# THE INFLUENCE OF HUMIC ACID ON THE MIGRATION PROPERTIES OF RADIONUCLIDES

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# THE INFLUENCE OF HUMIC ACID ON THE MIGRATION PROPERTIES OF RADIONUCLIDES

By

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# DECLARATION

This dissertation reports original research carried out in the Radiochemistry Department at the South African Nuclear Energy Cooperation (NECSA) in collaboration with the Centre of Applied Radiation Science and Technology (CARST) at the North West University (Mmabatho) between 2003 and 2004. It has not been submitted in part or in whole for a degree at any other university. Data presented here are original, and any other sources of data acquired through collaborative activities are fully acknowledged.

I. SEKOKO

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- Special thanks to the Almighty, the one who said "I have plans for you, plans that will not harm you but prosper you.
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# ABSTRACT

The storage or disposal of nuclear waste is one of the major concerns faced by governments, communities, and environmentalists. This radioactive waste, as a source of ionising radiation, represents a potential hazard to human health and must be carefully managed so as to reduce the associated risks to acceptable levels for both now and in the future. The migration of radioactive waste (radionuclides) in the environment is controlled by many factors, such as the interaction of the radionuclides with soil.

Humic acid (plant material) has substantial chelating properties for metal ions and can therefore considerably affect the migration behaviour of radionuclides in a soil layer. To manage the radioactive waste effectively, it is important to know the presence and interaction of humic acid with radionuclides released from radioactive waste repositories. The aim of this study is therefore to investigate the influence of humic acid on the distribution coefficients of radionuclides found in both Thabana and Vaalputs waste repositories.

The technique employed in this study is based on a laboratory batch method to study the influence of humic acid on the distribution coefficients of $^{131}I$ and $^{137}Cs$ on soil samples from Thabana and Vaalputs waste repositories at different concentrations. The results of this study show that $^{131}I$ and $^{137}Cs$ do not form any complexes with humic acid and therefore the presence of humic acid does not have a significant effect on the migration of $^{131}I$ and $^{137}Cs$.

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## Glossary of Terms

| | |
|---|---|
| Complexation : | Complexation or complex formation is the term used for a compound formed when a metal ion combines with an electron donor. This term is commonly used to refer to all types of interactions resulting in compound formation. If one or more ligands contain two or more donor groups, then the resulting structure is termed a chelate. |
| Colloids: | Solid material, limited to particle size of range smaller than 0,00024 mm (smaller than clay particles), in suspension. |
| $K_d$ values: | Distribution coefficients/partition coefficients ($K_d$ values) are a measure of sorption of contaminants into or onto soils and are defined as the ratio of the quantity of the adsorbate adsorbed per unit mass of a solid to the amount of the adsorbate remaining in the solution. The distribution coefficient or $K_d$ value is simply given by:<br>$K_d = C_{solid}/C_{solution}$ |
| Fulvic acid: | An alkaline-soluble portion of the degradation products from vascular plants that is generally of low molecular weight and does not precipitate at low pH. |
| Humic acid: | An alkaline-soluble portion of the degradation products from vascular plants that is generally of high molecular weight and precipitates at low pH. |
| Humic Complexation: | Also known as complex formation, and is the interaction of dissolved cations with humic acid molecules. |
| Low-level waste: | Waste containing enough radioactive material to require action for the protection of people, but not so much that it requires shielding in handling or storage. |
| Intermediate-level waste: | Waste requiring shielding. If it has more than 4000 Bq/g of long-lived (half-life of over 30 years) alpha emitters it is categorised as "long-lived" and requires more sophisticated handling and disposal. |

| | |
|---|---|
| High-level waste: | Waste that is sufficiently radioactive to require both shielding and cooling, that generates >2 kW/m$^3$ of heat and has a high level of long-lived alpha-emitting isotopes. |
| Radioactive waste: | Material that contains or is contaminated with radionuclides at concentrations or activities greater than clearance levels as established by the NNR (National Nuclear Regulator), and that has no use.<br>Radioactive waste can be classified according to radiological properties (quantity and type of radioactivity), physical properties (form in which the material occurs, i.e. gas, liquid or solid) and also whether it is heat producing or not. The hazard involved as well as the final disposal methods to be used for the waste also plays a part in the classification. |

## Symbols and Abbreviations

| | |
|---|---|
| BF | Backfill material |
| Bkrnd | Background |
| Calc | Calcrete |
| Gamma Spec | Gamma spectroscopy |
| Ha | Humic acid |
| Hs | Humic substance |
| ILW | Intermediate-level waste |
| LLW | Low level waste |
| RC | Red clay |
| ORNL | Oak Ridge National Laboratory |
| Rdncld | Radionuclide |
| Std | Standard |
| UV/VIS Spect | Ultraviolet-Visible Spectrophotometer |

# CHAPTER 1

# INTRODUCTION

# 1. INTRODUCTION

The storage or disposal of nuclear waste is one of the major concerns faced by governments, communities, and environmentalists.

Radioactive waste, as a source of ionising radiation, represents a potential hazard to human health and must be carefully managed so as to reduce the associated risks to acceptable levels both now and in the future. Radioactive waste disposed of in a repository should be isolated from the biosphere during the operational phase as well as during the phase referred to as the institutional control period.

Vaalputs is a national, near-surface, radioactive waste management facility that serves South Africa's needs for disposing of low- and intermediate-level short-lived radioactive waste generated by the Koeberg nuclear power station. Based on the proposed radionuclides inventory, the institutional control period must be three hundred years for this near-surface repository.

Vaalputs is situated some 100 km southeast of Springbok (600 km north of Cape Town) in the Northern Cape Province (Figure 1.1). It covers an area of about 10 000 ha, measuring 16,5 km from east to west and 6,5 km from north to south at its narrowest point and has a mean elevation of about 1 000 m above sea level. Namaqualand is characterised by rugged granite terrain with a well-developed drainage system towards the west. Bushmanland, on the other hand, is extremely flat, often with ill-defined drainage systems and is characterised by gently undulating consolidated sand dunes. Namaqualand falls within the winter rainfall area, with characteristic succulent vegetation, whereas Bushmanland falls within the summer rainfall area, with its own distinct flora of woody shrubs and grass. The climate is harsh and in summer the temperature can soar to 40 $^0$C or higher, whereas in winter freezing conditions and winds with a high chill factor are often experienced. Rainfall at Vaalputs is bimodal, with an annual average of about 74 mm per year. [*http//nlmjanp/nlmonline/vaalputsgallery.htm*]

The soil characteristics at Vaalputs are regarded as "clayey" due to the smectite, illite and koalinite present in the soil, together with large concentrations of chlorides and sulphates.

# VAALPUTS

**National Radioactive Waste Disposal Facility**

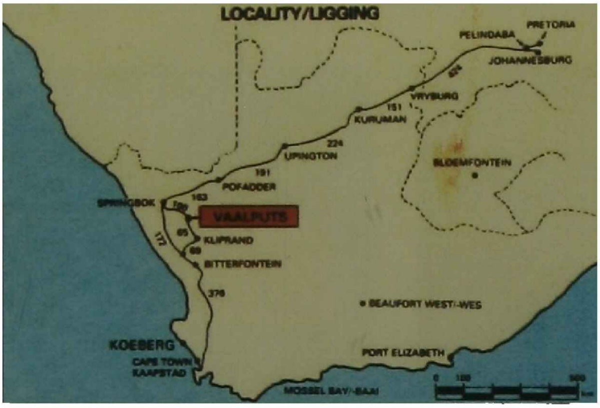


Figure 1.1: Vaalputs national waste repository.

The disposal of radioactive waste at Vaalputs is based on a multiple-barrier concept. The metal drums (LLW) and the cement drums (ILW) that are used for containing waste act as primary barriers. These containers are placed in a trench, which is then filled with backfill material consisting of a mixture of clays (Figure 1.2).

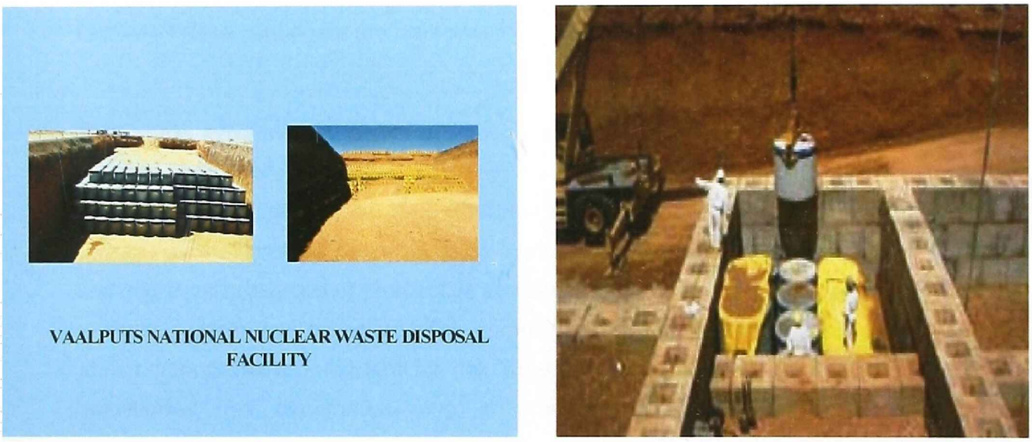


Figure 1.2(A): Cross-sectional diagram of waste disposal at Vaalputs showing the placing of cement drums in trenches before filling the trench and covering it with clay.

Figure 1.2(B): Cross-sectional diagram of waste disposal at Vaalputs showing the placing of cement drums in trenches before filling the trench and covering it with clay.

Another site in Pretoria, known as "Thabana", acts as a temporary storage facility for containers containing trans-uranic waste, radioactive waste from hospitals, industrial and agricultural waste, as well as radioactive waste from other research institutions such as universities. The disposal of radioactive waste at Thabana is currently by means of a multiple-barrier concept, where metal drums and metal pipes used for containing waste act as primary barriers. These containers are embedded in a shale environment.

This shale environment contains various plant residues, resulting in the possible formation of humic acid by means of a biological decaying mechanism. According to literature (Chapter 2) humic acids can form colloidal complexes with metals, resulting in an increase in the solubility, availability and migration properties of radioactive species through the environment when a waste container is breached. The complexation behaviour of humic acid with radionuclides is important for risk assessment of future nuclear waste repositories, the decommissioning of uranium mines, as well as for remediation and restoration of contaminated sites.

The information regarding the migration rate of radionuclides in these soils after deposition is important for several ecological reasons. Firstly, this rate controls the resident time of the gaseous radionuclides in the topsoil layer from where it can be released into the environment. Secondly, the rate of migration also determines how long the radionuclides will remain in the root zone of the soil where they can be taken up by plants and released to the environment, and thirdly, this rate determines the time period before the radionuclides reach the groundwater.

The influence of humic substances on the distribution coefficients of radionuclides is one of the most important parameters in determining the fate of radionuclides and for the treatment of these bonded pollutants in order to limit the migration in geological waste repositories. Many investigators have studied the migration of radionuclides by determining the distribution-coefficient values under the environmental conditions associated with the area of interest, and incorporating these values into migration models for safety assessment purposes. Unfortunately, literature results may not be applicable to Vaalputs because of the huge concentration of chlorides and sulphates present in the soil that could influence the radionuclide-humic interactions. It is also uncertain if the literature results would be applicable to Thabana owing to the large iron content in this shale environment.

For the determination of the interim safety of Thabana (shale environment) and the feasibility of the disposal of humic contaminated waste at Vaalputs, it is necessary to study the absorption behaviour of humic acid into different soils from Thabana and Vaalputs as well as the influence of this "affected" soil on migration properties.

In this study, the main emphasis will be on the interaction of a commercially available humic acid with soil and radionuclides, and its effect on the migration properties of radionuclides found at the nuclear waste repositories in South Africa (i.e. Thabana and Vaalputs). The research involves:

- Determining humic acid in soils and water samples from Thabana and Vaalputs
- Determining the absorption of commercially available humic acid into soil samples from Thabana and Vaalputs
- Determining the absorption of radionuclides into Thabana and Vaalputs soils
- Determining the absorption of radionuclides into experimentally humified soil samples from Thabana and Vaalputs
- Determining the absorption of humic-radionuclide complexes into Thabana and Vaalputs soils
- Investigating the influence of pH on the sorption behaviour of humic-radionuclide complexes

The results of this study will be used to determine the impact of humic acid on the migration/sorption behaviour of radionuclides. Based on these results, a decision can be made regarding the interim safety of Thabana (shale environment) and the feasibility of the disposal of humic contaminated waste at Vaalputs.

# CHAPTER 2

# LITERATURE STUDIES

# 2. LITERATURE STUDIES

## 2.1 Distribution Coefficients

### 2.1.1 Distribution-coefficient determinations

Adsorptions of dissolved radionuclides onto backfill in a waste repository (distribution coefficients/partition coefficients [$K_d$ values]) are used in transport and risk assessment modelling advective-dispersive equations.

Distribution-coefficient/partition-coefficient values ($K_d$ values) are defined as the ratio of the quantity of the adsorbate adsorbed per unit mass of a solid to the amount of the adsorbate that was present in the solution (*Liu et al* 1982).

The $K_d$ parameter is kinetically fast, reversible and independent of concentration of the sorbing solute and can be determined as follows:

$$K_d = C_{solid}/C_{aqueous} \quad (1)$$

The $C_{solid}/C_{aqueous}$ refers to solute concentration in the solid and aqueous phases respectively.

In dynamic models, sorption causes retardation of the nuclide relative to the transport of an ideal, non-interacting tracer. For this type of transport, a retardation factor can be defined as:

$$R = V_i / V_n \quad (2)$$

whereby V represents the mean advective velocity for either an ideal tracer ($V_i$) or the sorbing nuclide ($V_n$). For a porous solid with porosity $\varepsilon$, and specific density $\delta$ (kg.m$^{-3}$), the retardation factor can be described as:

$$R = 1 + K_d (1 - \varepsilon)\, \delta \quad (3)$$

It is therefore necessary to determine $K_d$ values in order to find:

- The resident time of the gaseous radionuclides in the topsoil layer from where it can be released into the environment
- The time period for radionuclides in the root zone of the soil where they can be taken up by plants and released to the environment
- The time period before the radionuclides reach the groundwater

Different absorption mechanisms into solids are possible, as indicated in Figure 2.1, and the distribution/partition coefficient ($K_d$) value is a summation of these different processes.

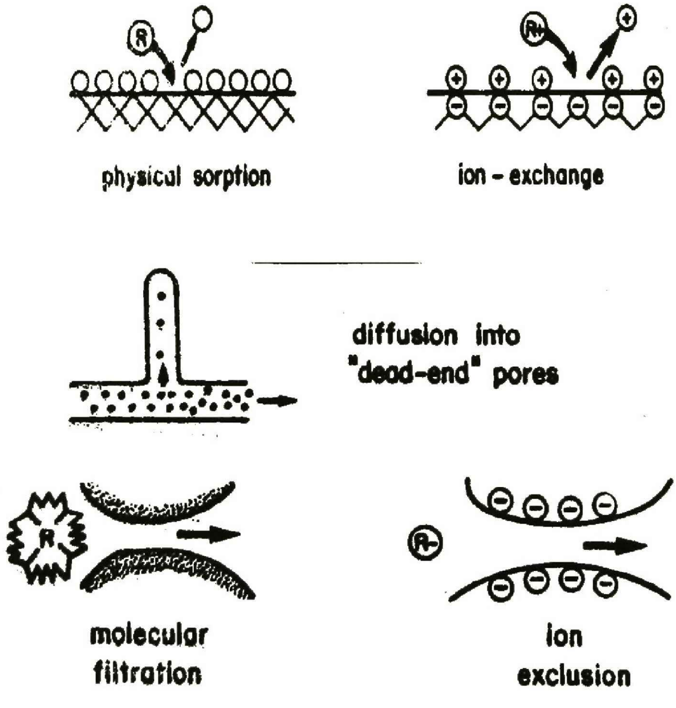


Figure 2.1: Different absorption mechanisms into solids

Other factors that may also influence $K_d$ values are: soil types, soil absorption sites available, presence of particulate matter and colloids, radionuclide concentration and the speciation of the contaminant in aqueous solution (*Johnson et al*). This therefore indicates that literature $K_d$ values are only valid for the mineralogy and geochemical conditions under which they were determined. It is therefore necessary to determine site-specific $K_d$ values (aqueous and geological conditions of the system) for Vaalputs/Thabana in order to model the migration of radionuclides through these waste repositories.

The general methods for determining $K_d$ values are: laboratory batch method, in-situ batch method, laboratory flow-through method and field-modelling methods.

At the recent Migration 2003 conference the need was expressed to standardise the determination of $K_d$ values in order to compare international values. The aspects that influence the determination of $K_d$ values and that need to be standardised are:

### 2.1.2 Concentration limitations

*Choppin (2003)* states that $K_d$ values in "older" databases are possibly incorrect because a macroscopic approach was followed (owing to instrument limitations) instead of the preferred nanoscopic approach. Under macroscopic conditions the use of high tracer concentrations could result in complex formation, precipitation and colloid formation that would negatively affect the distribution/partition coefficient ($K_d$) values. In a nanoscopic approach the tracer concentration is limited to $10^{-6}$ M, in order to limit the formation of colloids, complexes and precipitation reactions. *Choppin* therefore recommends that $K_d$ values should be determined using a nanoscopic approach (Tracer levels lower than $10^{-6}$ M).

*Alexander (2003)* indicates that the $K_d$ results for different uranium isotopes generated from "older" simplistic models have orders of magnitude different to those of experimental values. Results from second-generation models, which produce output parameters with less physical significance, are also questionable because, for instance, the calculated retardation factor also includes precipitation reactions. *Alexander* indicates in Figure 2.2(a) (based on literature values), that the sorption isotherm ($K_d$ values) tends to "plateau" with increasing tracer concentration. He suggests that $K_d$ values should be determined in the linear section of the absorption characteristics of an absorption site that corresponds to a tracer concentration lower than $10^{-6}$ M.

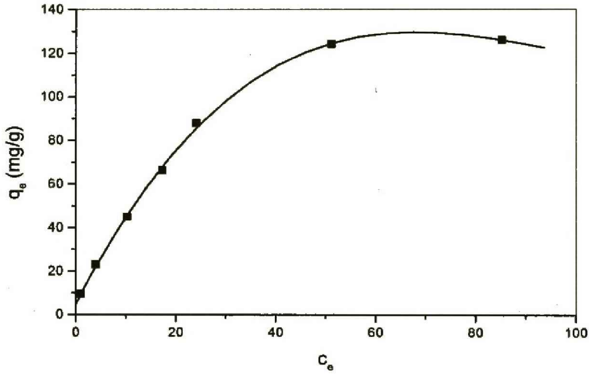


Figure 2.2(A): Linear section of the absorption characteristics of the absorption sites (*Alexander* (2003)).

*Wilson et al (2003)*, studied the sorption of Pu(Vi) into/onto magnetite by varying the pH (species) and plutonium concentrations. The results in Figure 2.2(B) indicate that Pu absorption decreases as the initial tracer concentration increases. As no evidence of any $PuO_2$ precipitation was observed, this lowering of absorption with increased tracer can be attributed to complex-formation.

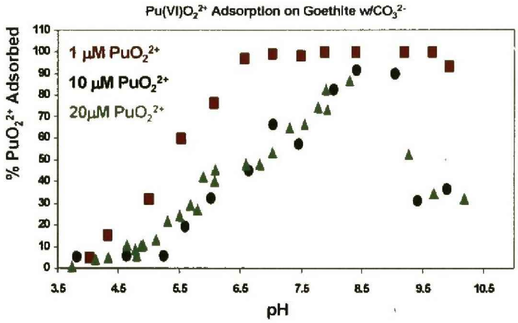


Figure 2.2(B): Adsorption of Pu (VI) $O_2^{2+}$ onto magnetite (*Wilson et al*, 2003).

*Lützenkirchen (2003)* studied the adsorption of uranyl onto quartz and compared the experimental results with theoretical results from surface complexation models. The results, see Figure 2.3, indicate that the modelled and experimental results correspond perfectly and that at lower uranyl concentration the highest adsorption onto quartz was measured. As in the previous study, this can be attributed to complex-formation.

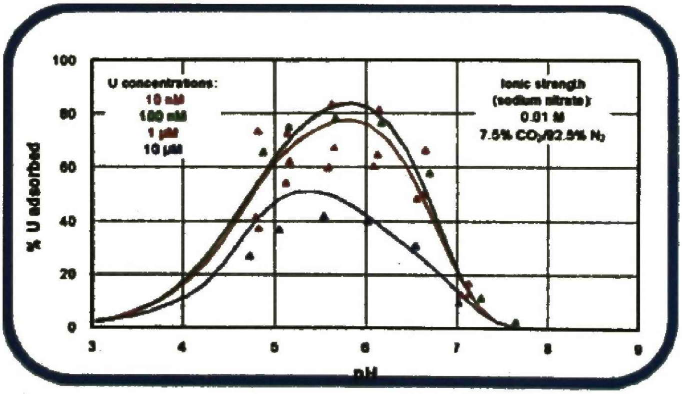


Figure 2.3: Modelling uranyl adsorption onto quartz - a comparative study between different surface complexation models and experimental data (*Lützenkirchen* (2003)).

### 2.1.3 Ionic strength

During the determination of $K_d$ values it is necessary to keep the ionic strength of the solution constant during the absorption process in order to eliminate any concentration gradients that could influence the absorption mechanisms. From literature results it is clear that $NaClO_4$ is the preferred ionic buffer.

*Missana et al (2003)* studied the absorption behaviour of cesium into FEBEX smectite at different ionic strengths. The experimental results from this study were compared with a surface complexation model and the results, see Figure 2.1.3(A), clearly indicated that there was an excellent correlation between the experimental and the modelled results. Another observation from the results is that the higher the concentration of the added ionic buffer, the lower the absorption. *Missana* explained this tendency (Figure 2.4(A) and 2.4(B)) as that a high ionic strength influenced the charge on the surface of the smectite, thereby influencing the absorption into the smectite.

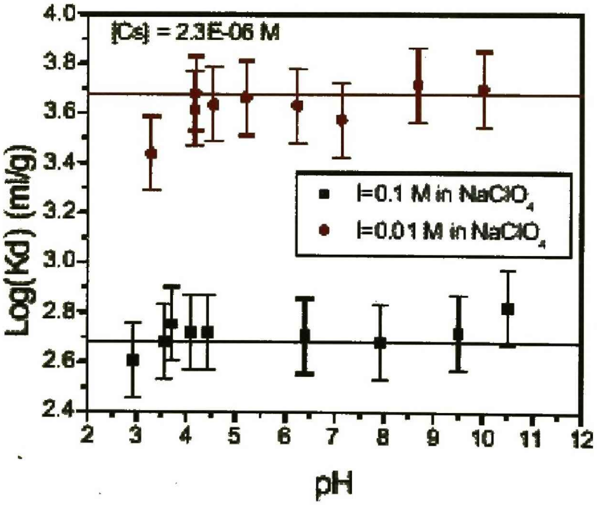


Figure 2.4(A): Sorption properties of Cs at different Ionic strengths onto/into smectite (*Missana et al.*)

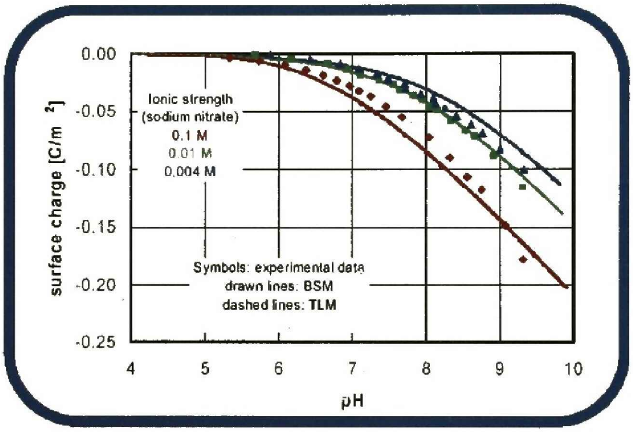


Figure 2.4(B): Influence of ionic strength on the surface charge of smectite (*Missana et al* (2003)).

