the far-field are mostly determined by very slow geophysical and geochemical—natural—processes. The properties of the near field sediments and the interactions of radionuclides with these sediments—the imposed processes—are determined by the very presence of the canister. This implies that the consequences of mechanical ruptures, heat gradients, and all other physical and chemical irregularities in the immediate vicinity of the canister that are a consequence of the emplacement, have to be studied.

The migration of radionuclides away from the canister and the consequences of the near-field and far-field processes and properties should then be incorporated in one migration model to allow safety assessment calculations of this option. The development of such a model was beyond the scope of this study.

However, before and overall model can be assembled the nature and
impact of occurring subprocesses must be evaluated. This research is a pre-
sentation of such a study, considering the effects of temperature on the
migration of radionuclides through the sediment of a specific dump site —
the Madiera Abyssal Plain — in the Atlantic Ocean.

Canisters with high-level radio-active waste may still radiate heat
when buried in deepsea sediment. The temperature field around a canister
will be one of the most dominating properties of the near-field situation
in the first decades of burial. The amount of heat radiated depends on the
age and concentration of the waste in the canister and slowly decreases
with time. The general expectation is that the half life of heat radiation
will be about 15 years and that the waste has a temperature of about 250°C
when it leaves the power plant (Percival, 1983), since temperature increases
with depth of the sediment (up to 54°C/100 m in these deposits, ..........198), the canister will reach the environmental temperature within 30 to
50 years, depending on the depth of burial and the age of the waste.

The temperature field has two main effects:
- It may induce a convection of interstitial water and it may change the
  chemical characteristics of the sediments and the interstitial water and by
doing so the sorption properties of the migrating nuclides. The influence
of the interaction of temperature and the occurrence of inhomogenities and
mechanistic irregularities on migrating nuclides are beyond the scope of
this study.
- The effect of temperature on diffusion is considered to be dependant on
  the change of Kd's and the temperature factor for the molecular diffusion
  coefficient \( D_M(T) = D_M(°C) + 3 \times 10^{-7} \ T \); \( T \) in°C, Duursma and Bosch, 1970).

The chemical and physical consequences of a hot source have been
studied seperately. The chemical study focussed on the effect of tem-
perature on the interstitial water chemistry of sterilized and non steri-
lized sediment samples from the Madeira Abyssal Plain and a study on the
influence of temperature on the sorption of the radionuclides plutonium,
neptunium and americium to these sediments. A theoretical and experimental
study on the sorption of cadmium and cesium to these sediments was per-
formed beforehand in order to assess the method. This study is reported
seperately in a paper (Wegereef et al., 1985).

The mathematical study included the effect of a hot canister on the
distribution of heat and the consequences for the occurrence of convection and other heat induced processes in a water saturated sediment.
3 - Materials and methods

3-1 Sediments

Sediments were obtained from the RGD (Rijks Geologisch Dienst), Haarlem and were stored at 4°C in their original p.v.c. core segments. They were examined for mineral composition at the Rijks Instituut voor Drinkwatervoorziening (RID), Leidschendam, using X-ray spectroscopy. Elemental analyses were performed at the ECN (Energie Onderzoek Centrum Nederland), Petten using neutronactivation analysis (van der Sloot and Zonderhuis, 1979).

Relative surface area (SA) was determined using the ethyleneglycol procedure of Dyal and Hendricks (1950). Cation-exchange capacity (C.E.C.) was determined using the sodium-exchange procedure as described by Duursma and Eisma (1973).

The fractions of Fe, Mn and Zn, bound to calciumcarbonate and bound to the clay minerals, were determined using the extraction procedure with sodium acetate followed by the extraction with sodium dithionate. The extracted kation in the fractions were determined with AAS (Atomic Absorption Spectrometry). The calciumcarbonate content was determined by adding acid and weighing the produced and reabsorbed CO₂. Porosity was determined by drying until constant weight at 55°C.

3-2 Incubation of sediment at 4 temperatures

All manipulations were carried out in a glovebox filled with N₂. Three sediments were used in this study: PCL 14/1, PCL 14/3 and PCL 32. Each sediment was manually homogenized thoroughly and portions of ~ 80 ml were put in a jar of poly-methyl-pentane (PMP) which is - according to the manufacturer - resistant to exposure at high temperatures for a long period. These jars were incubated in a vessel which was constantly purged with N₂ and kept moisted. Incubations were performed at 4°C, 35°C, 60°C and 90°C. A parallel series was treated likewise but was sterilized before incubation by γ-radiation at Gammaster, Veenendaal.

At days 26, 45, 79, 127, 169, 206, 239 and 266 jars with sterilized and 'natural' sediment were withdrawn from the large incubation vessel.
These jars were transferred to the glovebox and Eh and pH were measured in the sediment. Interstitial water was then squeezed out of the sediment in teflonized Schleicher & Schüll presses through a 0.45 μm filter using a pressure up to 9 bar.

Eh and pH were measured in the porewater, 1.00 ml is pipetted in a glass vial, the vial is closed with a rubber septum and the sample is stored in a freezer until detection for CO$_3^{2-}$. For this purpose is a small volume of HCl injected through the septum. The CO$_2$ in the air under the septum is measured with GC and CO$_3^{2-}$ is calculated.

Iron (II) was detected in 1.0 ml sample by mixing with 1.00 ml 0.1% phenanthroline. The colour is allowed to develop for 15 min and is measured at 510 nm in a spectrophotometer. Sulfide was detected in 2.0 ml sample by adding 20 μl of a solution of 1 g N,N-dimethyl-p-phenyl-diamine dihydrochloride in 500 ml 6 M HCl. Then 20 μl of a solution of 8 g FeCl$_3$ in 500 ml 6 M HCl was added. The colour is measured after 60 minutes at 670 nm in a spectrophotometer.

Silicate, phosphate, nitrate, ammonia and dissolved organic carbon and sulphate were analysed on a Technicon Autoanalyser AA II using standard procedures:

- Silicate (Koroleff, 1971): silicate reacts with molybdate to form silicomolybdic acid, this is reduced and forms a blue compound.
- Orthophosphate (Murphy and Riley, 1962): orthophosphate reactes with a potassium antimonyltartrate reagent, it gives a blue antimony-phosphate complex.
- Nitrate (Grasshoff, 1970): nitrate is reduced to nitrite, this is determined as an azo-dye after reaction with sulphanilamide and N-1-naphtyl-ethylenediamine.
- Ammonia (Koroleff, 1970): ammonia reacts with hypochlorit to monochloramine, this gives with phenol indophenol blue.
- Dissolved organic carbon (D.O.C.) (Schreurs, 1978): CO$_3^{2-}$ is washed out, the sample is destructed under U.V. and oxidized to CO$_2$, which is measured in an infrared spectrophotometer.
- Sulphate (Merks and Sinke, 1973): sulphate reactes with the barium methylthymolblue complex and releases methylthymol blue. This is measured spectrophotometrically.
3-3 Seawater

Standard seawater was prepared according to the FWPC (1969); 25.4 g NaCl, 10.0 g MgSO₄, 0.7 g KCl, 0.03 g H₃BO₃ and 0.2 g NaHCO₃ are added to one liter distilled water. The pH is adjusted to 8.2 with 0.2 N NaOH. Before using this seawater it was filtered through a 0.22 μm polycarbonate membrane filter and deoxygenated by boiling for 30 min while purging with N₂.

3-4 Radionuclides Pu, Np and Am

Radionuclides Pu-239, Np-237 and Am-243 were obtained in a solution of HNO₃. They were evaporated to dryness and were taken up in an appropriate amount of seawater. The pH was adjusted to 8.2. These stock solutions were allowed to age overnight and filtered the next day through a 0.22 μm polycarbonate filter. Six solutions of different plutonium concentration were prepared by spiking seawater with the stock solution. These solutions were added immediately to the sediment suspension.

The Np-237 stock solution developed a white precipitate. The above seawater was used to prepare the sub-solutions. These sub-solutions again developed a precipitate, so they were filtered through 0.22 μm polycarbonate filters just before they were added to the sediment suspension. The oxidation state of the neptunium in some of the batch experiments was detected after incubation by using the procedure of Foti and Freiling (1964). This procedure is based on the facts that: 2-thionyltrifluoroacetate (TTA) in benzene can extract Np (IV) from a dilute acid solution, but not Np (V) and Np (VI), while lanthanum fluoride carries Np (V) and Np (IV) but not Np (VI). The procedure is:

1) water and sediments are centrifuged.
2) 5.0 ml of the supernate is counted.
3) 4.0 ml is shaken together with 0.28 ml 12 M HCl and 2.3 ml 0.4 M TTA in a separating funnel for 10 minutes. The phases are allowed to separate and 3.0 ml of the organic phase (Np (IV)) and 2.0 ml of the aqueous phase (Np (V+VI)) are counted.
4) 5.0 ml is transferred to a centrifuge tube and the following reagents are added: 0.7 ml lanthanum-nitrate solution (2.5 mg lanthanum-nitrate per ml), 0.7 ml uranium-nitrate solution (2.0 mg uranium-nitrate per
(ml), 0.21 ml 12 M HCl en 0.7 ml HF.

5) The tube is shaken for 2 minutes and centrifuged. Then 3.6 ml of the supernate (Np (VI)) is counted. The precipitate (Np (IV) + (V)) is dissolved in 0.5 ml 2 M Al(NO₃)₃ + 1.4 ml 2 M HNO₃, and counted.

The americium stock solution did not develop a visible precipitate and was used to make six sub-solutions. These were used in the incubations at 60°C and 95°C. The remains of these six sub-solutions were filtered after a week through a set of two 0.15 μm polycarbonate filters. The americium was found to form a precipitate that settled on the top filter. About 70% of the activity remained in solution. Repeated filtration again removed about 30% of the activity out of the solution and these filtrates were used in the batch experiments at 60°C and 95°C.

3-5 Detection of Pu, Np and Am

Liquid scintillation counting was used for all radionuclides. An appropriate amount of radionuclide solution (in most cases 5.0 ml) was transferred to a glass counting vial. An equal volume Beckman EP1 scintillation liquid was added. The samples were counted integrally in a Packard-Becker Liquid Scintillation counter, gain 30, window 050-». Since both Np-237 and Am-243 have β-emitting daughters, Pa-233 (T½ = 27.0 days) and Np-239 (T½ = 2.35 days) respectively, these samples were counted after one month in order to let the daughters grow in to a stable mother-daughter ratio. After three months some countings of Np-237 were repeated to check the stability of these mother-daughter ratios.

Warning: In a first series of experiments we used plastic counting vials of Packard-Becker. These were found to give very high backgrounds which were increasing in time, probably due to a chemiluminescent reaction of the plastic (or the coating on the plastic) with the scintillation liquid.
Plate 3-1.
A glove box filled with N₂ was used in the studies in order to exclude interference of O₂.
3-6 Batch experiments

The experimental procedure used in this work was adopted from the constant shaking method as developed by Duursma and Bosch (1973). In order to perform the experiments at temperatures up to 95°C the method was modified as described below and some precautions were taken to control Eh.

Basically the method consists of the incubation of a known amount of sediment with a known amount of radionuclides. The radionuclide in solution is measured before and after the incubation and with this information Kds can be calculated (adsorption). A reverse procedure is equally possible (desorption).

3-6-1 Adsorption

Sediment is brought in seawater to a predetermined sediment concentration of about 250 mg/l. This concentration was checked by filtering a known volume of suspension over a 0.22 μm filter followed by drying and weighing of the filter. In order to maintain the existing Eh of the sediments and to avoid the exposure of the constituents of the solution to an excess of oxygen, the seawater was deoxygenated before using and all work was performed in a N₂ purged glovebox (see plate 3-1).

Aliquots of 19.0 ml were pipetted in glass vials and 1.0 ml of radionuclide solution was added. The vials were sealed by melting. Six radionuclide concentrations were applied and each experiment was performed in triplo. A parallel incubation of radionuclide in seawater without sediment was used as a check to determine the start- or 'blank' conditions.

Incubations were performed at 4°C, 35°C, 60°C and 95°C for 25 days. The samples were shaken, when possible, twice a day. Upon analysis, the vials were centrifuged for 30 minutes in a Sorvall centrifuge at 1500 rpm. They were opened and allowed to re-equilibrate at the incubation temperature in a water-batch for about 40 min. Samples of 5.0 ml were mixed with scintillation liquid and counted as described. The rest of the liquid was suctioned off and used to determine pH.
3-6-2- Desorption

Ten ml of fresh seawater was added to the pre-contaminated sediment, the vials were closed again and incubated for another 24 days under similar conditions. The samples were further manipulated as described above.

3.7. Column experiments

Column experiments were performed with tritium, cadmium and plutonium. The experimental procedures were adopted from HPLC technology but modified to meet our requirements: Arheodyne valves, teflon tubes, Omnifit fittings, watermantles and glass columns were applied. The columns were filled manually with wet sediment. The intention of these experiments was to test chromatographically the ionic transport through a column of seabed sediment. Cadmium was used as tracer with a standard set of glass columns of different length. These investigations were carried out in the Delta Institute. Later on the procedure was applied for chromatography of the radionuclides at the ECN. Dimensions of the glass columns were $\varnothing$ 4.1 mm while lengths varied from 13 mm to 52 mm. The columns were filled with sediment PCL 14/2.

The quality of the columns was tested by elution of a spike of tritiated water with seawater as eluens. Cadmium chromatography was performed in one of these columns (length 21.8 mm) at 20°C and at 90°C. A spike of 10 $\mu$l of 200 ppm Cd$^{2+}$ in seawater was brought on the column. The fractions were collected in a volume of 1.0 ml water, and acidified with HNO$_3$. Cadmium was analysed on a Perkin-Elmer AAS.

The column of 21.8 mm length was also used in the chromatography of Pu-239, but it was impossible to detect any activity in the elutes. This slow migration of Pu was already indicated by theoretical indications as shown in 4-5. To overcome this problem, teflon tubing with a very narrow inner diameter were used as column, dimensions: $r = 0.375 \text{ mm}$, $l = 1.5 \text{ mm}$. These columns were filled with 100 $\mu$l sediment PCL 14/3 suspension, containing 12.5 mg/ml sediment (on a dry-basis). A spiked sediment was prepared as follows: 250 $\mu$l of the Pu-stock solution ($442 \times 10^3$ cpm/ml) was incubated together with 6.0 ml sediment suspension, containing 2.0 mg/ml sediment. With a syringe 50 $\mu$l of this activated slurry was brought on the "column", the column was then eluated with seawater. Seawater, pH 8.2, was
pumped through the columns with a L.K.B. Vario Perpex II pump at a rate between 1 and 10 \( \mu l.min^{-1} \) depending on the permeability of the column.

The eluate was collected in fractions, which were subsequently counted. The column was cut into thin slices. The sediments were washed out of the slices in counting vials with acidified water (0.2 M \( \text{HNO}_3 \)) and counted. The slices of the tubing were weighed. Knowing the weight-length ratio, these served to measure the length of the column.

4. Results and Discussion

4-1 Sediments

The sediments used in this study originate from the Madeira Abyssal Plain (MAP), a potential site for waste disposal. The area is situated around 31° 21'N, 24°30'W, which is south of the Azores and south-west of Madeira. Sediment samples were provided by the RGD, Haarlem.

The geophysical, sedimentological, chemical and stratigraphical particulars of the area are given by Kuijpers (1981) and Duin and Kuijpers (1982): The average depth of the MAP is 5400 m, the area is not completely flat and abyssal hills rising up to 300 m above the seafloor do exist. The whole area is covered by a layer containing turbiditic and pelagic sediments. The sediment thickness ranges from 1750 m in the abyssal valleys to 250 m on the top of the abyssal hills. Sediments at a depth larger then ~ 500 m beneath the seafloor will be consolidated and lithified by the ongoing diagenetic processes. The sediments in the central part are of mixed turbiditic and pelagic origin, except for the elevated parts of the area which have generally not been subjected to turbiditic sedimentation. Turbiditic sediments are dominant in the northern part of the area, while pelagic sediments are dominant in the western parts, these area cannot be reached by the continental derived turbiditic sediments. Sand and silt do occur in very small and decreasing amounts going from east to west. Sedimentation rates range between 9 cm/1000 years when both turbiditic and pelagic sedimentation take place, down to 1 cm/1000 years when pelagic sedimentation alone occurs. The pressure at this depth does not force the calcium carbonate of depositing remains of plankton to go into solution so that sediments contain high amounts of calcium carbonate. Turbiditic sedi-
ments contain much organic carbon and are mostly anoxic while pelagic sediments contain more carbonate and less organic carbon and are mostly oxic.

So it appears that even within a small and geologically homogeneous area sediments have a variety of physical and chemical properties that can affect migration behaviour of radionuclides. The redox potential and pH control the speciation of radionuclides while anions like $\text{CO}_3^{2-}$ form complexes with actinides (Allard, 1982). The calcium carbonate content is the most important factor for these actinides to control sorption of marine sediments (Higgo et al., 1983). It is therefore beyond dispute to evaluate the chemical and physical properties of the sediments first.

Three sediments were used in the studies, they were collected at station 82PCL14, this is a pelagic sediment of the westernmost part, at station 80PCL19, this is a mixed pelagic, turbiditic and silt sediment of the central part and at station 82PCL32, this is a turbiditic sediment of the northernmost part of the area. These sediments were sampled during the "Tyro" trips in 1980 and 1982 but were not suitable for geological examination because of a failure during sampling that resulted in deformed or very short cores (see Duijn and Kuijpers, 1982). Tables I, II and III give particulars of the three sediments.

Sediment from station 82PCL14 is a grey to white pelagic sediment and consists largely of calcareous and siliceous remains. Calcite is again the most abundant (~ 40%) mineral and again kaolinite, montmorillonite and illite are the other minerals, quartz and smectite were not detected.

Sediment of station 80PCL19 is from an area with silt and sand deposition together with pelagic and turbiditic sediments. Mineral analyses did not show a large difference between this sediment and the other two. This sediment was used in earlier studies of Pu, En and Cd adsorption. (Appendix I and II).