### 2.1.4 Volume to solid ratio

*Lee et al (2003)* studied the absorption of uranium into compacted bentonite. The results indicated a decrease in the absorption of uranium with increasing dry bentonite. *Lee* explained this result as follows: the absorption of uranium into compacted bentonite depends on the presence of an anion exclusion mechanism, the size of uranium species in the solution, the charge on the bentonite surface, the porosity of the compacted bentonite, as well as the pore size of the compacted bentonite. He postulated that by increasing the dry mass for compaction, the resulting increase in the density of bentonite reduced the porosity as well as the pore size volume, thereby reducing the absorption into compacted bentonite.

*Tao et al (2003)* studied the absorption of cobalt in peat and the results, see Figure 2.5, indicated that the distribution coefficients for cobalt on peat decreased with increasing concentration of tracer.

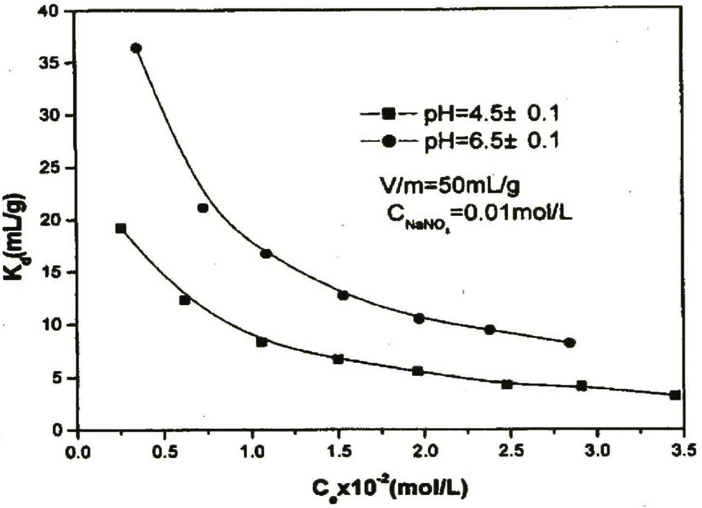


Figure 2.5: Distribution coefficients for cobalt on peat (*Tao* (2003)).

### 2.1.5 Formula to calculate $K_d$ values

Distribution coefficient/partition coefficient values ($K_d$ values) are defined as the ratio of the quantity of the adsorbate adsorbed per unit mass of a solid to the amount of the adsorbate that was present in the solution. The $K_d$ parameter is kinetically fast, reversible and independent of the concentration of the sorbing solute and can be determined as follows:

$$K_d = C_{solid}/C_{aqueous} \qquad (4)$$

For a porous solid with porosity $\epsilon$, and specific density $\delta$ (kg.m$^{-3}$), the retardation factor can be described as:

$$R = 1 + K_d\,(1 - \varepsilon)\,\delta \qquad (5)$$

At the recent Migration 2003 conference the need was expressed to standardise the determination of $K_d$ values in order to compare international values. In order to standardise the formula for calculations, *Dr. M. Masayuki* (1998) (Japan) proposed the following calculation algorithm:

$$K_d(m^3/kg) = \frac{(C_0 - C)}{C} * \frac{V}{W}$$

where:

$C_0$: Initial concentration ($Bq/dm^3$)

C: Final Concentration ($Bq/dm^3$)

V: Volume of the solution ($m^3$)

W: Weight of rock sample (kg)

In order to standardise the $K_d$ value determinations in porous structures *Dr. A.M. Jacobson et al (2003)* and *Dr. M.H. Baik et al (2003)* proposed the following formula:

$$Kd = \frac{([U_i]-[U_s])}{U_s} * \frac{10^3}{A(m)}$$

where:

$K_d$: Surface sorption coefficient

$[U_I]$ : Initial concentration of U

$[U_s]$ : Concentration of uranium in the solution phase

A ($cm^2$): Specific surface area of the mineral or uranium

m (g): Mass of the sample

Owing to the low specific surface area of the slate and Vaalputs clay it was decided to use the following proposed method (*Masayuki* (1998)) for this study:

$$K_d(m^3/kg) = \frac{(C_0 - C)}{C} * \frac{V}{W}$$

### 2.1.6 Recommended experimental method for measuring $K_d$ values

The general methods for determining $K_d$ values are: laboratory batch method, in-situ batch method, laboratory flow-through method and in-situ field method. At a recent conference ("Migration 2003") the need was expressed to standardise the experimental method of $K_d$ determination in order compare future international published values.

Dr. T Yamaguchi – Japan Atomic Energy Research Institute for $K_d$ Determinations, recommended the following experimental method:

- Prepare a solution with tracer concentration at nanoscopic level under a controlled atmosphere.
- Confirm the concentration of dissolved tracer (e.g. uranium) after 24 hours and after 48 hours in solution before experimentation to confirm equilibrium conditions.
- Add ionic buffer to preserve pH during experimentation.
- Perform absorption experiment.
- Confirm tracer concentration after 24 hours and 48 hours of contact with solid to confirm equilibrium conditions.
- Pass solution through a filter system to remove colloids and solid particles.
- Determine the $K_d$ values in solution in accordance with the method proposed by *Dr. M. Masayuki* by summarising every individual specie.

In this study the above experimental method was followed, except that the solution was centrifuged instead of filtered before determining the $K_d$ values. This change was necessary as small clay particles blocked the filters during the separation step.

## 2.2 Humic Substances

Humic substances are organic poly-electrolyte macromolecules found throughout the world and they derive from post mortal material such as rotten plants and dead animals (*Johnson (1978)*). They are probably the most widely distributed organic material products. The concentration of humic substances in soil is dependent on factors such as climate, pH, substrate material, topography and decay time. In soil the humic content varies from 0% to almost 10%. However, in water the humic content is measured as dissolved organic carbon (DOC), which can be up to 50 ppm in dark water swamps (*Jackson et al* (1978) and *Choppin* (1988)). *Higgo et al (1992)* indicated in his literature that humic substance comprised up to ~80% of dissolved organic carbon (DOC) in natural waters, and that they were known for their high complexation affinities.

Originally, the occurrence and nature of humic substances were regarded as issues of primarily academic interest. This situation has changed dramatically since studies of humics have gained recognition as important contributors to environmental science. Humic substances are affected by a number of biological and chemical transformation mechanisms, including microbial processes and photochemical degradation reactions. Some different roles of humic substances in the environment are specified by *Allard et al (1989)* as follows:

- A complexing agent or adsorbent for man-made pollutants (radionuclides)
- A complexing agent or adsorbent for naturally occurring substances
- A precursor of toxic substances in technical processes
- A precursor of toxic substances in natural processes
- A complexing agent for different heavy metals
- Interaction with biologically active substances, thereby modifying their impact on the environment

Humic matter is divided into three components, which are defined according to their solubility, namely:

- Humic acid: Soluble above a pH of approximately 3.5 (i.e. insoluble at pH values of less than 3.5)

- Fulvic acid: Soluble in both acidic and basic solutions (i.e. at all pH values)
- Humin: Insoluble at all pH values

### 2.2.1 Structure of humic acid

Humic acid has a high molecular weight (ranging from ten to several thousand daltons) and contains carboxylic, phenolic, amino and quinine groups. Aromatic nuclei of a low degree of condensation are also incorporated into parts of non-aromatic character (*Jackson et al* (1978*)*.

The structure of humic acid is distinctive in that it forms different biodegradation mechanisms. Recently chemically synthesised humic acid has been manufactured by different companies by using the same starting material and the synthesised molecules of humic materials, which share some structural and chemical characteristics (Table 2.1). Humic substances are complex, multi component structures, and cannot be described in specific molecular terms, but must rather be treated in a operational manner. This heterogeneity and the poly-electrolytic character of humic substances were not properly considered until a few years ago, and many problems remain unsolved (*Allard et al* (1989*))*. *Shin and Moon (1996)* proposed the structure in Figure 2.6 for the absorption of humic into clay particles.

The proposed structure in Figure 2.6 indicates that humic acid is a highly polymeric substance and can be characterised as a mixture of polymers containing aromatic and heterocyclic structures. The carboxyl and nitrogen groups in the structure react with metals, revealing the chelating properties as well as the buffering capacity of these humic complexes *(Czerwinski et al,* 1994 and *Rocha,* 1999).

# Clay mineral

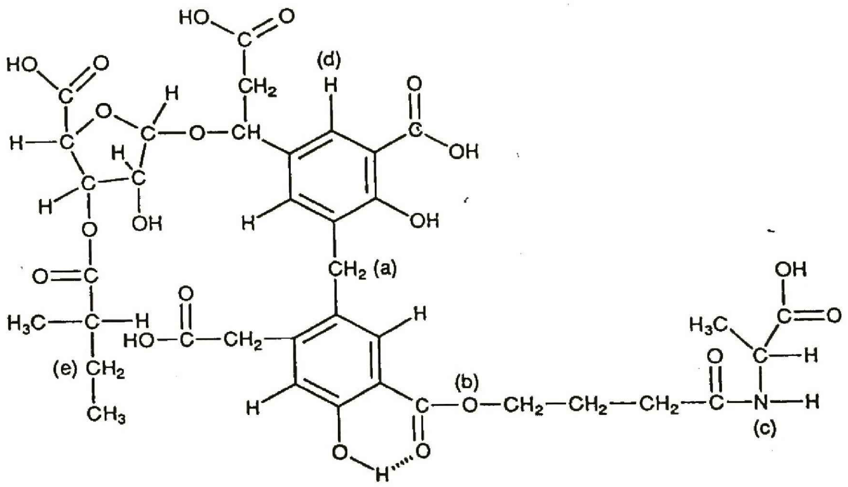


Figure 2.6: Proposed structure of humics absorbed into clay particles
(*Shin and Moon (1996)*).

**Table 2.1**: Elemental contents of commercial humic acids and selected humic acids from dopplerite, peat and leonardite.

| **Humic acid (Ha)** | ***C*** | ***H*** | ***O*** | ***N*** | ***S*** | ***P*** | ***Total*** | ***Ash (%)*** |
|---|---|---|---|---|---|---|---|---|
| K & K Ha | 63.25 | 5.17 | 32.22 | 0.68 | 4.49 | 0.15 | 106.0 | 22.48 |
| CPI Ha | 59.89 | 5.07 | 34.81 | 0.81 | 0.72 | <0.05 | 101.3 | 9.28 |
| Fluka-Tridom Ha | 65.79 | 5.51 | 37.79 | 0.71 | 3.16 | <0.05 | 113.0 | 32.82 |
| P & B Ha (Batch 1) | 63.88 | 5.69 | 35.23 | 0.80 | 3.04 | <0.05 | 108.6 | 24.77 |
| P & B Ha (Batch 2) | 62.84 | 5.38 | 34.99 | 0.80 | 3.68 | 0.05 | 104.9 | 15.01 |
| P & B Ha (Purified batch 2) | 61.87 | 4.45 | 28.92 | 0.89 | 3.35 | <0.05 | 99.5 | 4.44 |
| Aldrich Ha | 63.15 | 5.60 | 34.98 | 0.80 | 4.58 | <0.05 | 108.9 | 22.56 |
| Aldrich Ha Sodium salt | 68.98 | 5.26 | 43.45 | 0.74 | 4.24 | <0.05 | 122.7 | 31.21 |
| Aldrich (Purified to $H^+$ form) | 65.31 | 5.94 | 25.05 | 0.51 | 3.36 | <0.05 | 100.2 | 4.46 |
| Wyoming dopplerite | 61.16 | 4.39 | 43.59 | 1.61 | 2.36 | <0.05 | 113.1 | 31.02 |
| Irish peat | 60.70 | 5.22 | 32.59 | 1.29 | 0.90 | <0.05 | 100.7 | 1.05 |
| Leonardite Ha | 63.25 | 3.64 | 31.05 | 1.17 | 0.84 | <0.05 | 100.00 | 2.47 |

### 2.2.2 Complex-formation in solutions after humic-metal interactions

Humic substances are known to complex metal ions of groundwater constituents (e.g. $Fe^{3+}/Fe^{4+}$, $Ca^{2+}$), with the formation of colloidal matter as a final product (*Kim et al*, 1990). The description of metal-ion binding to humic substances is complicated for the following reasons:

- The stoichiometry of the reactions
- The competition between specifically bound ions
- The distribution of affinity constants
- The electrostatic interactions

Understanding humic-metal complexation is important in order to determine the fate of pollutants and contaminants in the environment. Humic acid acts as a negatively charged specie because of the ionisation of the acidic carboxylic and hydroxyl groups. Because of its negative charge, it is expected to interact with positively charged species to form complexes and to repel negatively charged anions. *Jackson et al* 1978 indicated that the metal-humate complex can be described as a polynuclear chelate with the cations binding predominantly onto the negatively charged ligand groupings in the humic acid's structure. The binding (interaction) of the metals is regarded as being predominantly ionic if the metals are very electropositive with low ionisation potentials for the valence electrons (*Livens*, 1991).

Although the interaction of metals with humic substances is regarded as being predominantly ionic, the binding can also be through a chelate interaction from the humic substance structure. The formation of this type of interaction between humic substances and chelatable metals in hazardous wastes depends for instance on the types of metal species, nature of humic substances, chemical types of metal species, structure of humic substances, chemical environment with respect to acidity-alkalinity, oxidation-reduction situation and the presence of competing species, e.g. calcium (Ca). (*McCarthy*, 1989).

Humic substances indicate that, of most functional groups present in humic acid, the carboxylic, hydroxyl and phenolic groups are responsible for the binding of metals (*Rocha*, 1999 and *Kupsch, et al*, 1996).

*Jackson et al*, 1978 indicated that humic acid contains two types of weak acidic groups: the carbonyl group that dissociates up to a pH range of 5–6 and the phenolic group that dissociates beyond pH 7. He also indicated that, at low pH, acidic and weakly acidic groups are thought to bind metals directly, but at a high pH, the metals form hydroxocomplexes that bind onto the humic acid.

*Czerwinski et al* (1994) indicated that the actinides interact strongly with oxygen donor sites in the humic acid structure. During this interaction, bound water is released and the electrostatic repulsion by the ionised anionic groups inside this macromolecule is reduced. This results in the formation of molecular aggregates that may lead to the formation of colloids. This type of colloid formation was confirmed by *Kim J.I et al* (1997), who indicated in his research that hydrolysis, carbonate complexation, colloid generation and other complexation reactions mainly govern the chemical behaviour of actinide ions in the presence of humic acid.

*Ephraim et al (1990),* studied the complex-formation of europium and cobalt with fulvic substances. He reported that these metals were selectively complexed by weakly acidic-phenolic groupings on the fulvic acid molecule.

### 2.2.3 Sorption studies involving humic acid in this study

The influence of humic substances on the distribution coefficients of radionuclides is one of the most important parameters in determining the fate of radionuclides and the treatment of these bound pollutants in order to limit the migration in geological-waste repositories. *Ibarra* (2003) indicated that the high values of radionuclide absorption into humic acid could pose a real problem regarding the mobilisation of radionuclides at a waste disposal site. Unfortunately, the values in the literature may be not applicable to Vaalputs due to the huge concentration of chlorides and sulphates that may complex the humic acid and influence the radionuclide-humic interactions. It is also uncertain whether the results can be applied to Thabana owing to the large iron content in this shale environment.

A short summary of available literature data is as follows:

*Benes et al (1998)* indicated that the absorption of uranium onto Cyprus clay at low pH conditions could be enhanced by the addition of humate. However, at higher pH values the addition of humate material suppressed the absorption. The results also indicated that at a fixed pH the absorption of uranium depended on the ratio of the uranium concentration to the amount of Cyprus clay. This result confirms the statements made in 2.1.3. A further interesting result is that, in the presence of a sufficient loading of humate (17 mg/g and more) onto clay, the uranium is mainly bound as an organic form of uranium-humate complex onto the surface of the clay mineral. In the absence of humic acid the uranium is absorbed directly via an ion exchange reaction into the clay.

Cesium in groundwater solution exists as cationic Cs over a wide pH and concentration range. It exists in the environment in a +1 oxidation state. Stable cesium is ubiquitous in the environment, with concentrations in soil of between 0.3 and 25 mg/kg, and the only stable isotope of cesium is $^{133}$Cs. Fission products include four (4) main cesium isotopes, with only $^{134}$Cs (half-life = 2.05 y), $^{135}$Cs (half-life = 3 * $10^6$ y and $^{137}$Cs (half-life = 30.23 y) occurring in significant concentrations 10 years after separation from nuclear fuels.

The aqueous speciation of cesium in groundwater is among the simplest of the contaminants being considered in this study. Cesium forms few stable complexes and is likely to exist in groundwater as the uncomplexed $Cs^+$ ion that adsorbs rather strongly onto most minerals, especially mica-like clay minerals (EPA, 1999, Vol. 2, pg. 46-49).

The extent to which the adsorption will occur depends on the concentration of mica-like clay minerals in the soil, and concentrations of major cations such as $K^+$, which has a small ionic radius as $Cs^+$. As part of a programme to investigate the interaction of actinide ions with humic acids, *Choppin et al*

*(1980)* studied the binding of calcium with humic acid. Calcium is a common cation in nature and will compete with the actinides for binding sites on humic acid.

According to EPA, vol. 2 (1999), there is little tendency of cesium forming complexes in soil/water environments, the formation of inorganic complexes is not a major influence on cesium speciation and the dominant aqueous species in most groundwater is the uncomplexed $Cs^+$ ion. Cesium can be associated with the OH-ions in a solution but the extension of this association cannot be estimated accurately. The uncomplexed Cs+ forms extremely weak aqueous complexes with sulphate, chlorite and nitrate.(EPA, vol. 2, 1999). EPA, vol. 2, pg. 47 also indicates that cesium will form weak complexes with humic materials because of low stability and the presence of competing cations (e.g. $Ca^{2+}$) at appreciably higher concentrations than that of cesium. EPA, vol. 2 also states that aqueous complexation of cesium is not thought to greatly influence its behaviour in most groundwater systems.

None of the common complex-forming agents found in groundwater (humic acid included) will form strong complexes with Cs.

*Lieser et al (1986.)* showed that $Cs^+$ ions can be absorbed into clay particles by means of an ion exchange mechanism.

In contrast with *Lieser's* results, *Fensenko et al (2001)* observed a nearly uniform $^{137}Cs$ distribution in upper horizons of hydromorphic humic soil. This indicates that high humic acid present in the soil could be responsible for the uniform distribution of $^{137}Cs$ in the soil. Studies by *Palágyi et al (2003)* showed that cesium has a lower migration rate (~five times lower) than strontium in arable top soils. This is attributed to the absorption of Cs into humic substances. Under deeper soil conditions the migration rate of $^{137}Cs$ increased, indicating an absence of humic substances.

EPA, vol. 2, 1999 indicated that mica minerals such as illite and vermiculite, which are present in the Vaalputs soil, tend to absorb cesium between their structural layers. It has been shown that such minerals tend to exhibit a very high selectivity for $Cs^+$ over other cations existing at much higher concentrations.

The data obtained by *Mc Henry (1954)* on the effect of cesium concentration and pH on cesium adsorption by calcareous soil containing mica-like minerals has been revised by the EPA, which indicated that the trace cesium concentration is essentially completely adsorbed above pH 4, and when placed in a high salt solution (e.g. 4 M of NaCl ), only 75% of the trace cesium was adsorbed and the adsorption was essentially independent of the pH over a wide range.

EPA, vol. 2 also indicates that cesium may also adsorb onto iron oxides and that those oxides do not fix cesium as mica minerals do, but instead they complex cesium to sites where abundance is pH-dependent.

In the soil many mica-like minerals have been weathered away, leaving minerals with a more pH-dependent charge. As the pH decreases, the number of negatively charged complexation sites decreases. It was emphasised that cesium formed weak complexes with humic materials or naturally occurring organic materials (EPA, Vol. 2, 1999).

Cobalt is found in waste repositories and it has a half-life of 5,272 a. Radioactive $^{60}Co$ is an important constituent found to migrate in waste repositories. *Ephraim et al* studied the complex-formation properties of natural organic acids and indicated that cobalt, zinc and europium were selectively complexed by the phenol grouping on the fulvic acid molecule. They assumed that a 1:1 cobalt-humic acid complex formed.

*Baek et al (2003b)* studied the sorption, desorption and migration of cobalt in the presence of humic substances onto clay. Results from this study indicate that cobalt interacts with the carboxyl groups in humic substances, and forms humic-cobalt complexes. It was also indicated that the surrounding pH has an effect on the solubility of humic substances. In acidic conditions, the carboxyl groups in humic substances undergo protonation, and cannot form complexes with cations such as cobalt and cesium.

*Kim et al (2003)* investigated the feasibility of using humic acid as a complexing agent for the removal of cobalt from waste streams. The equipment that was used to study the influence of the solution conditions such as pH, electrolyte and counter ions on the process is illustrated in Figure 2.7.

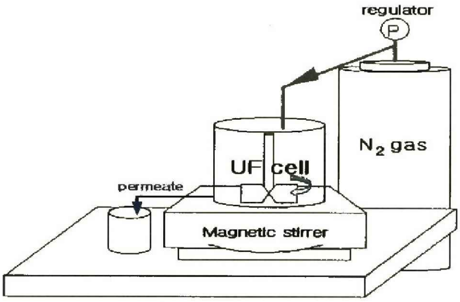


Figure 2.7: Equipment used by *Kim et al* (2003) to study the complexation of cobalt with humic acid.

The results from the study by Kim *et al* (2003) indicate that the removal of cobalt in solution increases with increasing humic substances (HS) (Figure 2.8). The apparent reason for this increase is the increased number of binding sites available for cobalt complexation. The results also indicate that cobalt removal increases when the pH increases from 4 to 8. This increase in complexation was attributed to the increase in the solubility of humic acid as well as cobalt hydroxide precipitation.

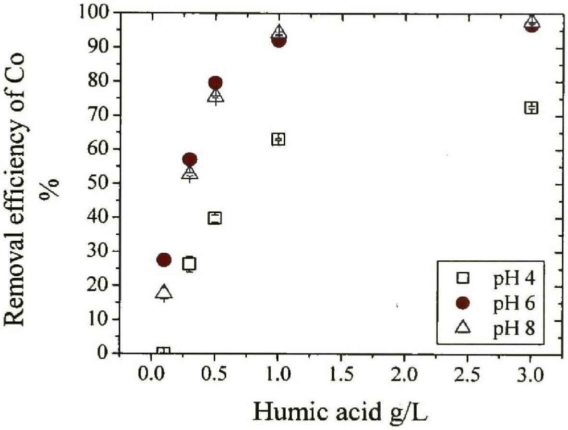


Figure 2.8: Representation of the effect of pH on cobalt removal (*Kim et al* (2003)).

*Dunigan* studied the effect of $^{85}$Sr, $^{60}$Co, and $^{137}$Cs absorption into humic acid. His results indicate that as the pH increases, an increasing amount of Sr is absorbed into the humic acid through complex-formation.

$^{99}$Tc is of great importance in nuclear waste disposal studies because it has a potential of contaminating the geosphere due to its very long half-life ($^{99}$Tc: (2.1*10$^{5}$ y) and high mobility. In the presence of a reducing solid phase that can act as an electron donor, the solubility can be limited by the reduction of a pertechnetate followed by the formation of a surface precipitate with low solubility. *Geraedts et al (2003)* indicated that, in the presence of dissolved organic substances like humic acid, the solubility of Tc is enhanced owing to the formation of mobile Tc-humic complexes. The mechanism involved is that the pertechnetate is reduced to Tc (IV) under reducing conditions and then combines with humic substances to form $TcO_2$–humic complexes..

*Sakamoto Y et al* (2003) also studied the influence of humic acid on the sorption behaviour of $^{99}$Tc on geological materials. Results indicated a decrease of distribution coefficients of $^{99}$Tc and $^{237}$Np on granite and tuff if the concentration of humic substances increases. This reduced absorption (Figure 2.9) is due to the formation of mobile Tc (iv) or Np (iv)-humate/fulvate complexes. The metal-humate complexes as proposed by *Sakamoto et al* are indicated in Figure 2.10.

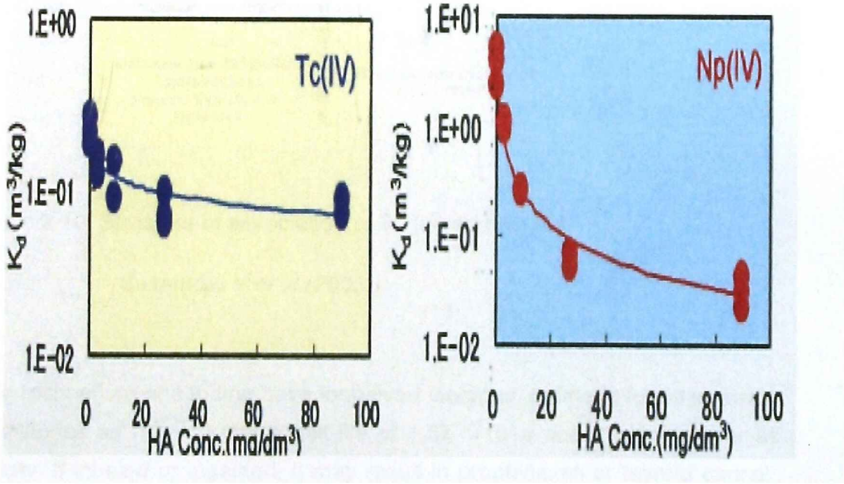


Figure 2.9: Influence of humic substances on sorption behaviour of $^{99}$Tc (iv) and $^{237}$Np (iv) on geological material (*Sakamoto. et al, 2003*).

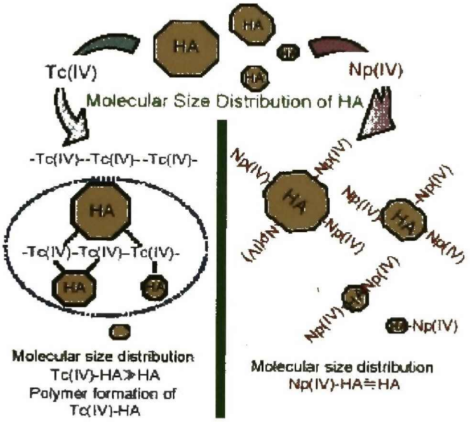


Figure 2.10: Structure of association of Tc (iv) and Np (iv)

*(Sakamoto Y et al (2003)).*

Both technetium and iodine have long-lived isotopes. Iodine is found in waste repositories as $^{129}$I. $^{129}$I has a half-life of 1,57 * $10^7$ a and it is known for its toxicity. If inhaled or ingested, it may result in prophylaxes or thyroid cancer. In our project, $^{131}$I was used instead of $^{129}$I. $^{131}$I and $^{129}$I are both isotopes. It is very difficult to study $^{129}$I using gamma spectroscopy as it gives minimum gamma rays compared with its isotope $^{131}$I. $^{131}$I was used as an anion and its interaction. *Torstenfelt et al (1985)* indicated that both iodine and technetium are anionic under oxidising conditions and therefore they would be expected to have only minor interactions with the solid phase and a mobility in water-saturated clay close to the self-diffusion of ions in dilute water solutions.

*Radcon (1988)* indicated that the interaction of radioactive iodine, e.g. $^{131}$I, with humic acid is independent of the pH (specie) and initial concentration of humic substances.

*Sakuragi et al* (2003) performed sorption experiments to study the uptake of Am(iii) and Eu(iii) in hematite (relevant to Thabana because of iron content in slate) in the presence of humic acid (Ha) in order to clarify the effects of ionic strength and pH on solid-solution partitioning in ternary Am(iii) /Eu (iii)-hematite-Ha systems. The results indicated that, in the absence of Ha,

Am(iii) /Eu(iii) sorption on pure hematite increased with pH and was insensitive to changes in ionic strength (Figure 2.11). However, in the presence of humic acid, the Am/Eu (iii) exhibited a constant retention of 100% over the whole pH region studied as well as at different ionic strengths.

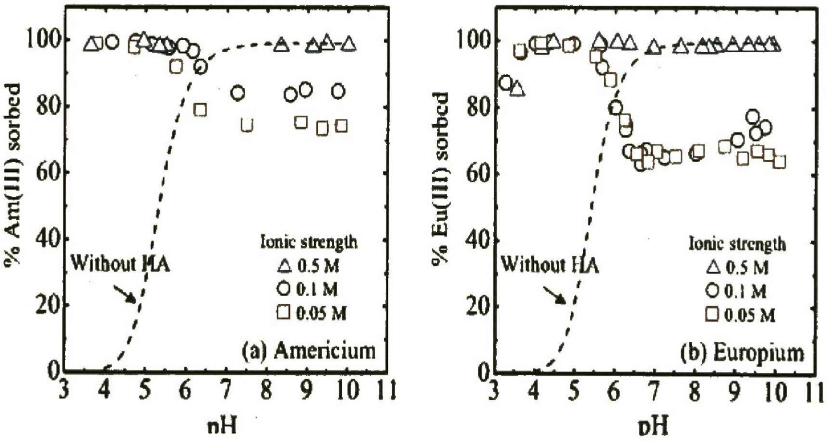


Figure 2.11: The effect of ionic strength on sorption of (a) Am(iii) and (b) Eu(iii) by hematite (1,0 g/dm$^3$) in the presence of humic acid as a function of pH (*Sakuragi et al* ).

*Tanaka et al (2003)* performed laboratory experiments to study the effects of humic substances on the mobility of $^{63}$Ni(ii) on packed granite or turf. Results indicated that a portion of $^{63}$Ni(ii) flowed through the column at the same rate as the injected influents, indicating that the transport of this $^{63}$Ni(ii) was not retarded. The amount of this non-retarding portion increased with increased concentration of humic substances in the influent. By determining the amount of Ni in the non-retarding portion, the schematic presentation of their results (Figure 2.12) indicated that humic acid as well as the humic-nickel complex did not absorb into granite, whereas nickel metal absorbed into granite. This result indicates that, in the presence of humic acid, non-absorbing complexes will form that will result in an increase in the migration rate of certain radionuclides.

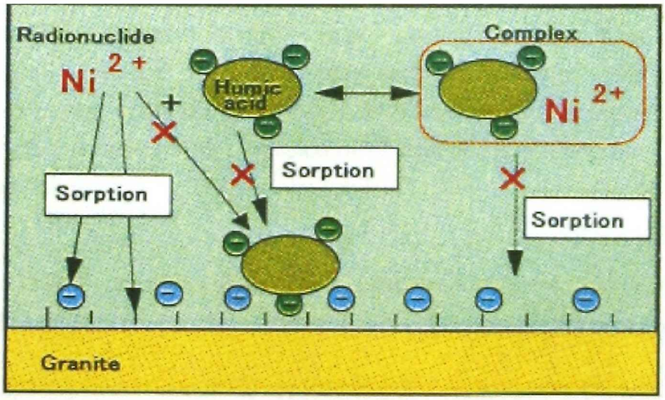


Figure 2.12: Sorption mechanism of Ni into granite in the presence of humic acid (*Tanaka T,* 2003).

*Moulin et al (1987)* studied the interaction of $Am^{3+}$ with humic acid and made the following remarks: "Actinides of all oxidation states (3+, 4+, 5+ and 6+) form strong complexes with natural organic humic and fulvic acids. However, actinide hydrolysis products (oxidation state 4+ species) and carbonate complexation of actinides (oxidation states 5+ and 6+) dominate over the formation of organic (humic) complexes". However, for trivalent actinides, humate complexes could be predominant and the effects on nuclide transportation would be most pronounced for this oxidation state. He also released a literature data review on the complexing properties of humic substances with actinides and cations present in groundwater.

$Pu^{6+}$ strongly form bicarbonate media by reducing $Np^{6+}$ to $Np^{5+}$ and $Pu^{6+}$ to $Pu^{4+}$ before forming complexes. Complexes between humic acid and uranium form without reducing $U^{6+}$ to $U^{4+}$. Therefore, the humic acid is not only effective as a reducing agent, but also complexes the 4+ and 6+ valence states. This humic-metal complex is very mobile. However, humic acid adsorbed strongly onto clay minerals, thereby reducing the actinide ions in groundwater.

Results by *Olofson* on the study of the absorption properties of actinide solutions ($Am\ (0H)_4^-$, $NpO_2\ (OH)_2^-$, and $Pu\ (OH)_5^-$) from low concentrations over a pH range from 3 to 12 into colloids indicated that Am and Pu were associated with colloid (>20 nm) formation in the pH range from 7 to 9. Np-colloid interaction was detected under similar conditions. This result was confirmed by the study done by *Kim* (1992), indicating that the anionic $PuO_2\ (OH)_3$ species absorb into colloids and that $Am(OH)_3$ increasingly forms complexes at pH >12.

*Choppin (1988)* observed that, in the presence of humic colloids, $U^{6+}$ was reduced to $U^{4+}$ and the reduced uranium was absorbed into humic colloids.

## 2.3 Influence of humic acid on colloid formation

Groundwater colloids occur naturally in all groundwater and they are composed of inorganic and organic molecular constituents or micro organisms and are chemically surface-active and readily absorb actinide ions, generating pseudocolloids of actinides. Colloids have a slow settling velocity and are transported over great distances. These colloids can increase the amount of actinides that can migrate in a natural aquifer system. Failure to account for this colloid migration as a potential vehicle for actinides can therefore lead to serious underestimates of the distances that actinides can migrate. Negatively charged colloids are expected to be more mobile than positively charged ones because a water matrix usually carries a negative charge. Mobile groundwater colloids that have been observed with a negative charge include organic molecules, layer silicates, silica-rich particles, bacteria, bacteria and iron oxide. They range in size from 10 mm to 10 µm.

Due to their high surface specific area per unit mass, they possess a high sorptive capacity for contaminants and are able to sorb onto solid surfaces (*James et al*). When humic molecule bind with metals, a less hydrophilic structures or aggregates are formed. If these aggregates are small enough (e.g. 45 ϒm), they may remain suspended in solution as colloids.

Humic colloids can also serve as a host for sorption of hydrolysed actinide ions onto the colloid surface, thereby forming "pseudocolloids". According to *Liesler (1986),* P. Paneth observed the formation of radiocolloids in the course of his studies on the separation of natural radioelements. The studies indicated that radiocolloids were formed in concentration ranges considerably lower than the concentration limits given by the solubility products.

*Picket et al (2003)* assessed the performance of the proposed US high-level waste repository at Yucca Mountain, as the potential effect of colloids on radionuclides transport needed to be considered (Figure 2.13). *Picket (2003),* indicated that modelled results showed that Pu would slowly desorb from colloids, and that this factor could enhance radionuclides migration.

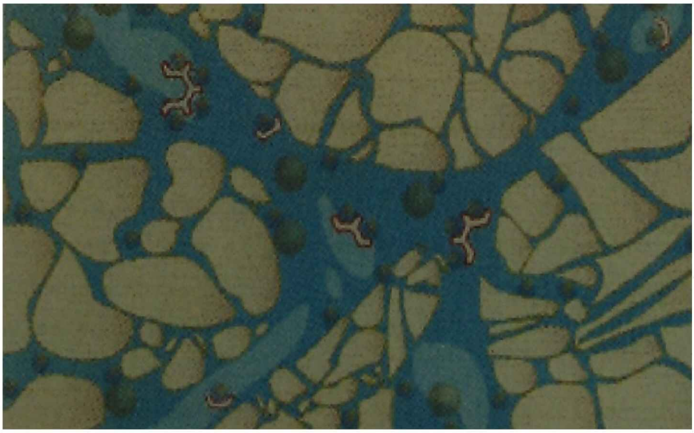


Figure 2.13: DOE illustration of conceptual model of colloid transport for use in performance assessment (*Picket D.A.*, 2003).

## 2.4 The influence of sulphate on the Vaalputs $K_d$ values

Owing to a known presence of sulphates and chlorides at Vaalputs, the influence of chlorides and sulphates needs to be accounted for. *Jackson et al 1978* described the interaction between sulphide species and organic species as complex. It was stated that the polysulphide ions serve as good acidity and redox buffers in reduced organic sediments. Reaction between humic materials and polysulphides serves to stabilise the organics by incorporating polysulphide chains into their structures. Polysulphides are strongly complexing ions in their own right and therefore their enhancing effects on the complexation properties of humic materials are likely to be significant. Interactions with metals would be expected to be strong and retentive against metal remobilisation. As the polysulphides are oxidised and soluble, subsequent aeration of such sediments would lead to the release of heavy metals (Jackson *et al* (1978).Humic material may also become more soluble and mobile as linking chains are destroyed.

## 2.5 Shale Environment

Shale makes up about half to three quarters of all sedimentary rocks on earth and it underlies more of the land surface than any other rock. Slate splits easily into thin plates along well-defined planes parallel to the original stratification (geocites.com) and the different settling processes that take place during sedimentation generally determine the different clay compositions in shale. Shale is formed from compacted mud and it contains widely variable amounts of minerals such as quartz, feldspar, clay minerals, rock fragments, calcite and occasionally other minerals. The degree of compaction in shale varies, e.g. younger, poorly sorted shale is less compacted than older varieties.

The clayey nature of shale gives it special geochemical significance as the small particles make it possible for colloidal processes and ion-exchange mechanisms to operate. For radioactive-waste consideration, an assessment of the organic matter present in the shale is important. It has been argued *(Meyer, 2001)/ (IAEA, 1983)* that the organometallic transport of radionuclides makes carbonaceous shale unattractive for consideration for a radioactive waste repository, yet it has also been argued that the reducing environment of these types of shale should be well suited for the retention of radionuclides and fission products. Examination of the rock cores recovered during the drilling of the injection well for the shale fracturing facility at Oak Ridge National Laboratory (ORNL) in *1983m,* shows that the shale is neither very porous nor very permeable. The measured permeability of cores of the disposal formation has values of 31 x $10^{-6}$ millidarcies in a vertical direction.

Investigations into the reducing characteristics of shale suggest that the reduced carbon and iron contents are sufficient to cause reduction and retention of any $M^{6+}$ actinides that might escape from hypothetically breached radioactive waste packages. Shale usually contains pyrite ($FeS_2$), which will interact with any $U^{6+}$ present, and the oxidised sulphur will trap any radioactive radium present.

The temperature distribution in the shale that results from the decay of injected radionuclides is a function of the specific activity of the waste, the orientation of the grout sheet, the total volume of waste injected, the thermal conductivity of the shale and the injection frequency. According to the IAEA (1983), the maximum allowable temperature in shale (before deterioration) is not exactly known. However, a mineralogical analysis of core samples and other evidence suggested that a temperature of at least 100 $^0$C, and probably higher, could be tolerated.

The shale surrounding the grout sheet at the ORNL site has a considerable ion-exchange capacity for cesium, strontium and transuranic radionuclides. The migration rate of these radionuclides through shale will be slower than the water percolation rate. Results indicate that these radionuclides will have been transmuted by radioactive decay long before they approach the surface since their rate of movement is so low. The rate of movement of strontium is less than that of the water flow by a factor of 700 to 12 000 (depending on the pH of the water) and the rate movement of cesium is lower by a factor of 14 000.

Based on the above laboratory experiments, subsurface injection has been used at the Oak Ridge National Laboratory to dispose of low-level waste

(LLW) for the past two decades. The process consists of mixing the liquid waste with cement and other additives to form slurry that is injected under pressure through a cased well into low-permeability shale at a depth of 300 m. The slurry spreads from the well along hydraulic fractures and sets to form irregularly shaped grout sheets up to 200 m in radius.

Over 1,8 x $10^7$ liters of slurry, containing more than 5,5 x $10^{16}$ Bq of radionuclides ($^{90}$Sr, $^{137}$Cs, $^3$H, $^{60}$Co, $^{106}$Ru and isotopes of Cm, U, Am and Pu), have been disposed of in this matter. The US Department of Energy decided to close the site in 1986, which provided a unique opportunity to study the fate of the injected waste. Initial results indicated that contaminated groundwater surrounded the grout sheets in the injection zone and extended at least 300 m from the injection well. Of the main contaminants ($^{90}$Sr and $^{137}$Cs) disposed of into the injection zone well, only $^{90}$Sr was present in groundwater. The reason for $^{137}$Cs being absent in the groundwater was that the rich illite mineralogy in the slate strongly absorbed the $^{137}$Cs, thus greatly retarding its migration. The discovery of contaminated groundwater in the injection formation was not expected because the cementitious grout had been designed to incorporate the radionuclide bearing wastes. According to *Haase*, the groundwater contamination was the main contributing factor in the decision to close this facility.

## 2.6 Analytical Determination of Humic Acid

### 2.6.1 UV-VIS spectrophotometer

The term "spectrochemical analysis" refers to a technique whereby the interaction of chemical species with electromagnetic radiation is determined and documented by means of a spectrum (Meyer, 2001). An ultraviolet-visible spectrophotometer was used in this study to characterise and study the absorption of humic acid into solids. A short description of the instrument is as follows:

The UV-spectrochemical instrument has an input device used to convert chemical information of a sample into information in the form of electromagnetic radiation. This device is known as a transducer and encodes the chemical information into another form, i.e. electromagnetic information. To decode or extract the chemical information encoded in the radiation, a second transducer, called the detector, is required. In the spectrochemical instrument, the function of a detector is to provide a measurable electrical signal that is proportional to some property, usually radiant power of a radiation incident upon the detector. In actual fact, the detector converts the information present in the electromagnetic radiation to another form that is more amenable to signal processing techniques. The electrical signal from the detector, which contains the encoded information about the sample, must next be rendered interpretable to a human observer. For this operation, a readout system is employed. The final output can take many forms, from simple meter deflection to columns; in our case, the spectra peaks. In the ultraviolet-visible spectrochemical technique there is also a frequency selector. A frequency selector separates or disperses electromagnetic radiation into relatively narrow bands of wavelengths or frequencies that can then be examined either individually or simultaneously to determine the encoded information about the sample.

A final indispensable component is the control system of the spectrochemical instrument. This device is responsible for coordinating all the events and operations that take place in the instrument, from selection and introduction of the sample to the readout signal, which the human operator usually performs.

The isolation, fractionation and concentration determination of humic acid was done by *Allard*, using different absorption ratios on the UV/VIS spectrophotometer absorption spectra. For instance, the ratio of absorption intensities at 465 nm and 665 nm (E4/E6) is widely used to determine the concentration of humic acid (Figure 2.1).

However, this ratio method is suspect as the ratio decreases with increasing huminification and increases again during the condensation of aromatic humic contents (Chen *et al* ,1977). The ratio is also governed by molecular size, which is again dependent on pH (speciation). Owing to the complex nature of humic acid, UV spectroscopy is of limited use for its characterisation (Kim *et al*, 1990).

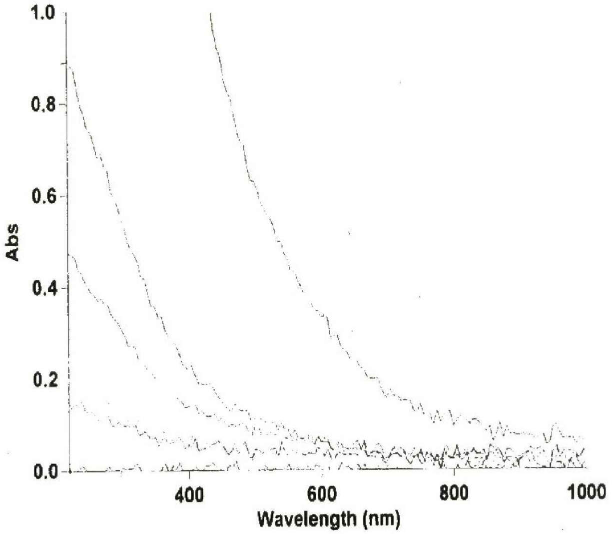


Figure 2.14: The UV/VIS spectrum of the Aldrich humic acid used in this study at different concentrations of humic acid.

### 2.6.2 Infrared spectroscopy

Infrared spectroscopy was employed by Kim *et al* (1990) to determine the humic acid structure. Typical features on the IR spectrums of different synthesised humic acids indicate hydrogen bound hydroxyl groups (3 400 cm$^{-1}$), carbonyl groups (1 725 cm$^{-1}$), carboxylic groups (1 400 cm$^{-1}$) and aromatic groups (1 630 cm$^{-1}$).

*McCarthy* (1989) also used infrared spectroscopy to characterise a commercial humic acid, and one of his observations was that humic acids appear to be partly in a salt form or complexed with metals. The infrared spectrum of the commercial humic acid corresponds remarkably with humic acid isolated from peat and soils. However, pronounced differences between these two classes of materials are revealed by $^{13}$C-NMR spectroscopy.

In this study, IR spectroscopy was not considered for determining humic acid concentration in this study owing to the complexity of the spectra and the presence of a water absorption band during the dissolution of humic acid salts to be used as a tracers.

### 2.6.3 Gamma spectroscopy

One of several forms of radiation is gamma radiation. It is emitted by many radionuclides such as cobalt, iodine, cesium, etc. Gamma spectroscopy is used to detect the presence of these radionuclides. These radionuclides may be natural or they may be released by various industries. They include activation products caused by the absorption of a neutron by molecules or fission products that occur following fission of nuclear fuel radionuclides such as U-235 and Pu-239.

A brief description is as follows: quantitative assessment of gamma emitting radionuclides in solid, liquid and gaseous samples can be made with high accuracy and sensitivity by a number of solid state detectors, such as germanium detectors. Solid-state detectors are often used to identify and quantify gamma-emitting radionuclides in effluent and environmental samples in and around a wide variety of facilities handling radioactive waste. The germanium detector is a gas-filled detector that utilises the ionisation produced in gas by the interaction of ionising radiation, which produces an electrical signal that indicates the presence of radiation and its energy and type.