Sediment from station 82PCL32 has a greenish to grey colour that turns grey on exposure to air oxygen. It is - although it is typical for these sediments - not complete anoxic and interstitial water did not contain sulfide. A complete gradient of interstitial water components in the top centimeters near the sediment-water interface is given by de Lange (Duijn and Kuijpers, 1982). The results of interstitial water characterisation are given in figures 1 to 10. Sediment properties at the start of the incubation are those after at least 8 months storage at 4°C and after mixing in a glove chamber filled with $\text{N}_2$. This long storage period might explain the
high Eh. A little over 50% of the sediment consists of CaCO$_3$ in the form of calcite. Other minerals present are kaolinite, montmorillonite and illite, but no quartz was found. Smectite was also reported to be present in these abyssal sediments (Higgo, et al., 1983) but it was not detected in all our sediments. The most striking feature in this sediment is the high Fe content (see table 2): ~11%.

All sediments consists of homogeneous and very fine (0.1 to 30 μm) material and all have a high porosity (about 70%) and water content (about 50%). This features are typical for the deepsea sediments. Table II gives the elemental composition of the sediment together with the interstitial water. Since interstitial water occupies about 50% of the volume, this will have consequences for the calculation of the dried sediment composition. De Lange reports the same quantities of K, Na, Ca and Mg in the interstitial water as in ocean bottom water, with only slight differences (Duin and Kuijper, 1982). This means that the elemental composition as given in table II has to be corrected for these main cations. It does not make much difference for Ca: a correction of ~0.04% is negligible, but corrections of ~1.1% for Na, ~1.3% for Mg and ~0.03% for K are important.

4-2 Incubation studies with deep sea sediments

Theoretical studies on the physical effects of canisters in the deep sea sediments (Delow, 1982) indicate that the sediment around a canister will tend to compact by a process called "thermal damping". This will of course, inhibit migration of radionuclides leaching away from the corroding canister. Our studies could not verify this process since it can only be studied by in situ experiments. Other studies on the effect of a hot canister on the chemistry of the seabed sediment however, indicate an opposite effect for nuclide migration: Seyfried and Janecky (1979) and Seyfried and Thornton (1982) found that a sediment-seawater mixture, when heated to 200° to 300°C at 500 bars showed a decreasing pH, an increased oxidation capability and a recrystallisation of the minerals. These circumstances favor low sorption constants for the actinides (Sanchez et al., 1981). This certainly holds when diffusion is the only mechanism for migration. Duursma and Eisma (1973) stated that

$$D_{\text{radionuclide}} = \frac{0.5 \times 10^{-6}}{K_{\text{radionuclide}}}$$  (4-1)
So that at low Kd's the migration will be enhanced.

The above results are valid for temperatures between 200 to 300°C and so called "red clays", which are pelagic sediments with hardly any calcium-carbonate.

The Madeira Abyssal Plain (MAP) sediments cannot be compared with the "red clays" and in our study we used only temperatures up to 90°C. Results of incubations of MAP sediments did not show spectacular changes in the chemical composition of the interstitial water, see figures 1 to 10. It must be kept in mind that the first values of all the incubation series were determined on non sterilized sediments that were already stored for more than 8 months at 4°C, so that values of the 4°C incubation series can be considered as an indication for the precision of the determinations.

In spite of the manufacture's assurance, the incubation jars were not resistant against temperatures of 90°C. The jars cracked and the contents dried out, so the results of the 90°C incubation were not reliable.

Sterilized and natural sediments were applied in the incubation to inquire the influence of microbial mineralisation on the chemistry of the interstitial water. At 35°C or even 60°C we might expect a faster rate of mineralisation resulting in a lower redox potential, a increased sulfide concentration, a decreased pH and an increased CO₂ concentration. This in particular in the sediments (82PCL32/2) with high organic carbon contents. This, however, could not be concluded from the data, rather the opposite is observed. A general trend is a higher concentration of silicate in the interstitial water at higher temperatures, which is clearly a chemical effect. The solubility of silicate is enhanced at higher temperatures and the new equilibrium is reached within the first days of incubation.

Ammonium increases after about 80 days of incubation in both sterilized and natural sediments at the incubation temperature of 60°C. The mechanism behind this phenomenon is not yet clear.

Organic carbon in the interstitial water of 'natural' sediment is much more stable—although at a low level—than in the sterilized sediments. This indicates that microbial processes play an important role for the existence of this component. The pH decreases at higher temperatures, as was also found by Seyfried and Janecky (1981), but their shift in pH was much larger possibly because of the fact that they used much higher temperatures.
4-3 The radionuclides Pu, Am and Np

4-3-1-Plutonium

It has been found that Pu (V) is the dominating oxidation state in seawater and that Pu VI is rapidly reduced to Pu (V) in carbonate rich solutions (Nelson, 1980). It was also found that 95% of all Pu in these circumstances was in the semi-solid state PuO₂ and all the soluble plutonium exists as the monovalent kation PuO₂⁺ (Allard, 1982).

In our experiments the solutions were centrifuged and then allowed to "age" for over a month. The supernatant was used for adsorption experiments and was diluted several times before the incubation started. No visible precipitation was observed in the dilution series, which made us assume that all Pu is present as PuO₂⁺.

4-3-2-Americium

Americium is generally expected to be in the III valent state under the circumstances used in our experiments (Allard, 1982). Americium solubility is reported to be highly dependent of pH and carbonate. In the absence of carbonate, pH is the solubility controlling factor according to the correlation:

\[ \log [\text{Am}] = -3.76 \pm 0.26 - (1.07 \pm 0.04) \text{pH} \quad (\text{Rai et al., } 1981) \] (4-2).

However, in carbonate-rich water like in our experiments, CO₃²⁻ is the main controlling factor for solubility and Allard (1982) reports the existence of soluble Americium compounds at p(Σ CO₃) = 3.3 and pH = 8 up to a concentration of 10⁻⁶ M.

Our equilibrium concentrations of the sediment-nuclide incubations range between 10⁻⁹.5 M and 10⁻¹¹.5 M, with starting conditions of around 10⁻⁸ M to 10⁻¹⁰ M, so these should be well below precipitation levels. Still - invisible - precipitation occurs, since filtering through two 22 µM filters retained a large part (~ 60%) of the activity on the upper filter. Repeated filtering again retained part (~ 60%) of the americium activity. Therefore it is possible that our sediment samples were partly incubated with solid Am(OH)₃ or Am₃(CO₃)₂ particles in low concentrations. These particles are however so small that they cannot be separated off by centrifuging. For reasons of counting efficiency, it was impossible to change to
lower starting concentrations, so this starting situation was maintained.

4-3-3-Neptunium

Under partial oxic conditions as used in our experiments, neptunium is present in the pentavalent state. This was checked with the method of Foti and Freiling (1964) in samples equilibrated with sediment. Allard (1982) reported the existence of negatively charged carbonate complexes, which might explain low Kds.

During preparation of the stock solution and the diluted solutions, a visible precipitate developed that was not examined further. Most probably it is NpO$_2^-$, which precipitates at high concentration. Because Neptunium-237 ($T_1/2 = 2.14 \times 10^{10}$ year) was used, we had to use high concentrations in order to maintain a proper counting efficiency.

4-4 Batch experiments

The sorption mechanism of radionuclides to sediments is composed of several independent processes (Anonymous, 1983):

- electrostatical adsorption; This process is induced by Coulombic forces of attraction between charged species in solution and the charged sites at the surface of the sediment particles. It is a rapid and reversible process. It is dependent of temperature, ionic strength, charge and the solution and substrate composition.

- specific adsorption; This process is due to the induction of specific adsorption sites on a mineral surface by the sorbent. This process is highly dependent of mineral surface, sorbate and solution composition, but also of temperature.

- chemical substitution; This process is due to chemical forces that results in precipitation, chemical bounding and other typical chemical reactions. These reactions are mostly irreversible. They depend on substrate and solution composition and temperature. Strictly speaking chemical substitution is not an adsorption process but rather an absorption process. It is difficult to distinguish from adsorption in experiments.

- physical adsorption; This process is largely independent of temperature and
chemical composition of the sorbent and of the ionic strength and composition of the solution. Complexing agents and pH of the solution have a large influence on this process. The physical sorption involves all non-specific forces of attraction, i.e. it comprises all forces of attraction other than electrostatic adsorption, specific adsorption and chemical substitution.

Table 4-V lists the types of sorption together with the impact of parameters on the types of sorption. It can be concluded from this table that the overall sorption is more or less dependent on temperature, which makes it worthwhile to study it in more detail. Temperature, however, is not the only parameter — and certainly not the most influential parameter. Most parameters are not subject to change during the experiments in the experimental set up that we used, except for Eh. Eh is very critical at this point, since changes in Eh can induce large changes in the qualities of other parameters too. It is therefore important to control Eh and to preserve the 'natural' level during the experiment. This was attempted by removing all oxygen from the seawater before starting the experiment and closing the incubation vials airtight by melting. Although we could not manage to achieve the exact Eh of the interstitial water of the sediment, which is around 200 to 250 mV, it was possible to maintain a fairly constant Eh in the vials ~ 300 mV: start and end Eh differed at the most 50 mV.

As can be concluded from above, sorption is a complex process which is not easily described by chemical and physical processes. The division in the various chemical and physical processes can hardly be quantified when using a simple technique like batch experiments. Therefore the "overall" sorption — which is at the end of the crucial parameter — is expressed as the distribution coefficient of a radionuclide between the solid phase and the liquid phase:

\[
\frac{x_i}{X-x_i} = K \frac{C_i}{C}
\]

(4-3)

where \(x_i\) = radionuclide sorbed to the sorbant (M/l)

\(X\) = sorbant sites (M/l)

\(K\) = distribution coefficient

\(C_i\) = radionuclide concentration M/l

\(C\) = concentration of ions competing for sorbant sites (M/l)

all processes are roughly described by this formula.
Since $X \gg x_1$, (4-3) becomes

$$\frac{x_i}{C_i} = K \frac{X}{C}$$  \hspace{1cm} (4-4)$$

$X/C$ is constant in seawater so

$$K_d \equiv K \frac{X}{C}$$  \hspace{1cm} (4-5)$$

and

$$K_d = \frac{x_i}{C_i}$$  \hspace{1cm} (4-6)$$

In batch equilibrium studies the $K_d$ can easily be calculated according to Duursma & Hoede (1967) from

$$K_d = \frac{(C_0 - C_t)}{C_t} \frac{M}{V}$$  \hspace{1cm} (4-7)$$

where $C_0$ = start concentration of the radionuclide *(M/l)*

$C_t$ = end " " " " *(M/l)*

$M$ = mass of the suspended sediment (g)

$V$ = volume of the suspension (ml)

$K_d$ = distribution coefficient (ml/g)

* or any activity concentration

Desorption studies were performed starting from the idea that $K_d$ can be calculated from a redistribution of radionuclides between sediment to which they were already adsorbed and new seawater. So:

$$K_d = \frac{C_0 - C_t + C_{dt}}{C_{dt}} \frac{V_d}{M}$$  \hspace{1cm} (4-8)$$

where: $C_{dt}$ = radionuclide concentration at desorption equilibrium *(M/l)*

$V_d$ = desorption volume (ml)

other parameters as in (4-5).

Figures 4-11 and 4-12 give the results of plutonium sorption experiments. Preceding experiments (see Appendices I and II) already showed large deviations in the determination of $K_d$ s of plutonium. Although triplicates were used now, and also precautions were taken to ensure constant $E_h$, it was still impossible to perform very accurate $K_d$ determinations. We still found a large range of $K_d$ s at the equilibrium concentration range $10^{-7.5}$ M/l
to $10^{-9.5}$ M/l. Kd values range between 5000 and 50000 ml/g for all the experiments, and no clear answer can be given to the question whether temperature has any specific influence on the adsorption of plutonium on both of these sediments. Too large differences were found within one temperature series. Desorption was higher in all cases than adsorption. This can indicate that adsorption was not completely finished at the time adsorption experiments were stopped and desorption experiments started, although the adsorption incubation lasted 3 weeks. Ranjon and Guegueniat (1984) reported higher Kd s at higher temperatures, which they seem to ascribe to the dissolution of insoluble plutonium complexes. Kd s were generally lower but this can be ascribed to sediment properties.

Figure 4-5 shows results of neptunium adsorption experiments. Again we found large deviations within one concentration series. Kd s range between 100 and 600 and they are evidently much lower than Kd s of Am and Pu. No unambiguous indications were found for the influence of temperature on adsorption.

Desorption measurements failed to give acceptable results since negative values were obtained for Kdes. This indicates that more neptunium was released from spiked sediment than was adsorbed. This is probably a result of inaccurate neptunium measurement due to the very low activity ($T^{99}_N = 2.14 \times 10^6$ year) of neptunium and the high activity of the daughter ($T^{237}_N = 27.0$ days).

Figures 4-13 and 4-14 show results of americium adsorption and desorption experiments. Most of the concentration series show constant Kd values with little deviation. Temperature seems to influence Kd; Kd s at 60°C and 90°C are 2 to 3 times lower than Kd s at 4°C and 35°C.

In preceding work (Wegereef, et al., 1985) we found an increasing Kd with decreasing temperature for cadmium. From this and the concentration series of cadmium, we could model the cadmium adsorption as a purely electrostatic adsorption process. It is most probable that americium too is adsorbed to the sediment by this coulombic interaction. Unfortunately we could not confirm this by concentration series into the high concentration range, since americium is insoluble at those levels. Even so, the lowering of sediment concentration was also difficult, because it yielded very high values - with large errors - due to the sediment effect (Aston & Duursma, 1973), which was already showed in earlier work (Appendix II).

Desorption experiments showed that sorption of americium is a reversible process, but again here large deviations in the values of Kd were found within one concentration series. Although Allard (1982; see section
3-4) reported enhanced americium solubilities due to the formation of negatively charged carbonate complexes at pH 8 and high carbonate concentrations, it is quite impossible to expect these negatively charged complexes to cause the high Kd s. Hence, it is doubtful whether these complexes existed in our experiments.

It can clearly be seen from the figures that the sediment characteristics play an important role in the sorption of americium and plutonium, while the neptunium sorption is not influenced by the sediment characteristics. Sediment PCL14/2 adsorbs 2 to 3 times as much plutonium and americium as the sediment PCL32/2.

This difference in Kd s is probably due to the mineral characteristics of the sediment. PCL32/2 is of turbiditic origin and contains higher levels of all trace and non-trace -for instance Fe- metals than sediment PCL14/2, which is of pelagic origin. Both contain about the same percentage of calcium carbonate, and all other relevant parameters of the incubated suspension are nearly the same, pH, Eh, ionic strength and ionic composition. The higher organic carbon of PCL32/2 can hardly influence the Kd s. The exchangeable ions of calcium carbonate and clay minerals differ too, see table III.

Other studies also report differences in Kd values for different sediment from the marine Atlantic deep sea (Higgo, et al., 1983).

We (van Geldermalsen and Duursma, 1983) also found a low adsorption of plutonium to estuarine sediments.

4-5 Column experiments

The migration of a solute through a column filled with sediment, is governed by the following processes: - convection by moving eluens - hydrodynamical dispersion - molecular diffusion - adsorption and desorption of solute with the sediment matrix.

Hydrodynamical dispersion and molecular diffusion are described by differential equations of the same form, so their effects can be added to give an 'apparent' diffusion term.

The transport equation in an one-dimensional porous medium is given by:
\[
\frac{\partial C}{\partial t} = D' \frac{\partial^2 C}{\partial x^2} - V_w \frac{\partial C}{\partial x} - \rho(1-\theta) \frac{\partial S}{\partial t} \tag{4-9}
\]

where: 
- \( S \) = solute concentration sorbed on matrix (\( \mu g/1 \))
- \( C \) = solute concentration in eluens (\( mg/ml \))
- \( D' \) = apparent diffusion coefficient (\( cm^2/sec \))
- \( x \) = distance along the flow path (cm)
- \( V_w \) = eluens velocity (\( cm/sec \))
- \( \rho \) = density of the sediment (\( g/cm^3 \))
- \( \theta \) = porosity of the sediment (\( cm^3/cm^3 \))
- \( t \) = time (sec)

Several models can be used to describe the last term of the equation but they can be divided into two main categories: equilibrium models and kinetic adsorption models. In order to simplify the analytical solution of the transport equation in a column the most commonly used expression for describing sorption is the linear adsorption isotherm: \( S = K_d C \) (formula 4-6).

This expression is deduced from an equilibrium model, it indicates that a few assumptions are made regarding the exchange process: - i) the sediment-solute and eluens are at equilibrium at any moment. In other words the exchange processes are instantaneous and reversible. - ii) No reactions occur with respect to the solute since all components for possible precipitates are below solubility level. - iii) \( \text{Eh and pH are constant to guarantee that speciation of the solute is at equilibrium.} \) - iv) The sediment has to be homogeneous with respect to sorption characteristics as surface area, exchange capacities, while the eluens has to have a constant composition.

Now
\[
\frac{\rho}{\theta} \cdot \frac{\partial S}{\partial t} = \frac{(1-\theta)\rho}{\theta} K_d \frac{\partial C}{\partial t} \tag{4-11}
\]

and (7) becomes:
\[
(1 + \frac{(1-\theta)\rho}{K_d}) \frac{\partial C}{\partial t} = D' \frac{\partial^2 C}{\partial x^2} - V_w \frac{\partial C}{\partial x} \tag{4-12}
\]
When the solute enters the column as a spike input, the Kd can be calculated by observing the elution pattern. The break-through peak of the solute is determined by $\frac{D'}{\theta}$, Kd and $V_w$. In practice these break-through curves are impossible to detect because of the high Kd values, which forces elution of the columns for months. This is impractical. Therefore, a numerical simulation was developed to evaluate the distribution of the solute sorbed to the sediment within the column. The boundary conditions are as above.