Germanium detectors: are semi-conductor diodes having a P-I-N structure in which the intrinsic (I) region is sensitive to ionising radiation, particularly X-rays and gamma rays. Under severe bias, an electric field extends across this intrinsic or depleted region. As the photons interact with the material within the depleted volume of the detector, charge carriers are produced. These charges are swept by the electric field to the P and N electrodes. The charge, which is proportional to the energy deposited in the detector by the incoming photons, is converted to a voltage pulse by an integral charge-sensitive pre-amplifier.

The energy resolution of the detector can easily be destroyed by leakage current induced noise and the detector must therefore be cooled. The cooling reduces the thermal generation of charge carriers, i.e. reverse leakage current, to an acceptable level. Liquid nitrogen, which has a low temperature (77 K), is often used as a cooling medium. The sensitive detector surfaces are always protected from moisture and other contaminants.

Sodium-iodide detector (NaI detector): NaI detection, also known as scintillation, consists of a sodium-iodide (NaI) crystal that is optically mounted to a photomultiplier tube. Incident radiation interacting in the NaI crystal will result in the production of light. The light is then transmitted into a photomultiplier tube where the light produces electrons. The electrons produced are then amplified in the phototube. The signal out of the phototube is transformed into a pulse that signifies the incidence of a photon; the pulse is then recorded by various means, which are easily available.

## 2.7 Summary of literature

"Thabana", acts as a temporary storage facility for containers containing transuranic waste, radioactive waste from hospitals, industrial and agricultural waste, as well as radioactive waste from other research institutions such as universities. In this shale environment, different plant residues are present resulting in the possible formation of humic acid by means of a biological decaying mechanism. According to literature humic acids can form colloidal complexes with metals, resulting in an increase in the solubility, availability and migration properties of radioactive species through the environment when a waste container is breached. For determining the interim safety of Thabana (shale environment) and the feasibility of disposal of humic contaminated wastes at Vaalputs, it is necessary to study the absorption behaviour of humic acid into different soil samples from Thabana and Vaalputs, as well as the influence of this "affected" soil on migration properties.

In this study, the main emphasis will be on the interaction of a commercially available humic acid with soil and its effect on the migration properties at the nuclear waste repositories in South Africa (i.e. Thabana and Vaalputs). The research involves:

- Determining humic acid in soils and water samples from Thabana and Vaalputs
- Determining absorption of commercially available humic acid into soil samples from Thabana and Vaalputs
- Determining absorption of uranium into Thabana and Vaalputs soil
- Determining the absorption of uranium into experimentally humified soil from Thabana and Vaalputs
- Determining the absorption of humic-uranium complexes into Thabana and Vaalputs soil

The $K_d$ parameter is important for estimating the potential for the adsorption of dissolved radionuclides onto backfill in a waste repository and it is used in transport and risk assessment modelling because it is simple to measure and understand. $K_d$ values are only valid for the mineralogy and geochemical conditions under which they are determined.

Standardisation of the measurement of $K_d$ values is also important as it has been indicated that certain $K_d$ values in older databases were obtained using a macroscopic approach owing to instrument limitations. The experimental method recommended by *Yamaguchi* (see 2.1.5) was used in this study and the $K_d$ values were determined using the formula recommended by *Masayuki* (*1998*) (see 2.1.4). The other parameters (based on international requirements (see 2.1)) used in this study were:

- Concentration limitations ($10^{-6}$ M)
- Ionic strength (0,01 M $NaNO_3$)
- Ratio of solids to water (1:10)

# CHAPTER 3

# EXPERIMENTAL

# 3. EXPERIMENTAL

## 3.1 Analytical Equipment and Chemicals Used in Study

Varian Cary 2300 Spectrophotometer (UV-VIS-NIR), Genie 2000 Gamma Spectroscopy, Electronic Analytical Balance (weighing balance) TB-200 (from Denver Instrument Company), Harlme Z200A Centrifuging Machine, Heidolph Reactor Jacket and Orion pH Meter, Model 410A.

Aldrich humic acid (Na salt) from Aldrich, lot 31620-091; radioisotopes: $^{137}CsCl_2$ (4,824 MBq mL$^{-1}$ in 0,1 M HCl), code CDZ72, purchased from Nycomed, Amersham and Na$^{131}$I (37 MBq mL$^{-1}$) manufactured at NECSA. Beckman reference buffers pH 4, pH 10 and pH 14.

## 3.2 Soil and Water Samples

### 3.2.1 Soil samples

Thabana Samples:

Thabana is located west of Pretoria at the Pelindaba site in the Northwest Province of South Africa. The soil at Thabana is generally regarded as slate and the area comprises weathered silk/dyke, plastic clay and fresh slate. For this study, groundwater and soil were collected from this site by auger drilling two vertical boreholes up to 180 m in depth. In order to eliminate any oxidation conditions, the surface of the soil core was cut away and only the inner part was used for studies. These soil samples were not milled. Particle-size determinations indicated that particle size ranged between 100 and 200 microns. In order to confirm homogeneity and the chemical composition of the different soil layers, triplicate samples were analysed by independent accredited laboratories. Cores of the soil were analysed and divided into five sections based on results. These sections were labelled according to their depth profiles: (i.e. A=7.7 m; B= 25 m; C= 32 m; D= 45 m and E=66 m) (see Table 3.1).

**Table 3.1**: Chemical composition of soil samples from Thabana used in this study.

| Chemical composition | Thabana Soil | | | | |
|---|---|---|---|---|---|
| | **A** Weathered silk/dyke | **B** Plastic clay | **C** Fresh slate | **D** Fresh slate | **E**** Fresh slate |
| | 2 m – 8 m | 10 m –25 m | 32 m – 47 m | 32 m – 47 m | 66 m – 180 m |
| pH | 7,1 | 7,1 | 7,1 | 7,1 | 7,1 |
| $Cl^-$ mg/l | 0 | 0 | 0 | 0 | 0 |
| $Ni^{2+}$ ppm | 67 | 28 | 68 | 40 | 48 |
| $Pb^{2+}$ ppm | 12 | 21 | 19 | 21 | 32 |
| $Ba^{2+}$ ppm | 495 | 772 | 791 | 426 | 496 |
| V ppm | 178 | 105 | 121 | 88 | 110 |
| Zr ppm | 84 | 140 | 148 | 163 | 121 |
| $Fe_2O_3$ % | 17,3 | 10,8 | 7,82 | 5,05 | 9,29 |
| MnO % | 0,05 | 0,02 | 0.,3 | 0,1 | 0,08 |
| $TiO_2$ % | 0,74 | 0,71 | 0,71 | 0,6 | 0,7 |
| CaO % | 0,07 | 0,6 | 0,19 | 0,75 | 0,06 |
| $K_2O$% | 1,96 | 2,5 | 3,57 | 1,95 | 3,04 |
| $P_2O_5$ % | 0,28 | 0,19 | 0,7 | 0,1 | 0,27 |
| $SiO_2$ % | 49 | 51,2 | 56 | 70 | 55 |
| $Al_2O_3$ % | 22 | 25,2 | 24,6 | 17,6 | 23,2 |
| MgO % | 0,2 | 0,2 | 1,5 | 0,2 | 0,1 |
| $NaO_2$ % | 0,2 | 0,2 | 0,3 | 0,3 | 0,3 |

**: Second borehole

Vaalputs samples:

Vaalputs is located in the Northern Cape Province of South Africa and is 120 km from Springbok, the nearest town. This site is currently used as a long-term storage facility for the disposal of low-level nuclear waste (LLW) and medium-level nuclear waste (MLW). For this study, groundwater and soil were collected from this site by auger drilling a 60 m borehole. In order to eliminate any oxidation conditions, the surface of each soil core was cut away and only the inner part was used for studies. These soil samples were not milled. Particle-size determinations indicated that particle size ranged between 10 and 200 microns. In order to confirm the chemical composition of the different sections, triplicate samples were sent to independent accredited laboratories for analysis.

Cores of the soil were analysed and three different sections were determined. These sections were labelled White Clay, Red Clay and Calcite. These samples have also different chloride and sulphate concentrations that can be considered "aggressive" chemicals that can be detrimental to waste packages.

**Table 3.2:** Chemical composition of soil samples from Vaalputs used in this study.

| | Kaolinite clay (backfill material) | Smectite/Illite clay ("deeper trench clay") | Calcrete |
|---|---|---|---|
| pH | 7.1 | 7.2 | 7.2 |
| $Cl^-$ mg/l | 814 | 870 | 870 |
| $Ni^{2+}$ ppm | 12 | 11 | 11 |
| $Pb^{2+}$ ppm | 26 | 26 | 26 |
| $Ba^{2+}$ ppm | 373 | 786 | 786 |
| V ppm | 71 | 0 | 0 |
| Zr ppm | 240 | 131 | 131 |
| $Fe_2O_3$ % | 368 | 322 | 322 |
| MnO % | 4 | 3 | 3 |
| $TiO_2$ % | 49 | 42 | 42 |
| CaO % | 434 | 39 | 39 |
| $K_2O$% | 214 | 183 | 183 |
| $P_2O_5$ % | 4 | 7 | 7 |
| $SiO_2$ % | 7270 | 7690 | 7690 |
| $Al_2O_3$ % | 760 | 960 | 960 |
| MgO % | 240 | 170 | 170 |
| $NaO_2$ % | 20 | 30 | 30 |

### 3.2.2 Water samples

Water samples used in this study were from the Thabana and Vaalputs sites and were extracted under a nitrogen atmosphere. These samples were placed in pre-treated polyethylene canisters (acid method) under nitrogen for transportation. Upon arrival at NECSA laboratories, these samples were placed in a refrigerator under a nitrogen atmosphere. In order to confirm homogeneity and the chemical composition of the groundwater from the sites, triplicates samples were sent to three independent laboratories for analysis. The average of nine analyses is listed in Table 3.3.

**Table 3.3:** Chemical composition of water samples used in this study.

| Concentration (mg/L or S/cm) | Vaalputs water | Thabana water |
|---|---|---|
| U (mg/l) | 0.2 | 0.1 |
| HCO (mg/l) | 414 | 308 |
| Ca (mg/l) | 60 | 60 |
| Mn (mg/l) | 0.8 | 0.89 |
| Co (mg/l) | 0.02 | 0.3 |
| Cu (mg/l) | <0.01 | 0.42 |
| Cl (mg/l) | 1060 | 46 |
| EC (µS/cm) | 4240 | 21 |
| F (mg/l) | 2.5 | 0.2 |
| Fe (mg/l) | 0.02 | 1.5 |
| Li (mg/l) | 0.06 | 0.05 |
| Mg (mg/l) | 51.0 | 33 |
| Ni (mg/l) | <0.01 | 0.40 |
| $PO_4$ (mg/l) | 1.00 | 0.2 |
| NO3- (mg/l) | <0.05 | 0.2 |
| pH | 7.5 | 7.0 |
| K (mg/l) | 18.7 | 0.6 |
| Na (mg/l) | 840 | 12 |
| $SO_4$ (mg/l) | 237 | 20 |
| TDS | 2392 | 284 |

## 3.3 Calibration of Equipment

### 3.3.1 pH meter

Three solutions were used to calibrate the pH meter, namely two reference buffer solutions of pH 4 and pH 7 and a Beckman Buffer solution of pH 10. The calibration method was as follows: The electrode was rinsed twice with distilled water and then blotted dry with soft paper and reimmersed in newly distilled water (pH 7). The pH meter was turned on, the water was stirred gently and the reading on the meter was allowed to stabilise. Once a stable reading was obtained, the pH meter was removed, rinsed with distilled water, blot-dried and put into the different buffer solutions for calibration. On completion of the calibration for all three solutions, the electrode was rinsed with distilled water, blot-dried and was ready for use.

The results obtained from the calibration showed that the meter has a maximum drift of 2,12%, allowing us to use the available meter.

### 3.3.2 Spectrophotometer

In order to study the influence of humic acid concentration on the absorption of radionuclides, standard solutions of humic acid were calibrated by using the UV/VIS spectrophotometer at wavelengths between 700 nm and 240 nm. Before any analysis, the instrument was calibrated with distilled demineralised water for a background signal. A known amount of humic acid salt was dissolved in demineralised water, Vaalputs water and Thabana water. The standards solutions were then calibrated using a Cary 2300 spectrophotometer in the spectrum range between 240 nm and 700 nm. Calibration curves were constructed by plotting the absorbency of the humic acid at different regions of the spectrum between 240 nm and 700 nm (regions chosen are: 274 nm; 285 nm; 350 nm; 465 nm; 495 nm; 520 nm and 665 nm) against the concentration of humic acid (see calibration results in Graph 4.1.1, Chapter 5). The same standard solutions were taken to an independent laboratory for a gravimetrical chemical analysis of the humic acid in order to calibrate for the UV-VIS instrument.

## 3.4 Preparation of Standard Solutions

### 3.4.1 Preparation of standard stock humic acid solution

Purified Na-salt humic acid from Aldrich was used to prepare standard humic acid solutions as follows: A known amount (0,3 g; 0,25 g; 0,2 g; 0,15 g; 0,1 g; and 0,05 g) of humic acid was dissolved in 1 L (one litre) of different water samples (Thabana, Vaalputs and demineralised) for humic acid standard solutions with concentrations of 0,3 g/L; 0,25 g/L; 0,2 g/L; 0,15 g/L; 0,1 g/L and 0,05 g/L demineralised water was used as a reference for the interaction behaviour of Thabana and Vaalputs water with humic acid.

### 3.4.2 Preparation of standard tracer solutions

Tracer solution of $Na^{131}I$ (37 MBq $mL^{-1}$) was manufactured at NECSA and $^{137}CsCl_2$ (4,824 MBq $mL^{-1}$ in 0,1 M HCl) was purchased from Nycomed, Amersham.

Different radioactive tracer solutions (stock solutions) were prepared by diluting these tracer solutions (1 mL) with 150 mL of demineralised water. Experimentation solutions were prepared by adding aquilots of 3 mL; 4 mL; 5 mL; 6 mL; 7 mL and 8 mL of these tracer stock solutions to Vaalputs, Thabana and demineralised water up to a volume of 150 mL per sample. These solutions were then pH adjusted as required.

Tracer solutions with humic acid complexes were prepared as above with Vaalputs and Thabana water containing humic acid (see 3.4.1).

In order to study the influence of pH (speciation) on the distribution coefficient ($K_d$ values), the experimental solutions (150 mL) were subdivided into three sets (50 mL each) and the pH of the tracer solutions was adjusted as follows:

- One set was for analysis at pH 7.
- For the second set, 0,1 M HCl was added to adjust the pH to 4.
- In the third set, $CaCO_3$ was added to adjust the pH to 10.

The tracer solution contained only a single tracer in order to eliminate the interdependence of the different tracers on each other.

### 3.4.3 Preparation of a humic saturated soil

Humic saturated soil was prepared as follows: 100 mL of the 0,3 g/L standard solution of humic acid was added to each of the different soil samples, thoroughly mixed and shaken for 48 hours (to ensure the absorption of humic acid into the soil samples). After this equilibration period, the solids were separated from the liquids by means of filtration. The soil samples were then dried in an oven at 90 $^0$C for a period of 90 minutes and transferred back into the respective containers for sorption studies. The amounts of humic acid absorbed into the soil samples were also measured.

## 3.5 Experimental Sorption Studies

Sorption studies of humic acid and radionuclides in soil samples were performed using the laboratory batch method. The following experiments were carried out:

- The absorption of humic acid into soil samples from Thabana and Vaalputs at pH 4; 7 and 10
- The absorption of radionuclides into unhumified soil samples at pH 4; 7 and 10
- The absorption of radionuclides into humidified soil samples at pH 4; 7 and 10
- The absorption of possible humic-radionuclide complexes into soil samples at pH 4; 7,2; and 10.

Distribution-coefficient values ($K_d$ values) were determined in triplicate and the same counting geometry was used for all samples.

The following procedure was followed to study the $K_d$ values:

After a weighed amount of a solid (1 g) and 10 mL of the "pH equilibrated" tracer solution had been put into (polyethylene) centrifuge tubes, the centrifuge tubes were immediately capped, shaken and placed in a jacket to be rotated end over end at 30 r/min. Absorption equilibrium was reached after 48 hours and the rotation was stopped. The centrifuge tubes were then placed in an upright position (Figure 3.1 and Figure 3.2) so that the different phases could separate. After a period of 24 hours the contents of the centrifuge tubes were centrifuged and the ratio of tracer distribution between the liquid phase and different solid phases (due to particle differences) was determined by gamma spectrometry using a NaI well detector.

The possibility of tracer absorption in the surface of the centrifuge tubes was checked by washing the tubes with 5% HCl and then determining the activity of the liquid solution as well as the centrifuge tubes by gamma spectrometry. The tracer absorption was negligible and is not included in the computation of the data.

The values of the distribution ratio ($K_d$) were calculated from the following relationship:

$$K_d(m^3/kg) = \frac{(C_0 - C_i)}{C} * \frac{V}{W}$$

V: Volume of the solution (mL)
M: Mass of the soil sample (g)

$C_o$: Initial concentration
$C_i$: Concentration at time

The amount of tracer ($C_o$-$C_i$) after equilibrium must correspond with the amount of tracer determined in the different soil particles before calculations are performed - if not, the results are ignored and the experiment repeated.

An example of a calculated result:

$C_o$: 100 Bq/mL of tracer in a 10 mL solution before start of experiment
$C_i$: 5 Bq/mL of tracer in a 10 mL solution after equilibration with 1 g of solid soil
$10^{-3}$ : Conversion of mL/g to $m^3$/g

$$Kd = \frac{V(10ml)}{M(1g)} \times \frac{C_0(100Bq/l) - C_i(5Bq/l)}{C_i(5Bq/l)} \times 10^{-3}$$

Figure 3.1: Time needed for the different solid phases to separate (from left to right): 1 hour, 2 hours, 4 hours, 8 hours, 12 hours,24 hours.

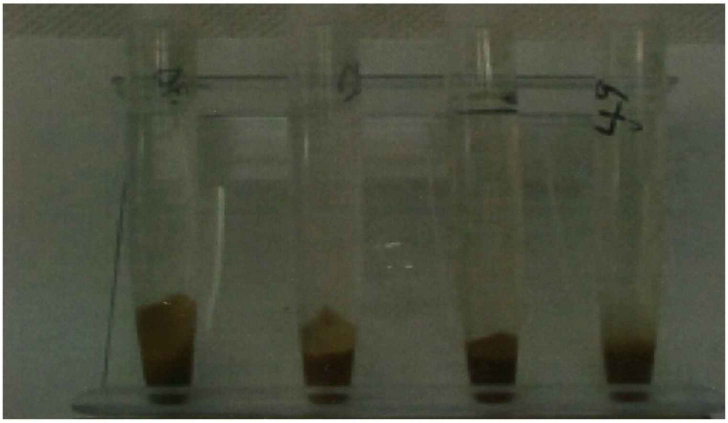


Figure 3.2: Three phases (coarse [200 micron], medium [20 micron] and fine [5 micron]) observed after centrifugation (from left to right): backfill, calcrete, "trench clay", river sand.

# CHAPTER 4

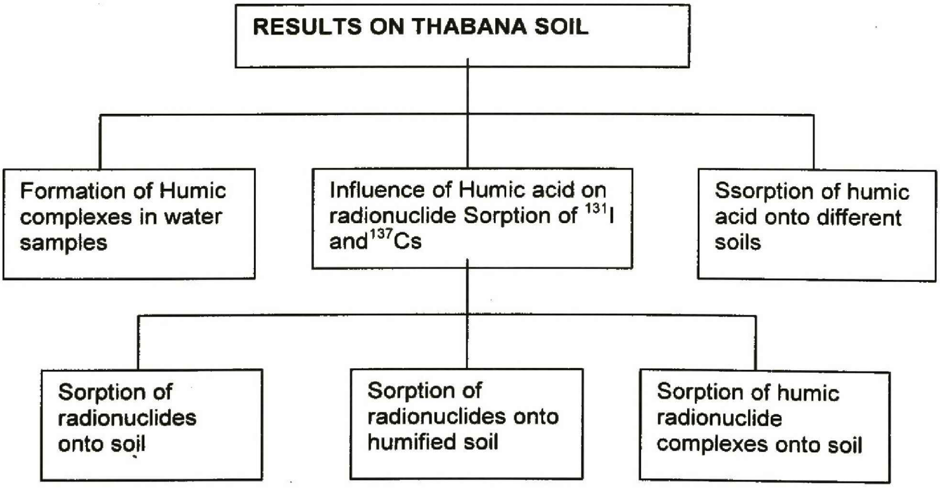
# RESULTS AND DISCUSSION
## Thabana studies

# 4. RESULTS AND DISCUSSION OF THABANA SOIL

In order to determine the influence of humic acid on the migration properties of radionuclides in South African waste repositories as well as the possible mechanisms involved, the following were studied:

- The possible formation of humic complexes in site-specific water sources
- The possible sorption of these humic complexes into soils at the waste repositories
- The absorption of radionuclides into soil samples
- The influence of redox conditions on the sorption of humic radionuclide complexes into soils
- The possible surface complexation reaction between absorbed humic acid on soil surfaces and radionuclides (absorption of radionuclide into humified soil samples)

The results in this chapter will be presented and discussed as indicated in the following schematic presentation:



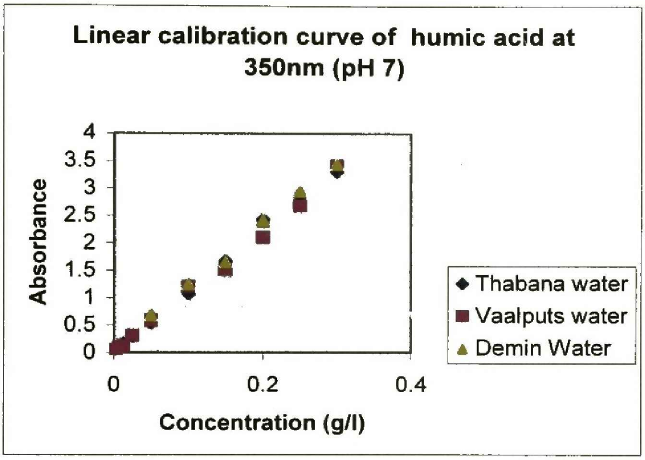
## 4.1 Investigation of Possible Humic Complex Formation in Thabana Water Solutions (Water Phase)

In order to determine the possible formation of humic acid complexes in the water samples used in this study, a known amount of humic acid salt was dissolved in demineralised water, Vaalputs water, and Thabana water. These solutions were then studied by using the Cary 2300 spectrophotometer in the 350 nm spectrum region (this appears to be the most sensitive region for humic acid standard used in this study).

The results in Table 4.1 and in Figure 4.1 indicate that regardless of the different water sources, the presence of high concentrations of chlorides and sulphates in the Vaalputs water and different humic concentrations, no significant differences in the sorption spectra of humic acid were observed.
If complex-formation had taken place, the legend field of humic acid would have been altered and consequently the electronic transitions at 350 nm would have been altered. The conclusion therefore is that no complexes could be observed in this pH region (6 and 8).