Most of the solute in the column is sorbed to the sediment due to high Kd values, so that $\frac{V}{V_r} >> D' - \frac{D'}{\theta}$. (4-14) and (4-12) becomes:

$$\left(1 + \frac{(1-\theta)p}{\theta}Kd\right) \frac{\partial C}{\partial t} = - V_w \frac{\partial^2 C}{\partial x^2}$$

(4-15)

So: $V_w/V_r = 1 + \frac{(1-\theta)p}{\theta}Kd$, (4-16)

is the retardation factor, where $V_r$ is the nuclide velocity. $V_w$ and Kd are now the main parameters that control the transport of the solute.

The distribution of the solute through the column after elution of an amount of eluens is numerically simulated: consider a stepwise elution of the eluens through the column. The column is divided in slices and at time $t=0$, slice $n=0$ is filled with solute that is sorbed homogeneously to the sediment.

The solute in the waterphase and the solute sorbed to the sediment in that part of the column are at equilibrium according to (4-6): $S=KdC$. In a first step, the eluens takes the solute in the waterphase to the second slice and the solutes in both slices are redistributed. These steps are repeated and after $x$ steps the distribution of the solute through the column is described as follows:

$$s(n,x) = c(0,0) * \frac{x!}{n!(x-n)!} \cdot \frac{1}{Kd^n} \left(\frac{Kd}{1+Kd}\right)^x$$

(4-17)

$x = V_r/V_p * 14$, $n=0$ to $13$.
where: \( S(n,x) \) = the amount of solute sorbed to the sediment in the \( n^{th} \) slice after elution of \((Ve/Vp) \times 14\) volumes of eluens.

\( C(0,0) \) = the total concentration of solute at time \( t=0 \) (or: \( Ve/Vp \times 14=0 \)) in slice \( n=0 \).

\( Kd \) = distribution coefficient (ml/g).

\( x \) = the amount of porewater volumes of one slice that passed through that slice (\( Ve/Vp \times 14 \)).

\( Ve \) = the elution volume.

\( Vp \) = the porewater volume of the total column.

\( n \) = the indicator of the slice, \( n=0 \) is the first slice, the columns were simulated with 14 slices (\( n=0 \) to \( n=13 \)).

The results of the column experiments were compared with the above numerical simulation and the optimal \( Kd \) value was found with a fitting procedure.

In an anticipating experiment to test the flow characteristics of columns with deep-sea sediment PCL14/3 of different length, the elution of a spike of tritiated water through columns of 13 mm, 29 mm and 50 mm length and 4 mm cross section was performed. Resulting elution patterns are plotted in figure 16. In order to compare elution patterns from columns of different length, the elution volume was normalised to the total column volume (\( Vt \)). The yield was approximately 100% and the symmetrical elution curves indicate excellent column characteristics with respect to uniform pore water movement. The elution of these columns with tritiated water was also chosen to check the porosity, but the results did not agree with the idea that the elution pattern could be explained by the porewater movement alone. Porosity determinations on basis of drying and weighing of the sediment material indicate a water content of 75% (v/v). Assuming \( Kd \) is 0, this would predict a relative elution volume (\( Vo = V(e)/V(t) \)) of 0.76. Where \( Ve= \) elution volume; \( Vt = \) total volume of the column.

Tritiated water was found to elute at a relative elution volume (\( Vr \)) of 1.00 ± 0.06 in the three experiments. It allows the calculation of a \( Kd \) for the tritiated water on basis of formula (4-16) since \( \frac{Vr}{Vo} = \frac{Vw}{Vr} \):

\[
1 + \frac{(1-\theta)\rho}{\theta} Kd = \frac{1.00}{0.76}
\]

\( \theta = 0.76; \rho = 1.45 \text{ g/cm}^3 \), so \( Kd = 0.69 \pm 0.01 \text{ ml/g} \)

This \( Kd \) can be explained by the exchange of eluating water with water that is strongly attached to clay minerals and the exchange of water with
cristal water of the calcium carbonate in the sediment.

Figure 4-17 shows the elution patterns of a spike of cadmium through marine sediment columns operated at 20°C and 90°C. Again elution volumes have been normalized to column volume. Only 2 to 3% of the applied cadmium is eluted in the first four relative elution volumes. This is probably a cadmium complex with a low charge that is only slightly retarded by the sediment. The bulk of the cadmium, more than 95%, stays on the column. Theoretical considerations lead to the conclusions that relative elution volumes of about 200 to 1400 can be expected when Kd's are adopted of about 100 to 700 ml/g. This would indicate very low and undetectable amounts of cadmium per fraction. These results were an indication that elution patterns of radionuclides with even higher Kd's would be hard to obtain unless very low levels of activity could be detected and long lasting experiments were put up. To overcome these obstacles columns were further miniaturized. Although all conditions were the same: a standard slurry was used, a standard teflon tube was used etc., the sizes of the columns did not seem to be uniform.

The column characteristics together with the chromatography conditions are given in Table 4-V. We see that column volumes calculated from tube length and those calculated from sediment weight in the slurry differ with a factor ~3. Figure 4-18 shows the activity of fractions collected from plutonium chromatography through marine sediments (82PCL14/3), operated at 20°C and 60°C.

It is striking that in elution patterns of both columns operated at 20°C there are two peaks indicating the elution of two forms of plutonium with a respective Kd value of 650 and 2200 ml/g. This is in contrast with the chromatography performed at 60°C, which lacks these peaks. However, these early break-through peaks are not representative for the bulk of the plutonium applied in these chromatographies, for they contain ~0.7% (A) to 0.6% (B) of the total applied activity.

A closer look into the sediments of the column itself provided more information on the migration of plutonium through the column. This was achieved by measuring the activity in slices of sediment, see figures 4-19 to 4-29. However, the method to cut the column tube into slices introduced an error since it was very difficult to perform an exact vertical separation of the slices due to the microscopic size of the column. Moreover, it was particularly difficult to determine the top of the column which might have introduced a relative large error in the value of the first slice of the top
Curves obtained with the numerical approach (formula 4-17) were fit in the experimental results in order to get an optimum Kd value. Table 4-VI shows the results of these best fitting Kd's together with the columns and elution characteristics.

The mean Kd for the 20°C experiment is $14.8 \times 10^5 \pm 12.6 \times 10^5$ ml/g and the 60°C experiment yielded $5.5 \times 10^5 \pm 4.7 \times 10^5$ ml/g. So although Kd's at 60°C are generally lower than at 20°C, as is also the case in cadmium adsorption to these sediment, the results are not unambiguous - due to the large variations.
**Table 4-1. Characteristics of sediments used in sorption experiments**

<table>
<thead>
<tr>
<th>Core Name</th>
<th>82 PCL 14/1</th>
<th>82 PCL 14/2</th>
<th>82 PCL 14/3</th>
<th>80 PCL 19/1</th>
<th>80 PCL 19/10</th>
<th>82 PCL 32/2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Position</strong></td>
<td>31°10.0N 25°35.7W</td>
<td>30°59'7N 30.4W</td>
<td>32°30.0N 24°08.7W</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sampling depth (m)</td>
<td>5370</td>
<td>-</td>
<td>-</td>
<td>5373.0</td>
<td>-</td>
<td>5368.0</td>
</tr>
<tr>
<td><strong>Physical</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porosity (v/v)</td>
<td>73</td>
<td>74</td>
<td>72</td>
<td>73</td>
<td>85</td>
<td>74</td>
</tr>
<tr>
<td>Water content (g/g)</td>
<td>51.5</td>
<td>49.5</td>
<td>49.4</td>
<td>50.9</td>
<td>52.1</td>
<td>47.0</td>
</tr>
<tr>
<td>Median grain size (µm)</td>
<td>0.2 to 35</td>
<td>-</td>
<td>-</td>
<td>0.2 to 35</td>
<td>-</td>
<td>0.2 to 35</td>
</tr>
<tr>
<td><strong>Cation exchange</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Capacity (meg/100 g)</td>
<td>2.83 (~6.8)</td>
<td>10.84</td>
<td>8.2 (~8.2)</td>
<td>16.64</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific surface area (m² g⁻¹)</td>
<td>65 (~65)</td>
<td>(~65)</td>
<td>52 (~52)</td>
<td>83</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Mineral**

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Pelagic</th>
<th>Mixed</th>
<th>Tubiditic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic C (%)</td>
<td>2.1 (2.1)</td>
<td>2.1 (2.1)</td>
<td>2.1 (2.1)</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>37.3 (41.8)</td>
<td>40.1 (45.8)</td>
<td>(~45.8)</td>
</tr>
<tr>
<td>Calcite</td>
<td>++ (+ +)</td>
<td>(+ +)</td>
<td>++ (+ +)</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>+ (+)</td>
<td>(+)</td>
<td>++ (+)</td>
</tr>
<tr>
<td>Illite</td>
<td>+ (+)</td>
<td>(+)</td>
<td>+ (+)</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>+ (+)</td>
<td>(+)</td>
<td>+ (+)</td>
</tr>
<tr>
<td>Vermicellite</td>
<td>+ (++)</td>
<td>(+ +)</td>
<td>+ (++)</td>
</tr>
<tr>
<td>Chlorite</td>
<td>- (-)</td>
<td>(-)</td>
<td>- (-)</td>
</tr>
<tr>
<td>Quartz</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

++ abundant; + present; - trace; - none
Table 4-II.

Elemental composition of sediments as determined by neutron activation analysis. The elements are expressed as percentages or ppm of dry sediment.

<table>
<thead>
<tr>
<th></th>
<th>82PCL14/1</th>
<th>82PCL14/2</th>
<th>82PCL14/3</th>
<th>80PCL49/1</th>
<th>80PCL19/10</th>
<th>82PCL32/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca (%)</td>
<td>21.4</td>
<td>22.1</td>
<td>22.5</td>
<td>22.1</td>
<td>18.1</td>
<td>20.9</td>
</tr>
<tr>
<td>Fe (%)</td>
<td>3.26(.7)</td>
<td>3.50(.7)</td>
<td>3.42(.6)</td>
<td>2.47(.6)</td>
<td>3.07(.7)</td>
<td>11.5(2)</td>
</tr>
<tr>
<td>Al (%)</td>
<td>3.32</td>
<td>3.64</td>
<td>3.80</td>
<td>3.13</td>
<td>4.85</td>
<td>4.39</td>
</tr>
<tr>
<td>Cl (%)</td>
<td>4.74</td>
<td>2.18</td>
<td>2.55</td>
<td>2.27</td>
<td>2.39</td>
<td>3.43</td>
</tr>
<tr>
<td>Na (%)</td>
<td>1.73</td>
<td>1.87</td>
<td>2.0</td>
<td>2.05</td>
<td>1.69</td>
<td>1.79</td>
</tr>
<tr>
<td>Mg (%)</td>
<td>1.36</td>
<td>1.39</td>
<td>2.24</td>
<td>0.89</td>
<td>1.17</td>
<td>1.17</td>
</tr>
<tr>
<td>Sr (ppm)</td>
<td>1140(190)</td>
<td>1150(190)</td>
<td>1290(190)</td>
<td>1380(270)</td>
<td>889(240)</td>
<td>3500(650)</td>
</tr>
<tr>
<td>Ba (ppm)</td>
<td>167(89)</td>
<td>187(115)</td>
<td>188(90)</td>
<td>331(110)</td>
<td>595(122)</td>
<td>1150(390)</td>
</tr>
<tr>
<td>Mn (ppm)</td>
<td>761</td>
<td>880</td>
<td>927</td>
<td>800</td>
<td>388</td>
<td>535</td>
</tr>
<tr>
<td>Ce (ppm)</td>
<td>65(2)</td>
<td>68(2)</td>
<td>60(2)</td>
<td>61(2)</td>
<td>56(2)</td>
<td>230(7)</td>
</tr>
<tr>
<td>Rb (ppm)</td>
<td>33(16.1)</td>
<td>29(10.4)</td>
<td>27(11)</td>
<td>43(13)</td>
<td>61(13)</td>
<td>128(44)</td>
</tr>
<tr>
<td>Cr (ppm)</td>
<td>58(4)</td>
<td>64(5)</td>
<td>59(5)</td>
<td>37(4)</td>
<td>94(4)</td>
<td>208(14)</td>
</tr>
<tr>
<td>Nd (ppm)</td>
<td>28(4)</td>
<td>31(4)</td>
<td>35(5)</td>
<td>24(4)</td>
<td>24(5)</td>
<td>91(12)</td>
</tr>
<tr>
<td>V (ppm)</td>
<td>65</td>
<td>84</td>
<td>99</td>
<td>50</td>
<td>77</td>
<td>82</td>
</tr>
<tr>
<td>Co (ppm)</td>
<td>21.5(0.9)</td>
<td>20.2(1.0)</td>
<td>18(.8)</td>
<td>12.4(.7)</td>
<td>9.71(.71)</td>
<td>55.4(2.4)</td>
</tr>
<tr>
<td>Sc (ppm)</td>
<td>9.5(0.1)</td>
<td>10.3(.1)</td>
<td>9.5(.1)</td>
<td>6.0(.1)</td>
<td>11.6(.1)</td>
<td>32.4(.4)</td>
</tr>
<tr>
<td>Th-Pa 233</td>
<td>6.2(.4)</td>
<td>5.9(.5)</td>
<td>5.8(.4)</td>
<td>6.2(.4)</td>
<td>7.6(.4)</td>
<td>22(1)</td>
</tr>
<tr>
<td>Hf (ppm)</td>
<td>3.2(.4)</td>
<td>3.3(.5)</td>
<td>2.8(.4)</td>
<td>3.5(.4)</td>
<td>2.4(.4)</td>
<td>10.2(1.3)</td>
</tr>
<tr>
<td>Cs (ppm)</td>
<td>1.89(.67)</td>
<td>1.56(.67)</td>
<td>1.18(.62)</td>
<td>.87(.47)</td>
<td>3.34(.83)</td>
<td>7.25(2.34)</td>
</tr>
<tr>
<td>Eu (ppm)</td>
<td>1.36(.26)</td>
<td>1.4(.31)</td>
<td>1.49(.28)</td>
<td>1.26(.26)</td>
<td>2.22(.125)</td>
<td>4.69(.76)</td>
</tr>
<tr>
<td>Ta (ppm)</td>
<td>1.29(.43)</td>
<td>.98(.56)</td>
<td>1.33(.54)</td>
<td>1.33</td>
<td>0(0)</td>
<td>3.98(1.36)</td>
</tr>
<tr>
<td>Lu (ppm)</td>
<td>.28(.04)</td>
<td>.28(.04)</td>
<td>.24(.05)</td>
<td>.38(.04)</td>
<td>.30(.04)</td>
<td>.78(.124)</td>
</tr>
</tbody>
</table>

1) Neutron activation analysis was performed on dried untreated sediments that originally contained about 50% (w/w) water (see Table X), no corrections were made for Cl− and for the counterions Na+, Mg++, K+ and Ca++ in this interstitial water.
Table 4-III.

Calcium carbonate exchangeable and clay mineral exchangeable Fe, Mn and Zn\(^1\) in Atlantic ocean sediments.

<table>
<thead>
<tr>
<th></th>
<th>PCL14/1</th>
<th>PCL14/2</th>
<th>PCL14/3</th>
<th>PCL19/1</th>
<th>PCL19/10</th>
<th>PCL32</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>ppm (2)</td>
<td>ppm (2)</td>
<td>ppm (2)</td>
<td>ppm (2)</td>
<td>ppm (2)</td>
<td>ppm (2)</td>
</tr>
<tr>
<td>calcium carbonate</td>
<td>3.06</td>
<td>3.02</td>
<td>3.61</td>
<td>2.66</td>
<td>-</td>
<td>2.33</td>
</tr>
<tr>
<td>clay mineral</td>
<td>1105</td>
<td>1348</td>
<td>1250</td>
<td>751</td>
<td>-</td>
<td>1548</td>
</tr>
<tr>
<td>Mn</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>calcium carbonate</td>
<td>53.7</td>
<td>50.4</td>
<td>50.7</td>
<td>20.7</td>
<td>-</td>
<td>10.1</td>
</tr>
<tr>
<td>clay mineral</td>
<td>12.5</td>
<td>15.5</td>
<td>13.6</td>
<td>5.47</td>
<td>-</td>
<td>72.3</td>
</tr>
<tr>
<td>Zn</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>calcium carbonate</td>
<td>0.48</td>
<td>0.46</td>
<td>0.62</td>
<td>0.31</td>
<td>-</td>
<td>0.33</td>
</tr>
<tr>
<td>clay mineral</td>
<td>0.41</td>
<td>0.40</td>
<td>0.41</td>
<td>0.35</td>
<td>-</td>
<td>0.51</td>
</tr>
</tbody>
</table>

1) Sediments were successively extracted with 1 N sodium acetate, pH 5.0 and with a 0.5 M citrate-acetate buffer pH 4.8, containing 0.3 M dithionate.
2) in ppm calculated on dry weight basis.
Table 4-IV.

Physico-chemical parameters and their influence on sorption of radionuclides to environmental substances.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Electrostatic sorption</th>
<th>Specific sorption</th>
<th>Chemical substitution</th>
<th>Physical sorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>appreciable</td>
<td>appreciable</td>
<td>appreciable</td>
<td>variable(1)</td>
</tr>
<tr>
<td>Eh</td>
<td>large(3)</td>
<td>large(3)</td>
<td>variable</td>
<td>variable(2)</td>
</tr>
<tr>
<td>Temperature</td>
<td>appreciable</td>
<td>appreciable</td>
<td>appreciable</td>
<td>small</td>
</tr>
<tr>
<td>Time</td>
<td>small</td>
<td>variable</td>
<td>variable</td>
<td>small</td>
</tr>
<tr>
<td>Speciation of nuclides</td>
<td>large</td>
<td>large</td>
<td>variable</td>
<td>large</td>
</tr>
<tr>
<td>Concentration of nuclide</td>
<td>large</td>
<td>large</td>
<td>large</td>
<td>small(4)</td>
</tr>
<tr>
<td>Concentration of complexing or competing solutes</td>
<td>large</td>
<td>large</td>
<td>large</td>
<td>large</td>
</tr>
<tr>
<td>Ionic strength of solution</td>
<td>large</td>
<td>variable</td>
<td>large</td>
<td>small</td>
</tr>
<tr>
<td>Properties of sorbent</td>
<td>large</td>
<td>large</td>
<td>large</td>
<td>small</td>
</tr>
</tbody>
</table>

1) depends on charge of nuclide-species, zero when uncharged.
2) depends on electroactivity of nuclide species.
3) if redox sensitive nuclides are involved.
4) at concentrations below saturation.