**Table 4.1:** The UV-VIS sorption values of humic acid in water.

| | Absorbance (350 nm) | | |
|---|---|---|---|
| **Concentration (g/L)** | **Thabana water** | **Vaalputs water** | **Demin. water** |
| 0.3 | 3.3 | 3.42 | 3.44 |
| 0.25 | 2.84 | 2.68 | 2.94 |
| 0.2 | 2.42 | 2.1 | 2.42 |
| 0.15 | 1.66 | 1.52 | 1.65 |
| 0.1 | 1.07 | 1.2 | 1.25 |
| 0.05 | 0.54 | 0.58 | 0.68 |
| 0.025 | 0.29 | 0.31 | ----- |
| 0.0125 | 0.16 | 0.12 | ----- |
| 0.00625 | 0.09 | 0.098 | ----- |
| 0.003125 | 0.06 | 0.06 | ----- |



Demin. Water = Demineralised water.

Figure 4.1: A linear calibration curve of a standard solution of humic acid at pH 7,2 using different water samples.

However, *Carter and Suffete* indicated that by changing the pH of a solution containing humic acid, the molecules would be aggregated due to hydrogen bonding and the ionisation of functional groups on the humic structure, thereby increasing the formation of complexes.

In order to determine the complex-formation of these "altered" humic acid structures at different redox conditions, the above experiment was repeated in other redox environments. However, the pH range between 4 and 10 was chosen for this experiment as literature (*Cha. H et al, 2003)* indicated that at a pH lower than 3,5, humic acid precipitated and at a pH higher than 10, the organic structure of humic acid started decomposing.

The results in Table 4.2 and Figure 4.2 indicate that at the two extreme specified redox conditions, the sorption of humic acid tends to decrease. No significant complex-formation was observed in the solutions and this result is attributed to the fact that humic acid starts precipitating at pH 4 and decomposing at pH 10.

**Table 4.2:** The UV-VIS sorption values of 0,15 g/L humic acid in different water samples and different redox conditions (pH 10).

| **0.15 g/L<br>Humic acid** | **Absorbance (350 nm)** | | |
|---|---|---|---|
| **pH** | **Thabana** | **Vaalputs** | **Demineralised** |
| 4 | 0.95 | 0.96 | 0.99 |
| 7 | 1.66 | 1.65 | 1.52 |
| 10 | 1.18 | 1.02 | 1.16 |

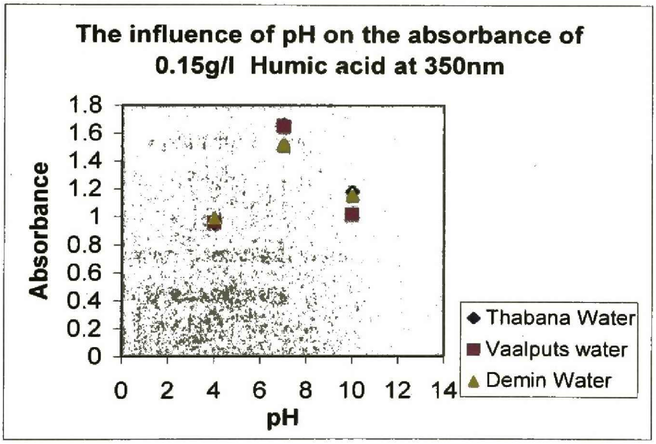


Figure 4.2: The influence of pH on the formation of humic acid complexes using different water samples.

The above results indicate that the formation of possible humic complexes in the research water samples is negligible and will not have an influence on the results of this study.

## 4.2 Sorption of Humic Acid into Different Thabana Soils

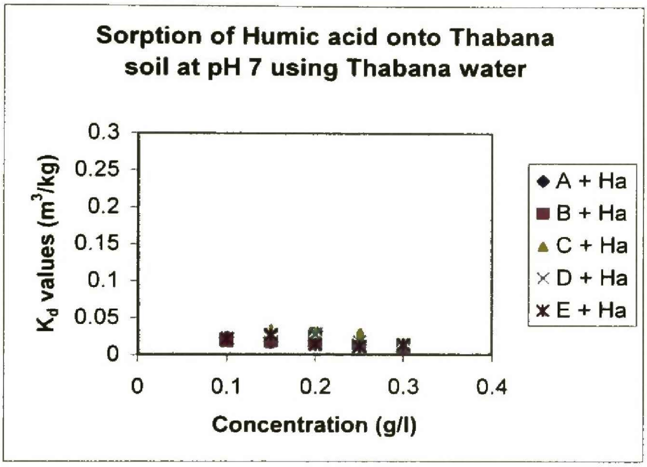
In order to determine the possible absorption of humic acid into slate, thereby reducing the number of available absorption sites for radionuclide absorption, a known amount of humic acid salt was dissolved in demineralised water and Thabana water. These solutions were then used to determine the absorption of humic acid into soil samples.

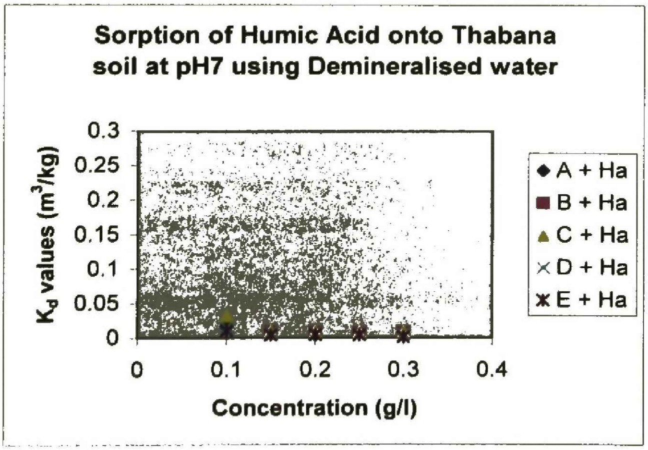
The results in Table 4.3 and Figure 4.3 indicate that the absorption of humic acid into different slate materials as encountered at Thabana is minimal. The results indicate that even in the presence of high concentrations, i.e. between 0,15 g/L and 0,3 g/L, a uniform distribution coefficient is observed. The $K_d$ values in this region are very low, indicating that the amount of humic acid absorbed into slate is very small and that the number of available absorption sites for radionuclide absorption has not been significantly altered in the presence of humic acid.

**Table 4.3:** The distribution-coefficient values of humic acid for Thabana soil using both Thabana water.

| Thabana water | | | | | |
|---|---|---|---|---|---|
| 350 nm | $K_d$ values ($m^3/kg$) | | | | |
| **Concentration (g/L)** | **A + Ha** | **B + Ha** | **C + Ha** | **D + Ha** | **E + Ha** |
| 0.3 | 0.012297 | 0.00976 | 0.01619 | 0.01037 | 0.013571 |
| 0.25 | 0.019583 | 0.016055 | 0.027867 | 0.0184 | 0.011515 |
| 0.2 | 0.030333 | 0.019157 | 0.030333 | 0.027813 | 0.0142 |
| 0.15 | 0.017213 | 0.019123 | 0.032564 | 0.024583 | 0.026889 |
| 0.1 | 0.022424 | 0.019722 | ---------- | ----------- | 0.021471 |

| Demineralised water | | | | | |
|---|---|---|---|---|---|
| 350 nm | $K_d$ values ($m^3/kg$) | | | | |
| **Concentration (g/L)** | **A + Ha** | **B + Ha** | **C + Ha** | **D + Ha** | **E + Ha** |
| 0.3 | 0.004576 | 0.007732 | 0.008696 | 0.004098 | 0.001467 |
| 0.25 | | 0.007093 | 0.007818 | 0.005393 | 0.004135 |
| 0.2 | 0.004235 | 0.008615 | 0.009516 | 0.006351 | 0.004405 |
| 0.15 | 0.009386 | 0.009643 | 0.009643 | 0.007188 | 0.003983 |
| 0.1 | 0.016042 | 0.17174 | 0.031667 | 0.01451 | 0.010833 |
| 0.05 | 0.038571 | --------- | 0.126 | 0.027778 | 0.024 |





A; B; C; D; E: Represents soil at different depths (Chapter 3)

Figure 4.3: Graphs of $K_d$ values ($m^3$/kg) of humic acid absorbed into different Thabana soils in the presence of Thabana and demineralised water.

As stated previously in section 4.1 by *Carter and Suffete*, redox changes would alter the humic acid molecules. So the experiment was repeated in different redox conditions to study the absorption of these "altered" humic acid structures into slate.

The results in Table 4.4 and Figure 4.4 indicate that no significant absorption of humic acid into slate was observed for the pH range between 5 and 10. This result confirms the previous results, namely that no altered complexes could be observed in these redox conditions. The conclusion therefore is that even if undetected "altered" humic acid structures do form, these structures do not absorb into slate and therefore the presence of any humic complexes present in the water used in this study will have a minimal effect on the results of this study.

However, results in Table 4.4 and Figure 4.4 also indicate that significantly different values for the absorption of humic acid into slate were observed at the low pH value of 4. This increased absorption at this pH is attributed to the fact that as humic acid starts precipitating, the amount of measured humic acid in solution decreases, resulting in increased absorption measurement, which includes the precipitation reactions.

The above results indicate that the $K_d$ values in the region (pH 5-10) are very low, indicating that the amount of humic acid absorbed into slate is very small and that the number of available absorption sites for radionuclide absorption has not been significantly altered in the presence of humic acid.

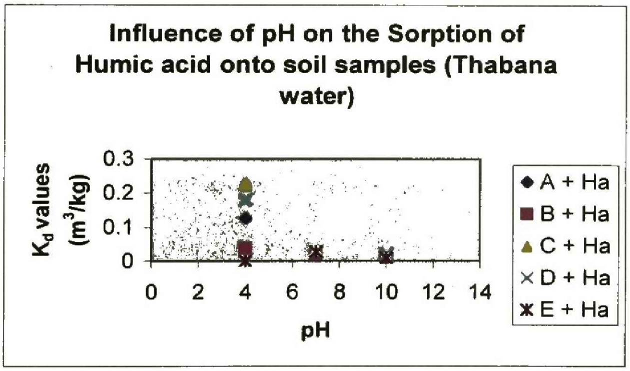
## 4.3 Absorption of Radionuclides into Thabana Soil

### 4.3.1 Influence of anionic radionuclide specie ($^{131}$I)

Iodine is found in waste repositories as $^{129}$I and it has a half-life of $1.57*10^{17}$a. In this project, $^{131}$I was used instead of $^{129}$I due to the difficulties in studying $^{129}$I. $^{131}$I has a shorter half life compare with its isotope $^{129}$I and this makes $^{131}$I very easy to work with.

**Table 4.4:** The absorption ($K_d$) values of humic acid into Thabana soil at different pH values.

| $K_d$ values ($m^3/kg$) | | | | | |
|---|---|---|---|---|---|
| **Thabana water** | | | | | |
| pH | A + Ha | B + Ha | C + Ha | D + Ha | E + Ha |
| 4 | 0.125714 | 0.0375 | 0.2275 | 0.18 | ----------- |
| 7 | 0.017213 | 0.019123 | 0.032564 | 0.024583 | 0.026889 |
| 10 | 0.01622 | 0.010702 | 0.020256 | 0.021053 | 0.009032 |
| **Demineralised water** | | | | | |
| pH | A + Ha | B + Ha | C + Ha | D + Ha | E + Ha |
| 4 | 0.0147 | 0.03125 | 0.2375 | 0.166786 | 0.033043 |
| 7 | 0.016 | 0.01714 | 0.031667 | 0.027778 | 0.024 |
| 10 | 0.0091 | 0.011481 | 0.011091 | 0.014681 | 0.017619 |



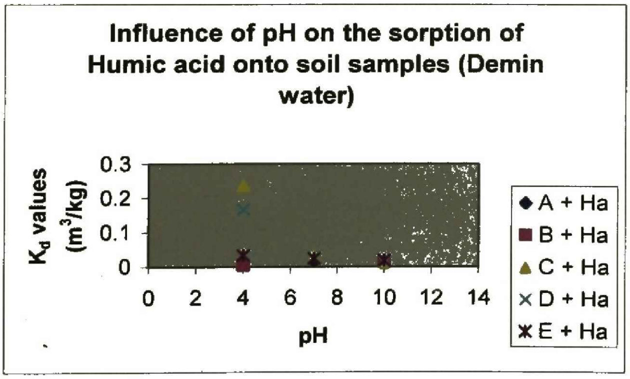


Figure 4.4: Graphs showing the influence of pH on the distribution coefficients of humic acid into different Thabana soils.

In the proposed structure of humic acid many double bonds are present that would result in a negatively charged humic acid structure and therefore it is expected that the anionic species would not form complexes with humic acid. The migration (absorption) of iodine would remain unaffected.

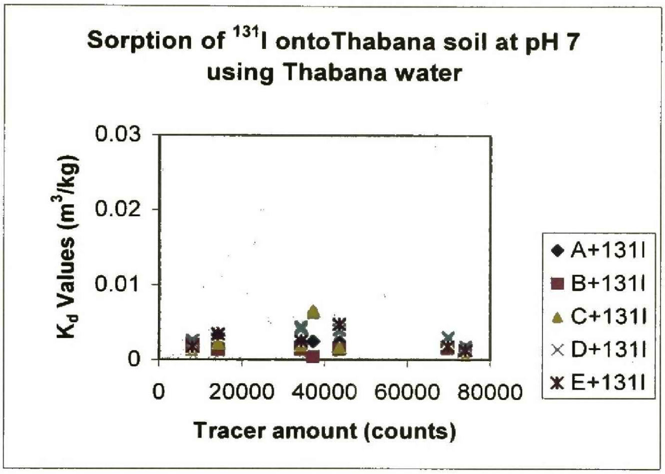
To confirm the above assumption regarding complex-formation and the migration properties, the absorption of $^{131}$I in the presence and absence of humic acid at different redox pH conditions into the different soil samples was studied.

#### 4.3.1.1 Absorption of iodine into Thabana soil at pH 7

The relatively low distribution-coefficient values in Table 4.5 and in Figure 4.5 that were obtained for the absorption of $^{131}$I into slate indicate that the anionic $^{131}$I does not absorb into Thabana soil even in the presence of different water sources.

**Table 4.5:** $K_d$ values (m$^3$/kg) of $^{131}$I absorption into Thabana soil samples.

| | **$K_d$ values (m$^3$/kg)** | | | | |
|---|---|---|---|---|---|
| | **(Thabana water)** | | | | |
| **Original Std. (Counts)** | **A+$^{131}$I** | **B+$^{131}$I** | **C+$^{131}$I** | **D+$^{131}$I** | **E+$^{131}$I** |
| 74040 | 0.001299 | 0.001009 | 0.000893 | 0.00175 | 0.001258 |
| 69840 | 0.002147 | 0.001577 | 0.002121 | 0.002968 | 0.001784 |
| 43535 | 0.002346 | 0.00142 | 0.001628 | 0.004016 | 0.0047 |
| 37148 | 0.002428 | 0.000328 | 0.006518 | ---------- | -------- |
| 34186 | 0.002346 | 0.001388 | 0.001902 | 0.004271 | 0.002461 |
| 14213 | 0.003267 | 0.001365 | 0.002161 | 0.003417 | 0.003417 |
| 8067 | 0.00206 | 0.002076 | 0.001526 | 0.002464 | 0.001705 |
| | **$K_d$ values (m$^3$/kg)** | | | | |
| | **(Demineralised water)** | | | | |
| **Original Std. (Counts)** | **A+$^{131}$I I** | **B+$^{131}$I** | **C+$^{131}$I** | **D+$^{131}$I** | **E+$^{131}$I** |
| 62169 | 0.001394 | 0.000534 | 0.00083 | 0.000902 | 0.000547 |
| 36489 | ------- | 0.002902 | ------- | -------- | 0.006968 |
| 28641 | 0.00136 | 0.001377 | 0.001382 | 0.002181 | 0.003484 |
| 19929 | 0.002777 | 0.003059 | 0.003114 | 0.002685 | 0.002685 |
| 8401 | 0.003585 | 0.002019 | 0.003029 | 0.003053 | 0.006319 |



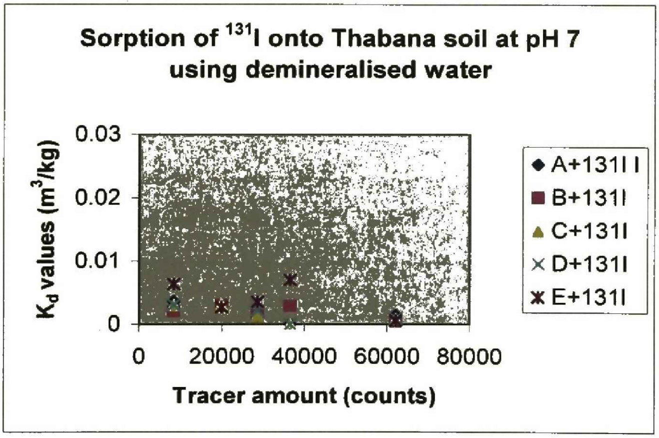


Figure 4.5: Graphs representing the distribution coefficients of $^{131}$I for Thabana soil using both Thabana water and demineralised water.

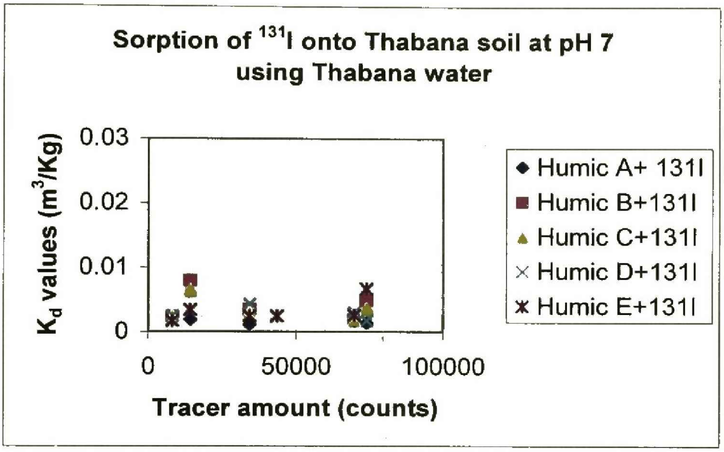
### 4.3.1.2 The absorption of $^{131}$I into humified Thabana soil at pH 7

Results in 4.2 above indicate that the amount of humic acid absorbed into slate is negligible and that the number of available absorption sites for radionuclide absorption is not significantly altered in the presence of humic acid. From these results, the distribution coefficients of iodine for humified Thabana soil were studied so as to investigate whether the presence of humic acid had altered the properties of the soil, thereby affecting the $K_d$ values.
The relatively low distribution values in Table 4.6 and in Figure 4.6 indicate that the anionic $^{131}$I does not absorb into artificially humified Thabana soil. This result confirms the results in 4.2, i.e. that the amount of humic acid that absorbed into slate was negligible and did not alter the absorption properties significantly in the presence of humic acid.

**Table 4.6:** $K_d$ values (m$^3$/kg) of $^{131}$I for humified Thabana soil samples.

| | **$K_d$ values (m$^3$/kg)** | | | | |
|---|---|---|---|---|---|
| | **(Thabana water)** | | | | |
| **Original Std. (Counts)** | **Humic A+ $^{131}$I** | **Humic B+$^{131}$I** | **Humic C+$^{131}$I** | **Humic D+$^{131}$I** | **Humic E+$^{131}$I** |
| 74040 | 0.001383 | 0.004897 | 0.003717 | 0.00175 | 0.006663 |
| 69840 | 0.001699 | 0.001905 | 0.001953 | 0.002968 | 0.00261 |
| 43535 | ---------- | ---------- | 0.045593 | ---------- | 0.002469 |
| 34186 | 0.001142 | 0.003542 | 0.00309 | 0.004271 | 0.002461 |
| 14213 | 0.001887 | 0.007946 | 0.006511 | 0.003417 | 0.003417 |
| 8067 | 0.002031 | 0.00238 | 0.002513 | 0.002464 | 0.001705 |

| | **$K_d$ values (m$^3$/kg)** | | | | |
|---|---|---|---|---|---|
| | **Demineralised water** | | | | |
| **Original Std. (Counts)** | **Humic A+ $^{131}$I** | **Humic B+$^{131}$I** | **Humic C+$^{131}$I** | **Humic D+$^{131}$I** | **Humic E+$^{131}$I** |
| 62169 | 0.000982 | 0.002205 | 0.001754 | 0.001003 | 0.000533 |
| 36489 | ---------- | 0.002663 | 0.002396 | 0.002921 | 0.002539 |
| 28641 | 0.001699 | 0.00256 | 0.00285 | 0.001581 | 0.002735 |
| 8401 | 0.003021 | 0.003511 | 0.003226 | 0.00324 | -------- |
| | | | | | |



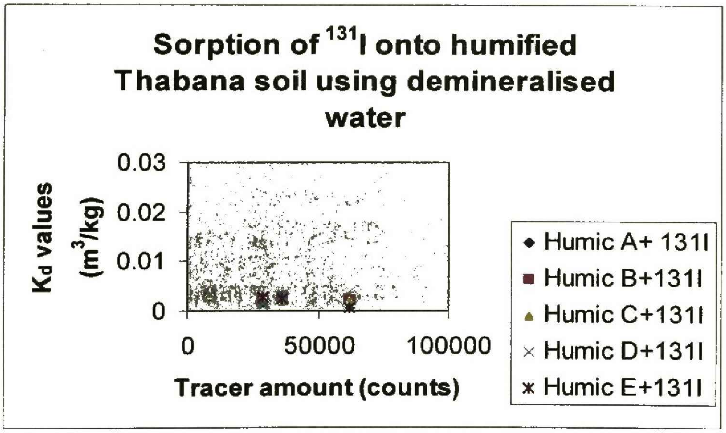


Figure 4.6: Distribution-coefficient (m$^3$/kg) data versus the tracer amount (counts) of $^{131}$I for humified Thabana soil at a neutral pH using both Thabana water and demineralised water.

### 4.3.1.3 The possible absorption of $^{131}$I –Ha into Thabana soil at pH 7

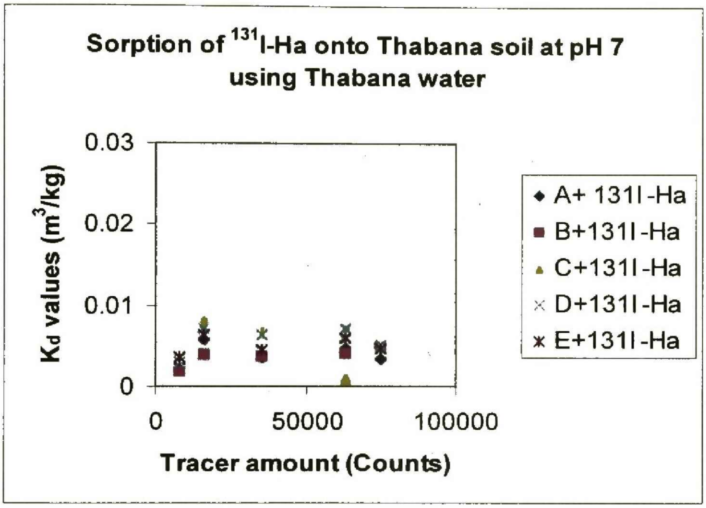
Humic acid has substantial chelating properties for metals, especially transition metals, and therefore considerably affects the sorption and migration of radionuclides in a soil layer. However, the chelation of humic acid with anoxic $^{131}$I is not well known and the absorption of such a specie into Thabana soil had to be investigated. In order to force the possible complex-formation, different concentrations of humic acid were added to the tracer, and in addition, in order to establish the formation of a chelated iodine specie, polarography was performed. However, the calculated results were unfortunately inconclusive because of the unknown molecular mass of the humic acid used and will not be reported.