**Table 4-5.**

Columns and chromatographic conditions used in plutonium elution experiments. Columns were made as follows: a glassfibre plug is placed in a teflon tube (0.75 mm) and 100 µl sediment (PCL4/3) slurry (12.5 mg/ml) is eluted through the tube. The sediment settles on top of a filter in the column and the column is ready to use. Columns used at 60°C were produced at this temperature too. The chromatography is started by adding 0.1 µg spiked sediment on the column.

Column volumes were calculated by two methods: 1e by using the weight to length ratio of the slices of the tube; 2e using the known amount of dry sediment in the slurry.

<table>
<thead>
<tr>
<th>Number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temperature (°C)</strong></td>
<td>20°</td>
<td>20°</td>
<td>22°</td>
<td>20°</td>
<td>20°</td>
<td>20°</td>
<td>60°</td>
<td>60°</td>
<td>60°</td>
<td>60°</td>
<td>60°</td>
<td>60°</td>
<td>60°</td>
</tr>
<tr>
<td><strong>Length (1) (mm)</strong></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.24</td>
<td>0.9</td>
<td>1.64</td>
<td>1.37</td>
<td>-</td>
<td>-</td>
<td>1.27</td>
<td>1.61</td>
<td>1.56</td>
<td>1.54</td>
</tr>
<tr>
<td><strong>Volume (1) (µl)</strong></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>.53</td>
<td>.39</td>
<td>.71</td>
<td>.62</td>
<td>-</td>
<td>.55</td>
<td>.69</td>
<td>.67</td>
<td>.66</td>
<td>.62</td>
</tr>
<tr>
<td><strong>Volume (2) (µl)</strong></td>
<td>3.33</td>
<td>2.59</td>
<td>2.00</td>
<td>2.00</td>
<td>2.00</td>
<td>2.00</td>
<td>2.00</td>
<td>2.00</td>
<td>2.59</td>
<td>2.00</td>
<td>2.00</td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td><strong>Elution volume (ml)</strong></td>
<td>8.6</td>
<td>8.2</td>
<td>5.8</td>
<td>7.2</td>
<td>15.5</td>
<td>15.0</td>
<td>62.0</td>
<td>75.0</td>
<td>53.1</td>
<td>15.0</td>
<td>196</td>
<td>97.1</td>
<td></td>
</tr>
<tr>
<td><strong>Elution time (min)</strong></td>
<td>71.35</td>
<td>10080</td>
<td><em>a</em></td>
<td>2580</td>
<td>9690</td>
<td>17280</td>
<td>10080</td>
<td>9047</td>
<td><em>b</em></td>
<td>6810</td>
<td>3000</td>
<td>15840</td>
<td>8640</td>
</tr>
<tr>
<td><strong>Elution pattern (7)</strong></td>
<td>yes</td>
<td>yes</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Sediment (dry) (mg)</strong></td>
<td>2.25</td>
<td>1.75</td>
<td>1.35</td>
<td>1.35</td>
<td>1.35</td>
<td>1.35</td>
<td>1.75</td>
<td>1.35</td>
<td>1.35</td>
<td>1.35</td>
<td>1.35</td>
<td>1.35</td>
<td>1.35</td>
</tr>
<tr>
<td><strong>Relative elution</strong></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>24.9</td>
<td>72.7</td>
<td>38.7</td>
<td>183.0</td>
<td>-</td>
<td>68.5</td>
<td>140.8</td>
<td>41.0</td>
<td>543.5</td>
<td>286.6</td>
</tr>
</tbody>
</table>

\( V(e)/V(p) \times 10^4 \)

*a* supply-tube failed (a ~ 615 min, b ~ 8655 min)
Table 4-VI.

The best-fitting distribution coefficients for plutonium adsorption calculated for the column experiments.

<table>
<thead>
<tr>
<th>Column no.</th>
<th>Elution temperature</th>
<th>Distribution coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>22°</td>
<td>4.0</td>
</tr>
<tr>
<td>4</td>
<td>20°</td>
<td>4.0</td>
</tr>
<tr>
<td>5</td>
<td>20°</td>
<td>32.0</td>
</tr>
<tr>
<td>6</td>
<td>20°</td>
<td>0.70</td>
</tr>
<tr>
<td>7</td>
<td>20°</td>
<td>16.0</td>
</tr>
<tr>
<td>9</td>
<td>60°</td>
<td>1.4</td>
</tr>
<tr>
<td>10</td>
<td>60°</td>
<td>4.0</td>
</tr>
<tr>
<td>11</td>
<td>60°</td>
<td>1.2</td>
</tr>
<tr>
<td>12</td>
<td>60°</td>
<td>11.0</td>
</tr>
<tr>
<td>13</td>
<td>60°</td>
<td>10.0</td>
</tr>
</tbody>
</table>
Figure 4-1. Characteristics of sterilized and non-sterilized sediments during incubation at 4°C, 35°C, 60°C and 90°C.
Figure 4-2. Characteristics of sterilized and non-sterilized sediments during incubation at 4°C, 35°C, 60°C and 90°C.
Figure 4-3. Characteristics of sterilized and non-sterilized sediments during incubation at 4°C, 35°C, 60°C and 90°C.
Figure 4-4. Characteristics of sterilized and non-sterilized sediments during incubation at 4°C, 35°C, 60°C and 90°C.
Figure 4-5. Characteristics of sterilized and non-sterilized sediments during incubation at 4°C, 35°C, 60°C and 90°C.
Figure 4-6. Characteristics of sterilized and non-sterilized sediments during incubation at 4°C, 35°C, 60°C, and 90°C.
Figure 4-7. Characteristics of sterilized and non-sterilized sediments during incubation at 4°C, 35°C, 60°C and 90°C.
Figure 4-8. Characteristics of sterilized and non-sterilized sediments during incubation at 4°C, 35°C, 60°C and 90°C.
Figure 4-9. Characteristics of sterilized and non-sterilized sediments during incubation at 4°C, 35°C, 60°C and 90°C.
Figure 4-10. Characteristics of sterilized and non-sterilized sediments during incubation at 4°C, 35°C, 60°C and 90°C.
Figure 4-11. Adsorption coefficients of PLUTONIUM-239 of two Madeira Abyssal Plain sediments at 4 temperatures and their relation to equilibrium concentrations. Results of batch experiments, a: 4°C, b: 35°C, c: 60°C and d: 90°C.

A: Adsorption coefficient of sediment PCL 14/2.
B: Adsorption coefficient of sediment PCL 32/2.
Figure 4-12. Desorption coefficients of PLUTONIUM-239 of two Madeira Abyssal Plain sediments at 4 temperatures and their relation to equilibrium concentrations. Results of batch experiments, a: 4°C, b: 35°C, c: 60°C and d: 90°C.
A: Desorption coefficients of sediment PCL 14/2.
B: Desorption coefficients of sediment PCL 32/2.
Figure 4-13. Adsorption coefficients of AMERICIUM-243 of two Madeira Abyssal Plain sediments at 4 temperatures and their relation to equilibrium concentrations. Results of batch experiments, a: 4°C, b: 35°C, c: 60°C and d: 90°C.

A: Adsorption coefficients of sediment PCL 14/1.
B: Adsorption coefficients of sediment PCL 32/2.
Figure 4-14. Adsorption coefficients of AMERICIUM-243 of two Hadeira Abyssal Plain sediments at 4 temperatures and their relation to equilibrium concentrations. Results of batch experiments, a: 4°C, b: 35°C, c: 60°C and d: 90°C.
A: Desorption coefficients of sediment PCL 14/2.
B: Desorption coefficients of sediment PCL 32/2.
Figure 4-15. Adsorption coefficients of NEPTUNIUM-237 of two Madeira Abyssal Plain sediments at 4 temperatures and their relation to equilibrium concentrations. Results of batch experiments, a: 4°C, b: 30°C, c: 60°C and d: 90°C.
A: Adsorption coefficients of sediment PCL 14/2.
B: Adsorption coefficients of sediment PCL 32/2.
Figure 4-16. Elution patterns of tritiated water from three columns of sediment PCL 14/3 of different length, A: 13 mm, B: 29 mm and C: 50 mm. The dimensionless relative elution volumes are displayed, $V(e)$ = the elution volume, and $V(t)$ = the total column volume.
Figure 4-17. Elution patterns of cadmium from a column of sediment PCL 14/3, length: 13 cm, operated at 2 temperatures. \( V(e) \) = elution volume and \( V(t) \) = total column volume (170 \( \mu l \)). A: 20°C; B: 90°C.

Figure 4-18. Elution patterns of plutonium-239 from columns of sediment PCL 14/3, operated at 2 temperatures. Information on the columns in Table 4-V. \( V(e) \) = elution volume, \( V(p) \) = pore water volume of the total column. A and B: 20°C; C: 60°C.
temp 22 °C, V(o) 5.8 ml, V(e) 2.0 or .51 ul, sediment 1.35 mg, eluted for 615 min.

Figure 4-19. The relative plutonium activity in sections of column number 3 (see table 4-V) of sediment FCL 14/3 before (the dotted rectangle) and after elution with seawater (the continuous rectangles), 1/L is the dimensionless length. Characteristics of the elution and the column are mentioned on top of the figure, see also table 4-V. The dashed lines connect the theoretical relative plutonium activity calculated with different distribution coefficients, A: 4.0 $10^2$ ml/g; B: 3.0 $10^2$ ml/g and C: 2.0 $10^2$ ml/g.

temp 26 °C, V(o) 7.2 ml, V(e) 2.0 or .53 ul, sediment 1.35 mg, eluted for 2580 min.

Figure 4-20. The relative plutonium activity in sections of column number 4 (see table 4-V) of sediment FCL 14/3 before (the dotted rectangle) and after elution with seawater (the continuous rectangles), 1/L is the dimensionless length. Characteristics of the elution and the column are mentioned on top of the figure, see also table 4-V. The dashed lines connect the theoretical relative plutonium activity calculated with different distribution coefficients, A: 4.0 $10^2$ ml/g; B: 3.0 $10^2$ ml/g and C: 2.0 $10^2$ ml/g.
temp 20 °C, V(o) 15.5 ml, V(e) 2.0 or .39 ul, sediment 1.35 mg, eluted for 8880 min.

Figure 4-21. The relative plutonium activity in sections of column number 5 (see table 4-V) of sediment PCL 14/3 before (the dotted rectangle) and after elution with seawater (the continuous rectangles), 1/L is the dimensionless length. Characteristics of the elution and the column are mentioned on top of the figure, see also table 4-V. The dashed lines connect the theoretical relative plutonium activity calculated with different distribution coefficients, A: 3.2 $10^3$ ml/g; B: 2.0 $10^3$ ml/g and C: 1.8 $10^3$ ml/g.

temp 20 °C, V(o) 15 ml, V(e) 2.0 or .71 ul, sediment 1.35 mg, eluted for 17280 min.

Figure 4-22. The relative plutonium activity in sections of column number 6 (see table 4-V) of sediment PCL 14/3 before (the dotted rectangle) and after elution with seawater (the continuous rectangles), 1/L is the dimensionless length. Characteristics of the elution and the column are mentioned on top of the figure, see also table 4-V. The dashed lines connect the theoretical relative plutonium activity calculated with different distribution coefficients, A: 7.0 $10^3$ ml/g; B: 6.0 $10^3$ ml/g and C: 5.0 $10^3$ ml/g.
temp 28 °C, V(e) 62.0 ml, V(o) 2.0 or .02 ul, sediment 1.35 mg, eluted for 10080 min.

Figure 4-23. The relative plutonium activity in sections of column number 7 (see table 4-V) of sediment PCL 14/3 before (the dotted rectangle) and after elution with seawater (the continuous rectangles), 1/L is the dimensionless length. Characteristics of the elution and the column are mentioned on top of the figure, see also table 4-V. The dashed lines connect the theoretical relative plutonium activity calculated with different distribution coefficients, A: 1.6 $10^7$ ml/g; B: 1.4 $10^7$ ml/g and C: 1.2 $10^7$ ml/g.

temp 68 °C, V(e) 20.8 ml, V(o) 2.0 or .55 ul, sediment 1.35 mg, eluted for 8055 min.

Figure 4-24. The relative plutonium activity in sections of column number 9 (see table 4-V) of sediment PCL 14/3 before (the dotted rectangle) and after elution with seawater (the continuous rectangles), 1/L is the dimensionless length. Characteristics of the elution and the column are mentioned on top of the figure, see also table 4-V. The dashed lines connect the theoretical relative plutonium activity calculated with different distribution coefficients, A: 1.8 $10^7$ ml/g; B: 1.6 $10^7$ ml/g and C: 1.4 $10^7$ ml/g.
temp 60 oC, V(e) 53.1 ml, V(o) 2.0 or .08 ul, sediment 1.35 mg, eluted for 8810 min.

Figure 6-25. The relative plutonium activity in sections of column number 10 (see table 4-V) of sediment PCL 14/3 before (the dotted rectangle) and after elution with seawater (the continuous rectangles), l/L is the dimensionless length. Characteristics of the elution and the column are mentioned on top of the figure, see also table 4-V. The dashed lines connect the theoretical relative plutonium activity calculated with different distribution coefficients, A: 6.0 \times 10^{-7} \text{ ml/g}; B: 5.0 \times 10^{-7} \text{ ml/g} and C: 4.0 \times 10^{-7} \text{ ml/g}.

temp 60 oC, V(e) 15.0 ml, V(o) 2.0 or .07 ul, sediment 1.35 mg, eluted for 3000 min.

Figure 4-26. The relative plutonium activity in sections of column number 11 (see table 4-V) of sediment PCL 14/3 before (the dotted rectangle) and after elution with seawater (the continuous rectangles), l/L is the dimensionless length. Characteristics of the elution and the column are mentioned on top of the figure, see also table 4-V. The dashed lines connect the theoretical relative plutonium activity calculated with different distribution coefficients, A: 1.2 \times 10^{-7} \text{ ml/g}; B: 1.1 \times 10^{-7} \text{ ml/g} and C: 1.0 \times 10^{-7} \text{ ml/g} and D: 0.9 \times 10^{-7} \text{ ml/g}.
Figure 4-27. The relative plutonium activity in sections of column number 12 (see table 4-V) of sediment PCL 14/3 before (the dotted rectangle) and after elution with seawater (the continuous rectangles). 1/L is the dimensionless length. Characteristics of the elution and the column are mentioned on top of the figure, see also table 4-V. The dashed lines connect the theoretical relative plutonium activity calculated with different distribution coefficients, A: $1.1 \times 10^{-3}$ ml/g and B: $1.0 \times 10^{-3}$ ml/g.

temp 60 oC, V(o) 97.1 ml, V(c) 2.0 or .62 ul, sediment 1.35 mg, eluted for 8640 min.

Figure 4-28. The relative plutonium activity in sections of column number 13 (see table 4-V) of sediment PCL 14/3 before (the dotted rectangle) and after elution with seawater (the continuous rectangles). 1/L is the dimensionless length. Characteristics of the elution and the column are mentioned on top of the figure, see also table 4-V. The dashed lines connect the theoretical relative plutonium activity calculated with different distribution coefficients, A: $1.0 \times 10^{-3}$ ml/g; B: $0.9 \times 10^{-3}$ ml/g and C: $0.8 \times 10^{-3}$ ml/g.
MATHEMATICAL MODELLING AND ITS APPLICATION TO EXPERIMENT
5. HEATFLOW IN SATURATED SEDIMENT.

5.1. Introduction.

The repository of a canister containing high level nuclear waste in a subseabed will only be an option if the radioactive decay is in the same order as the isolation rate of the canister. This isolation rate is the retardation of the release of radioactive isotopes from the seafloor to the overlying ocean water. So a study of this process must deal with the rate of isolation first, since the rates of radioactive decay are rather well known. Therefore the aim of this report will be the study of the effect of the rate of transport of nuclides in the seabed.

On the principle that the presence of the nuclides have no influence on the heat transport we can divide this study into two different parts. First we will discuss the effect of the heat produced by the ongoing degeneration of the isotopes, and the induced velocity field of the interstitial water. Secondly we will deal with the migration of the radionuclides through the porous seabed. The migration could be very well affected by the temperature or the velocity field.

5.2. Mathematical model.

The water saturated sediment is considered to be a porous medium in which free convection of interstitial water may occur. This convection must be determined because it possibly effects the migration or even the heat transfer.

In order to predict the effect of the heat source on the pore water movement a mathematical model is used. This model will be set up with an axisymmetrical coordinate-system, this system reflects the geometry of a buried canister in a large subseabed. However, we will only apply this model for the prediction of the effect of a heat source in the experimental drums, containing water saturated sediment.

We can describe the system by the conservation of mass, of momentum and of energy, and by an equation of state, by assuming the porous medium to be rigid, isotropic and homogenous, and the fluid density to be slightly dependent on the temperature only. We will use Darcy's law as equation of momentum. The fluid density is assumed to be linearly dependent on the tem-
temperature. According to the Boussinesq approximation the density variations are only accounted for in the buoyancy term. (Dagan, 1972 and Hickox et al., 1980).

The equations that describe the system are then respectively:

\[ \text{div} \mathbf{v} = 0 \]  \hspace{1cm} (5-1)

\[ \frac{u}{k} \mathbf{v} = - \nabla p + \rho_f g \]  \hspace{1cm} (5-2)

\[ \left( \frac{\rho c_p}{\rho_m} \right)_m \frac{\partial T}{\partial t} + \left( \frac{\rho c_p}{\rho_f} \right)_f \nabla \cdot \nabla T = \lambda_m \nabla^2 T \]  \hspace{1cm} (5-3)

\[ \rho_f = \rho_o \left[ 1 - \beta (T - T_o) \right] \]  \hspace{1cm} (5-4)

where \( \mathbf{v} \) is the superficial or Darcy velocity, \( p \) the pressure, \( g \) the acceleration of gravity, \( T \) the temperature and \( \rho \) the density. The parameters \( \mu, k, \rho, \lambda, \) and \( \beta \) are the viscosity, permeability, specific heat, thermal conductivity and the thermal expansion coefficient. The subscripts \( f \) and \( o \) indicate fluid and reference properties; the subscript \( m \) is given to mean properties of fluid and solid together; the relation is:

\[ \left( \frac{\rho}{\rho_o} \right)_m = \phi \left( \frac{\rho}{\rho_o} \right)_{\text{fluid}} + (1-\phi) \left( \frac{\rho}{\rho_o} \right)_{\text{solid}} \]  \hspace{1cm} (5-5)

where \( \phi \) is the porosity.

The temperature \( T \) in the equations (5-3) and (5-4) expresses the temperature in both solid and fluid; i.e. no difference is assumed between the temperature in the solid and the fluid \( T = T_s = T_f \). This is based on the assumption that the heat transfer between solid and fluid is sufficiently rapid so that the temperatures are in equilibrium.

As mentioned before the system is axisymmetric, so we chose cylindrical coordinates with the origin in the point source (figure 5-1). Because of the axisymmetry the azimuthal angle can be excluded.

Since the system is axisymmetric and the zero divergence is ensured by (5-1) a streamfunction \( \tilde{\psi} \) can be defined:

\[ v_r = - \frac{1}{r} \frac{\partial \tilde{\psi}}{\partial z} \]  \hspace{1cm} (5-6)

\[ v_z = \frac{1}{r} \frac{\partial \tilde{\psi}}{\partial r} \]  \hspace{1cm} (5-7)
where \( v_r \) and \( v_z \) are the Darcy-velocity components in the \( r \)- and the \( z \)-direction. Now taking the curl of Darcy's law (5-2), this equation becomes:

\[
\frac{1}{r} \frac{\partial}{\partial z} \left( \frac{1}{r} \frac{\partial \psi}{\partial r} \right) = -\frac{k g \rho_o \beta}{\mu} \frac{\partial T}{\partial r}
\]

(5-8)

Together with the energy equation these equations describe the system of heat transfer and convection in the porous medium. The addition of boundary conditions will complete the mathematical model. However, these conditions depend on the geometry of the experimental set up, so they will be dealt with in the concerning sections.

5.3. The small-scale drum experiment.

In a small-scale cylindrical vessel containing water-saturated sediment the temperature effect of a heat source in the centre is measured. This first and preliminary experiment was carried out with sieved sand and a constant heat production. A schematic outline is shown in figure 5-2.

The height (2L) of the vessel is 26 cm and the diameter (2R) is 20 cm. The temperature is measured by 12 probes, that are numbered as indicated in the figure. The heat is produced by a 10 Watt bulb. The electrical feeders of the bulb are situated vertically along the axis.

In order to calculate the temperature and the velocity field in the bulk of the drum we must add the specific boundary conditions to the equations (5-3) and (5-8). These conditions are i): the 10 Watt heat source in the centre, ii): the rate of heat loss and iii): the impermeability of the wall.

In case of a heat source with a constant production \( Q \) and a steady state the variables in the model can be changed into non-dimensional ones by putting:

\[
r = \frac{r}{R}
\]

(5-9)

\[
x = \frac{z}{R}
\]

(5-10)

\[
\psi = \frac{1}{a_e} \psi
\]

(5-11)
\[ \theta = \frac{\lambda m}{Q} R (T - T_0) \]  

(5-12)

where \( R \) is the radius of the vessel, \( Q \) the specific heat production of the point source and \( a_e = \frac{\lambda m}{(\rho c_p)^e} \), a thermal diffusion coefficient.

If the ratio between the buoyancy and the viscous forces are expressed in the Rayleigh number:

\[ Ra = \frac{k_\text{g} \rho \beta Q}{\mu d_e \lambda_m} \]  

(5-13)

then the equations of the system become:

\[ \frac{1}{r} \frac{\partial}{\partial r} \left( \frac{1}{r} \frac{\partial \psi}{\partial r} \right) - \frac{\partial \theta}{\partial x} = - Ra \frac{\partial \theta}{\partial r} \]  

(5-14)

\[ - \frac{1}{r} \frac{\partial^2 \psi}{\partial x \partial r} + \frac{1}{r} \frac{\partial \psi}{\partial r} \frac{\partial \theta}{\partial x} = \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \theta}{\partial r} \right) + \frac{\partial^2 \theta}{\partial x^2} \]  

(5-15)

Both equations are elliptic in \( \psi \) and \( \theta \) respectively, and thereby expression (5-15) is non-linear.

The boundary condition describing the heat loss is:

\[ \frac{\partial \theta}{\partial s} = \text{Bi} \theta \]  

(5-16)

where \( s \) expresses the local coordinate perpendicular to the wall and \( \text{Bi} = aR/\lambda \) is the Biot number.

This axisymmetry at the axis demands:

\[ \frac{\partial \theta}{\partial r} = 0 \quad r = 0 \quad (x \neq 0) \]  

(5-17)

\[ \frac{\partial \psi}{\partial r} = 0 \quad r = 0 \]  

(5-18)

The origin has been excluded in (5-17) because of the point source in this point. This exclusion is not necessary in (5-18) because the point source is no obstacle in the fluid flow.

The impermeability at the wall of the vessel will be expressed by a Dirichlet condition for the streamfunction:

\[ \psi = 0 \text{ on vessel wall and axis} \]  

(5-19)
At last the strength of the non-dimensional point source in the origin is:

$$ q = \frac{k \rho o \beta}{\mu a \lambda m} = Ra \quad r = 0 \text{ and } x = 0 \quad (5-20) $$

The complete mathematical model for this experimental geometry now consists of the equations (5-14) to (5-20).

An analytical solution for this model is not available. One of the difficulties is that the heat release from the source is mainly spherical, while the boundary conditions (concerning the vessel wall) are cylindrical. Another one is that the energy equation (5-15) is non-linear. Therefore we use a numerical method to solve these equations.

In order to apply a numerical method we have to split off the singularity caused by the constant heat production of the point source. The character of this singularity is known from Carslaw and Jaeger (1959):

$$ 0_\lambda = \frac{q}{4\pi |r|} \quad (5-21) $$

where $|r|$ is the distance to the source point.

The non-linearity of the energy equation is encountered by using Newton linearization. A finite difference method is chosen to calculate the solution numerically, i.e. a central difference method is used here (Mitchell and Griffiths, 1980).

In order to use this mathematical model and to make some comparative calculations we used parameter values as is given in table 5-I.
TABLE 5-I: Parameters used in the model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mu )</td>
<td>( 1.002 \times 10^{-3} )</td>
<td>kg/ms</td>
</tr>
<tr>
<td>( \rho_0 )</td>
<td>1000</td>
<td>kg/m³</td>
</tr>
<tr>
<td>( \beta )</td>
<td>( 2.1 \times 10^{-4} )</td>
<td>1/K</td>
</tr>
<tr>
<td>( \lambda_m )</td>
<td>1.5</td>
<td>W/mK</td>
</tr>
<tr>
<td>( (\rho c_p)_\ell )</td>
<td>( 4.18 \times 10^6 )</td>
<td>J/m³K</td>
</tr>
<tr>
<td>( g )</td>
<td>9.8</td>
<td>m/s²</td>
</tr>
<tr>
<td>( k )</td>
<td>( 2.5 \times 10^{-11} )</td>
<td>m²</td>
</tr>
<tr>
<td>( R )</td>
<td>0.10</td>
<td>m</td>
</tr>
<tr>
<td>( L )</td>
<td>0.13</td>
<td>m</td>
</tr>
</tbody>
</table>

The data for the fluid properties are taken from Batchelor (1967), while the geometrical parameters are related to the experimental configuration. The permeability is calculated according to Duursma and Bosch (1970), figure 27. The diameter of the sediment particle is 200 \( \mu \)m.

Using these parameters we will compare two special cases. In the first case the heat discharge will be at the top of the vessel, while in the second case this will be at the side wall. The bottom is insulated in both cases. The related data for these cases are given in table 5-II.

TABLE 5-II: Distinctive heat-transfer coefficients.

<table>
<thead>
<tr>
<th>Case</th>
<th>( Q ) [W]</th>
<th>( \alpha_L ) [W/m²K]</th>
<th>( \alpha_R ) [W/m²K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>106</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>0</td>
<td>2.65</td>
</tr>
</tbody>
</table>
The subscripts L and R of the heat transfer coefficients correspond respectively with the top and the side wall of the vessel.

The results of these two computations are given by the figures 5-3 and 5-4 respectively. The a-figures denote the temperature distributions along the axis and the side wall, while the b-figures show the distributions in radial direction at the bottom \((x = - L/R)\) and through the source \((x = 0)\). The dotted lines give the temperature distribution if no convection takes place.

In figure 5-5 a typical velocity pattern is displayed. The length of the arrows are an indication of the differences in the velocity magnitudes.

The figures 5-3 and 5-4 show, naturally, different temperature distributions. Yet the maximum velocities in the origin (in case 1: 7.5 cm/day and in case 2: 7.9 cm/day) are about the same, so we may conclude that, in order to set up the experiment with the highest maximum velocity, there is no significant difference between the two cases.

The main conclusion from both figures 5-3 and 5-4 concerns the difference between the temperature distributions with convection (solid lines) and without (dotted lines). This small difference shows that the effect of the fluid flow on the heat transfer is neglectable. In both cases is \(Ra = 0.95\).

The advantage of this conclusion is that the energy equation now becomes linear, because the convection term vanishes. So the temperature field can now be calculated seperately from the velocity field.

After this theoretical analysis we have carried out preliminary experiments. All walls of the vessel were fairly insulated, we have used three kinds of sediments. The ranges of the particle diameters \(d_p\) of these sediments are listed in table 5-III.

**TABLE 5-III: Particle size distribution of sediments used in the preliminary experiments.**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A:</td>
<td>(150 &lt; d_p &lt; 210)</td>
</tr>
<tr>
<td>B:</td>
<td>(105 &lt; d_p &lt; 150)</td>
</tr>
<tr>
<td>C:</td>
<td>(d_p &lt; 75)</td>
</tr>
</tbody>
</table>
The sediments A and B were obtained from the same supply of sand by sieving.

Each experiment lasted about 80 hours. The results are shown in figure 5-6. The subdivision a, b and c correspond to the A, B and C of table 5-III. The gaps in the graphs are caused by the fact that data were recorded in working hours. Because of the axisymmetry only the temperatures of the probes 3, 4, 7, 8, 11 and 12 are given.

We notice that the low temperature in the laboratory during the night (the gaps in the figure) has a considerable effect on the temperature in the vessel. The quality of the wall insulation was not sufficient; so the temperature changes in the laboratory interfered with the experiment. As a consequence of the fluctuation, the steady state temperature is not easy to give. Thereby, the deviation of the heat transfer coefficient \( a \) will be too large for an accurate comparison of the results of the model with the experimental data. Hence, for an appropriate comparison we need more accurate boundary conditions and a transient mathematical model.

Though a general comparison is not significant here, we can use these measurements to determine the heat conduction coefficient and the heat capacity of the bulk. For this purpose we use the transient temperature distribution of a point source in an infinite medium, given by Carslaw and Jaeger (1959).

\[
T - T_0 = \frac{Q}{4\pi \lambda_m r} \text{erfc} \left( \frac{r}{2\sqrt{a_m t}} \right) \tag{5-22}
\]

where \( r \) is the spherical distance to the source. This expression can be used for small values of the time \( t \) only. In that short period the influence of the boundary will be small.

An approximation of the parameters \( \lambda_m \) and \( (\rho_c)_m \) is made by using a standard parameter fitting method. Note that \( a_m = \lambda_m / (\rho_c)_m \). The results of this approximation method are listed in table 5-IV.
TABLE 5-IV: Result of Parameter fitting.

<table>
<thead>
<tr>
<th>Case</th>
<th>$\lambda_m$ [W/mK]</th>
<th>$(\rho c_p)_m$ [J/mK]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.0</td>
<td>2.7 $\times 10^6$</td>
</tr>
<tr>
<td>B</td>
<td>2.0</td>
<td>2.7 $\times 10^6$</td>
</tr>
<tr>
<td>C</td>
<td>1.2</td>
<td>2.9 $\times 10^6$</td>
</tr>
</tbody>
</table>

The theoretical courses of the temperature at point 3 are given in the figures 5-6 a, b, and c as solid lines. In all cases the stationary temperature of expression (5-22) is far below the system temperature. This is caused by the insulating of the vessel.

However, for small $t$, it appeared that the solid lines can cover the experimental values rather nicely.

Finally, from this preliminary experiment and its theoretical analysis we learned that at $Ra = 0.95$ the fluid velocity has negligible influence on the heat transfer. In order to make a rather good comparison of the theoretical model with the experimental data we must take care of two things i): the boundary conditions must be known, and ii): the model must be transient.

5.4. The large-scale drum experiment.

The configuration of the second experiment is again preliminary. In order to gain experience with a heat source of constant temperature a system of pipes have been used, while at the same time the effect of an injection of KCl-solution is measured. The concentration field as well as the temperature and velocity field are calculated by computer programs of the Delft Soil Mechanics Laboratory.

The heat source, used in this experiment, is a small piece of pipe with a diameter of 2.5 cm and a length of 10 cm.

This source is kept at a constant temperature by hot water, for instance 80°C. This water is externally heated by a 1000 Watt heating-bath.
which is connected to the source by two insulated small pipes.

The vessel used in this experiment is much larger than the one used in the first experiment. The height of the vessel is 1.80 m and the diameter is 1.30 m. As a consequence of these sizes the vessel is filled with unsieved sand. A schematic outline is given in figure 5-7.

After reaching the steady state for the temperature, 1000 ml 0.5 N KCl was injected near the heat source. The experiment lasted about a month and was terminated by removing the sediment in layers of 5 cm each. $K^+$ was determined in the interstitial water of several points in each layer.

This experiment was carried out before contacts with the Delft Soil Mechanics Laboratory resulted in the use of their codes LIGHTS (= Liquid Incompressible Geothermal Heat Transfer Simulator) and VERA.

LIGHTS computes the temperature and the velocity field based on the Boussinesq approximation. With this velocity field VERA calculates the migration of the injected nuclides using the constituent balance:

$$\frac{\partial (\phi C)}{\partial t} + \nabla \cdot (\nu C) = \nabla \cdot (E \nabla C)$$  \hspace{1cm} (5-23)

where

$\phi$ = porosity.

$\nu$ = Darcy velocity.

$C$ = concentration of nuclides.

$E$ = dispersion coefficient, includes hydrodynamic dispersion and molecular diffusion.

In both codes it is possible to give the parameters local values.

We learned from the experimental data that the outside temperature of the insulated input and output pipes was about $50^\circ$C. Therefore in the code model the source and pipes are supposed to be at a constant temperature, see figure 5-8a. The other boundary conditions are:

$$T = 20^\circ$C on top$$  \hspace{1cm} (5-24)

$$\frac{\partial T}{\partial n} = 0 \quad \text{on bottom and side wall.}$$  \hspace{1cm} (5-25)

($\partial/\partial n = \text{normal derivative}$)
\[ \psi = 0 \] on axis, bottom and side wall. \[(5-26)\]

\[ v_r = 0 \] on top. \[(5-27)\]

The last condition describes the water exchange between the sediment-bulk and the upper water layer.

With the permeability \( k = 1.1 \times 10^{-11} \, \text{m}^2 \) and the conductivity \( \lambda_m = 2.3 \, \text{W/mK} \) the temperature and the velocity field are computed. See figure 5-8b and 5-8c respectively. The steady state values (8b) of the experimental temperatures do not quite fit the theoretical temperature field. It can be noticed that the horizontal input and output pipes disturb the axisymmetry. For instance the \( 38^\circ\text{C} \) at point 3 is higher than the \( 37^\circ\text{C} \) at point 4. Most curious is the dissonant temperature at point 6: \( 26.3^\circ\text{C} \). The theoretical maximum velocity occurring near the heat source is \( 0.97 \times 10^{-5} \, \text{m/s} \) or 83.8 cm/day.

The boundary condition, used in VERA, at the side wall and the bottom is:

\[ \partial C / \partial n = 0 \] \[(5-28)\]

It was not clear whether \( \partial C / \partial z = 0 \) or \( C = 0 \) should be used for the condition at the top, or one like \( (hC - \partial C / \partial z) = 0 \), where a mass transfer coefficient \( h \) is imposed. We chose \( \partial C / \partial z = 0 \). So the injected nuclides are supposed to be transported from the pore water into the upper water-layer only by water exchange and not by diffusion.

The initial condition is \( C = 1 \) at the point of injection, as shown in figure 5-9a. The figure 5-9b and 5-9c show the concentration fields after 1 and 4 days respectively.

If, as in this case, a fluid exchange between pore water and upper water-layer takes place, then we perceive that the nuclides are mostly transported to this upper layer. The area enclosed by the isoconcentration line \( C = 0.01 \), for instance, is much smaller for \( t = 4 \) days than for \( t = 1 \) day; moreover this area has been moved upwards.

We can conclude from this large-scale drum experiment that the choice of tracer and its initial concentration is very important; i.e. the concentration of the tracer must be low enough to ensure that the thermal density differences of the fluid are not disturbed. The use of a system
with hot running water as a heat source did not work out well: the disturbance of the input and output pipes was too large in spite of the insulation. Electrical feeders will not disturb the temperature field that much, so we will use an electrical heat source in the next experiment again.