The relatively low distribution coefficients of the possible anionic $^{131}$I-humate complexes presented in Table 4.7 and in Figure 4.7 correspond with the results in Table 4.5 for $^{131}$I. This result therefore indicates that possible anionic $^{131}$I-humate complexes that could alter the absorption properties of $^{131}$I into Thabana soil are not significantly present.

**Table 4.7:** $K_d$ values ($m^3/kg$) of $^{131}$I-Ha for Thabana soil samples.

| Thabana water | | | | | |
|---|---|---|---|---|---|
| $K_d$ values ($m^3/kg$) | | | | | |
| **Original Std. (Counts)** | **A+ $^{131}$I -Ha** | **B+$^{131}$I -Ha** | **C+$^{131}$I -Ha** | **D+$^{131}$I -Ha** | **E+$^{131}$I -Ha** |
| 75009 | 0.00346 | 0.004911 | 0.004911 | 0.005111 | 0.004657 |
| 63119 | 0.00465 | 0.004072 | 0.000862 | 0.007207 | 0.006061 |
| 52187 | 0.066074 | 0.011082 | 0.075384 | 0.074829 | 0.023585 |
| 35376 | 0.003644 | 0.003703 | 0.006742 | 0.006437 | 0.004568 |
| 15869 | 0.005767 | 0.003896 | 0.008122 | 0.00706 | 0.006356 |
| 8122 | 0.002859 | 0.001786 | 0.003564 | 0.003001 | 0.003564 |

| Demineralised water | | | | | |
|---|---|---|---|---|---|
| $K_d$ values ($m^3/kg$) | | | | | |
| **Original Std Counts** | **A+$^{131}$I -Ha** | **B+$^{131}$I -Ha** | **C+$^{131}$I -Ha** | **D+$^{131}$I -Ha** | **E+$^{131}$I -Ha** |
| 57069 | 0.000373 | 0.000477 | 0.000782 | 2.79E-05 | 0.000124 |
| 27884 | 0.001704 | 0.001367 | 0.001547 | 0.001819 | 0.001219 |
| 20649 | 0.003976 | 0.003155 | 0.005674 | 0.00143 | 0.003403 |
| 8208 | 0.002579 | 0.001264 | 0.0023 | 0.00143 | 0.002167 |



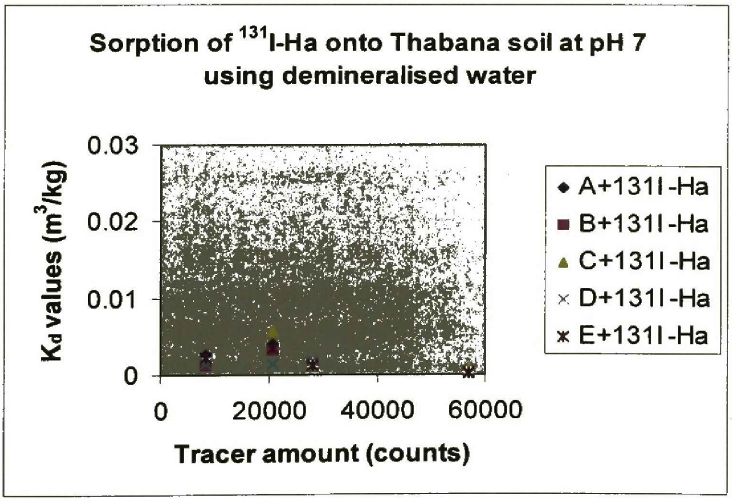


Figure 4.7: The distribution coefficients (m$^3$/kg) data versus the tracer amount (counts) $^{131}$I-Ha for Thabana soil at a neutral pH using both the Thabana water and demineralised water.

#### 4.3.1.4 The influence of redox conditions (different pH) on the absorption of $^{131}$I into Thabana soil

As the $K_d$ values for $^{131}$I absorption into different Thabana soil types are relatively similar (zero), it was decided to repeat all the above experiments in different redox conditions to study the absorption of iodine-humic complexes into Thabana soil. *Carter and Suffete* indicated that by changing the pH of a solution containing humic acid, the molecules would be aggregated due to hydrogen bonding and the ionisation of functional groups on the humic structure, thereby increasing the formation of complexes. The pH range between 4 and 10 was chosen for this experiment as literature (*Cha. H et al, 2003)* indicated that at a pH lower than 3,5, humic acid precipitates and at a pH higher than 10, the organic structure of humic acid starts decomposing.

The relatively low distribution coefficients presented in Table 4.8 and in Figure 4.8 indicate that the absorption of different $^{131}$I complexes into different Thabana soil types remains minimal even under different redox conditions. The results also indicate that, at the two extreme specified redox conditions, the absorption of humic acid tends to decrease. However, the values actually differ minimally and therefore it is difficult to confirm whether humic acid starts precipitating at pH 4 and decomposing at pH 10.

Interesting from the results is the "slight" increase in absorption for the possible humic-$^{131}$I complex, which could indicate the presence of these complexes. Unfortunately, it is very difficult to confirm this statement owing to the low absorption values and therefore it remains only a possibility.

**Table 4.8:** $K_d$ values of $^{131}$I on soil fraction A under different pH conditions using Thabana water (0.1g/l Ha) and an average of 16000 counts of tracer.

| | **$K_d$ values ($m^3/kg$)** | | |
|---|---|---|---|
| **pH** | **Soil A + $^{131}$I** | **Ha-A+$^{131}$II** | **Soil A + Ha-$^{131}$I** |
| 4 | 0.001469 | 0.001807 | 0.00361 |
| 7 | 0.002069 | 0.001628 | 0.00438 |
| 10 | 0.000453 | 0.000714 | 0.001636 |

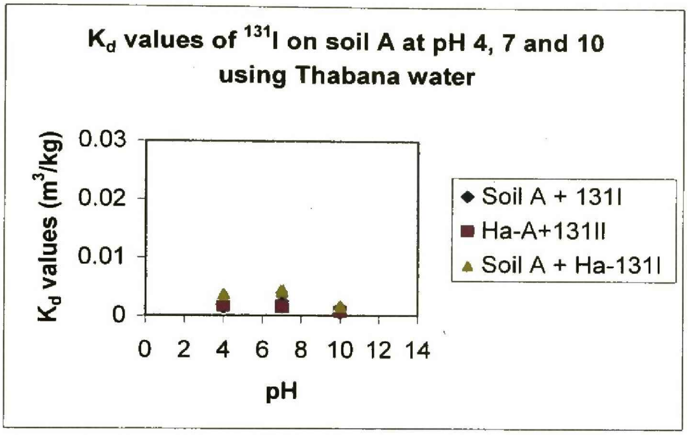


Figure 4.8: $K_d$ values of different iodine complexes for soil fraction A at different pH conditions.

### 4.3.2 Influence of cationic radionuclide specie ($^{137}$Cs)

$^{137}$Cs is often found in waste repositories as a fission product. It has a half-life of 30,1 years. It is regarded as one of the major contributors to the radiation hazards of spent fuel during the first 300 years after discharge from a reactor. It is also a suitable model element for studying the behaviour of uncomplexed divalent and monovalent cations.

Cesium in a groundwater solution exists as cationic Cs over a wide pH and concentration range. None of the common complex-forming agents found in groundwater (humic acid included) will form strong complexes with Cs and it is expected that no complexes with humic acid will form and the migration (absorption) of cesium will remain unaffected. In order to confirm the above assumption regarding complex-formation and migration properties, the absorption of cesium in the presence and absence of humic acid under different redox (pH) conditions into the different soils was studied.

#### 4.3.2.1 Absorption of cesium ($^{137}Cs$) into Thabana soil at pH 7

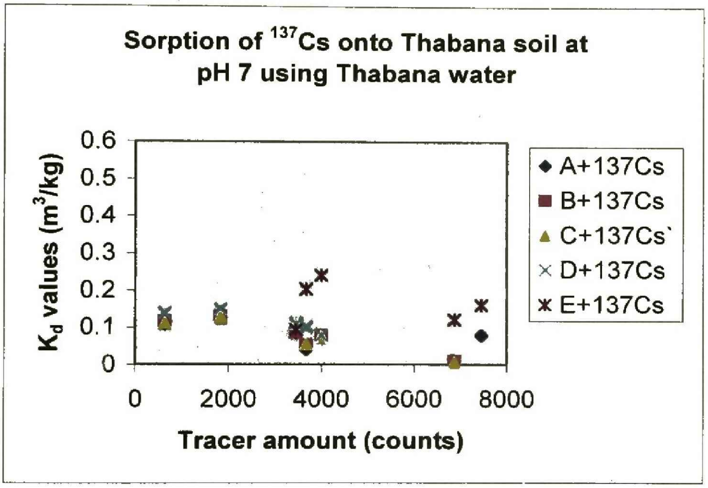
The distribution values in Table 4.9 and in Figure 4.9 indicate $^{137}Cs$ absorption into the different Thabana soils. This result compares with results of *D.G. Brookins,* who investigated the ability of shale and clay minerals to react with, and retain, radionuclides from spent fuel by locking the radionuclides into the mineral structures of the shale.

The results also indicate that the average absorption value for $^{137}Cs$ absorption into the different soils is slightly higher for demineralised water than for Thabana water. The differences in values are minimal, therefore the values are considered to be the same. If this small difference in values is real, a possible explanation for this result is that the presence of ionic species in the Thabana water favours the formation of $^{137}Cs$ complexes, thereby altering the absorption properties of $^{137}Cs$.

Table 4.9: $K_d$ values ($m^3/kg$) of $^{137}Cs$ for Thabana soil at pH 7.

| **Pure Soil types**<br>**$K_d$ Values ($m^3/kg$) Thabana water pH 7** | | | | | | |
|---|---|---|---|---|---|---|
| Rdnlcd set # | C (orig ) | A + $^{137}Cs$ | B + $^{137}Cs$ | C + $^{137}Cs$ | D + $^{137}Cs$ | E + $^{137}Cs$ |
| 1 | 7445 | 0.078949 | ---------- | ---------- | ---------- | 0.16 |
| 2 | 6867 | 0.009575 | 0.010102 | 0.006757 | ---------- | 0.121398 |
| 3 | 3995 | 0.075181 | 0.078778 | 0.076099 | 0.07819 | 0.23958 |
| 4 | 3666 | 0.040219 | 0.05299 | 0.055404 | 0.100422 | 0.202442 |
| 5 | 3450 | 0.08375 | 0.087734 | 0.109377 | 0.110209 | 0.093934 |
| 6 | 1827 | 0.137339 | 0.129466 | 0.129466 | 0.14887 | ---------- |
| 7 | 634 | 0.107407 | 0.1168 | 0.111923 | 0.138442 | ---------- |

| | **Pure soil types**<br>**$K_d$ values ($m^3/kg$) demineralised water at pH 7** | | | | | |
|---|---|---|---|---|---|---|
| Rdncld set # | Counts | A+$^{137}Cs$ | B+$^{137}Cs$ | C+$^{137}Cs$ | D+$^{137}Cs$ | E+$^{137}Cs$ |
| 1 | 3798 | 0.121875 | 0.08495 | 0.126129 | 0.126129 | 0.14192 |
| 2 | 1464 | 0.075614 | 0.062118 | 0.07044 | 0.082658 | 0.156364 |
| 3 | 1254 | 0.202542 | 0.206207 | 0.213929 | 0.235882 | 0.21 |
| 4 | 817 | 0.26233 | 0.345217 | 0.19425 | 0.167609 | 0.216944 |



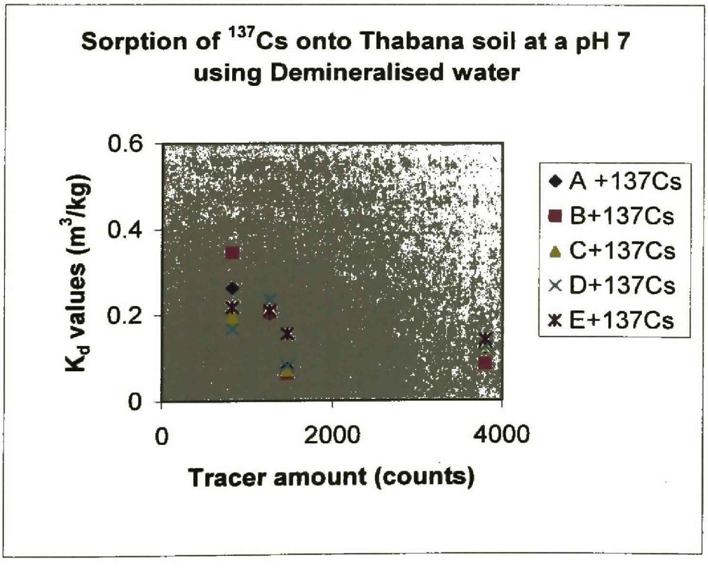


Figure 4.9: Distribution coefficients ($m^3$/kg) of $^{137}$Cs onto Thabana soil.

#### 4.3.2.2 The absorption of $^{137}$Cs into humified Thabana soil at pH 7

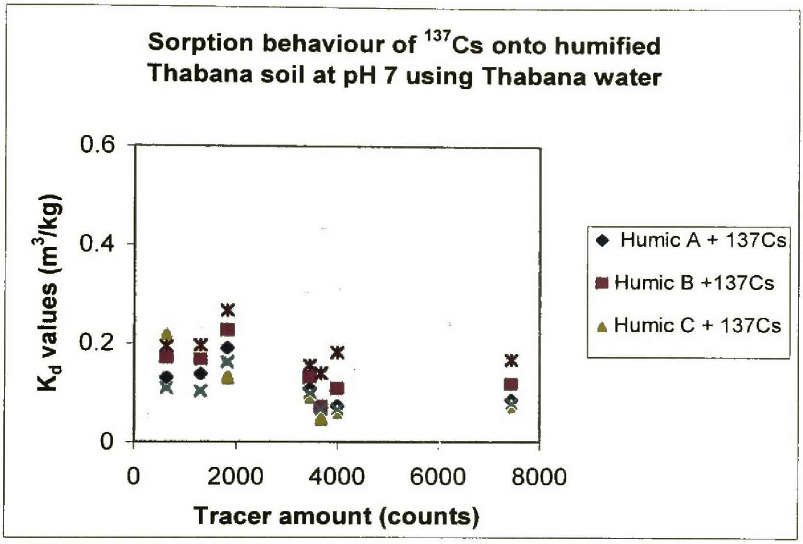
Previous results in section 4.2 indicated that the amount of humic acid that absorbed into slate was negligible and that the number of available absorption sites for radionuclide absorption would not be significantly altered in the presence of humic acid. As the results in 4.3.2.1 show a slight absorption of cesium into slate, it is important to investigate whether the characteristics of the slate is altered in the presence of humic acid.

The absorption of $^{137}$Cs into artificially humified Thabana soil was determined and the distribution values (Table 4.10 and Figure 4.10) do not show any significant difference from the values determined with pure Thabana soil (Table 4.9). This result confirms the results in section 4.2, namely that the amount of humic acid that absorbed into slate was negligible and did not alter the absorption properties of the soil.

**Table 4.10:** $K_d$ values ($m^3/kg$) of $^{137}$Cs absorption into humified Thabana soil samples.

| | **Thabana water** | | | | |
|---|---|---|---|---|---|
| | **$K_d$ values ($m^3/kg$) of $^{137}$Cs for humified Thabana soil** | | | | |
| Counts | Humic A + $^{137}$Cs | Humic B + $^{137}$Cs | Humic C + $^{137}$Cs | Humic D + $^{137}$Cs | Humic E + $^{137}$Cs |
| 7445 | 0.086563 | 0.119253 | 0.075871 | 0.078526 | 0.167262 |
| 3995 | 0.073229 | 0.109254 | 0.063981 | 0.066095 | 0.182067 |
| 3666 | 0.070927 | 0.072013 | 0.049417 | 0.066375 | 0.139633 |
| 3450 | 0.108557 | 0.133154 | 0.095505 | 0.099177 | 0.155865 |
| 1827 | 0.19069 | 0.227273 | 0.132734 | 0.162358 | 0.266818 |
| 1300 | 0.137727 | 0.168082 | 0.193125 | 0.103043 | 0.196349 |
| 634 | 0.130889 | 0.171143 | 0.216429 | 0.109623 | 0.194516 |

| **Demineralised water** | | | | | |
|---|---|---|---|---|---|
| **Humified soil** | | | | | |
| | $K_d$ values ($m^3/kg$) of $^{137}$Cs for humified Thabana soil | | | | |
| Counts | Humic A + $^{137}$Cs | Humic B + $^{137}$Cs | Humic C + $^{137}$Cs | Humic D + $^{137}$Cs | Humic E + $^{137}$Cs |
| 3798 | 0.0966 | 0.1296 | 0.0918 | 0.109 | 0.2259 |
| 1464 | 0.0536 | 0.07404 | 0.0497 | 0.0426 | 0.0704 |
| 1254 | 0.128 | 0.1293 | 0.1234 | 0.1429 | 0.1358 |
| 817 | ------ | 0.1999 | 0.1845 | 0.205 | 0.1676 |



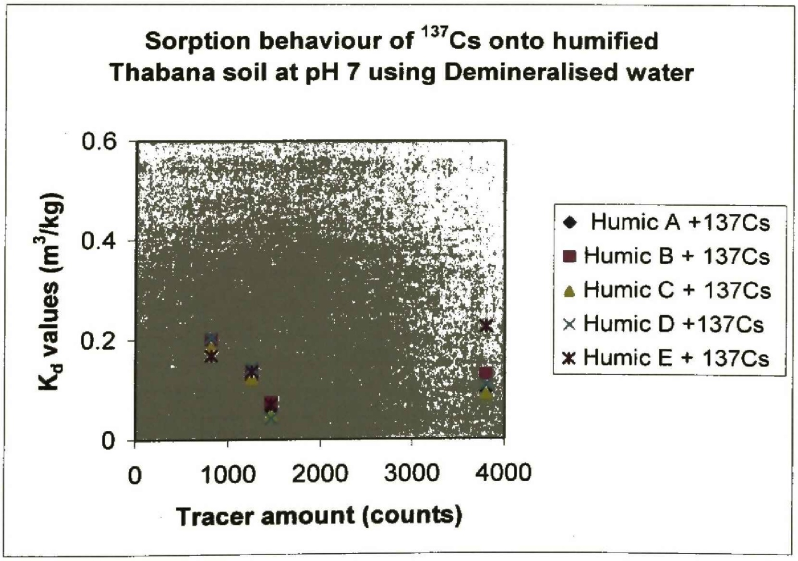


Figure 4.10: The distribution coefficients of $^{137}$Cs for humified Thabana soil at Thabana using Thabana water and demineralised water.

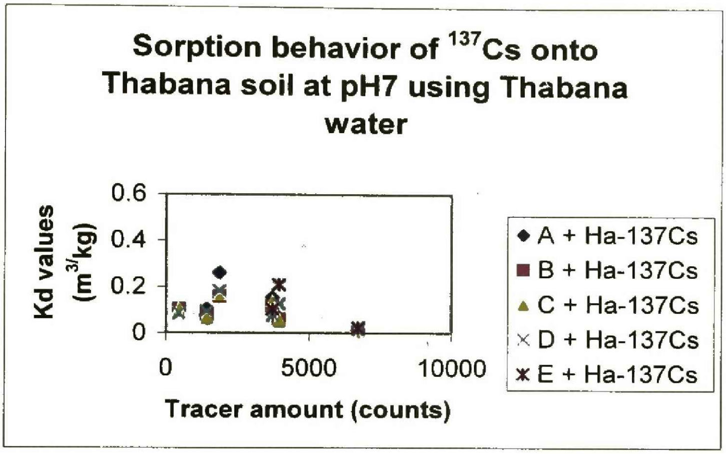
### 4.3.2.3 The absorption of $^{137}$Cs –humic acid complex into Thabana soil at pH 7

Humic acid has substantial chelating properties for metals, especially transition metals, and therefore could considerably affect the sorption and migration of radionuclides in a soil layer. However, previous results indicated that the chelating of humic acid with anoxic $^{131}$I could not be observed and therefore it was necessary to determine whether a humic-metal complex formed with a cationic specie like $^{137}$Cs and not $^{131}$I. As stated before, calculated results on this type of complex-formation were inconclusive owing to the unknown molecular mass of the humic acid used and would not be reported.

The distribution coefficients presented in Table 4.11 and in Figure 4.11 of the possible cationic $^{137}$Cs-humate complexes correspond with the results in Table 4.10 for $^{137}$Cs absorption into the same soil (in the absence of humic acid). This result therefore indicates that possible $^{137}$Cs-humate complexes are present but the absorption properties remain the same, or that no complexes formed. As indicated by *Tanaka et al*, that cesium species do not form complexes with humic acid.

**Table 4.11:** The distribution coefficients of Ha-Cs for Thabana soil.

| **Thabana water** | | | | | |
|---|---|---|---|---|---|
| | **$K_d$ values (m$^3$/kg) of $^{137}$Cs-Ha for Thabana soil** | | | | |
| Counts | A + Ha-$^{137}$Cs | B + Ha-$^{137}$Cs | C + Ha-$^{137}$Cs | D + Ha-$^{137}$Cs | E + Ha-$^{137}$Cs |
| 6720 | 0.008 | 0.0088 | 0.0074 | 0.007958 | 0.0224 |
| 3944 | 0.069 | 0.0616 | 0.0602 | 0.126944 | 0.209111 |
| 3717 | 0.1536 | 0.1176 | 0.1382 | 0.076042 | 0.104369 |
| 1867 | 0.2605 | 0.1581 | 0.1661 | 0.18051 | ---------- |
| 1423 | 0.1029 | 0.0778 | 0.0727 | 0.092374 | ---------- |
| 464 | 0.1004 | 0.106 | 0.106 | 0.086667 | ---------- |
| | | | | | |
| **Demineralised water** | | | | | |
| | **$K_d$ values (m$^3$/kg) of 137Cs-Ha for Thabana soil** | | | | |
| Counts | A + Ha-$^{137}$Cs | B + Ha-$^{137}$Cs | C + Ha-$^{137}$Cs | D + Ha-$^{137}$Cs | E + Ha-$^{137}$Cs |
| 4137 | 0.081325 | 0.078968 | 0.079352 | 0.088266 | 0.163096 |
| 1579 | 0.173605 | 0.129735 | 0.180241 | --------- | 0.197703 |
| 1587 | 0.263621 | 0.183537 | 0.22 | 0.230455 | 0.22 |
| 614 | 0.170588 | 0.217407 | 0.165429 | 0.160556 | 0.176061 |



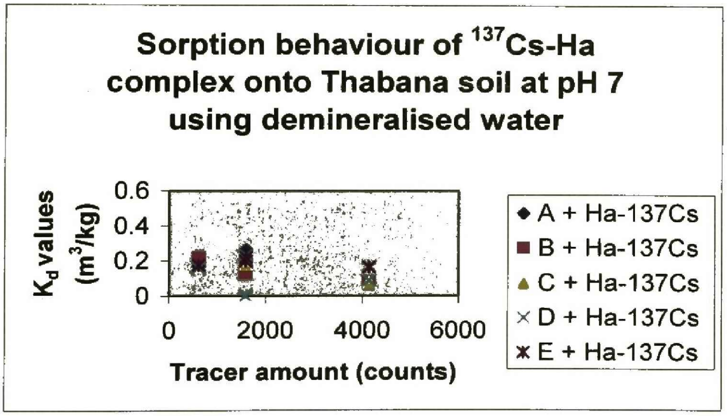


Figure 4.11: The distribution coefficients ($K_d$ values) of Ha-Cs for Thabana Soil using both Thabana water and demineralised water.