5.5. The half cylinder experiments.

After the preliminary experiments we now come to a final configuration of the experiments. The half of a PVC cylinder, which is divided along a plane through the axis, is kept fixed to the inner side of a water bath; the circular side of this half cylinder is facing to the interior of the water bath. The content of the half cylinder is water saturated sediment in which the measurements take place. The large amount of cooled water in the water bath will see for a constant temperature at the cylinder wall. The heat source in the front side of the water bath and at the same time on the middle of the cylinder axis provides the heat production in the sediment. A schematic outline of this experiment is given in figure 5-10.

The temperature effect in ocean clay as well as in fine sand is measured with this configuration. We have injected some red tracer to verify the free convection rate of the interstitial water in case of the fine sand. This was not performed in the clay because of the low permeability.

The diameter of the cylinder used in this experiment is 15 cm, while the height is 40 cm. The water bath in which the half cylinder is fixed is nearly cubical with a side length of 60 cm.

The heat source and the temperature probes are mounted in a transparent front, exactly at the centre of the cylinder axis. The fitting of the bulb is enclosed by the plexiglass, while the bulb glass and the probes are extending into the sediment. The advantage of this configuration is that the mutual distances of the source and the probes are constant and measurable, and not dependent on a possible compaction of the sediment. A thermostat on the bulb controls the temperature ($T_1$) of the heat source.

The insulation of the transparent front must be as good as possible, since only in that case the temperature field in the sediment will be axisymmetric. Therefore this front consists of two plexiglass plates separated by a thin layer of air.
The half cylinder inside the water bath is all surrounded by cooled water of constant temperature \( T_0 = 10^\circ C \). This water is constantly stirred so that an optimal boundary condition of constant temperature along the cylinder wall is ensured. Inside the cylinder on the top of the sedimental bulk there is a 2 cm water-layer. The presence of this layer allows a pore water exchange with the sediment.

In order to predict the temperature and the free convection rate of the pore water caused by the heat source we will deal with the theoretical model first. The two fundamental equations, viz. Darcy's law (5-8) and the energy equation (5-3), are valid here. From section 5.3 we learned that the convection term in the energy equation could be neglected. These two equations and the Rayleigh number now become:

\[
\frac{1}{r} \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial}{\partial r} \left( \frac{1}{r} \frac{\partial \psi}{\partial r} \right) = - Ra \frac{\partial \Theta}{\partial r} \quad (5-29)
\]

\[
\frac{\partial \Theta}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \Theta}{\partial r} \right) + \frac{\partial^2 \Theta}{\partial x^2} \quad (5-30)
\]

\[
Ra = \frac{k g \rho \beta B (T - T_0)}{\mu a_m l} \quad (5-31)
\]

in which the Rayleigh number is again the ratio between the buoyancy forces and the viscous forces. The non-dimensional coordinates \( r \) (the radius), \( z \) (the height in respect of the source), and \( \tau \) (the time) and the variables \( \Theta \) (the temperature) and \( \psi \) (the streamfunction) are respectively:

\[
r = \frac{r}{R} \quad (5-32)
\]

\[
z = \frac{x}{R} \quad (5-33)
\]

\[
\tau = \frac{a_m t}{R^2} \quad (5-34)
\]

\[
\Theta = \frac{T - T_0}{T_1 - T_0} \quad (5-35)
\]

\[
\psi = \frac{1}{a_m R} \psi \quad (5-36)
\]

The boundary conditions of this configuration describe the presence of the water layer on top of the sediment and the possibility of water ex-
change with the interstitial water. Besides this we have the dimensions and
the impermeability of the heat source, while the temperature of the source
and the low temperature of the wall are constant during the experiment.
Because of the transient character of the equations we also have an initial
condition here: the temperature field on the moment that the source starts
radiating heat. The mathematical descriptions of these conditions are:

\[ v_r = 0 \quad \text{on the interface between sediment and upper water} \quad (5-37) \]

layer.

\[ 0 = 1 \quad |x| < X_{\text{source}} \quad \text{and} \quad |r| < R_{\text{source}} \quad (5-38) \]

\[ 0 = 0 \quad \text{on the top, bottom and side wall of the cylinder.} \quad (5-39) \]

\[ 0(t=0) = 1 \quad \text{in the source.} \quad (5-40) \]

\[ 0(t=0) = 0 \quad \text{everywhere else in the sediment.} \quad (5-41) \]

In the finite difference method central differencing is used to
calculate the temperature and the velocity field numerically. The resulting
matrix equations will be solved by the Local Relaxation method of Botta and
Veldman (1982). In contrast with Young's overrelaxation method Botta and
Veldman's method does not operate with one optimal relaxation parameter but
with a set of appropriate parameters, one for each grid point.

In order to compare the temperature field of the model calculations
with the measured data we will use the parameters of the experimental
materials. The values of the parameters are listed in table 5-V.
TABLE 5-V: Parameters used in the transient model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mu )</td>
<td>( 1.002 \times 10^{-3} ) kg/ms</td>
</tr>
<tr>
<td>( \rho_o )</td>
<td>1000. kg/m³</td>
</tr>
<tr>
<td>( \beta )</td>
<td>( 2.1 \times 10^{-4} ) 1/K</td>
</tr>
<tr>
<td>( \lambda_m )</td>
<td>2.3 W/mK</td>
</tr>
<tr>
<td>( (\rho c_p)_m )</td>
<td>( 2.8 \times 10^6 ) J/m³K</td>
</tr>
<tr>
<td>( g )</td>
<td>9.8 m/s²</td>
</tr>
<tr>
<td>( k )</td>
<td>( 7.1 \times 10^{-12} ) m²</td>
</tr>
<tr>
<td>( R )</td>
<td>0.1 m</td>
</tr>
<tr>
<td>( L )</td>
<td>0.13 m</td>
</tr>
</tbody>
</table>

The physical properties of the fine sand \((d_{10} = 75 \mu m)\) that we obtained from Delft Soil Mechanics Laboratory, are already known. (DSML report, 1980: sand size III).

The results of the computations with these data are shown in the figures 5-11 and 5-12. These figures give the axisymmetric temperature and velocity profiles for the steady state, and are based on a source temperature of 60°C. The lines in figure 5-11 are the isotherms of the temperature field, while in figure 5-12 the closed lines are streamlines and the dotted lines are isotachs. These isotachs indicate the points of equal (absolute) velocities. The directions of these velocities are of course along the streamlines.

In order to compare the theoretical results with the measurements we will determine the temperature courses at 1 and 2 cm from the heat source during the heating up of the sediment. The comparison with the measurements is shown in figure 5-13. The solid lines are the theoretical courses, while the measured temperatures at points 2, 4, 6, and 8 are indicated by symbols.

The temperatures of points 2, 4, 6, and 8 are shown only since the temperatures of the upper points 1 and 5 coincide with those of 4 and 8.
respectively; and the temperatures of the lower points 3 and 7 coincide with 2 and 6 respectively, located at the right side of the source.

The agreement of experimental and theoretical values is rather good. The mutual differences of the experimental observations could be caused by a small deviation of the source location from the centre point between the temperature probes. A 1 mm deviation of the source gives a mutual difference of 2 mm for the two probes on either side of the source. Another effect might be a local disturbance of the geometry by the presence of the thermostat (with a diameter of 4 mm) near the heat source.

This experiment is carried out with sediment from the MADEIRA ABYSSAL PLAIN as well. The data for the heat conduction coefficient is determined experimentally by the Delft Soil Mechanics Laboratory. Especially the temperature dependency is considered. The sediment porosity is about 60% to 65% and the conduction coefficient is measured at a temperature of 10°C and a temperature of 70°C. The results are listed in table 5-VI.

| TABLE 5-VI: Conduction coefficient measurements (in W/mK). |
|-----------------|-----------------|-----------------|-----------------|
| temperature     | saturated pore  | porosity        |
| °C              | sediment water  | %               |
| 10.             | 0.87            | 0.58            | 60-65           |
| 70.             | 0.92            | 0.66            | 60-65           |

The heat capacity is only measured at 20°C: \((\rho c_p)_m = 4.7 \times 10^6 \text{J/m}^3\text{K}\). There was no indication that this capacity would vary significantly with the temperature and we learned that the sensitivity of the conduction coefficient for the system is much greater than that of the heat capacity (pers. communication, L.H. Brush: Sandia Laboratories in Albuquerque USA).

In relation to the experimental results in table 5-VI we may conclude that the dependency of the conduction coefficient on the temperature is mainly affected by the pore water. For an easy verification the values of the conduction coefficient of water are listed at 10°C and 70°C. These values are taken from Batchelor (1967).
Using these measured values and the geometrical data from table 5-V we obtain the result as is shown in figure 5-14. In this figure the relative temperature is plotted against the time in hours. Again the symbols denote the experimental results and the lines the results of the model calculations at 1 cm and 2 cm distance from the heat source.

The results of the model calculation of the temperature course at the 1 cm point is only partly coinciding with the measured course. It is not clear why this happens, because in case of the steady state (after 3 hours from starting-up) the values of the parameters $\lambda_m$ and $(\rho c_p)_m$ have no influence on the temperature level in that point. However, especially in that period this deviation is most apparent. On the other hand the temperature course at a point with distance 0.9 cm is almost completely coinciding with the course at point 8 (the crosses). In case of the courses at points 2 cm away from the source, the conformity between model and experiment is rather good.

The conclusion of this section is that we may say that the temperature field in the sediment can be rather well predicted, although the temperature field will be somewhat disturbed in case of a half circular configuration. This leads to the assumption that the velocity rates also ought to be predicted by the model. The verification of this assumption was the aim of the following experiment. We will discuss the results in the next chapter.
Figure 5-1

Cylindrical coordinate system
Figure 5-2
Schematic outline of the small-scale drum experiment
Figure 5-3
Heat exchange on top

Ra = 0.95 and Q = 10 Watt

a) Axial temperature distribution
on r = 0 and r = 1

b) Radial temperature distribution
on x = -L/R, 0, L/R

Figure 5-4
Heat exchange on side wall
Figure 5-5
Axisymmetric flow pattern
The direction and the length of an arrow indicate the direction and the magnitude of the velocity in the concerning point.
FINE SAND 150-0.125 Mm (a)
- THERMISTER 11
- THERMISTER 12
- THERMISTER 17
- THERMISTER 18
- THERMISTER 3
- THERMISTER 4
- ERFC THERM

FINE SAND 100-0.125 Mm (b)
- THERMISTER 11
- THERMISTER 12
- THERMISTER 17
- THERMISTER 18
- THERMISTER 3
- THERMISTER 4
- ERFC THERM
Figure 5-6

Measurements in sediments, heated by a 10 Watt source

a) Particle diameters $150 \, \mu m < d_p < 210 \, \mu m$

b) Particle diameters $105 \, \mu m < d_p < 150 \, \mu m$

c) Particle diameters $d_p < 75 \, \mu m$
Figure 5-7
Schematic outline of the large-scale drum experiment
The pipes drawn at an oblique angle are in fact perpendicular to the cross section.
Figure 5-8
Large-scale drum experiment
Source at 80°C, pipes at 50°C.

a) Model situation
b) Experimental and theoretical field
c) Theoretical velocity field
Figure 5-9
Large-scale drum experiment
Injection of dissolved tracer at the source.

a) Initial concentration field
b) Concentration field after 1 day
c) Concentration field after 4 days
Figure 5-10 a
Perspective view of the experimental configuration with the half cylinder. The heat source and the thermisters are visible in the centre.

Figure 5-10 b
Schematic front view of the experimental configuration
Figure 5-11
Temperature profiles from a heat source with constant temperature

$$\text{THETA} = \frac{T - T_0}{T_1 - T_0}$$
Figure 5-12
Flow pattern with permeable boundary at the sediment/water layer interface
Solid lines are streamlines, dotted lines are isotachs.
Figure 5-13
Theoretical and experimental temperature courses in fine sand, 1 cm and 2 cm from the heat source
Figure 5-14
Theoretical and experimental temperature courses in atlantic clay at 1 cm and 2 cm from the heat source
6. NOTES ON A THRESHOLD VALUE FOR THE PRESSURE GRADIENT.

After the verifications of the theoretical temperature field the same experimental configuration was used to compare the theoretically predicted velocity rates with the real velocities in the sediment. In order to realize this a pink tracer was injected 5 cm above the heat source. The supply of tracer is such that the concentration at the point of injection is constant. Because there is no sorption by the fine-sand particles this tracer shall be transported by the pore water flow.

The migration of this tracer can be observed through the transparent front plate, and the shape of the pink area will give an indication of the velocity rate.

Using the data of the fine sand that is given in table 5-V we determined the velocity field shown in figure 5-12. In this field the maximum velocity is 46.1 cm/day and occurs just along the vertical wall of the heat source. Model calculations done by DSML showed that if we suppose a constant relative concentration 1.0 at the injection point (which is 5 cm above the heat source and on the cylinder axis), the tracer will be visibly transported to the water layer on top of the sediment.

However, after starting the injection of the tracer into the sediment with a steady temperature field, the migration process appeared to be a pure diffusion process. This effect can be seen in the figure 6-1. Picture 6-1a is taken just after starting the injection, while 6-1b shows the situation after 45.5 hours. According to the calculations the vertical migration upward should be greater than downward, this is in contrast with the picture, which shows an equal migration to both sides.

The conclusion from this experiment is that there is no interstitial water flow around the injection point under these circumstances. Therefore we want to discuss the idea of a threshold value for the pressure gradient.

The effect of a threshold value for the pressure gradient was incorporated in the model. Calculations with this extended model gave some interesting results.

This threshold value could be caused by a minimum friction that must be overruled before the fluid starts flowing, comparable with the phenomena of friction in the kinematics of solids.
From Darcy's law (5-2):

\[
\frac{\mu}{k} \frac{\partial v}{\partial z} = -\nabla p + \rho_f g
\]  

(6-1)

it is clear that, if a threshold value for the pressure gradient exists, this can be translated into a threshold value for the velocity. The translation factor is proportional to the permeability \(k\), so a threshold velocity will depend on the particle size in the sediment.

In order to give an indication of the effect of a threshold value we have adapted the model by using the magnitude of the local velocity. The model itself will determine the boundary of the area in which the pore water flows, while outside this area the water is supposed to be at rest. This area is found by a numerical iteration process.

Calculations with this adapted model have been made for two cases: \(V_{\text{threshold}} = 1 \text{ cm/day}\) and \(V_{\text{threshold}} = 3 \text{ cm/day}\). The results are shown in figure 6-2 and 6-3 respectively. The physical properties are the same as used to calculate the flow pattern in figure 5-12. The velocity rates are of course not quite reliable but give a rough indication of the effect of the threshold value.

Figure 5-12 shows the pattern with \(V_{\text{threshold}} = 0 \text{ cm/day}\). Comparison with figure 6-2 (\(V_{\text{threshold}} = 1 \text{ cm/day}\)) shows that the pattern is hardly changed, only the area with the low velocities has been cut off. However, pore water exchange with the layer on top of the sediment is not occurring any more. Figure 6-3 shows that with \(V_{\text{threshold}} = 3 \text{ cm/day}\) the cylinder wall is not reached by the flowing pore water, so the wall does not disturb the flow pattern at all.

A notable result is that with \(V_{\text{threshold}} = 0 \text{ cm/day}\) the maximum velocity is 46.1 cm/day, while with \(V_{\text{threshold}} = 3 \text{ cm/day}\) this maximum is decreased to 26.5 cm/day. In the last case the quantity of flowing water along the heat source is obviously too small to induce a velocity of 46.1 cm/day.

A cautious conclusion from these calculations may be that, when a threshold value for the pressure gradient exists, the maximum occurring velocity could be much lower than the predicted values based on the classical Darcy model.
A condition for the occurrence of this phenomenon in the seabed is, that there is no interstitial advection before the emplacement of the canister. When there is advection, then the flow is already exceeding the threshold value.

The study of this phenomenon will be continued in future at the department of Applied Mathematics of the Twente University of Technology. An experiment will possibly be set up to prove the existence of such a threshold pressure gradient.
Figure 6-1
Front view of the tracer injection experiment.
The white cable is leading to the heat source.

a) Situation just after starting the injection

b) Situation 45½ hours after starting the injection
Figure 6-2
Flow pattern when threshold velocity is 1 cm/day
Solid lines are streamlines, dotted lines are isotachs.
Figure 6-3
Flow pattern when threshold velocity is 3 cm/day
Solid lines are streamlines, dotted lines are isotachs.
7. MIGRATION OF ISOTOPES IN SATURATED SEDIMENT.

7.1. Introduction.

The low concentrations of radioactive nuclides in pore water have a neglectable influence on the heat transport and the rate of convection, but the movement of the pore water can be most significant for the rate of migration. Therefore the migration process can be treated as a process that takes place in a porous medium of which the temperature and velocity field are already determined and known.

In this section we will deal with the phenomena that control the migration process. The phenomena are reflected by the terms in the differential equation that describes that process. By comparison of the order of magnitude of these terms the effects can be weighed against each other. The phenomena considered here are sorption, diffusion and convection.

Although the decay of the radioactive isotopes is also one of the important phenomena we will neglect this effect here, because the decay will only cause a positive (from mother isotopes) or negative (to daughter isotopes) contribution to the local concentration of the concerned radioactive isotope. This is rather easily taken into account in a large computer code. On the contrary it is true that the half life of these isotopes prescribe the lifetime of the total migration process.

Beside these modelling aspects of the migration we will discuss an extension of the Langmuir sorption model as a result of the batch experiments with cadmium. An expression has been derived, using the assumption that sorption is a chemical exchange equilibrium, that describes the sorption distribution coefficient $K_d$ as a function of the isotope concentration in solution. It was even possible to incorporate the temperature in the expression as well.