### 4.3.2.4 The influence of redox conditions (different pH) on the absorption of $^{137}$Cs into Thabana soil

*Carter and Suffete* indicated that by changing the pH of a solution containing humic acid, the molecules would be aggregated owing to hydrogen bonding and the ionisation of functional groups on the humic structure, thereby increasing the formation of complexes. In order to study this phenomenon, the absorption experiments of cesium into Thabana soil (soil type C) in the presence of humic acid were repeated for the pH range between 4 and 10.

The distribution coefficient results in Table 4.12 and in Figure 4.12 indicate that the absorption of cesium into Thabana soil remains the same even in the different redox environments (radionuclides alone, radionuclide with humic acid and radionuclide on humified soil). This result confirms that cesium species do not form complexes with humic acid. The lower absorption value at pH 4 can be attributed to the fact that humic acid starts precipitating at pH 4.

**Table 4.12:** The influence of pH on the sorption behaviour of $^{137}$Cs for soil sample C. (0.1g/l Ha) at an average of 10 000 counts of $^{137}$Cs tracer).

| | $K_d$ values ($m^3/kg$) | | |
|---|---|---|---|
| pH | Soil C +$^{137}$Cs | Ha-soil C + $^{137}$Cs | Soil C + 0.1 Ha-$^{137}$Cs |
| 4 | 0.19595 | 0.17463 | 0.16646 |
| 7 | 0.26243 | 0.26473 | 0.28678 |
| 10 | 0.27211 | 0.29779 | 0.26552 |

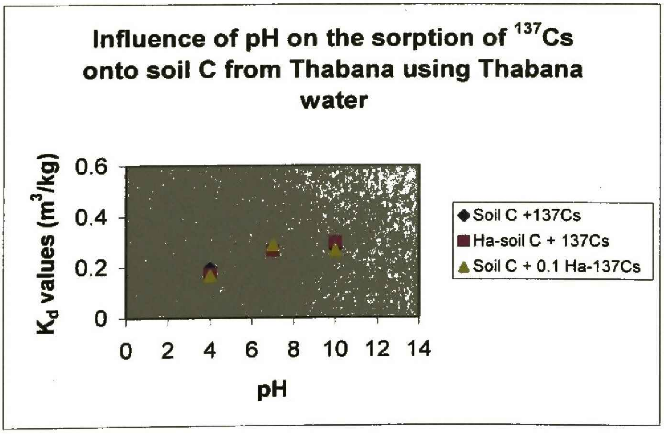


Figure 4.12: The distribution coefficients of $^{137}$Cs for soil C at different pH values.

# CHAPTER 5

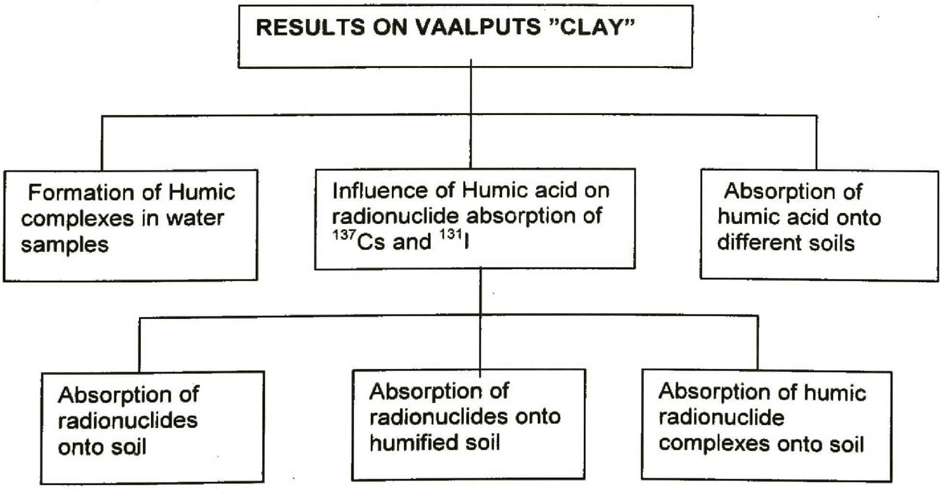
## RESULTS AND DISCUSSION
### Vaalputs studies

# 5. RESULTS ON VAALPUTS SOIL

The influence of humic acid on the migration properties of radionuclides at the South African waste repositories as well as the possible mechanisms involved was also carried out for Vaalputs. The following were studied:

- The possible formation of humic complexes in site-specific water sources (Vaalputs water)
- The possible absorption of these humic complexes into soils at the waste repositories
- The absorption of radionuclides into soil samples from Vaalputs
- The influence of redox conditions on the absorption of humic radionuclides complexes into soils
- The possible surface complexation reaction between absorbed humic acid on soil surface and radionuclides (absorption of radionuclides into humified soil samples)

The results in this chapter will be presented and discussed as indicated in the following schematic presentation:



## 5.1 Investigation of Humic-complex Formation in Vaalputs Water

In order to determine the possible formation of humic acid complexes in the water samples used in this study, a known amount of humic acid salt was dissolved in demineralised water, Vaalputs water, and Thabana water. These solutions were then studied by using the Cary 2300 spectrophotometer at the spectrum region of 350 nm. (this appears to be the most sensitive region for humic acid standards used in this study).

The results in Table 4.1 and in Figure 4.1 indicate that regardless of the different water sources, the presence of high concentrations of chlorides and sulphates in the Vaalputs water and different humic concentrations, no significant differences in the absorption spectra of humic acid were observed. These results indicate that humic complexes that form in the research water samples under the specified redox conditions are negligible and will not affect the results of this study (for more detail, see section 4.1).

## 5.2 Absorption of Humic Acid into Different Vaalputs Soils

In order to determine the possible absorption of humic acid into clay, thereby reducing the number of available absorption sites for radionuclide absorption, a known amount of humic acid salt was dissolved in demineralised water and Vaalputs water. These solutions were then used to determine the absorption of humic acid into soil samples.

The results in Table 5.1 and Figure 5.1 indicate that the absorption of humic acid into different materials (clay and calcrete) as encountered at Vaalputs is minimal. The results indicate that even in the presence of high concentrations, i.e. between 0,15 g/L and 0,3 g/L, a uniform distribution coefficient is observed. The $K_d$ values in this region are very low, indicating that the amount of humic acid absorbed into clay is very small and that the number of available absorption sites for radionuclides absorption has not been significantly altered in the presence of humic acid.

**Table 5.1:** Distribution-coefficient values of humic acid for Vaalputs soil.

| | **Vaalputs water** | | |
|---|---|---|---|
| **350 nm** | **$K_d$ Values ($m^3$/kg)** | | |
| **Conc. (g/1)** | **RC + Ha** | **Calc + Ha** | **BF + Ha** |
| 0.3 | 0.071485 | 0.08 | 0.053333 |
| 0.25 | 0.085714 | 0.066571 | 0.06 |
| 0.2 | --------- | 0.053636 | 0.079333 |
| 0.15 | 0.074444 | 0.056087 | 0.121538 |
| 0.1 | 0.14 | 0.09 | --------- |

| | **Demineralised water** | | |
|---|---|---|---|
| **350 nm** | **$K_d$ values ($m^3$/kg)** | | |
| **Conc. (g/L)** | **R.C + Ha** | **Calc + Ha** | **BF + Ha** |
| 0.3 | 0.055625 | 0.019717 | 0.007697 |
| 0.25 | 0.043571 | 0.016471 | 0.00505 |
| 0.2 | 0.053692 | 0.021846 | 0.010097 |
| 0.15 | 0.086875 | 0.033056 | 0.012302 |
| 0.1 | 0.077692 | 0.0356 | 0.021667 |
| 0.05 | 0.058235 | 0.028667 | 0.014167 |

Rc: red clay
Calc: Calcrete
Bf:Backfill
Ha:Humic acid

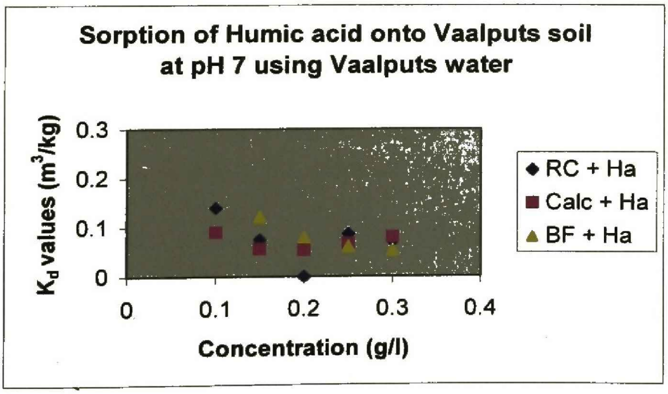


Figure 5.1 (a) Distribution of humic acid for Vaalputs soil using both Thabana water and demineralised water

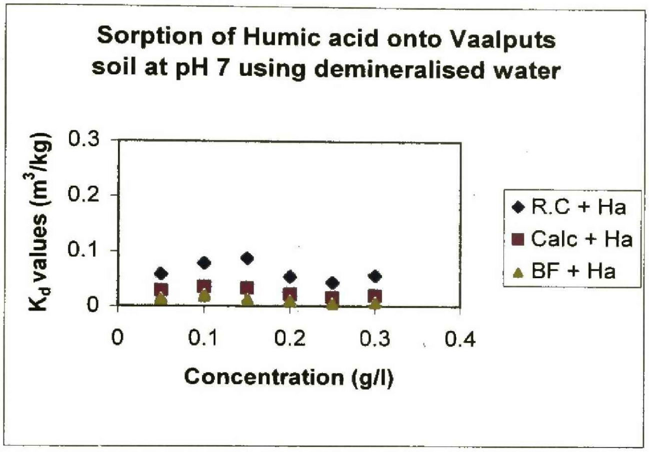


Figure 5.1 (b) Distribution of humic acid for Vaalputs soil using both Thabana water and demineralised water

As stated by *Carter and Suffete* (see section 4.1), redox changes will alter the humic acid molecules. So the experiment was repeated for different redox conditions to determine whether these "altered" humic acid structures would influence the absorption properties of clay.

The results in Table 5.2 and Figure 5.2 indicate that no significant absorption of humic acid into clay was observed for the pH range between 5 and 10. The conclusion is therefore that even if undetected "altered" humic acid structures do form, these structures do not absorb into clay and therefore the presence of any "free" humic acid in the water will have a minimal effect on the results of this study.

**Table 5.2:** The absorption ($K_d$ values) of humic acid into Vaalputs soil at different pH values.

|  | **Vaalputs water** |  |  |
|---|---|---|---|
|  | **$K_d$ values ($m^3/kg$)** |  |  |
| pH | RC + Ha | Calc +Ha | BF + Ha |
| 4 | 0.03599 | 0.04235 | 0.05 |
| 7 | 0.14 | 0.053636 | 0.079333 |
| 10 | 0.046667 | 0.036364 | 0.029231 |

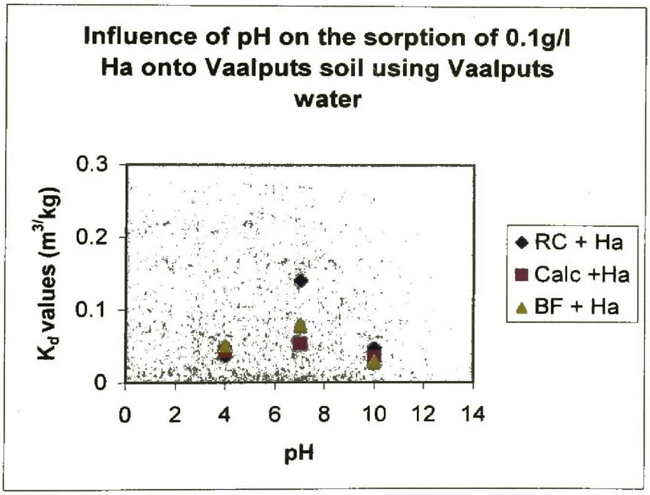


Figure 5.2: Influence of pH on the distribution coefficients of humic acid for different Vaalputs soils.

## 5.3 Absorption of Radionuclides into Vaalputs Soil

### 5.3.1 The absorption of $^{131}$I

In this project, $^{131}$I was used instead of $^{129}$I owing to the difficulties of studying $^{129}$I. $^{131}$I has a shorter half-life than its isotope $^{129}$I, making $^{131}$I very easy to work with.

The proposed structure of humic acid contains many double bonds, which would result in a negatively charged humic acid structure, and therefore it is expected that the anionic species would not form complexes with humic acid. The migration (absorption) of iodine would remain unaffected.

To confirm the above assumption regarding complex-formation and migration properties, the absorption of $^{131}$I in the presence and absence of humic acid under different redox pH conditions into the different soil samples was studied.

#### 5.3.1.1 The absorption of $^{131}$I into Vaalputs clay soil

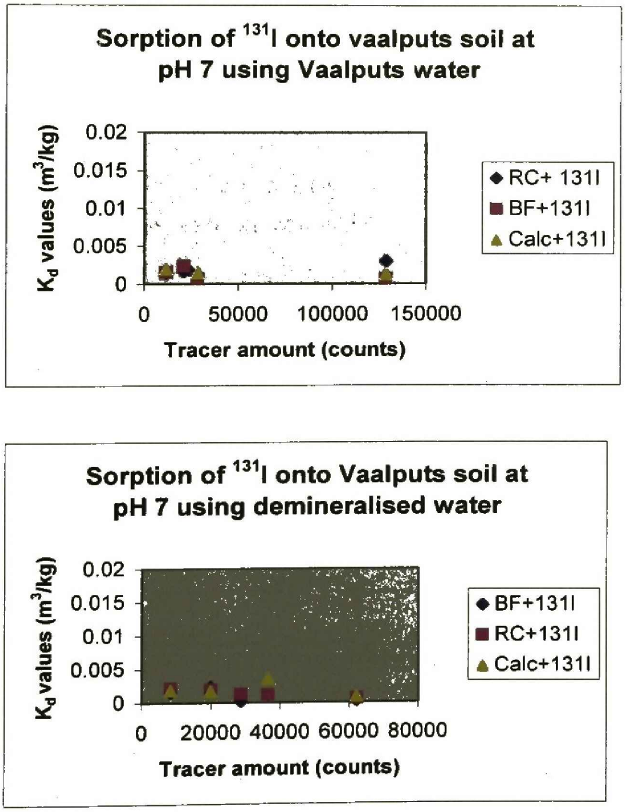
The relatively low distribution-coefficient values in Table 5.3 and in Figure 5.3 obtained for the absorption of $^{131}$I into clay indicate that anionic $^{131}$I does not absorb into Thabana soil even in the presence of different water sources.

**Table 5.3 (a):** $K_d$ values of $^{131}$I for pure Vaalputs soil using Vaalputs water.

| Vaalputs water<br>$K_d$ values ($m^3$/kg) | | | |
|---|---|---|---|
| **Counts** | **RC+ $^{131}$I** | **BF+$^{131}$I** | **Calc+$^{131}$I** |
| 128669 | 0.002982 | 0.000692 | 0.00125 |
| ------- | ------- | 0.000606 | 0.001516 |
| 28416 | 0.000926 | 0.000699 | 0.001443 |
| 23607 | 0.001834 | ------- | ------- |
| 21149 | 0.001595 | 0.00234 | ------- |
| 11644 | 0.001374 | 0.001532 | 0.001906 |

**Table 5.3 (b):** $K_d$ values of $^{131}I$ for pure Vaalputs soil using demineralised water.

| | Demineralised water | | |
|---|---|---|---|
| | $K_d$ values($m^3/kg$) | | |
| Counts | BF+$^{131}I$ | RC+$^{131}I$ | Calc+$^{131}I$ |
| 62169 | 0.000166 | 0.000617 | 0.000838 |
| 36489 | 0.001067 | 0.001147 | 0.003524 |
| 28641 | 0.000209 | 0.001301 | --------- |
| 19929 | 0.002362 | 0.001973 | 0.001674 |
| 8401 | 0.001489 | 0.002213 | 0.001836 |


Sorption of $^{131}I$ onto vaalputs soil at pH 7 using Vaalputs water

Sorption of $^{131}I$ onto Vaalputs soil at pH 7 using demineralised water

Figure 5.3: Distribution coefficients of $^{131}I$ for Vaalputs soil using both Vaalputs and demineralised water under environmental conditions

### 5.3.1.2 The absorption of $^{131}I$ into humified Vaalputs soil

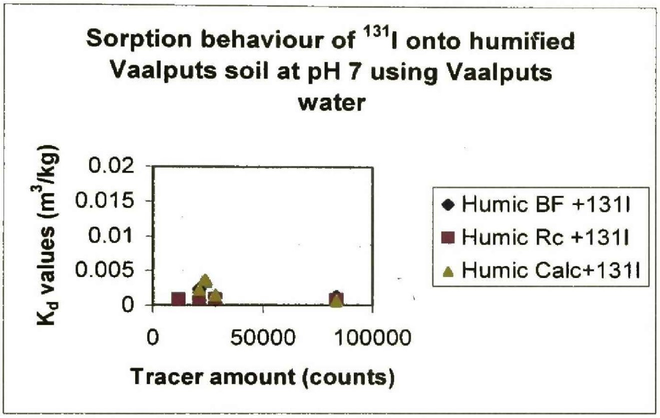
Previous results indicated that the amount of humic acid absorbed into clay was negligible and that the number of available absorption sites for radionuclides absorption would not be significantly altered in the presence of humic acid. In order to determine whether the characteristics of clay in the presence of humic acid would be altered to permit $^{131}I$ absorption, experiments were performed on artificially humified Vaalputs soil.

The relatively low distribution values in Table 5.4 and in Figure 5.4, which correspond with the values in Table 5.4, indicate that anionic $^{131}I$ does not absorb into artificially humified Vaalputs soil and that the absorption into any soil from the Vaalputs region is negligible. The results, which are the same for both demineralised and Vaalputs water, indicate that no significant polymerisation (complex-formation at high concentrations of chlorides) has taken place in the Vaalputs water and that the migration of $^{131}I$ will remain unaffected by the presence of humified soil.

**Table 5.4:** $K_d$ values ($m^3/kg$) of $^{131}I$ for humified Vaalputs soil samples.

| Vaalputs water | | | |
|---|---|---|---|
| | $K_d$ values ($m^3/kg$) | | |
| **Counts** | **Humic BF +$^{131}I$** | **Humic Rc +$^{131}I$** | **Humic Calc+$^{131}I$** |
| 83479 | 0.001266 | 0.000865 | 0.000635 |
| 28416 | 0.000699 | 0.000945 | 0.001443 |
| 23607 | -------- | ---------- | 0.003693 |
| 21149 | 0.00235 | 0.000986 | 0.00229 |
| 11644 | | 0.000884 | -------- |

| Demineralised water | | | |
|---|---|---|---|
| | $K_d$ values ($m^3/kg$) | | |
| **Counts** | **Humic BF +$^{131}I$** | **Humic Rc +$^{131}I$** | **Humic Calc+$^{131}I$** |
| 83479 | 0.001266 | 0.000865 | 0.000635 |
| 28416 | 0.000699 | 0.000945 | 0.001443 |
| 23607 | ---------- | ---------- | 0.003693 |
| 21149 | 0.00235 | 0.000986 | 0.00229 |
| 11644 | -------- | 0.000884 | -------- |



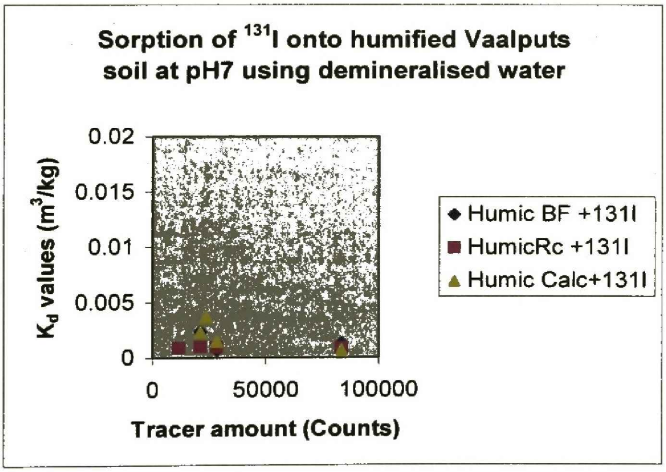


Figure 5.4: $K_d$ values of $^{131}$I for humified Vaalputs clay using both Vaalputs and demineralised water.

### 5.3.1.3 The possible absorption $^{131}$I–Ha into Vaalputs soil

Humic acid has substantial chelating properties for metals, especially transition metals, and therefore may affect the sorption and migration of radionuclides in clay. However, the chelation of humic acid with anoxic $^{131}$I is not well known and the absorption of such specie into Vaalputs clay had to be investigated. In order to force the possible complex-formation, different concentrations of humic acid were added to the tracer and in addition, in addition, polarography was performed in order to establish the formation of chelated iodine. However, the calculated results were inconclusive owing to the unknown molecular mass of the humic acid used and will not be reported.

The relatively low distribution coefficients presented in Table 5.5 and in Figure 5.5 of the possible anionic $^{131}$I-humate complexes indicate that possible anionic $^{131}$I-humate complexes that could alter the absorption properties of $^{131}$I into Thabana soil are not significantly present.

**Table 5.5:** $K_d$ values ($m^3$/kg) of I-Ha for Vaalputs soil samples using both Vaalputs water and demineralised water.

| | **Vaalputs water** | | |
|---|---|---|---|
| | **$K^d$ values ($m^3$/kg)** | | |
| **Counts** | **BF +$^{131}$I-Ha** | **RC +$^{131}$I-Ha** | **Calc +$^{131}$I-Ha** |
| 85642 | 0.001601 | -------- | 0.002464 |
| 72407 | 0.007272 | 0.003823 | 0.007255 |
| 42324 | 0.00673 | --------- | 0.008633 |
| 25868 | 0.000922 | 0.000866 | 0.001829 |
| 19384 | 0.001545 | 0.001835 | 0.00408 |
| 11282 | 0.001323 | 0.001152 | 0.002432 |

| **Demineralised water** | | | |
|---|---|---|---|
| **$K_d$ Values ($m^3$/kg)** | | | |
| **Counts** | **BF+ $^{131}$I -Ha** | **Rc+$^{131}$I -Ha** | **Calc+$^{131}$I -Ha** |
| 57069 | 0.000213 | 0.000296 | 0.001195 |
| 35912 | 0.002345 | 0.001249 | ---------- |
| 27884 | 0.001112 | 0.001408 | 0.002701 |
| 20649 | 0.002048 | 0.002259 | 0.003472 |
| 8208 | 0.00157 | 0.002238 | 0.002875 |

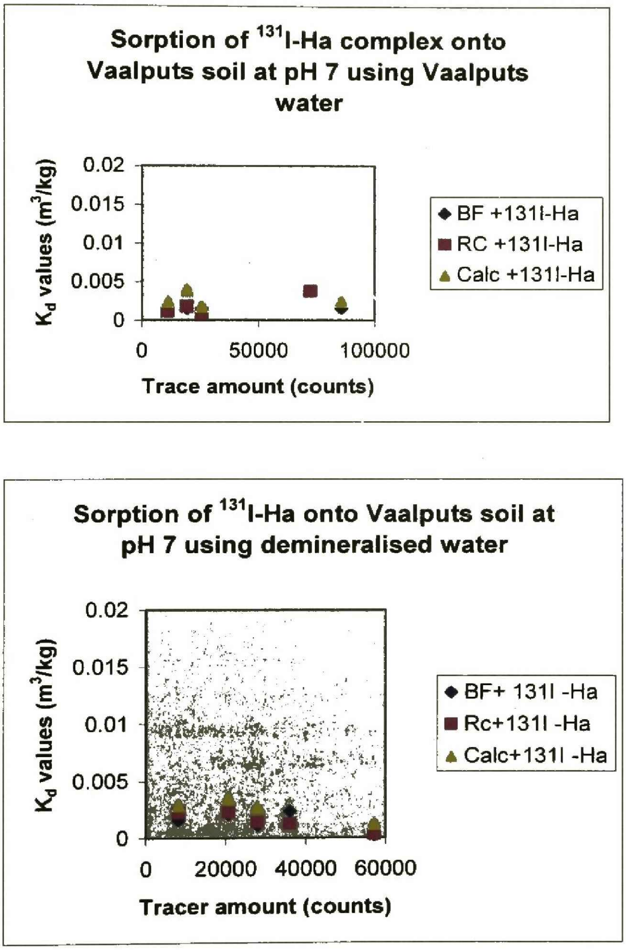


Figure 5.5: Influence of pH on the $K_d$ values of $^{131}$I.

### 5.3.1.4 The influence of pH on the absorption of $^{131}$I into Vaalputs soil

$^{131}$I and its complexes do not sorbs into different soil types from Vaalputs at pH 7 and as $^{131}$I is encapsulated in cement waste containers, the above experiments were repeated under higher redox conditions. According to *Carter and Suffete,* by changing the pH of a solution containing humic acid, the molecules will be aggregated owing to hydrogen bonding and the ionisation of functional groups on the humic structure, thereby increasing the formation of complexes. Again the pH range between 4 and 10 was chosen for this experiment as literature (*Cha. H et al, 2003)* indicated that at a pH lower than 3,5, humic acid precipitated and at a pH higher than 10, the organic structure of humic acid started decomposing

The relatively low distribution coefficients presented in Table 5.6 and in Figure 5.6 indicate that the sorption of different $^{131}$I complexes into different soil types from Vaalputs remains minimal even under different redox conditions.

**Table 5.6:** The influence of pH on the sorption of $^{131}$I onto Vaalputs soil (0.1g/l Ha) and an average of 10 000 counts)

| | **Vaalputs water** | | |
|---|---|---|---|
| | **$K_d$ values ($m^3/kg$)** | | |
| **pH** | **RC+$^{131}$I** | **HA-RC+$^{131}$I** | **RC+$^{131}$I -Ha** |
| 4 | 0.001329 | 0.00231 | 0.002981 |
| 7 | 0.001968 | 0.005613 | 0.004973 |
| 12 | 0.001657 | 0.001976 | 0.00155 |

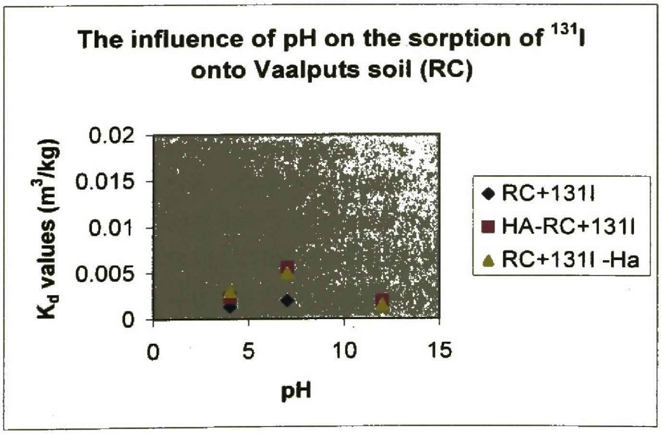


Figure 5.6: The influence of pH on the $K_d$ values of $^{131}$I for Vaalputs soil.

### 5.3.2 Sorption of cesium ($^{137}$Cs) onto soil samples

$^{137}$Cs is often found in waste repositories as a fission product. It has a half-life of 30,1 years, and is regarded as one of the major contributors to the radiation hazards of spent fuel during the first 300 years after discharge from a reactor. It is also a suitable model element for studying the behaviour of uncomplexed divalent and monovalent cations.

Cesium in groundwater solution exists as cationic Cs over a wide pH and concentration range. None of the common complex-forming agents found in groundwater (humic acid included) will form strong complexes with Cs and it is expected that no complexes with humic acid will form and the migration (absorption) of cesium will remain unaffected. In order to confirm the above assumption regarding complex-formation and migration properties, the absorption of cesium into the different soils in the presence and absence of humic acid under different redox (pH) conditions was studied.

#### 5.3.2.1 Absorption of cesium ($^{137}$Cs) into Vaalputs clay at pH 7

The distribution values in Table 5.7 and in Figure 5.7 indicate that $^{137}$Cs does absorb into the different Vaalputs clays. The results also indicate that the average $^{137}$Cs absorption value for Vaalputs water is higher than for demineralised water. A possible explanation for this is that the presence of ionic species in the Vaalputs water favours the formation of $^{137}$Cs complexes that absorbs onto the clay, thereby increasing the absorption properties of $^{137}$Cs.

**Table 5.7:** $K_d$ values ($m^3/kg$) of $^{137}Cs$ onto Vaalputs soil at pH 7.

| | **Vaalputs water** | | |
|---|---|---|---|
| | **$K_d$ values ($m^3/kg$)** | | |
| **Counts** | **BF + $^{137}Cs$** | **RC + $^{137}Cs$** | **Calc + $^{137}Cs$** |
| 38696 | 0.148916 | ---------- | ---------- |
| 24089 | ---------- | 0.461409 | 0.122649 |
| 8127 | 0.133841 | 0.436974 | 0.15125 |
| 6240 | 0.182 | 0.168797 | 0.462727 |
| 3666 | 0.75375 | 0.442593 | 0.823182 |
| 3398 | 0.347684 | 0.437105 | 0.455479 |
| 1603 | 0.219 | 0.257167 | --------- |

| | **Demineralised water** | | |
|---|---|---|---|
| | **$K_d$ values ($m^3/kg$)** | | |
| **Counts** | **BF + $^{137}Cs$** | **RC + $^{137}Cs$** | **Calc + $^{137}Cs$** |
| 3798 | 0.556866 | 0.470759 | 0.436824 |
| 1464 | 0.162235 | 0.170741 | 0.121892 |
| 1254 | 0.295854 | 0.295854 | 0.199 |
| 817 | 0.292593 | 0.230294 | 0.11194 |

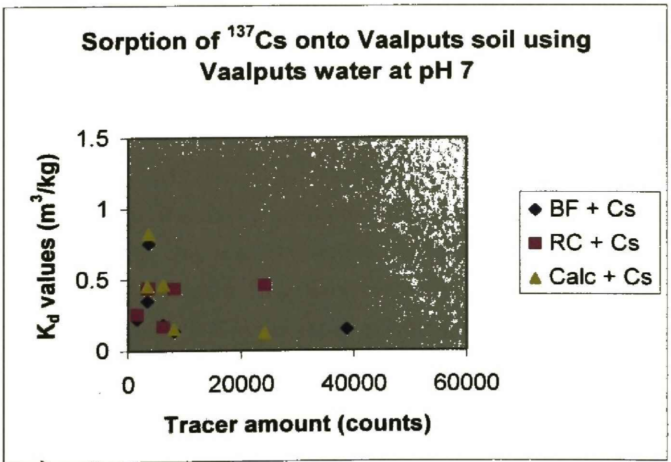


Figure 5.7 (a): Distribution coefficients ($m^3/kg$) of $^{137}Cs$ for Vaalputs soil using Vaalputs water

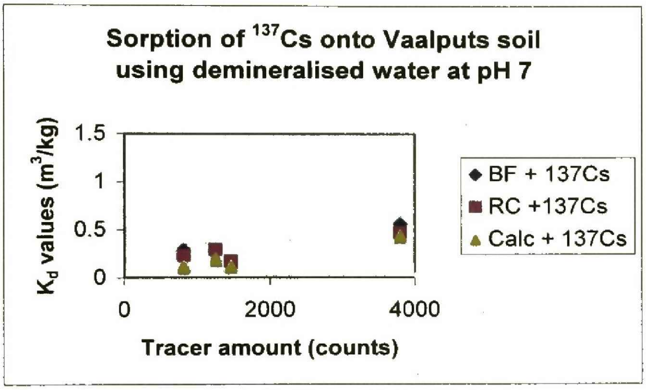


Figure 5.7 (b): Distribution coefficients (m$^3$/kg) of $^{137}$Cs for Vaalputs soil using demineralised water

### 5.3.2.2 The absorption of $^{137}$Cs into humified Vaalputs soil

The results in section 5.2 indicate that the amount of humic acid that absorbed into clay is negligible and that the number of available absorption sites for radionuclide absorption will not be significantly altered in the presence of humic acid. Therefore the absorption properties should remain the same.

In order to confirm the above statement, the absorption of $^{137}$Cs into artificially humified Vaalputs clay was determined. The distribution values (Table 5.8 and Figure 5.8) compare favourably with the values determined for pure Vaalputs clay (Table 5.7). This result confirms the results in section 5.2, i.e. that the amount of humic acid that absorbed into clay is negligible and did not alter the absorption properties of the soil.

The results also indicate that the average $^{137}$Cs absorption value for Vaalputs water is lower than for demineralised water. A possible explanation for this is that the presence of ionic species in the Vaalputs water favours the formation of $^{137}$Cs complexes that do not absorb into the clay, thereby decreasing the absorption properties of $^{137}$Cs.

**Table 5.8:** $K_d$ values ($m^3$/kg) of $^{137}$Cs absorption onto humified Vaalputs soil Samples.

| | Humic soil (Vaalputs water) | | |
|---|---|---|---|
| | $K_d$ values ($m^3$/kg) | | |
| Counts | Humic BF + $^{137}$Cs | Humic RC + $^{137}$Cs | Humic Calc + $^{137}$Cs |
| 38696 | 0.324162 | 0.892005 | 0.089747 |
| 24089 | --------- | 0.865964 | 0.259452 |
| 17431 | --------- | --------- | 0.580881 |
| 3666 | 0.980811 | 0.7232 | 0.93 |
| 3398 | 0.431299 | 0.482464 | 0.437105 |

| | Humic soil (Demineralised water) | | |
|---|---|---|---|
| | $K_d$ values ($m^3$/kg) | | |
| Counts | Humic BF + $^{137}$Cs | Humic RC + $^{137}$Cs | Humic Calc + $^{137}$Cs |
| 3798 | 0.431628 | -------- | -------- |
| 1464 | --------- | 0.130769 | 0.090966 |
| 1254 | 0.25125 | 0.275 | 0.159459 |
| 817 | 0.271724 | 0.262333 | 0.216944 |

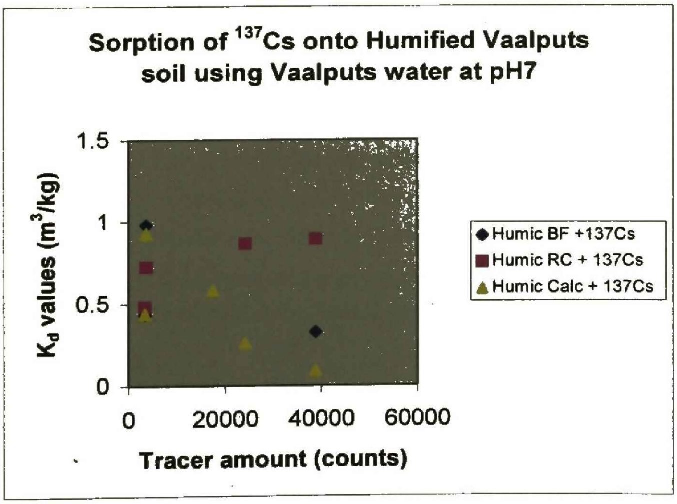


Figure 5.8 (a): The distribution coefficients of $^{137}$Cs for humified Vaalputs soil using Vaalputs water

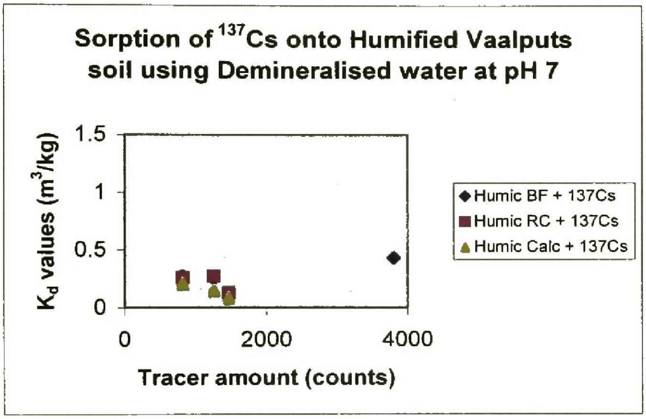


Figure 5.8 (b): The distribution coefficients of $^{137}$Cs for humified Vaalputs soil using Vaalputs water and

5.3.2.3 The absorption of $^{137}$Cs-humic complexes into Vaalputs soil

Humic acid has substantial chelating properties for metals, especially transition metals, and therefore could considerably affect the sorption and migration of cesium in a clay layer. The results in 5.2.2 indicate that the formation of $^{137}$Cs complexes decreases the absorption of $^{137}$Cs into clay. *Tanaka et al* commented that cesium species do not form complexes with humic acid. However, as the chelation of humic acid with $^{137}$Cs in the presence of ionic species (Vaalputs water) is unknown, the absorption of such species (if present) into Vaalputs soil had to be investigated.

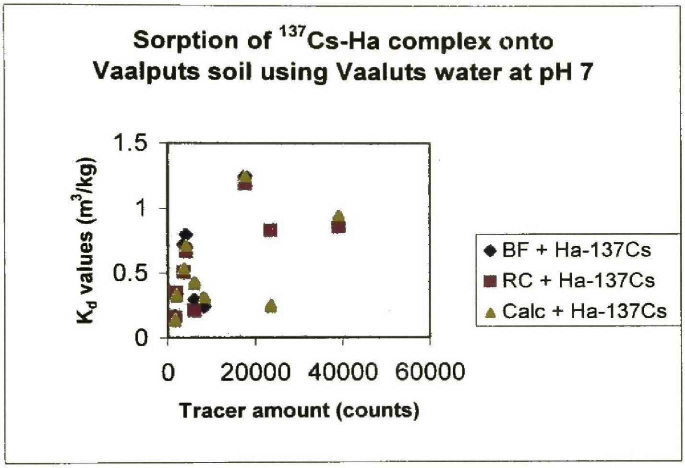
The distribution values in Table 5.9 and in Figure 5.9 compare favourably with the values determined for pure Vaalputs clay (Table 5.7), with only Cs present as radionuclide. As no significant decrease in the absorption could be observed, this result therefore indicates that $^{137}$Cs-humate complexes may be present and that the absorption properties remain the same as for the Cs-ionic complexes observed in Vaalputs water, or that no complexes formed.

**Table 5.9:** The distribution coefficients of Ha-$^{137}$Cs complex onto Vaalputs soil.

| | Vaalputs water | | |
|---|---|---|---|
| | $K_d$ values ($m^3$/kg) | | |
| **Counts** | **BF + Ha-$^{137}$Cs** | **RC + Ha-$^{137}$Cs** | **Calc + Ha-$^{137}$Cs** |
| 39161 | ---------- | 0.854481 | 0.945146 |
| 23500 | ---------- | 0.832294 | 0.254342 |
| 17757 | ---------- | 1.189797 | 1.249362 |
| 8328 | 0.238597 | ---------- | 0.312791 |
| 6213 | 0.293073 | 0.214296 | 0.433786 |
| 4264 | 0.794528 | 0.666825 | 0.712712 |
| 3717 | 0.718824 | 0.50625 | 0.536618 |
| 2105 | 0.335082 | 0.352931 | 0.335082 |
| 1723 | 0.171882 | 0.158922 | 0.145225 |

| | Demineralised water | | |
|---|---|---|---|
| | $K_d$ values ($m^3$/kg) | | |
| **Counts** | **BF + $^{137}$Cs** | **RC +$^{137}$Cs** | **Calc + $^{137}$Cs** |
| 3798 | 0.556866 | 0.470759 | 0.436824 |
| 1464 | 0.162235 | 0.170741 | 0.121892 |
| 1254 | 0.295854 | 0.295854 | 0.199 |
| 817 | 0.292593 | 0.230294 | 0.11194 |

The fact that the absorption values for the demineralised water system (no ionic species present) is the same as the Vaalputs water, confirms that cesium species do not form complexes with humic acid in the presence of chlorides and sulphates.



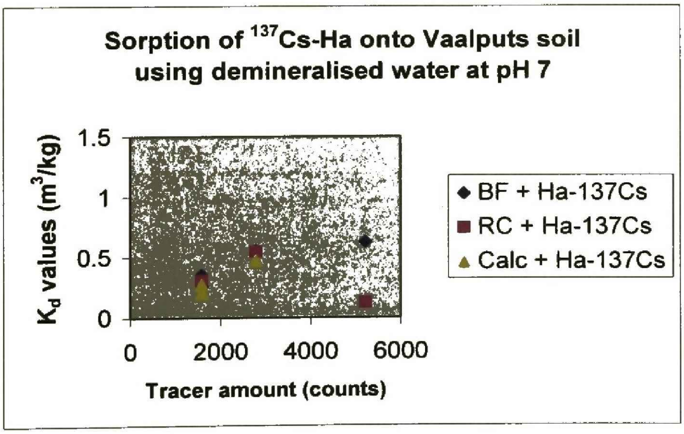


Figure 5.9: The distribution coefficients ($K_d$ values) of Ha-Cs for Vaalputs soil using both Vaalputs water and demineralised water

### 5.3.2.4 The influence of redox conditions (different pH) on the absorption of 137Cs into Vaalputs soil

*Carter and Suffete* indicated that by changing the pH of a solution containing humic acid, the molecules would be aggregated owing to hydrogen bonding and the ionisation of functional groups on the humic structure, thereby increasing the formation of complexes. In order to study this phenomenon, the cesium absorption experiments on Vaalputs clay in the presence of humic acid were repeated for the pH range between 4 and 10.

The distribution coefficient results in Table 5.11 and in Figure 5.10 indicate that the absorption of cesium into clay remains the same even under different redox environments (radionuclide alone, radionuclide with humic acid and radionuclide on humified soil). This result is only possible in the absence of complex-formation and therefore confirms literature that cesium species do not form complexes with humic acid.

**Table 5.3.4:** The influence of pH on the sorption of $^{137}$Cs onto Vaalputs soil (Using 0.1g/l Ha an average of 10 000 counts of $^{137}$Cs in Vaalputs water.

| | **Vaalputs water**<br>**$K_d$ values ($m^3/kg$)** | | |
|---|---|---|---|
| **pH** | **RC + Cs** | **Humic RC + Cs** | **RC + Ha-137Cs** |
| 4 | 0.233626 | 0.689747 | 0.354877 |
| 7 | 0.15125 | 0.1405 | 0.312791 |
| 10 | 0.10612 | 0.19301 | 0.228012 |

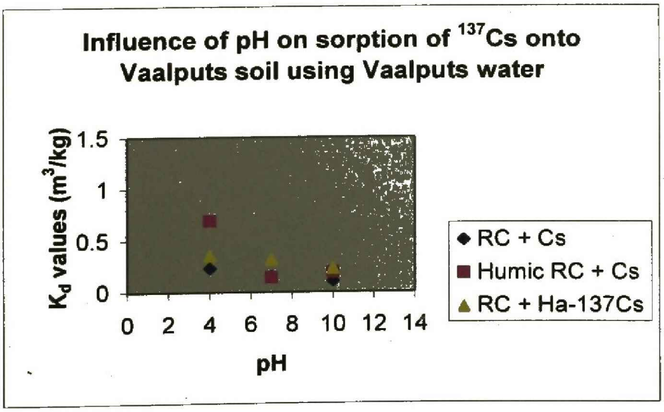


Figure 5.3.4: The influence of pH on the sorption of Cs onto Vaalputs soil.

# CHAPTER 6

# CONCLUSIONS AND RECOMMENDATIONS

## CONCLUSIONS AND RECOMMENDATIONS

Humic acid (plant material) has substantial chelating properties for metal ions and therefore may considerably affect the migration behaviour of radionuclides in a soil layer. To manage radioactive waste effectively, it is important to know the presence and interaction of humic acid with radionuclides released from radioactive waste repositories. The aim of this study was therefore to investigate the influence of humic acid on the distribution coefficients of radionuclides found in both Thabana and Vaalputs waste repositories.

The technique employed in this study was based on the laboratory batch method to study the influence of humic acid on the distribution coefficients of anionic $^{131}$I and cationic $^{137}$Cs for soil samples from the Thabana and Vaalputs waste repositories.

The absorption of the anionic $^{131}$I specie onto both Thabana soil and Vaalputs clay was studied and from the results obtained, it can be deduced that iodine does not absorb onto either Thabana soil or Vaalputs clay. As no significant effect was observed on the $K_d$ values in the presence of humic acid or humified soil it is assumed that the anionic characteristics of iodine (anionic exclusion theory) resulted in these low distribution coefficients.

Distribution coefficients indicated that the cationic $^{137}$Cs species does absorb onto both Thabana and Vaalputs soil thereby reducing migration. The results also indicate that the average $^{137}$Cs absorption value for Vaalputs water is higher than for demineralised water. A possible explanation for this is that the presence of ionic species (chlorides and sulphates) in the Vaalputs water favours the formation of $^{137}$Cs complexes that absorb onto clay, thereby increasing the absorption properties of $^{137}$Cs. No significant additional effect was observed for the $K_d$ values in the presence of humic acid or humified soil and it is therefore assumed that Cs does not form complexes with humic acid.

Although potentiometeric titrations of all the tracer solutions was done in order to confirm any of the complexations that might occur between humic acid and the tracer species used, the calculated results from this potentiometric data were unfortunately inconclusive owing to the unknown molecular mass of the humic acid used. It is therefore recommended that the characterisation of humic acid (elemental composition and structure) by different techniques should be performed in order to establish any possible complex-formation. Although the results in this study indicate that humic acid would not have a significant effect on the migration of cesium or iodine for both Thabana and Vaalputs soil, it is recommended this research should be repeated for the other, "problematic", $^{99}$Tc and $^{14}$C radionuclides in the waste repositories. It is also recommended that future studies should concentrate on the influence of humic acid on the distribution coefficients of uranium and other transurinic radionuclides in order to determine the feasibility of Vaalputs as a High Level Waste (HLW) repository.

# CHAPTER 7

# LITERATURE REFERENCES

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