7.2. Modelling aspects of migration.

The partial differential equation describing the migration is already used in previous sections. In this case we will discuss several aspects of it. The equation is based on the conservation of mass and is for
instance given by Hickox e.a. (1980):

\[
\frac{\partial}{\partial t} \left\{ \phi C + (1-\phi) \rho_s C_s \right\} = D \nabla^2 C - v \cdot \nabla C + S \tag{7-1}
\]

in which the variable \( C_s \) is the concentration of the adsorbed isotope and \( C \) the concentration in the fluid, while \( v \) is the Darcy velocity. The parameters \( \phi \), \( \rho_s \), and \( D \) are the porosity, density of the solid and the effective diffusion coefficient respectively. In \( S \) the terms are represented, e.g. by radioactive decay; but, as mentioned before, we will neglect this term.

In order to express \( C_s \) as a function of \( C \) it is usual to define an equilibrium distribution coefficient \( K_d \):

\[
K_d = \frac{C_s}{C} \tag{7-2}
\]

This coefficient is the ratio between the concentrations of the sorbed isotopes and the isotopes in solution. Using a parameter \( K \), often called sorption coefficient as well,

\[
K = \frac{(1-\phi)}{\phi} \rho_s K_d \tag{7-3}
\]

the differential equation obtains the rather simple parabolic form:

\[
\frac{\partial}{\partial t} \left\{ (1+K)C \right\} = D \nabla^2 C - v \cdot \nabla C \tag{7-4}
\]

The dispersion and the molecular diffusion are accounted for in the effective diffusion coefficient \( D \). This effective diffusion coefficient can be written, with the usual description of the dispersion, like:

\[
D = D_0 + \alpha |v| \tag{7-5}
\]

as is given by Hickox e.a. (1980). \( D_0 \) denotes the effective molecular diffusion, while the second term expresses the dispersion with \( \alpha \) a dispersion coefficient and \( v \) the Darcy velocity.

In this equation (7-4) it is supposed that the physical properties of the medium are homogenous. Although this is not true in reality, e.g. the dispersion as a part of the effective diffusion coefficient is depending on
the velocity distribution, it is possible to weight out some global effects of this process.

In the following step of simplification we will even suppose that the sorption coefficient \( K \) is neither depending on the time \( t \) nor on the concentration \( C \). In this case we may write the equation as follows:

\[
(1+K) \frac{\partial C}{\partial t} = D V^2 C - V \cdot VC
\]  

(7-6)

When we write this equation in its non-dimensional form, in which the terms are of order \( O(1) \) and the coefficients give the magnitude of these terms, we obtain:

\[
(1+K) \frac{\partial C}{\partial \tau} = \hat{V}^2 C - \left( \frac{UL}{D} \right) \hat{V} \cdot \hat{V} C
\]  

(7-7)

Here \( \hat{V}^2 \) is the Laplace operator for the non-dimensional variables and \( \hat{V} \) the normalized Darcy velocity related to a characteristic velocity \( U \). The new time variable \( \tau \) is defined by:

\[
\tau = \frac{Dt}{L^2}
\]

The characteristic length \( L \) in the seabed situation should be the depth of the buried canister. However, it is very difficult to give a characteristic velocity \( U \) that applies for the entire \( L \) meters. From calculations based on the validity of Darcy's law and the Boussinesq approximation, it is clear that further away from the source the rate of the pore water velocity decreases rapidly. Therefore we will only consider compartments of unit length, so \( L = 1 \) meter.

From equation (7-6) it is clear that by weighing out of the diffusion term against the convection term, the rate of sorption is of no consequence. So the Peclet number \( Pe = UL/D \) expresses the ratio between the convection and the diffusion.

If we suppose that the transport by convection can be neglected as \( Pe < 0.01 \), then with \( D = D_0 + \alpha U \) for \( U \) holds:

\[
U < \frac{D_0}{100 \, L - \alpha}
\]  

(7-9)

Using \( \alpha = 6.1 \) m, \( D_0 = 0.01 \text{ m}^2/\text{yr} \), as is done by Hickox et. al. (1980), and
L = 1 meter then we obtain that $U$ is well below 0.1 mm/yr.

Hickox et al. (1980) learn too, that the maximum velocity in the seabed will be below 0.1 mm/yr after about 100 years, which is the maximum velocity that occurs near the canister. The velocity in the field further away from the source will of course have been decreased below this value long before that. This means that if we suppose that the canister has some larger dimensions as it has in reality, we can neglect the transport of the nuclides by convection.

The modelling enlargement of the canister dimensions is dependent on the area of the field in which the flow rate stays below 0.1 mm/yr. A better measure would be the distance that a fluid particle can cover with a velocity larger than 0.1 mm/yr. The period of ± 100 years is small compared with the period of more than 10 or 100 thousand of years, that it takes the isotopes to reach the oceanfloor. So a migration model based on diffusion and sorption only, can be applied if the dimension of the canister is somewhat enlarged.

Especially when there exists a phenomenon like the threshold pressure gradient as is described in chapter 6, the maximum velocity that is possibly induced will be lower or even be zero. In case of a small cell as is shown in figure 6-3 the dimensions of the canister should enclose this area. It is most likely that in this case the enlargement of the canister could be more confined.

It is true that existence of threshold value for the pressure gradient must still be proved, but in a homogeneous seabed without previous advection it can be stated that the diffusion and sorption dominate the migration process of the isotopes through the seabed.

### 7.3. Diffusion influenced by sorption.

After discussing the effect of convection on the migration process in this section we will deal with sorption in relation to diffusion. In this case the equation that describes the migration process is:

$$\frac{\partial}{\partial t} \{(1 + K)C\} = \nabla \cdot D \nabla C \quad (7-10)$$
Here \( D_0 \) is supposed to be dependent on the location in the field, since it is dependent on the variation of the temperature. From Duursma and Eisima (1973) we learn that in the range of 0 to 50°C the temperature dependence of this coefficient, which is empirically determined, is:

\[
D_0(T) = (0.026 T + 0.45) \times 10^{-5} \text{ cm}^2/\text{sec} \tag{7-11}
\]

where \( T \) is in centigrades. So \( D_0 \) varies with a factor 2 or 3 in this range.

The sorption coefficient \( K \) depends not only on the temperature, but varies with the local concentration in the fluid as well. This relation has been studied for several metal elements during this project. This research led to a more accurate description of the sorption distribution coefficient for cadmium.

In case of interactions of elements to sediment by Coulombic forces (see table 4-IV) mostly called electrostatic sorption, a much used expression is the Langmuir relation. The expression is as follows:

\[
K_{d} = \frac{C_s}{C} \frac{a}{1+bC} \quad (7-12)
\]

in which \( a \) and \( b \) are constants, and \( C_s \) and \( C \) are the already defined concentrations. A well described foundation for the use of this Langmuir expression is given by Duursma and Hoede (1967).

Several expressions for the sorption distribution coefficient dependent on the kind of binding are known in the literature; e.g. the Freundlich distribution (Duursma and Hoede, 1967), (Harmsen, 1979):

\[
K_{d} = K C^\frac{1}{n} - 1 \quad (n > 0) \tag{7-13}
\]

and the formula given by Dubinin and Radushkevitch (1947), (or: NEA Workshop, 1983):

\[
K_{d} = \frac{b}{C} \exp (-\gamma \varepsilon^2) \tag{7-14}
\]

with:

\[
\varepsilon = RT \ln(1 + \frac{1}{C})
\]
in which b and γ are constants.

Results of adsorption experiments with cadmium are shown in figure (7-1) (Duursma et. al., 1982; van Geldermalsen and Duursma, 1984). The $K_d$ sorption coefficient was measured at several temperatures, but for this moment we will only deal with the values of $50^\circ C$. For this case we will apply a complete theoretical expression of the sorption relation, which is:

$$K_d = \frac{a_1 + b_1 C}{1 + d_1 C + e_1 C^2} + \frac{a_2 + b_2 C}{(1 + d_2 C)^2}$$

(7-15)

where $a_1$, $b_1$, $d_1$, $e_1$, $a_2$, $b_2$ and $d_2$ are parameters that might depend on the temperature, but are constants here. The fully extended derivation of this accurate expression will be published soon (J.W. Wegereef et al., 1985).

When we use here the constants given in table 7-1 this expression gives a more close description of the experimental data than by using the Langmuir relation; see figure 7-2.

TABLE 7-1: Parameter values of cadmium adsorption at $50^\circ C$.

<table>
<thead>
<tr>
<th>$K_d$ parameters for (7-15)</th>
<th>$K_d$ parameters for (7-16)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_1$ = 300</td>
<td>$a_1$ = 320</td>
</tr>
<tr>
<td>$b_1$ = 684</td>
<td>$b_1$ = 0.032</td>
</tr>
<tr>
<td>$d_1$ = 0.70</td>
<td>$a_2$ = 245</td>
</tr>
<tr>
<td>$e_1$ = 0.065</td>
<td>$b_2$ = 0.13</td>
</tr>
<tr>
<td>$a_2$ = 510</td>
<td>$a_3$ = 560</td>
</tr>
<tr>
<td>$b_2$ = 350</td>
<td>$b_3$ = 8.485</td>
</tr>
<tr>
<td>$d_2$ = 3.8</td>
<td></td>
</tr>
</tbody>
</table>

A more practical expression derived from the foregoing formula can be written as:
\[ K_d = \frac{a_1}{1+b_1 C} + \frac{a_2 C}{1+b_2 C^2} + \frac{a_3}{1+b_3 C} \]  

(7-16)

in which \( a_1 \) and \( b_1 \) are again constants that might vary with the temperature. In figure 7-2 the line with larger intermittances shows the sorption relation (7-16) with data of the second column of table 7-I.

These preceding relations could be derived by the assumption that the sorption process is mainly controlled by covalent binding in which several chemical equilibrium processes play a role. It is known from Le Chatelier and van 't Hoff that these equilibrium processes depend on the temperature. Using this relation we were able to describe the sorption relation not only as a function of \( C \) at a certain temperature, but as well as a function of temperature. This relation is the same as (7-15) but now with temperature dependent parameters. These parameters are defined as:

\[
\begin{align*}
a_1 & = \frac{Q_2 K_{22}}{(1+L)} \\
b_1 & = \frac{Q_2 K_{12}}{(1+L)^2} \\
d_1 & = \frac{K_{22}}{(1+L)} \\
e_1 & = \frac{K_{12}}{(1+L)^2}
\end{align*}
\]

\[
\begin{align*}
a_2 & = \frac{(K_{11} + K_{21}) Q_1}{(1+L)} \\
b_2 & = \frac{K^2_{11} Q_1}{(1+L)^2} \\
d_2 & = \frac{K_{11}}{(1+L)} \\
e_2 & = \frac{K_{12}}{(1+L)^2}
\end{align*}
\]

(7-17)

in which all parameters \( K_{ij} \), \( Q_i \), and \( L \) depend on the temperature as:

\[
\text{parameter} = \exp \left( \alpha + \frac{\beta}{T} \right)
\]

(7-18)

with \( \alpha \) and \( \beta \) are constants, and \( T \) the temperature in Kelvin.

In figure (7-3) again the symbols show the results of the batch experiments, in which \( K_d \) is determined at 37, 50, 75 and 90\(^\circ\)C. The curve in this figure shows the relation as is described by (7-16), (7-17) and (7-18) and the parameters of table 7-II. The values of table 7-II are results of an advanced parameter fitting method, which is developed by de Bruin (1984).
During the experiments the pH is almost constant, therefore in the derivation of the used expressions the assumption has been made that the sorption process is not influenced by pH variations, although this method can deal with it. The pH variation should then be taken in account as a chemical reaction that controls the sorption process. For a more detailed description of this method we refer to an article that will be published (J.W. Wegereef et al., 1985).

We have discussed the sensitivity of both parameters $D_o$ and $K_d$ on the temperature and the local concentration $C$ of the isotope in solution. More information about the $K_d$'s of the transuranes Pu, Np and Am is given in chapter A. We were not able to verify whether the adsorption coefficients of these radionuclides could be fitted with this method within this project. The method allows a wide range of applications, although it seems to be impossible to find an expression to fit the experimental data at first sight.

7.4. Effects of sorption and decay in a release model for a buried source.

The discussions in the previous sections have shown that the paramet-
ers that control the migration process of the radioactive isotopes through the seabed depend very much on the conditions (e.g. temperature). In order to get a rough idea of the effect of sorption and decay together on the release of radioactive nuclides to the ocean water we used a simple model of images to simulate this process.

In this model the diffusion coefficient and the sorption distribution coefficient $K_d$ are supposed to be constant during the entire process, while the waste is supposed to be buried unpacked. Hence the material can migrate directly into the seabed.

The unpacked waste is no rude limitation in the overall system. The system modelling of the System Analyses Task Group (1980) shows that the time the canister is intact can be neglected in comparison with the migration time of the isotopes in the sediment. The canister will exist for several hundreds of years, while the sediment transit time is in orders of ten thousands of years.

To simulate the release of the isotopes to the ocean water we assume that the isotope concentration at the seafloor (as a boundary condition for the sediment) is zero. The gradient of the concentration will then give the release rate of the isotopes.

For a mass $s$ buried in an infinite medium the concentration distribution is given by Duursma and Hoede (1967). Using the method of images to meet the boundary condition at the seafloor, the following expression of the distribution is obtained:

$$C(z,r,t) = -\frac{2s}{(4\pi Dt)^{3/2}} \sinh \frac{2zd}{4Dt} \exp\left(-\frac{(r^2 + z^2 + d^2)}{4Dt}\right)$$

(7-19)

Here $D$ is the diffusion coefficient, $t$ the time, $d$ the burial depth in the seabed and $(r,z)$ are cylindrical coordinates with $z = 0$ on the seafloor and the waste position being $z = -d$, $r = 0$.

The effect of sorption is included in the diffusion coefficient:

$$D = \frac{D_0}{(1+K_d)}$$

(7-20)

where $D_0$ is the pure diffusion coefficient and $K_d$ the adsorption coefficient in the sorption model given by Duursma and Hoede (1967).

Integrating the concentration gradient along the surface $z = 0$ we find the total flux of mass from the seabed per unit of time:
During the migration, however, the radioactive mass $s$ will decay. The rate of decay can be expressed as:

$$s = s_o e^{-\lambda t} \quad t \geq 0 \quad (7-22)$$

Here the $s_o$ is the initial radioactive mass of isotopes, and $\lambda$ is the decay coefficient, defined by $\lambda = (\ln 2)/t_{\text{half}}$ with $t_{\text{half}}$ the half-life. The radioactive fractional outflux with respect to a unit of waste ($s_o = 1$), including the effect of decay will now be given by:

$$\Phi(t) = \frac{4\pi D d_s}{(4\pi D t)^{3/2}} \exp\left(-\frac{d^2}{4Dt}\right) \quad (7-23)$$

If all the nuclides released from the seabed would be caught into one reservoir then the total radioactive fraction in the reservoir would be:

$$\Phi(t) = e^{-\lambda t} \cdot \text{erfc}\left(\frac{d\sqrt{K_d+1}}{2\sqrt{D_o} t}\right) \quad (7-24)$$

The erfc is the complementary error function and $t$ is the time since the burial took place. In this expression the $D$ has been replaced by the sorption equivalent $(7-20)$. In case of no decay: $\lambda = 0$.

With these two last expressions $(7-23)$ and $(7-24)$ we will discuss the influence of the burial depth on the radioactive release from the seabed in case decay and/or sorption are involved. The value used for the plain-diffusion coefficient is $D_o = 0.01 \text{ m}^2/\text{year}$. This value is commonly used, for instance by Hickox et al. (1980).

The values $(K_d + 1) = 1, 100$ and $10,000$ and $t_{\text{half}} = 5,000, 10,000$ and $20,000$ were used for adsorption coefficients and half-life times respectively. A burial at 30 and 60 m was simulated to observe the effect of depth.

Figure 7-4 shows the curves for the cumulative fraction of the buried waste released from the seabed into the ocean water if no decay was involved. The three curves on the left in the figure are the distributions of the decay factors in $(7-24)$.  

$$\Phi(t) = \frac{4\pi D d_s}{(4\pi D t)^{3/2}} \exp\left(-\frac{d^2}{4Dt}\right) \quad (7-21)$$
This figure shows that for \((K_d + 1) = 10.000\) and \(t_{\text{half}} = 5.000\) years both the burial at 30 m and 60 m show that the radioactivity of the released nuclides is almost completely decayed. However for \(K_d + 1 = 1\) and \(t_{\text{half}} = 20.000\) years the released fraction is still rather radioactive. For this case, Figure 7-5 shows the difference between a 30 m and 60 m burial. Not only the peak fraction is shifted but also the peak value is 10 times lower. Hence, if the burial depth would be 60 m instead of 30 m the released amount of still radioactive isotopes with \(t_{\text{half}} = 20.000\) years is 10 times lower.

Another point of interest is the yearly release fraction. Figure 7-6 b, c and d shows the distributions of the yearly released fractions of the radioactive isotopes. As a reference Figure 7-6a shows the release fractions without decay. The other figures show that if the time of the release-peak is of the same order of the half-life then the maximum yearly release is hardly affected by the decay. However if the half-life is very small in comparison with the release-peak time, the release fraction is hardly radioactive. See for instance the curve for \(K_d + 1 = 100\) and the burial depth of 30 m: in Figure 7-6a this curve shows \(t_{\text{peak}} = 10^6\) with a maximum value of \(10^{-7}\), while in Figure 7-6b for a half-life of 5.000 years the maximum value does not exceed \(10^{-20}\).

Conclusions.

- In case of large \(K_d\) and low \(t_{\text{half}}\)-values the radioactive release from the seabed is not sensitive to the sorption coefficient \(K_d\) and the burial depth.

- In case of low \(K_d\) and large \(t_{\text{half}}\) values the radioactive release from the seabed is hardly sensitive to the sorption coefficient \(K_d\) or the burial depth; the release peak will only be shifted in time.

- In case of a \(K_d\) value that causes a release-peak time in order of the half-life of the isotope, the sorption coefficient \(K_d\) or the burial depth will have a considerable effect on the radioactive release from the seabed.
It must be noted that all conclusions are under condition that there is no interstitial water-movement. If so, the sediment transit time will be shorter so that the isotopes with a shorter half-life will already contribute to the radioactive release from the seabed.
Figure 7-1
Batch measurements of sorption with cadmium in Atlantic clay
Figure 7-2

Sorption isotherms of Cd at 50°C

Langmuir, expression (7-15), expression (7-16), and experimental values
Figure 7-3
K_a-curves (7-15) for different temperatures in comparison with batch measurements of Cd
Figure 7-4
Cumulative released fraction without decay, and decay factors

Figure 7-5
Cumulative released fraction
Figure 7-6
Decay effect on annually released radioactivity

7-6 a) No decay

7-6 b) Half-life of 5,000 years
7-6 c) Half-life of 10,000 years

7-6 d) Half-life of 20,000 years
8 - Literature


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MIGRATION PROCESSES IN MARINE SEDIMENTS CAUSED BY HEAT SOURCES: SIMULATION EXPERIMENTS RELATED TO DEEP SEA DISPOSAL OF HIGH LEVEL RADIOACTIVE WASTES

By E. K. Duursma et al. (EUR 8710)
MIGRATION PROCESSES IN MARINE SEDIMENTS CAUSED BY HEAT SOURCES: SIMULATION EXPERIMENTS RELATED TO DEEP SEA DISPOSAL OF HIGH LEVEL RADIOACTIVE WASTES

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4 REFERENCES

Remark: The intention of this scientific research topic is not related to any political decision for or against disposal of radioactive substances in the sea. According to the regulations of the Royal Netherlands Academy of Arts and Sciences, which are equally valid for her Delta Institute for Hydrobiological Research, and those of the Technical University of Twente, all results are free accessible.
ABSTRACT

Higher temperatures (from 4 to \(80^\circ\text{C}\)) cause changes of \(K_d\) values for different elements like those studied: Cd and Pu-239. For Cd this was a reduction by a factor 10 for the temperature range 4-80°C while the preliminary data for Pu show for a range of 4-140°C not yet large differences, although all \(K_d\)’s were higher than those of the literature. This has to be investigated more in detail.

The results on convection experiments, steered and followed by model calculations, demonstrated that the convection of pore water of \(10^{-11}\ \text{m} \ \text{s}^{-1}\) can be achieved in days at temperature differences of \(70^\circ\text{C}\).

The so far achieved results allowed model calculations on the relationship between the safe-burial depth and both the temperature related \(K_d\)’s and convection coefficients. An inverse square root relationship might be used for the increase in burial depth and the \(K_d\)’s or apparent diffusion coefficients.

Although the limited amount of results only allow premature conclusions, reduction of \(K_d\)’s, due to heat, seems to be possible, in spite of the fact that this is not a general phenomenon for each radio-isotope.
Commission of the European Communities

International symposium on the behaviour of long-lived radionuclides in the marine environment

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TEMPERATURE EFFECTS ON SORPTION OF Cd, Eu, Pu AND AM ONTO ESTUARINE AND MARINE SEDIMENTS

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Abstract

TEMPERATURE EFFECTS ON SORPTION OF Cd, Eu, Pu AND AM ONTO ESTUARINE AND MARINE SEDIMENTS.

The effect of temperature (4° to 140°C) on sorption of Cd, Eu-152, Pu-239 and Am-243 onto Atlantic and estuarine sediments was studied using a batch equilibrium technique. The sorption distribution coefficient ($K_d$) of Cd showed an inverse dependency of temperature for the sediments. $K_d$: 1400 at 4° and 90 ml.g$^{-1}$ at 90°C for Atlantic sediment and 65 at 4° and 15 ml.g$^{-1}$ at 90°C for estuarine sediment. Equilibrium was reached within 2 days and coulombic interaction of Cd with the sediment surface of the calcium carbonate was apparently the main mechanism for cadmium adsorption. Temperature showed the same effects on sorption of Pu-239 to these sediments, indicating the same sorption mechanism. However, $K_d$ s were much greater: $10^5$ to $10^6$ ml.g$^{-1}$. Raising the temperature had a small effect on the adsorption of Eu-152, $K_d$: $6.8 \times 10^4$ at 4° and $4.5 \times 10^4$ ml.g$^{-1}$ at 80°C for Atlantic sediment, which would indicate that chemosorption is the main sorption mechanism here. Sorption equilibrium constants for Am were greater than $8 \times 10^6$ ml.g$^{-1}$ and no influence of temperature was found, perhaps due to imprecise instrumentation.

* Communication nr 265 of the Delta Institute for Hydrobiological Research.
This work was supported by the Dutch Ministry of Economic Affairs under contract number TW-83/TA-Z/112: jfk.
1. Introduction

An option for disposal of high radioactive waste is to put it in canisters and to dump these in the seabed sediment. A disadvantage is that new canisters radiate heat which causes elevation of temperatures in the nearby area and induces convection of the interstitial water of the sediments. Migration of radionuclides away from the canister is thus possibly enhanced (Hollister et al., 1981). Sorption onto the sediment will obstruct migration, but there is little known about the effects of temperature on sorption of radionuclides to seabed sediments. These must be evaluated first in order to produce relevant information for modeling studies.

Traditionally the sorption equilibrium of ions is described by the formula:

$$\frac{x_i}{X-x_i} = K \frac{c_i}{c} \quad (1)$$

in which $x_i$, $X$, $c_i$ and $c$ are the concentrations of the sorbed radionuclide, the ligands on the sediment surface, the radionuclide in solution and the seawater ions competing for adsorption. $K$ is the distribution coefficient. Since $X \gg x_i$, the formula becomes:

$$\frac{x_i}{c_i} = K \frac{X}{C} \quad \text{or} \quad \frac{x_i}{c_i} = K_d \quad (2)$$

In batch equilibrium studies $K_d$ (the sorption equilibrium coefficient) can easily be calculated (Duursma & Hoede, 1967) from

$$K_d = \frac{(c_o - c_f)c_f}{c_o} \cdot \frac{M}{V} \quad (3)$$

in which $c_o$, $c_f$, $M$ and $V$ are the start concentration, the equilibrium concentration in solution, the mass of the suspended sediment and the volume of the suspension.

This is a study of the sorption of Pu-239, Am-243, Eu-152 and Cd to sediments of the Oosterschelde estuary in the Netherlands and sediments of a selected dumpsite in the Atlantic Ocean at a range of temperatures from 4°C to 14°C, and incubated for more than 50 days at various concentrations.

2. Experimental

Sediments were characterized according to standard procedures (Duursma and Eisma, 1973). Batch equilibration under controlled temperature conditions were used to study the sorption behaviour of Atlantic Ocean and Oosterschelde sediment to Cd, Pu, Eu and Am. The Atlantic sediment was provided by Dr.
A. Kuypers, R.G.D. (the Dutch Governmental Geological Service) from core 82 PCL 14 collected in the Western Madeira Abyssal Plain in 1982. Estuarine sediment was from the Oosterschelde estuary in the Netherlands. A standard seawater solution according to Kalle (Grashoff, 1976) to which 45 μ M.l⁻¹ NH₄⁺, 7 μ M.l⁻¹ PO₄³⁻ and 1 μ M.l⁻¹ NO₃⁻ was added to approximate interstitial water conditions, was used in all experiments. CdCl₂ (1 g.l⁻¹) in 2.5 % HCl (Merck) was used to produce a range of Cd²⁺ concentrations from .1 to 20 mg.l⁻¹ in seawater, pH 8.0 Polypropylene tubes with screw-on stoppers were used to incubate 3 ml sediment suspension together with 6 ml of a Cd-solution. Each series was done in triplicates. Concentration series were allowed to incubate at several temperatures (4, 20, 50, 75 and 90° C). The samples were incubated in stoves and shaken regularly. The sediment was centrifuged after specific time intervals and Cd²⁺ was measured using a Perkin-Elmer AAS.

Eu-152, Pu-239 and Am-243 were obtained in .1 N HNO₃. Stock solutions containing 0.1 mCi.ml⁻¹ in seawater were prepared, adjusted to pH 8.0, and filtered before using. Pu and Eu activity in the filtrates were nearly the same as in the stocks but Am activity dropped to nearly 1 μCi.ml⁻¹. These filtered stocks and a 1:1 and a 1:4 dilution were applied in the tests. Teflon Oakridge type centrifuge tubes and Teflon Parr bombs were used in studies with radionuclides. A 2 ml sediment suspension (.44 mg Atlantic seabed sediment or 27 mg Oosterschelde sediment) was incubated with a 16 ml radionuclide solution. Samples were incubated at various temperatures ranging from 4 to 140° C. The sediments were centrifuged after various time periods, the pH and Eh were checked and an aliquot of 1 ml was subtracted and counted in a liquid scintillation counter. Sediments were resuspended and allowed to incubate further. Desorption of Pu-239 was determined by centrifuging the suspension and discarding the supernatant. Clean seawater was then added and the suspension was equilibrated for 7 days at 20° C, after which the activity of the solution as well as of the sediment was counted.

3. Results and Discussion

Table 1 shows the characteristics of the sediments. Figures 1 and 2 reproduce the effects of temperature on cadmium adsorption to Oosterschelde and Atlantic sediments. There is an extinct effect on the adsorption to both sediments that can be explained by thermodynamical principles. Cd²⁺ does not precipitate as CdCO₃ since K₅ is not constant over the concentration range used. Although
sorption processes are generally explained in terms of ion exchange mechanisms, this seems unlikely here because both sediments have cation exchange capacities in the same order of magnitude while \( K_d \) s differ with a factor of 15. Coulombic interaction with the sediment surface of the calcium carbonate i.e. the forming of insoluble complexes on either surfaces, is a more likely explanation, since the real surface areas as well as the calcium carbonate contents of both sediments and the \( K_d \) s have the same order of magnitude. Although it may not be clear as to what surface the Cd sorbs, it is evidently an exothermal process since the shift of the sorption equilibrium \( (K_d) \) to lower values at higher temperatures indicates a negative reaction enthalphy according to the thermodynamic principle

\[
\frac{d \ln K}{dT} = \frac{\Delta h}{RT^2}
\]

\( \Delta h \) being the reaction enthalphy. This is best illustrated by the sorption to Atlantic sediment at low equilibrium concentrations. Here \( X \gg x \) (formula 1) and Cd acts as a trace metal. Radionuclides were applied below this concentration level, see table 2.

Figures 3 and 4 show the results of sorption experiments with Pu-239. The sorption to Atlantic sediment \( (K_d : 10^6 \text{ ml.g}^{-1}) \) was not influenced by raising the temperature; this in contrast to sorption to Oosterschelde sediment \( (K_d : 10^6 \text{ ml.g}^{-1} \text{ at } 40^\circ \text{C and } 10^5 \text{ ml.g}^{-1} \text{ at } 80^\circ \text{C}) \), but care must be taken since standard deviations are large at high \( K_d \) s. This is due to errors in sediment mass and to low equilibrium concentrations. \( K_d \) s are lower for Oosterschelde sediment than for Atlantic seabed sediment, which implies the same sorption mechanism for Pu as found for Cd; in other words, a coulombic interaction of Pu with the sediment surface or the calcium carbonate. This explanation is supported by the fact that adsorption is almost reversible.

Figure 5 shows the results of Eu-152 incubation with the sediments at 2 temperatures. Equilibrium seems to be established within 3 days and \( K_d \) increases with temperature. This indicates that sorption of Eu is not ruled by simple coulombic interaction alone as with Cd and Pu. It is an endotherm process which indicates chemosorption as the most possible mechanism for adsorption. Eu sorption is therefore irreversible, which is confirmed by other studies (Kenna, 1981). The pH influences adsorption considerably. After 30 days of incubation the pH was lowered to pH 4 which induced a decrease in \( K_d \).

Sorption equilibrium constants of Am to both sediments were approximately \( 8.10^6 \text{ ml.g}^{-1} \) and probably greater. Temperature did not influence this. However,
sorption measurements with this method were inaccurate since start concentrations were very low due to the insolubility of Am. Nearly all activity was removed by filtering the stock solution before performing the sorption tests. This caused equilibrium concentrations near or beyond the detection limit of the liquid scintillation counter.

4. Conclusions

The influence of temperature on the sorption of radionuclides to marine sediments is not yet fully understood, although general trends may be drawn from the results. Eu is sorbed better at elevated temperatures, which indicates partially irreversible sorption. Sorption of Pu tends to be lower at higher temperatures as was clearly shown for Cd, this indicates a coulombic interaction with the sediment. Am does not seem to be influenced by temperature changes. \( K_d \) values of Pu and Am are in the range of \( 10^6 \text{ ml g}^{-1} \). The batch equilibrium method is not the best method to study sorption of radionuclides with high \( K_d \)s at high temperatures, since this forces either to use low sediment concentrations or very low equilibration concentrations. Both induce inaccurate results.

References


Figure 1  Effect of Cadmium concentration on the adsorption equilibrium constants of marine sediment at various temperatures.
Figure 2  Effect of Cadmium concentration on the adsorption equilibrium constants of estuarine sediment at various temperatures
Figure 3  Effect of time and temperature on adsorption equilibrium constants of trace Pu-239 to estuarine sediment, O-O: 4°C, △-△: 20°C, O-0: 80°C. Bars indicate standard errors.
Figure 4  Effect of time and temperature on adsorption equilibrium constants of trace Pu-239 and marine sediment.

X: 4°C, Δ-Δ: 27°C, ○-○: 80°C, o-o: 140°C.

Δ, ○-○ and θ-θ indicate the desorption equilibrium constants at 20°C of sediments previously used for adsorption of 4°C, 80° and 140° C, respectively.
Figure 5 Effect of time and temperature on adsorption equilibrium constants of Eu-152 to estuarine and marine sediments.

Estuarine sediment: ○--○: 4°C, □--□: 80°C.

Marine sediment: ○--○: 4°C, △--△: 80°C, after 30 days the pH of these incubations were lowered to pH 4.0: △--△: 80°C.
<table>
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<th>Oosterschelde sediment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CORE B2 PCL 14*</td>
<td></td>
</tr>
<tr>
<td>Depth (m)</td>
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<td>0.3</td>
</tr>
<tr>
<td>Depth of sediment within the core (m)</td>
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<td>0.1</td>
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<tr>
<td><strong>Physical</strong></td>
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<td></td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>75</td>
<td>47</td>
</tr>
<tr>
<td>Median grain size ((\phi))</td>
<td>&gt; 3.75</td>
<td>3 (\pm) 1.5</td>
</tr>
<tr>
<td>Water content (%)</td>
<td>52</td>
<td>22</td>
</tr>
<tr>
<td>Surface area (m(^2)g(^{-1}))</td>
<td>65</td>
<td>4.9</td>
</tr>
<tr>
<td>Cation exchange capacity (meg. 100 g(^{-1}))</td>
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<td>8.2 (\pm) 0.2</td>
</tr>
<tr>
<td><strong>Mineral</strong></td>
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</tr>
<tr>
<td>Organic C (%)</td>
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<tr>
<td>CaCO(_3) (%)</td>
<td>(&lt; 62)</td>
<td>(&lt; 5)</td>
</tr>
<tr>
<td>Kaolinite</td>
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<tr>
<td>Chlorite</td>
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<td><strong>Porewater (approximate-concentrations)</strong></td>
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<tr>
<td>NH(_4) ((\mu M. 1(^{-1})))</td>
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<tr>
<td>NO(_3) ((\mu M. 1(^{-1})))</td>
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<td>17</td>
</tr>
<tr>
<td>pH</td>
<td>7.4</td>
<td>7.8</td>
</tr>
</tbody>
</table>

+++ = most abundant  
* = present  
* = none  
* * More information on the sedimentology of the Madeira Abyssal Plain in Kuypers, 1982.

**TABLE 1.** Characteristics of sediments and pore water of sediments used in sorption experiments.
<table>
<thead>
<tr>
<th></th>
<th>Activity ( \text{Ci.ml}^{-1} )</th>
<th>Concentration ( \text{M.l}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pu-239</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stock</td>
<td>(0.139 \ 10^{-3} )</td>
<td>(0.66 \ 10^{-6} )</td>
</tr>
<tr>
<td>1:1</td>
<td>(0.078 \ 10^{-3} )</td>
<td>(0.37 \ 10^{-6} )</td>
</tr>
<tr>
<td>1:4</td>
<td>(0.030 \ 10^{-3} )</td>
<td>(0.14 \ 10^{-6} )</td>
</tr>
<tr>
<td><strong>Am-243</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stock</td>
<td>(1.52 \ 10^{-6} )</td>
<td>(1.30 \ 10^{-9} )</td>
</tr>
<tr>
<td>1:1</td>
<td>(0.85 \ 10^{-6} )</td>
<td>(0.73 \ 10^{-9} )</td>
</tr>
<tr>
<td>1:4</td>
<td>(0.51 \ 10^{-6} )</td>
<td>(0.22 \ 10^{-9} )</td>
</tr>
<tr>
<td><strong>Eu-152</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stock</td>
<td>(0.47 \ 10^{-3} )</td>
<td>(4.8 \ 10^{-9} )</td>
</tr>
<tr>
<td>1:1</td>
<td>(0.20 \ 10^{-3} )</td>
<td>(2.0 \ 10^{-9} )</td>
</tr>
<tr>
<td>1:4</td>
<td>(0.11 \ 10^{-3} )</td>
<td>(1.1 \ 10^{-9} )</td>
</tr>
</tbody>
</table>

**TABLE 2** Start concentrations of the radionuclides used in the adsorption experiments.
S. BONOTTO

In sediments bacterial growth would be affected by temperature which could be the influence of a bacterial population on the observed Kd of the sediment?

L.A. GELDERMALSEN

Elevated temperatures of the sediments will certainly have a positive influence on the bacterial growth. This growth and other changes of chemical characteristics due to high temperatures during a prolonged period of time does probably influence sorption properties of the sediment. Other studies are inquiring this. It was the intention of this study to bring temperature-dependent adsorption data into the temperature induced migration model around a canister and I think that even when growth or other chemical changes occur the data are still an approach of the field situation and are usable in the model.